PDL HANDBOOK SERIES

Additives for Polyolefins

Getting the most out of Polypropylene, Polyethylene and TPO

Michael Tolinski

pdl
Plastics Design Library

William Andrew is an imprint of Elsevier
Linacre House, Jordan Hill, Oxford OX2 8DP, UK
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA

First edition 2009

Copyright © 2009 Michael Tolinski. Published by Elsevier Inc.

The right of Michael Tolinski to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone: (+44) (0) 1865 843830, fax: (+44) (0) 1865 853333, e-mail: permissions@elsevier.com. Alternatively visit the Science and Technology website at www.elsevierdirect.com/rights for further information

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-81-552051-1

For information on all Elsevier publications
visit our website at elsevierdirect.com

Typeset by Macmillan Publishing Solutions
(www.macmillansolutions.com)

Printed and bound in United States of America

09 10 11 12 11 10 9 8 7 6 5 4 3 2 1

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER BOOK AID International Sabre Foundation

Table of Contents

Section I: Overview of Polyolefins and Additives

Section II: Environmental Resistance

Section III: Mechanical Property Enhancement

Section IV: Appearance Enhancement

Section V: Processing Aids

Section VI: Other Modifications of Form and Function

Section VII: Conclusion: Incorporating Additives

Preface

Some people connected to the plastics industry (I hope I am not alone) may have developed a slightly obsessive habit: turning plastic containers or components upside down to check the resin's identity on the article's material identification mark. The results of this investigation are usually not surprising; the feel and type of the article often by themselves immediately indicate that its material is some form of polypropylene (PP) or polyethylene (PE). What *is* often surprising is the diversity of form, texture, color, and stiffness various polyolefin (PO) articles have.

The versatility of POs is explained well by textbooks as being the result of complex polymerization methods that use carefully developed catalysts to create a certain polymer morphology and molecular weight distribution. This is true, but what often are less discussed are the additives that provide essential material qualities for each particular application. To the uninitiated, additive formulations might seem like magic recipes that only compounding experts or resin producers can be entrusted with.

But additives are what make polymers usable "plastics," and some knowledge about them is essential for plastics processors and industrial users. With PE and PP, additives often determine whether an untried application will be possible or profitable. Additives can affect the bottom line just as other raw materials do. And properly chosen, they can extend POs into new markets and applications for end users.

This book is for these end users and the supply chain that supports them. It is for molders and extruders who want to know how additives can be used to cut costs or expand markets. It is for compounders who need a quick-reference guide that covers additive types outside their range of expertise. It is for processors with mechanical engineering backgrounds who are not familiar with (or typically do not use) the terms of organic chemistry. It is for material-selection engineers and designers who need a sense of what properties are offered by sometimes confusing collections of long chemical names and various trade names. This book is also for laboratory characterization technologists who need to understand what is inside the plastics they analyze. And finally, it is for researchers and students who need an overview of PO additives that stays within the context of their end use, rather than in-depth analysis of chemical and structural relationships based on theory and laboratory work.

As much as possible, this book focuses on PO additives in wide general use over the past decade or two. It also covers recently developed additives that reveal the trends and interests of the industry. The book's content is based on material reported by experts in this field; much is distilled from recent industry conferences and publications. Sources are referenced liberally, and I have tried to summarize each source's findings using consistent terminology and sometimes simplified technical language. This keeps the focus on the performance of the additives in the polymer, rather than on their background chemical structures or mechanisms. For practicality, this book is organized by property (which was sometimes difficult, since different kinds of additives can be used to improve a given property, and individual additives can affect more than one property).

The book is in some ways structured as a handbook in that it tries to make it easy for the reader to find solutions for specific property requirements. However, it does not have the comprehensiveness of a complete handbook that covers all additives ever used with POs (along with their chemical formulas). Rather it focuses on additives currently important in the industry and new additives of increasing interest, such as nanofillers and environmentally sustainable materials. Given the continuing changes in the consumption and production of PO plastics and the broad use of the materials, undoubtedly some additive families may seem to be over- or under-represented, depending on the needs of a reader's specific sector.

As much as possible, each chapter emphasizes the value each relevant additive brings to PE or PP, rather than its chemical makeup, complex mechanisms, or the history of its development. When possible, similar additives are compared by capability or relative costs to help reveal the situations and strategies that dictate their use. The book also contains a number of short case studies about companies that have used or developed a particular additive to achieve a desired result.

Although the book attempts to report these cases and developments accurately, no reader should expect to achieve the exact results in their use of the technology. Depending on each reader's raw materials and application, an additive may perform worse (or better) than what is indicated in the text. Trade names and particular brands of additives are reported as examples of commercially available materials, not to recommend these products or to imply that these products are the only current, state-of-the-art materials available. New additive variations are being created all the time, and this book cannot provide nearly as effective advice for formulating particular applications as consultation with industry experts. This book at best should be read as a guide on the kinds of materials readers might discuss with their suppliers and customers or evaluate in their processes and products; no guarantees can be made about whether an additives approach mentioned here will work well in a specific process or application.

The research work behind this book started in the 1990s, even before the idea for the book was proposed. After a short manufacturing engineering career during which I had my first practical experiences with PO-based materials, I first wrote about PP's increasing presence in automotive applications for a (short-lived) plastics trade journal in 1999. When writing other articles since then, I have been consistently surprised by the relatively rigorous market applications that these supposedly "cheap commodity plastics" have been able to handle, largely because of additives and reinforcements.

However, my experience and probably no one person's experience could encompass all the uses of POs and their additives. So the content of this book is based on the work of hundreds of plastics industry experts around the world who have written and presented on additives developments. My own industry career in plastics and product engineering, though essential for creating this book, is dwarfed by the experience and achievements of these experts. Thus, serving essentially as an editor, I have tried to compile and summarize their published materials and reference their findings carefully in the text. I have also tried to provide a balanced view when authors or source materials are not consistent in their information, and I have tried to avoid ambiguous uses of terminology by consistently using the clearest, simplest choices of terms. Whenever a reported fact sounds surprising, hunting down the original sources referenced here (many of which are quickly available via a simple Internet search) may be a worthwhile exercise.

Like most people in the plastics industry, I am grateful for the number of thoughtful publications and conference presentations that our busy colleagues offer. I am also grateful to the perceptive editors at plastics trade publications who are skilled at seeing and noting the specific trends in our industry. We are lucky to work in an industry composed of people of so many different skills.

In particular, I want to thank specific people that were involved in the creation of this book or in my career leading up to it: industry publication editors such as Jim Destefani, Roger Ferris, Dan Domoff, Martin Scrivener, and Millicent Treloar (an acquisitions editor who originally approached me with the book idea). I am also thankful for my significant other throughout the book's composition period, Shaqe Kalaj—her own work ethic and moral support were inspiring and indispensable.

Mike Tolinski, February 2009

1

SECTION I

Overview of Polyolefins and Additives

CHAPTER 1

Introduction

This brief introduction will cover broader issues with polyolefins (POs) that justify this book's central focus on PO additives. As with forthcoming chapters, this chapter begins by listing some general guiding questions (and the sections in which they are discussed):

- (1.1) Why are POs important enough to focus on as a distinct segment of the plastics industry?
- (1.2) Why are additives critical for the overall success of POs?
- (1.3) What are some recent issues in PO use and production that have been influencing the use of additives?

1.1 IMPORTANCE OF POs

Plastics would not be so common in daily life if not for the technologies behind one general family of polymers—POs. Since World War II, daily life in both industrialized and developing societies has become radically changed by these carefully formulated organic materials, which are based on deceptively simple molecular structures built only from carbon and hydrogen. With polyethylene (PE) and polypropylene (PP), products once made from other materials became cheaper and often more durable. Innovative products that never existed before became possible (and affordable) and other products became lighter, brighter, and more user-friendly. And food and water could be packaged and transported in new, flexible ways (with even the modest PO water bucket contributing much to a community that otherwise could afford few other industrial products).

The sheer total volume of POs that are used reflects their importance. PE and PP make up over half of the +150 million metric tons of thermoplastics demanded worldwide (with PE accounting for nearly two-thirds of all POs). This consumption is equivalent to roughly 15 kg of PO product per year for each person on earth. So, given this demand for POs and the range of product types available with these versatile materials, it is likely that most people in the world now come into contact with an article made from PE or PP at least once each day [1-1, 1-2].

The production and use of POs in the world continues to grow, though at changing growth rates over time. PP, fueled by its particular versatility and improved properties, continues to grow ahead of other resins. PP has maintained an annual average growth rate of 6%–7% since 1980. Annual growth has since fallen off to under 3% in the 2000s, although some experts have now predicted a return to continued growth at 7% to over 8%. PP production capacity is expected to lead this growth by doubling during the period from 2008 to 2013 due to plant expansions in the Middle East. PE's growth rate, likewise, has been over 6% in the late 1990s/early 2000s. This growth has fallen below 1% since, though it may rise back to 6% by 2010, following the trends of a recovering global economy, new production capacity, and new food packaging and other applications. Meanwhile, both PE's and PP's growth will be supported by more efficient processing aids, stabilizers, and other additives that are being introduced into the market [1-3, 1-13, 1-14, 1-15].

1.2 IMPORTANCE OF PO ADDITIVES

Given their low cost, PE and PP have traditionally been categorized as "commodity plastics." But this is misleading; in fact, POs have been used for some engineering applications for years. Their properties continue to be expanded by the use of material additives whose contributions for improving properties are often under-reported and poorly understood. (In this book, "additive" will be used generally to refer to any material intentionally added to the base PO resin to influence the resulting compound's properties.)

Although the molecular weight and polymer structure of POs can be carefully controlled by advances in polymerization techniques, these advancements account for only part of the property improvements in commercial PE and PP grades. Reaction catalyst technologies are critical for providing many desired physical properties and processing characteristics, but they cannot address all the issues POs face during processing and service. And they cannot enhance many of the properties that make PO materials serious candidates for applications once controlled by more expensive engineering plastics. Additive reinforcements such as glass fibers, for example, will likely continue to be the main way PP is strengthened for its most extreme engineering applications.

Meanwhile, markets are driving improvements in low-cost, nonengineering applications of POs, such as packaging. But now, just efficiently enclosing a food item or other product is no longer enough; the packaging itself must communicate a product brand's unique qualities. Better reactor technologies have been heralded as providing high-clarity resins allowing new packaging uses, but new additives are at least as important for creating clarity or subtle effects in color or design that sells the packaged product. As these demands increase, traditional additives will continue to be challenged by alternative additive technologies.

1.3 RECENT ISSUES IN USING ADDITIVES

Even though they have been used commercially since only the mid-twentieth century, POs, and thermoplastic materials in general, have reached a certain maturity. Processors and designers are no longer excited by their basic capabilities; instead they ask, "How can I make more effective use of these materials?"

Consequently, the plastics industry has seen the wall thickness of plastic articles become thinner, though still stiff. The industry has seen greater demands for tougher materials with greater resistance to environmental factors. And it has faced the need for "leaner," more flexible processing, adding additives nearer the point of final molding or extrusion to tailor compound properties. Meanwhile, the industry has also seen more complex additives become available whose purpose and cost-effective use are not always adequately explained or demystified by suppliers.

Below, five key current issues are identified and discussed that relate to the choice and use of PO additives. These are the underlying themes of this book.

1.3.1 Matching property requirements with additive type and amount

Complicated and changeable relationships exist between resin supplier, compounder, processor, and end user. But operations of all sizes benefit from using materials at effective economies of scale, which depend on market volume, plant size, processing rates, and many other factors. For example, high-volume operations for diverse markets may tend to purchase standard additive formulations that cover a wide range of properties. Companies in smaller volume or specialized markets may rely more on compounders to provide custom formulations or masterbatches. And, in the interest of increased processing flexibility, all processors may seek options for adding additives to resin in-line or nearer the process that forms the final product [1-4].

For efficiency and flexibility, operations also benefit from purchasing only the additives required for the properties they actually need. Additive type or amount can be adjusted to provide no more than the required property that is demanded over the actual expected lifetime of the product (e.g., adding only just enough stabilizers to protect the product's appearance throughout its limited shelf-life). But this efficiency requires a good understanding of additive capabilities [1-5].

Achieving this flexibility also often requires blurring the lines between compounder and converter. A processor might start adding more different kinds of additive concentrates from masterbatch suppliers, rather than buying a fully compounded resin grade from a compounder. Or a processor might even bring its own compounding line in-house, if costs favor the expansion [1-6].

1.3.2 Doing more with less material

Over the last decade especially, calamities of weather and war have pressured petroleum and natural gas prices upward, and this has periodically shifted the cost of PO feedstocks in radical ways. Minimizing the amount of PO in a product is one way to soften the blow of major raw material cost changes [1-2].

Overall, higher energy prices (and environmental concerns) have created more calls for the "lightweighting" of products, especially in the transportation industries. For users of metal components, one satisfactory solution has been to switch to lightweight plastics when possible. But now the burden rests on all industries, including plastics, since an energy factor is attached to the production and transportation of all products, and all stand to benefit from energy savings and reduced emissions.

Thus, plastics manufacturers and end users need to use additives creatively to extend resin properties. In durable applications, longer-lasting, low-density PO products support the goals of material and energy efficiency. These materials require better fillers and reinforcements for increased mechanical properties and additives that protect the base polymer from degradation through longer product lifetimes. Unfortunately, a company's material-selection process does not always fully take into account all the properties required over the complete lifetime of a plastic product. Here, long-term testing and design-of-experiment (DoE) methodology are used to help identify the property contributions of each ingredient in a formulation. For example, DoE can be used to optimize a formulation by showing how much different levels of impact modifier, filler, or other additives, along with various processing conditions, affect the performance of a thermoplastic olefin (or thermoplastic polyolefin, TPO) in a rigorous automotive application [1-7, 1-8].

Other issues relevant to energy and the environment can influence additive selection. For instance, interest is growing in the use of an alternative plant-based fiber reinforcements and fillers. These agricultural products (produced mostly by solar energy) reduce the energy or "carbon footprint" of plastics production. And they reduce material densities and handling hazards, as found with glass-filled POs, for example. This interest has also led to more extreme ideas for using waste organic materials, such as scrap leather, as PO fillers. Moreover, interest in improved PO recyclability will continue and increase. Greater recycling will require better methods for compatibilizing resins of different morphology or rheology to create useful products that are equivalent in properties to virgin materials. Still the costs of these approaches have to be weighed against their overall benefits, and often the "greenest" and cheapest approach of all may be simply to reduce the amount of plastic in each packaged product [1-11, 1-12].

1.3.3 New properties for new markets

POs are still young enough materials that new markets remain to be conquered by them. New reactor technologies and additives are allowing them to penetrate markets currently dominated by other plastics. For example, transparent PP with improved clarifying additives can now compete with PET bottles in certain packaging applications. And improved PP-based TPOs in the automotive industry are becoming the norm for exterior and interior plastics on vehicles, replacing metals or other plastics.

However, new successful applications for POs tend to increase consumer expectations. For outdoor applications, this means POs will require better ultraviolet light-resistance (e.g., for large playground equipment or storage units) made possible with light stabilizers. And indoors, expectations continue to increase for durability and appearance. Here, additives supply new aesthetic features to POs, increasing the market appeal of plastics. These include pigments that bring bright hues to colored products to attract the eye and even fragrances to attract the nose. Thus the phrase "it's just cheap plastic" is not being overheard now nearly as often as it was in the 1970s. (No longer can plastics afford to be seen as "cheap.")

1.3.4 Unintended additive interactions

To enhance polymer properties, additives must interact with the polymer matrix and the mechanisms that tend to stress or degrade it. Unfortunately, they may also interact with other additives or the external environment in unexpected ways. One additive might improve property X while hurting property Y (or while diminishing a different additive's effect on improving property Y).

These complex interactions create challenges for the compounder, processor, and end user, and also help reinforce the mysterious and sometimes controversial public image of plastics in general. Accordingly, some additives' and polymers' interactions with consumers' health and the environment are often questioned by skeptical environmental organizations. This makes an understanding of these materials' health and safety effects essential for the industry, so that industry experts can communicate authoritatively with these organizations and government regulators. In the interest of protecting consumers, regulators are sensitive to the sometimes hazardous nature of some additives (even though the hazard may exist only when the additive is in its pure bulk form).

Perhaps inevitably, regulators and other external forces influence plastic industry trends in additive selection. In Europe, REACH registration is requiring manufacturers to document the properties of materials they plan on using. Restriction of Hazardous Substances (RoHS) directives in the European Union (EU) and China are targeted at restricting the use of heavy-metal and halogenated ingredients in electrical and other applications. Legislation in the EU, California, and elsewhere is already tending to discourage or stop the production and overall use of brominated fire retardants, for instance. The registration of the toxicological effects of more popular additives, such as antimicrobial agents, has also been targeted. And overall, there currently seems to be a trend toward industry limiting the use of an additive or material even before scientific studies about its health effects are completed [1-3, 1-9, 1-10].

So for better or worse, regulations play a role in dictating additive choice. They can create major obstacles (or at least extra paperwork) for suppliers, even when they have a new material that the industry and consumers want. But there may be opportunities lying behind these obstacles. And to some extent, additive makers and users are victims of their own success by being able to adapt so many substances for plastics use, and thus creating so many new applications visible to public speculation.

1.3.5 Faster processing

The last but not the least-important issue concerns speed. POs, which are so often used in high-volume commodity applications, are being processed with faster, computer-controlled equipment and tooling. Competition is driving this need for speed. A simple example is a molder who requires a PP margarine tub to be molded at a certain cycle time on a high-speed injection molding press; if it is not, the molder cannot be competitive and profitable at the same time, and the job cannot be considered a "winner." With processing machines getting faster all the time, PO formulations include additives that help processors reach their productivity goals using processing aids, nucleating agents, and other additives.

Productivity is a final overarching theme of this book. Here, additive selection can play a multi-faceted role for success. But among all the decisions made in a manufacturing operation, decisions about materials are often the hardest to make, especially by those who are closest to the process. Engineers or technicians who are comfortable with how a certain material runs or performs may feel that adjustments to the material's formulation are unreasonably risky. However, such changes do not have to be stressful and much can be gained at the bottom line.

CHAPTER 2

Trends in Polyolefin and Additive Use

Even though it is more difficult to identify current trends than to review data and history from the past, this chapter will attempt to highlight plastics industry trends relevant to POs late in the first decade of the twenty-first century. The chapter will bring together data and predictions from a number of industry sources whose skill and credibility are based on their abilities to observe and explain developments in the plastics industry.

The chapter will also dig down to the specific applications of POs based on recent developments in commercialized PO compounds and applications. It is organized according to the following guiding questions:

- (2.1) What are some production and pricing trends that are affecting the overall market for POs?
- (2.2) What are some overall trends in the production and use of polymer additives?
- (2.3) What are some current issues related to compounders—the companies that add the value of additives to raw resin?
- (2.4) What are some specific additives-related trends in specific applications for PE, PP, and TPO?

2.1 PO MARKET TRENDS

By virtually all estimates, the use of PE- and PP-based resins is expected to continue to grow worldwide, especially as less-developed regions grow their economies. The only uncertainty is the rate at which PO use will grow and where the fastest growth rates will occur. Multiple factors will determine where and how much PO resin will be produced, converted, and consumed. As briefly discussed below, fossil-fuel prices will affect the growth and pricing of these resins, as will new production capacity—with a kind of fluctuating give-and-take occurring between oil-price increases, PO production capacity, and demand growth.

2.1.1 Growth vs. volatility

Compared with other polymer families, PO production has grown fairly steadily since the 1990s. And POs are gradually taking on a greater share of new applications than commodity resins such as PVC and polystyrene. For example, in 1999, US production of PP overtook the yearly production of PVC and has gradually widened its lead ever since. The low densities of POs, compared with other commodity resins such as PVC, likewise, have given POs a cost-per-volume advantage. Meanwhile, intra-PO changes have also occurred, with US production of linear low density polyethylene (LLDPE) overtaking LDPE in 1998, rapidly increasing to the 12 billion pounds per year level, while LDPE remained at 8 billion pounds [2-1, 2-4].

However, this growth has occasionally caused disparities between new capacity for POs and fluctuating demand (although in some PO sectors, such as packaging, demand remains strong and steady). This global growth situation, along with spikes in oil prices and the occasional natural disaster, has created sometimes chaotic resin pricing swings in recent years. The year 2008 stands out for its volatility with spiking oil prices causing a 30% increase in PP pricing followed by a double-digit decline later in the year. Future new capacity starting in 2009 for manufacturing POs in the Middle East will likely change the pricing picture, with the capacity increase there for PP expected to be 22% by 2011, softening prices. However, questions remain about the types of PO produced with this new capacity (the ratio of HDPE to LLDPE, for example) and how it will affect prices specifically in different local markets around the world [2-2, 2-4, 2-8].

Changes in pricing relationships have also occurred during this period of growth and volatility. High-density polyethylene, low-density polyethylene, and polypropylene film prices (per pound) have matched each other in recent years, with LLDPE prices tracking 5–10 US cents/pound lower. In sheet extrusion, PP and HDPE prices have similarly tracked and matched each other, until PP started tracking at slightly higher prices in 2006. Similarly, injection molding grades of PP homopolymer have increased to holding a 5–10 cent/pound premium over general-purpose HDPE molding grades during most of the period since 2006 [2-7].

2.1.2 Future resin growth and prices

As recent history indicates, oil prices will particularly affect future PO pricing—even though most PO feedstocks are based on natural gas. PO prices have tended to track crude oil prices increases, and oil price volatility can be extreme (peaking at over $140 per barrel in 2008, before sinking quickly to below $40). This volatility has reportedly caused more makers of PP to switch to using less-expensive, natural gas-based ethane as a monomer feedstock rather than oil-based naphtha, for example [2-6].

Various estimates have pointed to continued demand growth for POs. For instance, PP-maker Dow Chemical has estimated PP growth averaging around 4.5% through 2015; alternatively, LyondellBasell ties PP growth rates to 1.5 times GDP growth. This demand growth varies greatly by region, with annual growth rates for PE at 2%–3% for North America and Western Europe and 7%–9% for the Middle East, China, and India from 2006–2011; and growth rates for PP in 2012 estimated at 2% for North America, 10% in China, and 11% in India. After 2015, the price/demand situation for POs and all polymers might change radically, with predicted $300/barrel oil prices ultimately affecting the prices and availability of once-cheap petrochemical-based products. By then, the availability of resin alternatives to commodity POs, such as bio-based resins, might also be significant enough to affect the PO market [1-14, 2-8, 2-9, 2-10].

Despite their growth in demand, there is no doubt that radical price changes of POs cause uncertainty about the market and complicate the long-term planning of PO makers, converters, and end users. However, POs will likely remain significantly lower in cost per volume of resin than other commodity resins, as they currently are. And, as mentioned later in this book, some inexpensive additions of additives can be used to help offset resin cost increases when they arise in the future [1-13, 2-23].

2.2 OVERALL TRENDS IN ADDITIVES PRODUCTION AND USE

Because many polymer additives are likewise based on petrochemicals, additive use and production is tied to oil prices as well. Additives are often more expensive than the resins they are used in; yet these additives can provide synergistic value-added functions to raw resin that offset their own costs. With the goal of increasing value when loaded in polymers, recent overall trends indicate both lower loadings of more-effective high-priced additives and higher loadings of low-cost additives, such as fillers and reinforcements [2-13].

The use of polymer additives, of course, follows the growth of the polymers they are used in. As with POs, the global growth rate of polymer additives varies by region, with about 4% global growth, but 10% in China and 12% in India. Thus, additive suppliers are consolidating and shifting operations to these regions. Also like POs themselves, the consumption of PO additives, such as stabilizers, is growing faster than with PVC additives. However, PVC still consumes by far the majority of all polymer additives produced, since roughly 40%

or more of most PVC grades are plasticizers or other additives. In contrast, POs use about 10% of all plastics additives produced [2-5, 2-11, 2-13].

Additives used at high volumes in POs and other polymers include inorganic fillers, which make up over half the market share of polymer additives. The most-used fillers are calcium carbonate ($CaCO_3$), titanium dioxide, talc, and aluminum trihydrate (ATH flame retardant). $CaCO_3$ dominates as a plastics filler; in the United States, the volume of $CaCO_3$ for plastics in 2007 (1.7 million metric tons) reportedly outweighed the volume of all other fillers combined, while ATH is the fastest-growing filler, with a 5.5%–7% annual growth rate (compared with other fillers growing at about 2%–5%). Meanwhile, organic fillers and fibers, such as wood, given that their cost per pound is about one-third that of PO resin, have been used in highly filled PO composites for durable construction material applications [2-5, 2-12].

Inorganic fillers and reinforcements have relatively more stable prices that themselves are only indirectly connected to fossil-fuel prices. This allows them to act as reliable hedges against raw resin price changes. Thus, PP compounds filled with talc or glass fiber, for instance, only tend to track the price of propylene monomer (which itself tracks with oil prices), rather than some wildly fluctuating filler price index as well. Moreover, filler/fiber price relationships tend to be stable, with 30% glass fiber-reinforced PP compounds tracking consistently at about $0.20/pound higher than 20% talc-filled PP [2-3].

Performance additives such as antioxidants (AOs), heat and light stabilizers, antistatic agents, and other functional additives used at relatively low concentrations are likewise growing, though at different rates. Given their high volumes and susceptibility to oxidation, POs consume over half of all AOs used for plastics, with about two-thirds of AOs used at primary resin producers and one-third by compounders. For light stabilizers, over 60% are used by POs, 40% by PP alone, and over half are added to resin by compounders. Light stabilizers, in particular, are growing faster than fillers and other additives at over 7% per year [2-12, 2-13].

Additives are often integrated with resin by compounders and converters using masterbatch concentrates. The masterbatch market for delivering colorants or other additives is composed of color, additive, white and black masterbatches, roughly in order of global market value. As with polymer additives, the highest growth rates for masterbatch use are in Asia and Eastern Europe (10%–12%), with only slow 3% growth in mature markets in North America and Western Europe, which already rely heavily on masterbatches [2-12].

2.3 TRENDS IN RESIN COMPOUNDING

As the primary means in which most additives are added to resin, compounders are extremely challenged by shifts in material prices and supply-chain geography.

Independent compounders supply custom and proprietary compounds or otherwise specialize in compounding filled/reinforced, color-matched, flame-retarding, antistatic, or masterbatch compounds. Compounding functions are also performed by primary resin suppliers, by additives or masterbatch suppliers, and by some large processors, internally or in-line with forming processes [2-16].

PP and PE are the two most-compounded polymers at North American compounders. About 75% of all polymers supplied to compounders in North America are POs (with PP itself making up over half of the total). "Technical polyolefin" compounding is increasingly being focused on by compounders who specialize in adding fillers, reinforcements, and modifiers to materials for automotive and appliance use [2-14, 2-15, 2-17].

However, compounders' jobs have been made more difficult by increased energy costs, higher raw materials costs, and higher transportation costs, as their customers and markets have moved farther away from traditional manufacturing regions. Recently, these costs have eaten away at margins and have caused industry consolidation, mergers, or outright plant closings. Resin and additives cost increases are difficult to manage or to pass on to customers, leaving compounders to shoulder the burden of price volatility. These pressures have driven compounders and processors to find more cost-effective formulations in less-expensive forms that still fulfill product requirements, but high costs also prevent the development of new additives or formulations [2-18].

2.4 TRENDS IN SPECIFIC PO APPLICATIONS

POs are processed using virtually every known thermoplastic conversion method. In some applications, such as film, pipe, or rotational molding, POs are the dominant materials; in others, such as the injection or compression molding of highly reinforced composites, they are only starting to show their value. In summary, there are currently five major application sectors that consume the most POs:

1. Film and sheet are the major forms in which PE is used, including shrink/stretch film, food packaging, pouches, and blown-film bags and liners. In North America, PE is by far the most-used film/sheet plastic material followed by PP. For shrink/stretch film in the United States, for example, over 75% is LDPE, rather than PVC. PE film and sheet also sees significant use in industrial thermoforming applications, as does PP for thermoformed packaging [2-19, 2-20].

2. Injection molding is of great importance for the most often injection-molded plastic, PP, and, to a lesser extent, HDPE. Molded PO applications include housewares, closures and caps, containers, and cups, as well as additives-intensive, engineering-type automotive applications for PP and TPO [2-21].

3. For blow-molded products, HDPE, PP, and LDPE are used by the greatest percentage of companies—and they are even more commonly blow-molded than PET is. Large containers for industrial and agricultural chemicals and other nonfood bottles are the leading blow-molded applications for POs, though many of these applications are often so ubiquitous or so common that they are easily overlooked as important PO uses [2-22].
4. Profile extrusion consumes huge volumes of POs for water and gas pipe and wire and cable coverings and insulation. Again, this is another "hidden" use of POs.
5. Fibers for various purposes consume large quantities of POs, especially PP. Often used in very visible applications, PO fibers must be properly stabilized to prevent yellowing (Chapter 3).

These sectors have matured and become implanted as producing everyday products that are mostly taken for granted by consumers and the general public. However, there are some trends for POs in various markets where the materials are providing new and unexpected product enhancements, largely possible through the use of additives. Some of these additives have not yet come into common use and do not even fit easily into the chapter categories in this book. But they do indicate that many opportunities remain for adding value to commodity resin applications; this chapter concludes by summarizing several trends below from three major market sectors.

2.4.1 Packaging trends

Plastic packaging made up over one-third of the $130 billion US packaging industry in 2007, with flexible packaging (mainly plastic based) as 18% of the total and rigid plastic packaging at 17%. The usefulness of POs for this packaging is so strong that even in down markets, PO compounds converted into various forms for packaging continue to grow in demand. Through the first half of 2008, for example, sales gains of 4%–9% were reported for PP cups and containers and HDPE, LDPE, and LLDPE, packaging, nonpackaging, and food packaging film, respectively. And rigid plastic (mainly PO) caps and closures—a multibillion dollar market in the United States alone—are expected to continue to grow through 2015 [2-2, 2-24, 2-26].

A number of current trends and interests signaled by the industry and public are likely to dictate future packaging designs. Some of these trends are summarized below.

- *Thinner packaging:* Environmental concerns for reducing packaging waste, as well as the industry's interest in reducing raw resin costs in each product, have led to thinner gauges in flexible, thermoformed, and molded packaging. Additives can help in these efforts somewhat by allowing improved more stable processing (Chapters 11–12) or better nucleation and strength (Chapter 10).

- *Improved aesthetics:* Color and clarity in a package have become even more important for allowing the differentiation of brands and products. The clarity of PP, in particular, has drawn more attention, given that clarified PP can be a more cost-effective alternative to PET for certain blow-molded containers (see Chapter 10). Other organoleptic (sensory) features in a PO package can draw consumer attention to various packages. These features include more attractive decoration or “special-effects” coloration (Chapter 9) or even specific odors encapsulated in the resin compound to enhance a consumer’s use of the product—whether it is a food package, toy, or waste bag (see Chapter 17) [2-23, 2-27].
- *Enhanced barrier properties:* With both small, single-serving flexible packages and rigid beverage bottles, packaging resin design is typically expected to keep out oxygen and to keep out (or in) moisture to extend shelf life and improve product quality. This barrier resistance often requires an added barrier layer (ethylene vinyl alcohol copolymer, EVOH or metallized foil) or a coating or fluorination treatment. Additives, such as nanofillers, have been proposed as the next step for POs to provide greater barrier properties without added material layers.
- *Retortable food packaging:* Flexible, heat-sterilized retort pouches are becoming more popular for restaurant, hotel, and military food packaging—offering sometimes years of storage of preprocessed food, plus food reheating with high-temperature retort treatments. These packages typically require complex, multimaterial, multilayer designs, but improved heat-resistance and barrier properties in the PO layers will allow all plastic package designs, longer shelf lives, and quicker retort treatments at higher temperatures [2-28].
- *“Active” packaging:* There is also greater interest in food packaging that adjusts the atmosphere or chemistry within the package itself to enhance food freshness and shelf life. These additive agents typically include oxygen scavengers, moisture scavengers, ethylene scavengers, or carbon dioxide absorbers or emitters. Oxygen scavengers, for example, support a clear package’s barrier layers by absorbing excess oxygen the food is exposed to, limiting spoilage and damage to food appearance or nutrition. These are typically ingredients susceptible to oxidation added into the package layers; examples of these additives and their uses in PO packaging are given in Case 2.1[2-30, 2-31].

CASE 2.1 PO FOOD PACKAGING ADDITIVES FOR CONTROLLING THE INTERNAL PACKAGE ENVIRONMENT [2-32, 2-33]

Problem: Food shelf life, appearance, taste, and nutrition are negatively affected over time, even when it is inside plastic barrier packaging.

Objective: Packaging that controls the atmosphere inside the package to prevent food damage.

Solution: Additives for PO packaging that control the buildup of gases that cause rotting and mold growth.

Flexible PO packaging is effective for clearly displaying and protecting the foods they contain. Yet even though these packages physically isolate the food, the environment inside the packaging can still damage the food, affect its aging process, or contribute to mold growth, limiting shelf life.

Phoenix Plastics Co., Inc. has developed additives that control the environment inside the film packaging, thereby controlling the ripening process of fresh fruits and vegetables, for example. In particular, ethylene is a gas emitted by plant materials, accelerating ripening or rotting. The company's Celspan ethylene-scavenging additive concentrates are said to control ethylene levels, while also limiting fungal growth.

For packaged bread, mold growth and insect infestation are the biggest threats. Here the company's developmental ReNovus additive, used at 3%–4% in PE bread bag film, inhibits mold and insect activity by migrating to the inner surface of the bag, reportedly lengthening shelf life to several weeks.

- *Increased needs for medical packaging:* Over one-third of all plastics used for medical plastics applications in North America are POs; these see their heaviest use in lower-end medical products, such as thermoformed trays, pouches, sterile wrap, and syringes. The demand for each of these products is expected to grow, especially in developed countries with aging populations. These products have different needs than other packaging, however, including resistance to multiple sterilization treatments and infectious environments. For this reason, extra AOs are needed for resisting sterilization radiation (Chapter 16) and antimicrobial additives may become more useful for preventing microbial growth (Chapter 17) [2-25, 2-29].
- *Improved recyclability:* Greater interest in reduced environment footprints has led to greater interest in more single-polymer, recyclable packaging that incorporates more recycled content. POs are relatively compatible with each other, especially when blended together in multimaterial constructions such as multilayer films or blow moldings, and the high volumes of POs used ensure a constantly high volume of PO recyclate available for reuse.

2.4.2 Automotive trends for POs

Decades ago, few would have expected the automotive sector to be such a large consumer of POs—lowly "commodity" materials. But vehicle applications have become a high-end market for PP and TPOs (compounds of PP, rubber, and filler) and this sector has driven the growth of these materials into other engineering-type applications.

Smaller cars will likely become more popular in the near future and for them, PP-based compounds have already become major materials. Several car models now contain well over 50 kg of PP, and in at least a few small cars, over half the plastics content is PP-based. In the future, it should become increasingly common to see 100–150 kg of thermoplastics in all cars and light trucks—40% or more of which are PO materials. And now, perhaps more than ever, the auto trends mentioned below will capitalize on the properties of these materials:

- *Lower costs:* Compared with engineering resins, PP-based materials have lower costs, and on a cost-per-strength basis and cost-per-volume basis, are competitive with all conventional materials used in vehicles. New PO production capacity in the future should only help in keeping their costs relatively lower.
- *Lighter weights:* Given the threat of increasing oil prices and new regulations (especially in the United States) for auto fuel economy, automakers are exploring all options for decreasing vehicle weight. Their efforts will be supported by the inherently low densities of PO compounds and the resulting lightweight components (with even lower densities possible from foaming) relative to other plastics and materials.
- *Paint-free colored surfaces:* Painting unwantedly creates costs and VOCs; accordingly, suppliers have made progress in producing pigmented, molded-in-color PO compounds having gloss levels from low to high. Challenges remain in improving weatherability and in integrating these parts with current auto-body painting processes (Chapter 9).
- *Engineering composite strength:* Reinforced PP compounds using long glass fibers will slowly allow these new kinds of low-cost, lightweight composites to be used for more structural applications in automotive. High strength and panel stiffness values will also come from cost-efficient microtalc or nanocomposite compounds (Chapters 7 and 8).
- *Stiffness plus low-temperature impact:* With their use growing at about 10% per year, TPOs can provide varying levels of impact resistance and varying flexural modulus values and are tailored for particular applications, from the most extreme exterior bumper fascia parts to softer interior components (Chapters 7 and 8). Other additives pair these properties with scratch-resistance (Chapter 17).
- *Recyclability and sustainability:* All PO-based plastic interior or exterior part systems, theoretically at least, allow potentially easier recovery and reuse of components or shredder "fluff" when a vehicle's lifetime is over. Reduced environmental footprints are also being sought with the use of plant-based fillers and fibers for plastics.

Finally, another more forward-looking trend relates to the more sophisticated material design and selection strategies used by the industry. These analytical strategies take into account the contributions of all the components in a compound and how they affect total raw ingredient costs, physical properties, processing rates and yields, and environmental footprint (life cycle costs) [2-34, 2-35, 2-36, 2-37, 2-38].

According to these trends, more exterior panels and interior and under-hood structures are likely to be made from PP/TPO or new kinds of PO-based materials. Ultimately, the only thing limiting more PO use in automotive may be the extent to which automakers can shift consumers' ideas about what a car should look like—away from the idea that a car can only be a formed sheet-metal box—and toward more designs based mainly on plastics.

2.4.3 Construction and infrastructure application trends

Construction and infrastructure projects consume large quantities of raw POs, and unlike packaging, these applications expect the PO products to last for decades. PO-based pipe, wire and cable coverings, and wood-plastic composites (WPCs) are the major consumers of resin, and new outdoor applications are being created regularly. For pipe and tubing, HDPE and PP are among the leading plastics along with PVC and ABS. For wire and cable, POs are slowly displacing PVC as commodity materials. PO-based WPCs are situated as good uses for recycled PE and PP, and US demand for WPC decking is doubling every five years. Meanwhile, agricultural films have become more specialized outdoor applications for PE, as have weatherable, sealable TPO membranes for building roof systems. Each application has its own particular concerns, but they all have similarities in what end users are ultimately looking for from PO compounds [2-39].

- *Higher throughputs and quality:* Most infrastructure PO applications are now mature extrusion-based applications (with WPCs maturing quite quickly over the last 10 years)—meaning that their most important improvements may come simply from faster throughputs and higher yields. Here, better processing lubricants (Chapter 12), foaming agents (Chapter 13), coupling agents (Chapter 14) and cross-linking agents (Chapter 15), and processing equipment options (Chapter 18) all have contributions to make.

- *Longer lifespans:* Outdoor or underground environments make particular demands of POs in these applications. Additives for PO piping must not reduce the material's long-term environmental stress-cracking resistance, and some can enhance the PO cable insulation's resistance to aging and embrittlement. Also, for cable coverings and WPCs, resistance to rot or organism attack is required for longer-life parts (and for WPCs, to justify their higher costs than wood). Here, antifungal and pest-repelling additives can be of assistance (Chapter 17). Other outdoor uses require special attention to light-absorbing additives and stabilizers in the compound (Chapter 4).

- *High temperatures and flame retardance:* Wire and cable coverings, in particular, require long-term heat stabilization or cross-linking (Chapters 3 and 15) as well as flame-retarding additives (Chapter 5). Cross-linking also supports new PE applications in hot-water plumbing.

Other additives-related trends are supported by colorants and new additives specifically formulated for each application. For example, additives even add special properties that turn large-scale uses, such as agricultural film, into engineered applications (see Case 2.2) [2-40, 2-41].

Trends for the various additive families covered in this book are shown in Table 2.1. These trends indicate that POs are becoming more specialized, with their formulations more carefully designed for each end use. Less often than ever does the term "commodity resin" seem appropriate for these engineered materials.

CASE 2.2 LIGHT-ABSORBING OPTIONS FOR PE AGRICULTURAL FILM [2-42, 2-43, 2-44, 2-45, 2-46]

Problem: Uncontrolled amounts of solar radiation and heat can interfere with the healthy growth of crops.

Objective: Agricultural films that control the amount of radiation that crops are exposed to.

Solution: Solar radiation-modifying additives in PO 'ag' films.

Agricultural films are high-volume PE products engineered to produce specific growing conditions for the plants they shelter or protect. To do this, they often rely on additives that modify the amount of heat and light the plant receives; these additives are becoming even more specialized in filtering specific kinds of light. This type of functionality for greenhouse "ag films" also can help keep plants free of certain diseases or even manipulate the behavior of insects that interact with the plants. A few examples of types of ag-film additives below reflect these trends.

Ultraviolet (UV) light absorbers, quenchers, and stabilizers are additives that not only protect the PE greenhouse film itself, but they also diffuse the light coming through the film, improving crop quality. However, the stabilizers must be protected from halogen- and sulfur-based agrichemicals, including pesticides. Vibatan masterbatches from the Viba Group (Italy) are said to provide pesticide-resistant UV stabilization for greenhouse/ag films.

Photoselective agents allow only certain light wavelengths to reach the crops. This controls the plant growth, thus enhancing quality and yields. For example, Ciba's SmartLight RL 1000 additive for film uses luminescence to transform part of the UV energy spectrum from the sun into visible red light wavelengths, which better promote the photosynthesis of certain flowers such as roses. It reportedly has shortened growing cycles, enhanced flower color, reduced spider pests, and increased yields.

Thermal-film additives help to keep the crops cool during the day by blocking infrared energy from the sun. As alternatives to white-washed films or other shading mechanisms, heat-reflecting additives contained in masterbatches for clear film are available from Techmer PM; these are said to reduce the temperature in the area sheltered by the film by several degrees.

Table 2.1 Summary of Current Trends Influencing the Development and Selection of PO Additives

Additive Type	Book Chapter	Key Issues	Relevant Usage Trends
Antioxidants and heat stabilizers	3	Reducing oxidation and long-term discoloration from additive interactions	Higher-temperature PO processing and applications
UV light stabilizers	4	Limited weatherability of POs, interactivity of light stabilizers with other additives	More outdoor-exposed POs using noninteracting forms of HALS and UV-screeners
Flame retardants	5	Greater use of FR POs, restrictions on halogen-based FRs	Nonhalogen FRs; synergies from combined FR additives
Electrical property-modifying additives	6	Application limitations from migrating antistatic agents	Nonmigrating permanent antistats
Fillers and reinforcing fibers	7 and 8	Engineering-type applications for POs (especially PP and TPO), more interest in "sustainable" fillers and fibers	Greater use of cellulose-based fiber reinforcements, of long-glass fiber reinforcement, and of nanofillers and specialty fillers
Colorants	9	Limited color strength, product differentiation, molded-in alternatives to painting	Special-effects colorants, more efficient pigments, new colorant forms (e.g., dyes for POs)
Nucleation and clarity	10	High crystallization and processing rates, high haze in cloudy PE and PP	Nucleating agents for higher properties, clarifying nucleators for clearer PP containers
Processing aids	11 and 12	Limits on equipment productivity and processing speed, excessive downtime and startup times	Multifunctional processing aids for specific situations
Foams	13	Internal vs. external foaming agents, foam cell size consistency	Easier-to-control foaming agents, finer cell sizes possible
Coupling and compatibilizing agents	14	High filler contents difficult to integrate with PO matrix, limited property gains from fibers	More options for grafted and nongrafted agents
Recycling and biodegradability	14	Nonoptimized PO recycling, disputes about agents that promote biodegradability	Better approaches for integrating regrind, better-defined capabilities of "biodegradability" additives
Cross-linking	15	Expansion of PE into higher-heat applications	Better control when using cross-linking agents
Sterilization and radiation resistance	16	Growing use of POs in medical applications, radiation-intensive sterilization treatments	Better antioxidants and stabilization against radiation
Surface aesthetics	17	Better scratch-resistance and other surface properties needed in automotive, etc., odor-enhanced POs	Additive combinations for surface enhancement, slip agents, encapsulated odor additives

(Continued)

Table 2.1 (Continued)

Additive Type	Book Chapter	Key Issues	Relevant Usage Trends
Antimicrobial agents	17	Infection-free medical PO surfaces, germ- and odor-free consumer POs	New agents and options for killing or repelling organisms
Blending and mixing additives issues	18	Filler dispersion, less reliance on compounders, worker health and safety	Equipment setups and additive forms suit specific situations

2

SECTION II

Environmental Resistance

CHAPTER 3

Antioxidants and Heat Stabilization

Throughout the compounding, molding, and extrusion processes they are exposed to, POs face conditions that tend to degrade their polymer chains and change their properties. The heat and stress of the processing environment can initiate oxidation and degradation processes in the polymer well before the finished product has been packed for shipment. Further, thermal exposure in the application itself gradually adds to the total “heat history” of the material, leading to degradation unless adequate heat stabilizers have been added. To maintain a resin’s original molecular weight and mechanical properties throughout its planned processing and design lifetimes, AOs are essential ingredients in a PO compound.

This chapter is structured much like others that follow in this volume. After a basic explanation of the mechanisms of oxidation and degradation in POs, the chapter reviews the roles and purposes of various families of AO additives. Then the chapter attempts to put some commercially available additives into perspective, using rough comparisons of their properties in real applications, using industry data and case histories.

Again, the purpose of this chapter and the following ones is not to educate readers to become additive research chemists, but rather to inform plastics processors on how, when, and why certain additives are used to achieve specific property goals cost-effectively.

In summary, this chapter will address these questions:

- (3.1) Why are AOs needed for POs, and how do they work?
- (3.2) What are the basic families of primary and secondary AOs used for thermal stabilization?
- (3.3) What are some important factors to consider when choosing commercially available AOs, and what are some examples of AOs that illustrate their most interesting recent developments?

3.1 IMPORTANCE OF AOs AND STABILIZERS FOR POs

In polymers, auto-oxidation, or autoxidation, is caused by the creation of free radicals (reactive molecular species with unpaired electrons). Autoxidation is a circular, self-propagating process that, unless interfered with by AOs, gradually leads to increasing degradation of the polymer. Such degradation is almost always unwanted, except when the material is intentionally designed to degrade after its service life is complete. Degradation mechanisms are complex and some are still not completely understood, although the property-damaging effects of autoxidation are obvious [3-3].

POs are susceptible to degradation by free radicals via breaking or cleavage of their polymeric chains (that is, chain scission) or by cross-linking between chains. These reactions lead to changes in molecular weight, molecular-weight distribution, mechanical properties, and appearance. Because of molecular structure differences, the tendency toward chain scission is more pronounced in PP than in PE (leading to reduced molecular weight), while cross-linking tends to predominate especially in unbranched types of PE [1-1, 3-4].

Molecular weight changes in the polymer and degradation can also create changes in the resin's organoleptic properties (color, taste, and odor). Given that exposure to oxygen is greatest at the surface of a plastic product, a product's cosmetic properties are the most visibly affected, with oxidation creating a cracked and/or powdery, chalked surface. This can be particularly disastrous with films and fibers, which have relatively high surface area per volume [3-4].

Autoxidation via free radicals can be initiated by heat, mechanical stress, metal catalyst residues, and radiation—conditions faced to differing degrees during resin production, compounding, processing, and throughout the lifetime of the product. Driven by heat and the presence of oxygen, autoxidation proceeds through a series of *initiation*, *propagation*, and *branching* chain reactions, graphically illustrated in Figure 3.1 and summarized as follows:

- Heat, light, shear, and catalyst residues tend to strip hydrogen from the polymer chain (RH) to form alkyl free radicals (R•).
- Oxygen combines with the free-radical species to create new reactive species, including peroxy radicals and hydroperoxides ($O_2 + R\bullet \rightarrow ROO\bullet + RH \rightarrow ROOH + R\bullet$) and other fragment species (H_2O, H_2, H_2O_2).
- The hydroperoxides (ROOH), in turn, are themselves reactive, creating new free-radical species, such as hydroxy and alkoxy radicals ($ROOH \rightarrow \bullet OH + RO\bullet$).

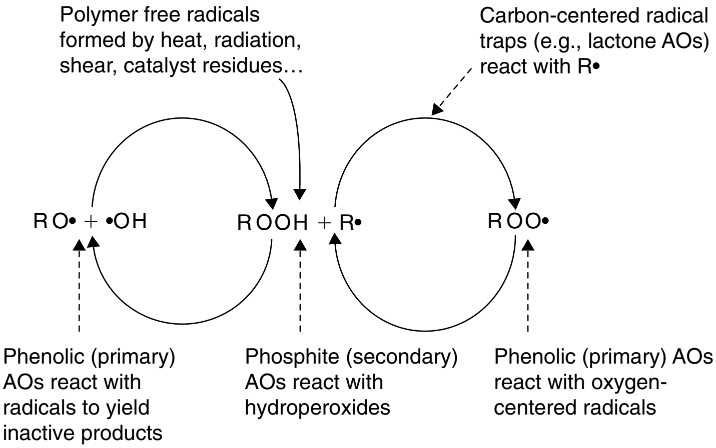

FIGURE 3.1

Autoxidation mechanisms. A simplified visual representation of the self-propagating autoxidation cycles of a polymer; dotted lines indicate the points in the mechanism where various AOs interfere with the process by deactivating various products.
Source: Adapted from [3-26] and other sources.

This process can self-terminate, but generally at a much slower rate than it propagates in the steps shown earlier. Depending on how effectively this self-initiating and self-propagating process is slowed and inhibited by AOs at certain points in the cycle (also in Figure 3.1), and on how much oxygen is available, it may slowly, progressively, and catastrophically degrade the polymer as the peroxy and alkoxy radicals decompose.

Propagation ultimately leads to chain scission or cross-linking. For example, when alkyl free radicals are near each other, enough to combine with each other, the result is cross-linking, which increases viscosity. Otherwise, the macromolecular chains are weakened and cut at their reactive free-radical points, lowering their average molecular weight and increasing melt flow. This destabilizing effect on melt-flow index usually becomes more and more pronounced after several extrusion passes. However, AOs help keep melt-flow properties stable. Figure 3.2, for example, compares the melt flow of an unstabilized HDPE with formulations made with various AO packages. Here, degradation is indicated by the reduced melt flow of the unstabilized material, while the stabilized materials' melt-flow readings stay relatively consistent [1-1, 3-1, 3-2, 3-3, 3-4].

Over the service life of a PO, heat-induced degradation can cause losses of multiple desired mechanical properties and increased embrittlement. This is shown in Figure 3.3, which compares long-term heat aging (LTHA) of heat-stabilized

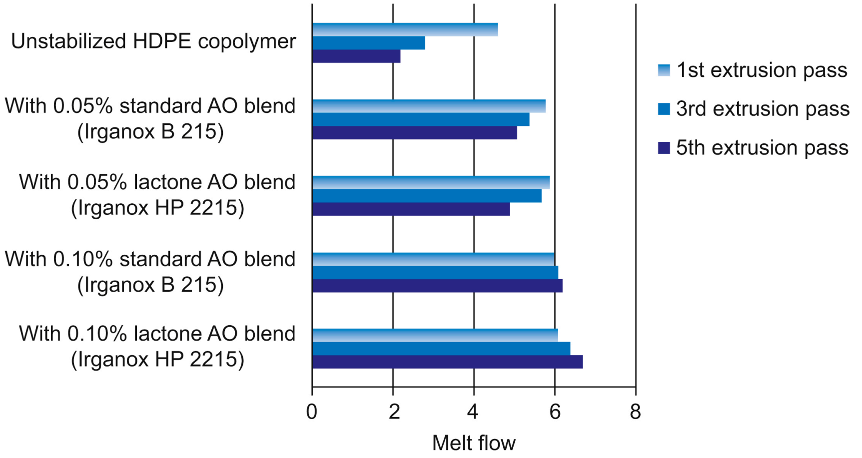

FIGURE 3.2

Melt-processing stabilization of AOs. Unstabilized HDPE shows large changes in melt-flow index with each extrusion pass. However, phenolic/phosphite AO blends without and with a lactone AO component (Ciba Irganox B 215 and HP 2215) reportedly keep the melt flow more consistent after repeated extrusion passes. Source: Adapted from [3-18].

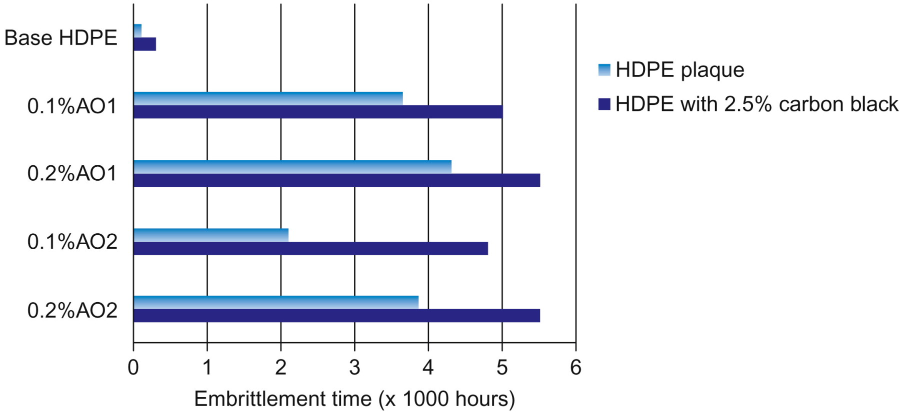

FIGURE 3.3

Long-term heat-aging effects of heat stabilizers. Along with melt-processing stability, different AO formulations and concentrations can extend the useful lifetimes of heat-exposed products well past that of unstabilized base HDPE. If fillers such as carbon black are added, heat-resistance to embrittlement may be extended even longer.
Source: Adapted from [3-25].

materials with a "base" polymer. Here, the time-to-embrittlement of the material is much extended by various AO packages and carbon black filler.

Thus given their susceptibility to autoxidation, commercial PP and PE require stabilizers to be useful; the question then becomes, which stabilizers and in what combinations?

3.2 PRIMARY AND SECONDARY AOs

AOs tend to interfere with the propagation of free-radical reactions that break polymer chains. Primary AOs do so by "scavenging" or consuming free radicals, while secondary AOs react with secondary hydroperoxide species created during autoxidation, preventing them from further degrading the polymer. To some extent for some additives, the characteristics of primary and secondary AOs overlap with each other (as do those of AO heat stabilizers and the ultraviolet light-stabilizing additives discussed in the next chapter) [3-4].

3.2.1 Primary AOs (radical scavengers)

In short, a primary AO stabilizes free radicals by donating a hydrogen atom, essentially "covering" the radical's unpaired electron and making the chemical species once again stable. The AO, in return, becomes a radical. But because of its structure, it is more stable than other radicals and prevents the chain reaction of radical propagation from continuing (and eventually it may react with other free radicals to form completely stable chemical species). Primary AOs act similarly on the products of autoxidation, including radicals that have combined with additional oxygen atoms (alkoxy or peroxy radicals) [1-1, 3-4].

Some primary AOs mainly supply melt-processing stability; others provide longer-term stability to protect the product over its lifetime. Decisions about which AO to use are typically made high up in the vertical production chain of polymer, depending on each PE or PP grade's expected processing and use. This section overviews the basic kinds of primary AOs, with further discussion of their effective uses later in this chapter [3-2].

Hindered-phenol AOs

Hindered-phenol AOs are the most popular primary AOs. They are called "hindered" because each molecule's reactive hydroxyl (OH) group is attached to its phenolic ring at the point where it is sterically shielded by hydrocarbon units connected to each neighboring carbon atom in the ring. Its structure allows the molecule to donate a hydrogen atom from its OH group to deactivate free radicals, transforming itself into a stable, inactive phenoxy radical that prevents the initiation of new radicals in the polymer. Higher processing or application temperatures tend to require phenolic AOs with higher-molecular-weights (generally ranging from 200 to over 1000), added to the polymer in percentages up to 0.5%. Added at an adequate level where they can overwhelm the side-reactions that propel the free-radical degradation cycle, phenolic AOs can provide both melt-processing stability and long-term thermal stability [1-1, 3-2, 3-4].

However, as phenolic AOs are themselves oxidized, some unintended changes in the resin's properties become evident, such as gas fading or yellowing caused by prolonged processing or exposure to nitrogen oxide pollutants or gamma radiation. At high temperatures, hindered phenols can also react with oxygen to create peroxy radicals that cause degradation. Moreover, acidic metal catalyst residues left over from polymerization can also oxidize these AOs, unless *acid scavengers* are included in the additive package. For POs, these are typically hydrotalcite-based antacids and calcium stearate and zinc stearate [1-1, 3-2, 3-3, 3-9].

Alternative AOs

Alternative AOs for providing melt-processing stability include natural or synthetic *vitamin E* (as α-tocopherol, its active form). As a safe, biocompatible alternative for food and health product packaging and human-contact applications, vitamin E is a fast-acting, hindered-phenolic AO that stabilizes via a complicated reaction mechanism analogous to its reactions in a living body. It is more expensive than other phenolic AOs, though it can be used in lower concentrations (0.025% or lower) [1-1, 3-5].

In vitamin E, nature has created a chemical structure that is a far more efficient radical trap than standard phenolic AO structures used for polymers. Thus it can be used at roughly one-quarter the loading of standard phenolics, and it reportedly resists the typical melt-processing temperatures of PE and PP (with its stability reduced above 280 °C). However, its oxidation products' tendency to discolor (yellow) PP is equal or slightly higher than the discoloration from standard phenolic AOs. Fortunately, the co-addition of a phosphite secondary AO (see later) can help counter the color-change effect (the mechanisms are complex and are covered in [3-5]).

Vitamin E has also been used as an AO to provide postradiation sterilization stability for body-contact medical applications (e.g., see Case 3.4 at the end of this chapter).

Phenol-free stabilizers

Phenol-free stabilizers provide the benefits of phenolic-based AOs without the threat of discoloration from gas fading. These are often based on *hindered amine* chemistries, which serve as free-radical scavengers and are usually referred to as hindered amine light stabilizers (HALS) because of their specialized roles, discussed in the next chapter. As a "phenol-free" alternative, high-molecular-weight HALS grades are also effective in providing long-term heat stability. HALS can be a more effective AO at low temperatures than phenolics. However, during service aging, HALS have been shown to create a gradual decline in mechanical properties (particularly in PP), rather than a sudden decline after a long period of little change, as with phenolic AOs (which are consumed by the autoxidation process). A HALS's effect on properties might be explained by its AO mechanism. After the HALS molecule oxidizes and loses its reactive hydrogen atom from its hindered amine location, the resulting active nitroxide (nitroxyl radical) then interrupts the autoxidation cycle through a series of reactions. In these reactions, the nitroxyl species partially regenerates itself until it gradually loses its radical-scavenging efficiency [3-2, 3-4, 3-5].

AO chemistries based on *lactones* (benzofuranones) or *hydroxylamines* are free-radical scavengers or traps that, when used with a phenolic AO or instead of it, reduce discoloration in color-critical applications. Lactones are also said to be less sensitive to variations in melt processing and recycled-material content, which itself often carries a long heat history and significant degradation. Lactones' stabilization is said to be highly efficient, since the chemistry appears to donate hydrogen directly to carbon-centered free radicals (R•) as shown in Figure 3.1. This reduces the overall amount of primary AOs needed to stabilize peroxy radicals (ROO•) that would otherwise be formed. Lactones have thus been described as stopping autoxidation before it has a chance to start. It has also been reported that lactones can donate hydrogen atoms to phenoxy radicals to "regenerate" the phenolic AO in the system, allowing this AO to continue to protect the polymer over the long term [3-2, 3-8, 3-26].

3.2.2 Secondary AOs (peroxide decomposers)

The propagating reaction of autoxidation creates hydroperoxides (ROOH), a relatively unstable species which must be reduced by AOs into more-stable alcohol (ROH) forms. Secondary AOs decompose these species by allowing themselves to becoming oxidized (taking the oxygen from the ROOH). Used in combination with primary AOs, secondary AOs are often referred to as "synergists," because their interaction with primary AOs greatly enhances the protection the polymer receives. Secondary AOs become cost-effective when they can lower the required amount of more-expensive primary AOs. And some high-performance, phosphite-based secondary AOs have even been shown to maintain a resin's color and melt-flow properties in PP when used as the sole processing stabilizer—without any primary phenolic AO in the formulation [1-1, 3-3, 3-4, 3-12].

Phosphite-based AOs

Phosphite-based AOs support melt-processing stability by accepting oxygen atoms from hydroperoxides, becoming themselves phosphates and leaving behind stable alcohol species. However, they are susceptible to reactions with water (hydrolysis) to form acids, causing melt-flow changes, black specks, corrosion, and breakdowns of other additives or materials encountered in service or in processing. Accordingly, different kinds of phosphites are available with bulky molecular structures that hinder their phosphorous atoms and resist hydrolysis. Generally, phosphites with higher-phosphorous content are more active and provide better process stability than lower-phosphorous grades [1-1, 3-2, 3-5, 3-12].

In combination with primary AOs in POs, phosphites help retain the melt-flow properties and color stability through repeated processing passes better than each AO can do alone. This helps limit the amount of primary AO that is consumed in processing dramatically. Moreover, phosphites and hindered-phenol AOs can be combined as dry blends to simplify handling and feeding [3-5].

Tris nonylphenyl phosphite (TNPP)

Tris nonylphenyl phosphite is one of the oldest and most often used phosphite stabilizers for polymeric materials. In liquid form, it is economical to use even at over twice the loading of alternative dry phosphites, and its liquid form has advantages in handling and metering. It is used in LLDPE bags and food packaging and HDPE blow-molded drums and box wrapping film [3-5, 3-6].

Even though TNPP has been approved for food-contact uses by the US FDA and European Food Agency and other agencies, studies have been directed at determining the potential toxicity of its nonylphenol content. Though not conclusively found to be a threat to human health, nonylphenol's potential toxicity to aquatic life has raised concerns about its accumulation in the environment. Excess nonylphenol is stripped from TNPP during its production, cutting its concentration down to as low as 0.1% or lower. And although TNPP generally resists hydrolysis, a small amount of hydrolysis during polymer processing and in the environment will create nonylphenol as a product of TNPP. Thus the material is being reevaluated in a risk assessment under the European Union's Existing Substance Regulatory (ESR) program. In response to the attention, in recent years, a range of alternative phosphites in liquid and solid form have become available, including those that are able to brand themselves as inherently "100% nonylphenol-free" [3-6, 3-7].

Unfortunately, most phosphites have a tendency to hydrolyze in the presence of moisture, causing clumping, handling and feeding problems, and potentially black specks in the resin. However, pentaerythritol-based phosphites are effective for stabilizing POs, and these reportedly have overcome some problems with hydrolysis [3-2, 3-5, 3-9, 3-12].

Thioester-based AOs

Thioester-based AOs are sulfur-based secondary AOs that are often called *thiosynergists* when combined with primary AOs. Like phosphites, thiosynergists transform reactive peroxide groups into alcohol groups, supporting long-term thermal stabilization. For example, distearyl thio dipropionate (DSTDP) fights LTHA when used in combination with a hindered-phenol primary AO. However, due to the odors they create, sulfur-based AOs tend to be used less than phosphites [3-2, 3-3, 3-4].

3.3 FACTORS DETERMINING AO SELECTION

In materials-selection situations of all kinds, decisions about additives often come down to making compromises between desired performance and cost. Notably, decisions about AOs and stabilizers for POs are complicated by a number of factors, including:

- the basic application requirements, such as the anticipated melt-processing and service temperatures, whether an AO is needed more for melt stability or for long-term heat stability in service (or both), whether the resin will be in contact with food or not, and aesthetic concerns (such as restrictions of discoloration or odors);
- the additive's performance in terms of PO type (e.g., PP homopolymer or copolymer; HDPE, LDPE, LLDPE, and so on) and on the product form the PO is processed into (film, sheet, injection-molded part, rotationally molded part, etc.);
- interactions between an AO and other additives, including synergistic effects (in which two additives provide greater performance than the sum of each), and antagonistic effects (in which the summed effect is lessened as one co-additive reduces the effectiveness of another);
- the physical forms in which an additive is available (e.g., liquid, powder, or preblended forms), and how this form cost-effectively integrates with the point in the production process where the additive is added;
- the degree to which additive selection depends on the production practices at the resin supplier or compounder (such as whether the material can be purchased at adequately cost-effective volumes; whether a current supplier relationship exists for acquiring a material, whether the facilities are available for receiving and safely storing the additive, etc.);
- the degree to which the choice of additive depends on the expert opinions, experience, and "comfort level" of formulators (or the degree to which a new additive is established enough in real-world applications to justify the risk of using it);
- the potential environmental or health hazards of an additive during processing or in the final product—whether they be well-documented threats or suggested/perceived potential threats that are causing the industry to avoid using a given type of additive.

On a case-by-case basis, various other complications will also likely arise that will tend to limit a formulator's additive options.

Table 3.1 Some Commercial Primary AOs

Type	CAS Number	Commercial Grades[a]	Molecular Weight	Melting Point (°C)	Form[b]	PO Application Notes
Phenolic	6683-19-8	Anox 20, Songnox 1010, Irganox 1010	1178	110–125	p, g	Often referred to as “AO-1” in the literature, a general-purpose processing AO with LTHA for PE and PP
Phenolic	2082-79-3	Anox PP18, Songnox 1076, Irganox 1076	531	49–53	p, g	General-purpose AO for PE and PP
Phenolic	41484-35-9	Anox 70, Songnox 1035, Irganox 1035	642	63–73	p, g	Primary and secondary AO; long-term stability for black PE and PP (pipe and wire and cable)
Phenolic	1709-70-2	Anox 330, Irganox 1330	775	244	p, g	Long-term stability for PP and HDPE tape and pipe
Phenolic	32687-78-8	Lowinox MD24, Songnox 1024, Irganox MD 1024	553	221–232	p, g	Metal deactivator (copper chelating properties) for filled PP and wire and cable HDPE
Phenolic	847488-62-4	Songnox 1077 LQ	470	liquid	l	Liquid AO for PE
Phenolic	27676-62-6	Songnox 3114, Anox IC-14, Irganox 3114	784	218–223	p, g	For color-sensitive applications such as PP fiber
Hindered Amine	192268-64-7	Chimassorb 2020	2600–3400	120–150	pellets	Light stabilizer for POs also provides long-term thermal stability for filled PP articles
Lactone	181314-48-7	HP 136	350	97–130	n/a	Used in blends with other AOs for stabilizing PP and PE
Vitamin E	10191-41-0	Irganox E 201	431	liquid	l	Bio-friendly liquid AO for PE packaging; effective at low concentrations

Source: Adapted from [3-10, 3-11, 3-17, 3-18, 3-21]

[a] *Suppliers: Songwon Industrial Co. Ltd. (Songnox), Chemtura Corp. (Anox, Lowinox), Ciba Specialty Chemicals, Inc. (Chimassorb, HP, Irganox)*

[b] *p = powder, l = liquid, g = granular*

This section will attempt to explain the key AO selection issues being currently discussed in industry, including some application examples to illustrate the complexities of making additive decisions for heat stabilization. As a supporting reference, Tables 3.1–3.3 provide information about various heat stabilizers representing a range of commercially available products, including

Table 3.2 Some Commercial Secondary AOs

Type	CAS Number	Commercial Grades[a]	Molecular Weight	Melting Point (°C)	Form[b]	PO Application Notes
Phosphite	31570-04-4	Alkanox 240, Songnox 1680, Irgafos 168	646	181–187	p, g	Referred to as "P-1," general-purpose melt-flow and color protection during processing for PE and PP
Pentaerythritol diphosphite	26741-53-7	Ultranox 626, Songnox 6260	604	170–180	p, g	High-performance melt-flow and color protection during processing
Pentaerythritol diphosphite	154862-43-8	Doverphos S-9228	853	225	P	High-molecular-weight; thermal, color and hydrolytic stability for PP and PE
Phosphite	26523-78-4	Weston TNPP, Doverphos HiPure 4 TNPP	688	liquid	L	High-purity (low-nonylphenol) hydrolysis-resistant liquid AO for PE and PP
Phosphite	n/a	Weston NPF 705	n/a	liquid	L	Nonylphenol-free TNPP substitute for PE
Thiosynergist	123-28-4	Songnox DLTDP, Naugard DLTDP	515	38–41	p, f	General-purpose thiosynergist for PE and PP
Thiosynergist	693-36-7	Songnox DSTDP, Naugard DSTDP	683	63–69	p, f	General-purpose low-volatility thiosynergist for PE and PP
Thiosynergist	29598-76-3	Naugard 412S	1162	47	P	High-performance thiosynergist with LTHA in filled PP, and PP and HDPE pipe

Source: Adapted from [3-10, 3-11, 3-12, 3-13, 3-14, 3-18]

[a] Suppliers: Songwon Industrial Co. Ltd. (Songnox), Chemtura Corp. (Alkanox, Ultranox, Weston, Naugard), Dover Chemical Corp. (Doverphos), Ciba Specialty Chemicals, Inc. (Irgafos)

[b] p (powder), l (liquid), g (granule), f (flake)

widely used commercial AOs and their key applications. The tables indicate the wide ranges of molecular weights and melting temperatures of available AOs. (*Note*: generic designations for AOs such as "AO-1," "AO-2," "P-1," etc. are mostly avoided in this text because of occasional inconsistencies in these usages in industry literature.)

Table 3.3 Some Commercial AO Blends for POs

Type	CAS Number	Commercial Grades[a]	Form[b]	PO Application Notes
Phenolic + phosphite	40601-76-1, 31570-04-4	Anox BB2777	p, g	Processing and gas-fade protection for PP film and pipe
Phenolic + phosphite	6683-19-8, 31570-04-4	Songnox 11B	p	Melt-processing, color, and long-term thermal stabilization for PE and PP
Phenolic + phosphite	6683-19-8, 26741-53-7	Ultranox 817	pellet	Long-term prevention of molecular weight degradation and discoloration for BOPP film and HDPE rotational moldings
Phenolic + phosphite	2082-79-3, 154862-43-8	Dovernox D-711	p, g	High-performance stabilizer blend for PE and PP
Lactone + phenolic + phosphite	181314-48-7, 6683-19-8, 31570-04-4	Irganox HP 2215	g	Effective PP and PE processing stability for demanding applications
Lactone + amine + phosphite	181314-48-7, 65447-77-0, 31570-04-4	Fiberstab L 112	p	Process stabilization for low-gas-fade PO fiber applications
Hydroxylamine + phosphite	143925-92-2, 31570-04-4	Irgastab FS 301	g	Nonphenolic processing stabilizer with color and gas-fade control for PP fibers and moldings

Source: Adapted from [3-10, 3-11, 3-15, 3-16, 3-19, 3-20]
[a] *Suppliers: Songwon Industrial Co. Ltd. (Songnox), Chemtura Corp. (Anox, Ultranox), Dover Chemical Corp. (Dovernox), Ciba Specialty Chemicals, Inc. (Irganox, Fiberstab, Irgastab)*
[b] *p (powder), l (liquid), g (granule), f (flake)*

The case studies from industry inserted below show how critical factors in additives decisions come together and are (usually) resolved. These cases are based on published industry source materials and they show how different AOs fit certain situations. Obviously, even very similar situations in the future could significantly differ from these cases; thus, these stories can only at best be a guide for what kinds of benefits certain AOs may offer in a related case. Additives specialists are continually developing new packages and all appropriate suppliers should be consulted for their possible heat stabilization solutions.

3.3.1 Thermal and color requirements in melt processing and in service

Making basic, cost-conscious choices regarding AOs focuses on whether an AO provides all necessary stabilizing properties to the resin—without supplying

CASE 3.1 AOs TO PREVENT GAS FADING IN FIBERS [3-29, 3-30]

Problem: Especially when stored, PP fibers containing phenolic-based AOs tend to show problematic color changes due to gas fading.

Objective: A stabilization system that prevents gas fading.

Solution: A nonphenolic stabilizer replacement that limits gas-fading and color changes while providing equivalent or better process-stabilizing and performance properties.

Makers of PP fiber products have both practical shelf-life and use-life concerns about color formation, especially since traditional phenolic stabilizers in PP cause gas fading due to interactions between the phenols and atmospheric pollutants, such as NO_x (nitrogen oxide) gases. Fibers and knitted products have high surface areas exposed, making them more vulnerable to gas fading in the warehouse and elsewhere. Fibers that display gas fading often have to be sold at a discount or worse, but fiber that is resistant to gas fading potentially could be sold at a premium price.

Accordingly, Ciba Specialty Chemicals developed a new phenol-free stabilizer for fiber, designated Irgastab FS 533. To properly evaluate the product for gas fading, Ciba knitted PP yarn containing the AO at 0.12% loading into the form of fabric “tubes.” The resulting color formation measurements (yellowing index and ΔE)—both after fiber spinning and after exposure of the knitted fabric in a gas-fade chamber—were reportedly one-third to one-half those of traditional phenolic/phosphite systems.

The phenol-free alternative does come with a cost penalty, but the company argues that its expense can be justified through cost-avoidance, that is, it reduces the amount of off-specification material that would otherwise have to be scrapped because of color. This allows products containing the additives to be positively differentiated in the market.

Reported findings about the nonphenol additive show other potential benefits, including:

- Melt-flow index stabilization that is roughly equivalent to traditional phenolic AOs used in fiber grades.
- Better long-term thermal stability than phenolics.
- When formulated with a HALS additive, better UV light resistance than a phenol/HALS system.

more than what’s actually needed. Formulators and materials-specifying experts might consider whether melt-processing stability is the priority for a product or if long-term thermal stability is also needed. They might need to decide how much a key measurement of AO performance—such as melt-flow rate—can change after multiple processing passes. The product’s long-term exposure to heat may need to be decided on in terms of numbers that can be compared with actual performance data. And the amount of color change that is allowable needs to be defined to prevent unexpected changes in a product’s appearance. Such decisions might require, for example, choosing a higher-molecular-weight phenolic AO for withstanding higher service temperatures or for better color retention, or perhaps choosing a different kind of AO altogether (as in Case 3.1).

3.3.2 AO selection by PO type and finished product form

Supplier product guides often do provide guidance as to which AO fits which PO form and application [e.g., 3-10, 3-11, 3-23, 3-24]. However, typically, a given AO is not completely restricted to a narrow use; unfortunately, this complicates acquiring an understanding as to what *the best* commercial AO is for a particular application. Industry literature does suggest some specific AO products for specific materials in specific forms (as shown in Tables 3.1–3.3), whether they be fiber, film, extrude pipe, wire and cable coverings, or molded forms of PP, HDPE, LDPE, or LLDPE. But tapping the expertise and experience of additive suppliers may be crucial when deciding on the formula for a specific application (as in Case 3.2).

3.3.3 AO physical forms and handling

The form in which an AO is purchased depends on handling practices at the facility and its equipment and on the AO's pricing and availability, as well as on stabilization performance and on how well the additive can be dispersed in the polymer. Other unique characteristics about AOs may cancel out these factors, depending on the processing environment. For example, the hydrolysis of phosphite AOs in liquid form (such as TNPP) is typically lower than with phosphites stored and used in solid form, because the liquid form has a lower surface area exposed to humidity. (Yet TNPP has its own limitations in the marketplace that deter its use, discussed later) [3-13].

Other factors include worker exposure to AOs when feeding them in dust form and proper dispersion of the AO in the resin. Addressing both issues are preblended additives in pellet form, which have become increasingly available since the 1990s. In particular, Great Lakes/Chemtura's patented and trademarked "no dust blends" (NDBs) are concentrated less-hazardous forms combining multiple additives, without a carrier resin. Primary and secondary stabilizers neatly packaged as NDBs reportedly allow more controlled feeding and better dispersion, resulting in less than half as much increase in a resin's melt-flow rate after multiple extrusion passes, compared with formulations that use powder blends [3-9, 3-31].

NDBs can contain highly concentrated combinations of AOs, acid scavengers (metal stearates), light stabilizers (HALS and UV absorbers), and other additives. For delivering phosphite AOs, NDBs are said to provide better combinations of processing stability and hydrolytic stability than phosphites in powder forms. Also, NDBs reportedly allow the least-expensive phosphites to perform more effectively, saving the costs of using more expensive AOs in powder form, for equivalent performance [3-30].

3.3.4 Synergies and antagonistic interactions

One way to compare the synergistic and antagonistic interactions between different AOs is to observe how they behave when used in preblended forms, in which reactions can occur thousands of times faster than when they are mixed independently into the polymer. In terms of synergies, phenolic primary AOs and phosphite secondary AOs reportedly do work well together in these

CASE 3.2 WIRE AND CABLE AOs [3-4, 3-25]

Problem: Long-term heat stabilization of HDPE for wire and cable applications requires high levels of AOs, but these can interfere with intended cross-linking mechanisms and cause migration/extraction problems.

Objective: Determine which stabilizers provide the best properties for wire and cable HDPE.

Solutions: Phenolic AOs with sulfur-bridging in their chemical structure and AO packages containing metal deactivators.

PE grades used in wire and cable applications encounter high service temperatures, and the oxidizing conditions they face during service require high loadings of AOs to prevent degradation. AOs that are commonly used include high-molecular-weight phenolic and phosphite stabilizers for good long-term heat-aging properties. Unfortunately, some stabilizers slowly extract themselves from the polymer matrix and do not necessarily prevent degradation resulting from the polymer's reactions with the copper wire it protects.

Complicating this application is that these grades are typically, intentionally cross-linked for better performance. Cross-linking provides enhanced mechanical properties, resistance to stress cracking, and toughness for the wires and cables, and it is usually created via peroxide additions (or by electron beam irradiation or moisture curing with silanes). However, high levels of hindered-phenol AOs can interfere with cross-linking mechanisms. So researchers at Great Lakes Chemical Corp. (now part of Chemtura) compared the performance of structurally different phenolic AOs in HDPE wire and cable compounds to understand the trade-offs in performance.

The researchers studied the AOs' interaction with peroxide additions added at 0.5% to promote cross-linking at 180°C. To compare AOs, they looked at the torque of the equipment used for processing each formulation, which indicated how much each AO affected cross-linking. The maximum torque and maximum change in torque were compared with a formulation containing no AO.

The best processing performance was achieved by two low-molecular-weight AOs whose structures contain sulfur atoms that connect or "bridge" its phenolic components. In contrast, the nonsulfur AOs achieved equivalent performance only when they were loaded at much higher loadings (0.4%–0.6%, compared with 0.1%–0.2%).

Researchers also looked at the heat-induced embrittlement time of HDPE plaques made with the stabilizers during oven aging at 120°C. Generally, they found that high-molecular-weight AOs outperformed low-weight sulfur AOs in standard HDPE. However, when testing *cross-linked* plaques for embrittlement, the lower-weight sulfur AO was also found to be the most effective. The researcher surmised that one plausible explanation is that the sulfur-containing AO becomes grafted on the polymer backbone during cross-linking and does not volatilize or come out of the polymer matrix. (Along with heat-aging problems, migration and blooming of the AOs at the surface can make printing and coating the surface difficult, causing aesthetic problems and build up on tool surfaces.)

Finally, the researchers considered the PO's contact with copper wire over a cable's 50-year lifetime, and how this contact can contribute to "metal-catalyzed thermal failures." Although the real-world tendency of a cable to oxidize over the long term is difficult to measure in testing, these researchers' evaluations showed that phenolic AOs, combined with a metal deactivator or chelator (see Table 3.1, for example), are effective in providing long oxidative induction times at high temperatures.

In summary, the work indicated several conclusions about AOs for wire and cable POs:

- For non-cross-linked PE compounds, higher-molecular-weight AOs "provide adequate performance during processing and LTHA."
- However, in cross-linked PE and carbon black compounds, lower-molecular-weight, sulfur-bridged phenolic AOs provide comparable or better performance than high-weight AOs.
- An AO combined with a metal deactivator or chelator provides critical "synergistic" improvements against oxidation in LTHA.

blends. Phenolic/phosphite blend ratios from 20:80 to 40:60, for example, reportedly have provided the best improvements in melt viscosity, thus providing the best melt stabilization. By contrast, when HALS are added with phenolic AOs, the result can be multiple-times greater color formation [3-9].

Moreover, the hydrolysis of phosphite AOs is a handling problem that can be influenced by blended co-additives. Since hydrolysis is an acid-catalyzed reaction, hydrotalcite antacids blended in a pellet with the phosphite tends to help slow down hydrolysis [3-9].

And the effects of fillers or pigments in the compounded resin may also need to be considered in terms of how they interact with the performance of AOs. For example, recent studies have confirmed that certain grades of titanium dioxide (TiO_2), a commonly used light-scattering pigment in resins, have a tendency to "deactivate" phenolic stabilizers and cause UV-light-accelerated color changes. Researchers have noted that these acid–base reactions can be reduced with the addition of HALS or greater amounts of hindered-phenolic AO, or with the use of TiO_2 particles with a modified surface chemistry [3-32].

3.3.5 Cost

For many companies and applications, perhaps the most important factor is cost; unfortunately, cost is also the most elusive factor to discuss in concrete terms. Cost issues are rarely clarified in the technical literature, and suppliers typically guard their pricing information until it is necessary to quote it to a real customer (and then their quotes may depend not only on the additive type, but also its form and packaging, the total volume and purchased quantities, and perhaps on other volume-based agreements between a company and a given supplier).

Moreover, rapid changes encountered in recent years in fossil-fuel prices, raw feedstock prices, and the global chemical industry infrastructure and supply base mean that price relationships calculated today, likely, won't stay the same next year (or even the next month). However, a certain truism will always hold—decisions about additives based on the cost must always be weighed against what value the additive will actually provide for the resin product. In particular, a few specific trade-offs might be considered as follows:

- *Relative, per-resin-kilogram cost*: Formulators might determine what loading of an AO is needed and compare that with another product's loading to achieve equivalent performance—and then compare the net costs of each AO blend per kilogram of resin. A more expensive additive at a lower loading may actually be less costly to use than a common additive. For example, an AO blend containing a lactone, phenolic, and phosphite AO might show itself to be cost-effective when compared with a simpler alternative.

- *Flexibility*: Inventories affect costs; thus, an issue may exist as to whether sourcing or stocking multiple additives for different applications is cost-effective when one additive at different loadings may cover several applications.

- *Customer acceptance*: For example, for a given human-contact application, the benefits of being able to tell customers that a resin uses a "bio-" or "green"-sounding vitamin E AO may outweigh any cost penalties of sourcing this additive. Inversely, using an additive package that is susceptible to gas fading may cause problems for the end user customer in the long run, threatening future business relationships.
- *Process productivity/cost reductions*: Are there processing costs that the choice of a premium additive could reduce, offsetting the additive's cost and providing even greater returns? For example, can line speeds be increased with the additive? Scrap reduced? Higher recycled content levels made feasible by a stronger AO? (See Case 3.3, for example.)

3.3.6 Environmental, food-contact, and health and safety considerations

Food-contact approvals from the US FDA and other agencies have been achieved for most of the relevant AOs available from major suppliers. Nonetheless, since AOs can be extracted from POs, they are always under scrutiny from regulatory agencies as to any possible health effects. Concerning health and "green" issues with additives, a proactive rather than reactive stance benefits companies that produce or use resins, so that they might anticipate controversies that could arise concerning particular additives or materials that they are accustomed to using. Such proactivity could allow producers time to find substitute additives, in case objective arguments about the current additives in question are ineffective at quelling fears and negative customer perceptions about a company's materials and products.

For example, concerns exist about the environmental effects of nonylphenol from the hydrolysis of TNPP, first discussed in Section 3.2.2. These concerns have led some producers to develop liquid TNPP substitutes that can be guaranteed as being inherently nonylphenol-free, such as a liquid phosphite AO from Chemtura (Weston NPF 705 in Table 3.2). Alternatively, a formulator might choose a "high-purity" TNPP that is said to offer with much lower levels of free, volatile nonylphenol. Producers such as Dover Chemical argue that such a TNPP can be cost-effectively used because of the greater percentage of TNPP in each lot. Decisions about using these kinds of alternatives, inevitably, require comparing the costs of using an unfamiliar AO with the possible indirect costs of being known as a user of materials that are associated with environmental risks or harm [3-7, 3-13].

Meanwhile, more POs are demonstrating the value they can bring to medical applications and products that come into intimate contact with the human body. Thus, perhaps even more pressure is falling on additive and resin producers to

CASE 3.3 AOs FOR EASIER FILM PROCESSING [3-8, 3-26]

Problem: To compensate for the penalties of higher resin costs, producers of biaxially oriented PP (BOPP) film seek productivity improvements in their melt-processing and converting operations.

Objective: Determine which processing benefits new AO chemistries can bring to this industry segment.

Solution: New stabilizer packages containing lactone AOs expand BOPP film's processing window, providing opportunities for increased line productivity.

Film producers make the most money by running their film lines at the highest possible speeds while producing a product with consistent properties. One approach for achieving enhanced productivity may lie in the use of improved polymer additive packages. Thus, developers from Ciba Specialty Chemicals have come up with AO alternatives for optimizing BOPP film-line productivity.

For BOPP, the right type and amount of phenolic and phosphite AO depends on the processing temperatures they encounter (typically 210–300°C). The higher the temperature is, the more processing stabilizer is needed to prevent changes in rheology and melt strength. Pressures to increase line speeds to cut costs demand higher extruder temperatures and more flexibility in extruder settings; this requires better melt stabilization. At the same time, in this more-demanding processing environment, a good AO system must be able to prevent additional degradation in the recycled edge-trim material used in the process, and be less sensitive to variations in recycled material use.

With BOPP, any lack of stability of the resin will be evident during film stretching, downstream from the extruder. By stabilizing the polymer's molecular weight distribution, a good AO can help widen the stretch processing window in terms of its allowable temperature range and in terms of the amount a film can be stretched without breaking or sagging. And of course, the AO must improve these characteristics while preventing color formation.

Given these concerns, Ciba determined that lactone-based chemistries can improve performance when added to conventional stabilizers (see Table 3.3, for example). Lactone's carbon-centered free-radical stabilization mechanism (see Figure 3.1) helps increase the efficiency of phenolic primary stabilizers, resulting in a polymer/stabilizer system that is less sensitive to variations, with reduced color formation as well.

In BOPP production trials, researchers reported that the inclusion of a "boosting" lactone stabilizer ingredient provided similar film haze, clarity, and elongation properties as with common phenolic/phosphite-based AO blends without lactone. However, the lactone blends did this at 800–1000 ppm loadings, compared with 1500 ppm for the control blend. Moreover, the lactone blends created films with higher elastic modulus values, in both the transverse and machine directions, possibly due to better thickness uniformity and control in processing.

The lactone blends also expanded the processing window for film stretching. The highest machine-direction stretch ratio before break for the two lactone-grade films tested was 5.4:1 and 5.7:1, compared to 5.1:1 for the non-lactone film. And in the transverse-direction stretching, the temperature window expanded by 16°C–17°C, compared with 14°C for the non-lactone film.

"This improved performance may be related to the better ability of the lactone-boosted system to protect the molecular architecture of the resin during processing," reported the researchers. They suggest that the lactone prevents chain-scission processes from destroying the "rich web" of long PP "tie molecules" that maintain film stability during stretching. This promotes strain-hardening and deters necking and stress concentrations.

The earliest commercial users of lactone AO packages for BOPP have reportedly realized one or more of the following:

- improved "on stream" time at high line speeds, and less downtime from less breakage,
- easier line start-ups,
- less scrap,
- greater potential downgauging opportunities,
- better film quality and color overall,
- less sensitivity to recycled material in the process.

CASE 3.4 BIOCOMPATIBLE AOs [3-5, 3-27, 3-28]

Problem: Stricter regulations and the greater use of POs for medical and human body-contact applications require biocompatible grades of materials.

Objective: Develop biological-based AOs for these expanded uses.

Solution: Vitamin E, an effective "bio-friendly" AO alternative.

As medical products made from POs come into even more intimate contact with the human body, concerns are likely to increase about additives that exude to the surface of the plastic. For primary heat stabilizers, this opens opportunities for additives that are both "generally regarded as safe" and biological in nature, such as forms of vitamin E (α-tocopherol), one of the most effective AOs in living biological systems.

In the 1990s, vitamin E was first considered as a possible heat stabilizer for plastic blood-storage containers, since it is nontoxic and appears to suppress the rupture of red blood cell membranes (hemolysis). Vitamin E has since become commercially available for stabilizing a number of PE applications.

One recent use of vitamin E is by resin supplier Ticona in a grade of ultra-high molecular weight PE (UHMWPE) used for orthopedic implants in joint replacements. This grade, in particular, must be able to resist intense sterilization treatments without oxidizing. The vitamin E is also said to improve implant wear by preventing oxidation of the implant within the body. Moreover, the oxidation products of tocopherol do not appear to show any biological activity in living systems.

With its antioxidizing reactivity and consumer-friendly perception, vitamin E could be brought into less-specialized human-contact applications—to the extent that its tendency to yellow POs can be reduced by phosphite co-additives. And although it is more costly per kilogram, this liquid AO requires only about one-quarter the loading percentage of standard phenolic AOs.

confirm the safety of their formulations, and to develop new biocompatible additives.

Examples such as Case 3.4 only scratch the surface of all the complicated decisions industry experts are making about additives. Future chapters, here, will present other similar cases, some of which inevitably affect the choice of AOs, given the potential for interactions between additives.

CHAPTER 4

Ultraviolet Light Protection and Stabilization

UV light can be particularly damaging to the polymer backbone of POs, and for UV-exposed products, this degradation takes precedence over heat-induced degradation focused on in the previous chapter. To varying degrees, UV light especially affects products that have most or any of their service lives outdoors. It can cause yellowing or otherwise unintended color changes, while also degrading the materials physically, causing surface chalking, cracking, loss of gloss, and lower mechanical properties (Figures 4.1 and 4.2). Moreover, UV light that is allowed to pass through a packaging material may damage the product contained inside, and even lower the nutritional value of contained foods or beverages. Thus, UV-blocking, -absorbing, and -stabilizing additives receive much deserved attention from additive developers and users [3-3, 4-1].

This chapter provides a basic description of UV's effects on POs, and how different additives interfere with UV degradation. The different roles and mechanisms of various commercially available additives are related to each other in terms of effectiveness, relative costs, and interactions with other additives. (Since UV stabilization is an ever-developing field of continuously "new and improved" additives, emphasis will be given to more recently commercialized additive types.) UV stabilizer use in different PO applications will be presented, and case studies will show how companies have been able to fight the effects of UV in real applications.

In summary, this chapter will address these questions:

- (4.1) How does UV light damage polyolefin polymers? How do anti-UV additives help protect polymers?
- (4.2–4.4) What are the practical differences between UV blockers, absorbers, and stabilizers?
- (4.5) What are some important factors to consider when choosing commercially available light stabilizers, and what are some examples of how they have been used in specific situations to create resilient, weatherable polyolefin products?

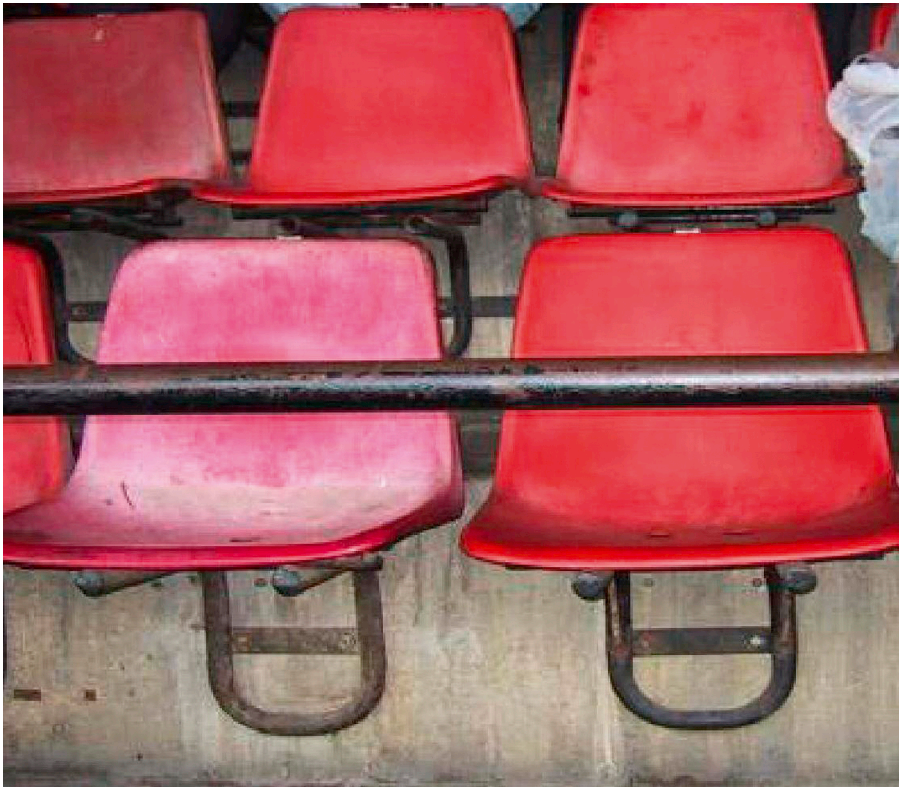

FIGURE 4.1

Effects of outdoor UV exposure. Stadium seating in particular can show discoloration and whitening (at left) from UV light exposure. (Photo reproduced by permission of Ciba Corp.)

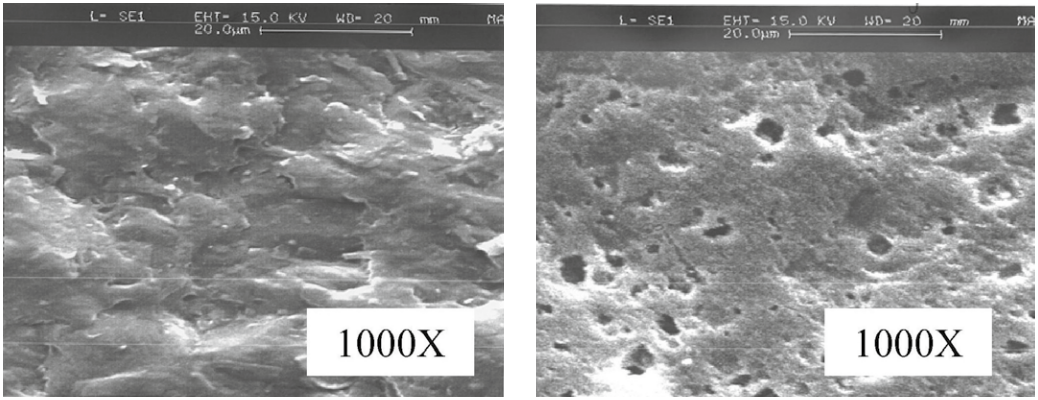

FIGURE 4.2

Surface degradation from UV exposure. Micrographs show how 6000 hours of UV weathering degrades a sample's surface (at right), causing pores and loss of gloss, compared with the unexposed sample on the left. (Photos reproduced by permission of Ciba Corp.)

4.1 UV DEGRADATION OF POs

The initiation of degradation via UV light depends on the presence of UV-absorbing species (chromophores) mixed in with the polymer. Since saturated polyolefin molecules do not themselves absorb much UV light directly, the most damaging UV is absorption by chromophores such as catalyst residues, pigments, or generally any organic molecules containing double bonds. These molecules release some of the UV energy they absorb by breaking bonds and releasing free radicals, which begin a degradation cycle similar to the autoxidation processes discussed in the previous chapter. This degradation cycle, first summarized in Chapter 3, is repeated below in slightly different terms:

- UV energy is absorbed by chromophores such as pigments or catalyst residues, creating broken bonds and free radicals (R•).
- Oxygen combines with free-radical species to create new species, including peroxy radicals and hydroperoxides, which are reactive with the polyolefin chain (RH) itself (O_2 + R•→ROO• + RH→ROOH + R•), as well as other fragment species (H_2O, H_2, H_2O_2).
- The hydroperoxides (ROOH) in turn are themselves reactive and create new free-radical species, such as hydroxy and alkoxy radicals (ROOH→•OH + RO•).

Aided by the photo-oxidation from UV light energy, the degradation process results in chain scission (predominant in PP) or cross-linking reactions (predominant in PE). Photo-oxidation mainly takes place at the surface of an unprotected resin, but it can occur deep within the solid material if the UV energy is not blocked by elements within the resin. Either way, the resin changes induced by this degradation can range from minor to catastrophic; for example, it has been proposed that chain scission in particular leads to increased crystallization in the polymer and creates internal and surface voids, resulting in cracks, embrittlement, and loss of gloss [4-7].

POs are generally degraded by UV wavelengths of 290–300 and 310–340 nm (310–360 nm for PP). Without some sort of internal protection or stabilization, POs can lose properties relatively quickly under sunlight or UV exposure. For instance, HDPE in the form of 1.5-mm plaques can lose 80% of its impact strength in just 2000 hours of accelerated weathering [4-2].

Different polyolefin structural forms react differently to UV. Highly branched LDPE tends to degrade more readily than LLDPE or HDPE, and overall, degradation takes place more easily within the amorphous phase of a polymer than in the crystalline phase. Moreover, PE and PP photo-oxidation behaviors are different enough that the same additive approach for protecting PE may not work the same in PP, even in the same applications. For example, a common stabilizer in a thin section of PE can be far more effective than when it is used in thin PP. Likewise, other stabilizers may be more or less effective, or change a product's color more or less, when used in PE or in PP. And even different forms of PP—homopolymer and copolymer—can differ in their sensitivity to UV when using the same stabilizer [4-3, 4-7, 4-21, 4-26, 9-30].

There are several ways in which additives prevent or interrupt the degradation processes initiated by UV. Bulky additives act as shields, physically screening or blocking UV light from penetrating deeply into the polymer. These additives and other organic chemicals also partially absorb the UV energy themselves (or the UV energy stored by chromophores) and release it in ways that are not harmful to the polymer. Or stabilizers may interrupt the degradation cycle itself, by scavenging free-radical species or the peroxides they create. Table 4.1 summarizes the various kinds of additives and their mechanisms.

4.2 UV BLOCKERS, SCREENERS, AND ABSORBERS

The terminology used when referring to UV screeners and absorbers (UVAs) sometimes overlaps. UV screeners physically block, reflect, and scatter UV radiation while also absorbing it to some degree, while nonblocking organic UVAs efficiently absorb UV energy and convert it to harmless forms.

To be effective, an absorber/screener should interact with UV light across the damaging part of the spectrum, ideally from 250 to 400 nm wavelengths. (Absorbing light above 400 nm, in the violet-blue part of the visible light spectrum, tends to create a shift toward yellow in the resin color.) UV blockers or screeners typically include carbon black and other pigments or fillers that make resin opaque. Titanium dioxide in particular is a useful pigment/filler, since, like carbon, it is inexpensive and can efficiently block and absorb some UV across the damaging range of the light spectrum. (For this reason, some grades of TiO_2, especially those designed for UV stabilization, are referred to by some suppliers as UVAs.) [3-5]

4.2.1 UV-blocking and -absorbing fillers and pigments

Along with blocking and scattering UV light, useful UV-stabilizing pigments and fillers absorb some UV and convert it into heat. However, these are the least effective of UV additives—their usefulness lies in their cheapness, stability, and simplicity for opaque or semi-translucent applications.

Carbon black absorbs all wavelengths of UV light and converts it into heat, while physically blocking UV penetration. For UV-stabilizing effectiveness, various grades of carbon black can be compared in terms of impurity level (affecting taste or odor), particle size, dispersability, and moisture absorption in the compound (which can cause defects in the final part) [4-4].

Table 4.1 Some Commercial UVAs and HALS-Based Light-Stabilizing Additives [4-7, 4-13, 4-24, 4-26, 4-27, 9-30]

Generic Designation	CAS Number	Commercial Grades*	Polyolefin Application Notes
UVA-1	1843-05-6	Chimassorb 81, Cyasorb UV-531	Food-use compliant
UVA-2	25973-55-1	Tinuvin 328, Cyasorb UV-2337	Molded PP/TPO; low metal interaction
UVA-3	3896-11-5	Tinuvin 326	Food-use compliant
UVA-4	2725-22-6	Cyasorb UV-1164	Low volatility, high solubility in POs
UVA-5	5232-99-5		
UVA-6	178671-58-4		Food-use compliant
HALS-1	52829-07-9	Tinuvin 770, Uvinul 4077	Molded PP
HALS-2	167078-06-0	Cyasorb UV-3853	Low-molecular-weight; color and gloss protection; synergies with high-weight HALS and UVAs
HALS-3	124172-53-8	Uvinul 4050 H	Low-molecular-weight, monomeric; FDA food-contact approved
HALS-4	64022-61-3		Lower basicity
HALS-5	91788-83-9		Thin PP
HALS-6	129757-67-1	Tinuvin 123	Liquid
HALS-7	71878-19-8, 70624-18-9	Chimassorb 944	High-molecular-weight, less migratory
HALS-8	65447-77-0	Tinuvin 622	High-molecular-weight and oligomeric; low volatility/migration
HALS-9	82451-48-7	Cyasorb UV-3346	High-molecular-weight, oligomeric; long-term, low-color; 1- to 2-year greenhouse films
HALS-10	193098-40-7	Cyasorb UV-3529	Low acid reactivity, low volatility, compatible with other UVAs/HALS; artificial turf and greenhouse films
HALS-11	152261-33-1	Uvinul 5050 H	Low basicity and interactivity with processing aids and paint systems
HALS-12	106990-43-6	Chimassorb 119	High-molecular-weight, monomeric; low volatility/migration; color retention in pigmented POs
HALS-1 + HALS-7	see above	Tinuvin 791	
HALS-7 + HALS-8	see above	Tinuvin 783	Tapes and thin products
HALS-8 + HALS-12	see above	Tinuvin 111	
HALS-9 + UVA-4	see above	Cyasorb THT 4611	Long-term protection, efficient, low-color, extraction-resistant

**Trademarked product names from Ciba Specialty Chemicals (Chimassorb, Tinuvin), BASF (Uvinul), and Cytec Industries (Cyasorb).*

Inorganic pigment fillers such as titanium dioxide, zinc oxide, and cerium and iron oxides block and scatter UV light and/or convert UV energy into heat. These pigment/filler preparations do not migrate through the resin like many organic UV stabilizers. TiO_2 in particular is often used for its reflective or scattering qualities that prevent UV light from reaching chromophores far below the resin product's surface. Depending on the particle size and absorption characteristics desired, loadings of these fillers may be needed at up to a few weight percent concentrations for UV resistance [3-3, 4-1].

Generally, smaller sizes of nonagglomerated filler particles are the most effective at blocking UV. For example, as reported by pigment supplier Croda, 200-nm pigment-grade TiO_2 is a relatively poor barrier to UV and has poor absorption, in comparison with 100-nm "ultrafine" grades that provide greater UV absorption and allow more visible light to be transmitted (increasing transparency and lowering haze). These particles are also said to resist re-agglomerating over time (reducing product clarity), unlike other fine metal oxide products. An alternative to TiO_2, zinc oxide, provides less absorption over the UV spectrum, but it does not catalyze chemical reactions as TiO_2 does, so it is better for long-term applications. These additives are supplied in liquid, concentrate, and masterbatch forms [4-1, 4-5].

Screeners have their pros and cons. They may reflect damaging light near the surface, in effect concentrating the energy in the resin there and causing severe surface degradation. However, various UV-blocking pigments or fillers can be combined with more efficient organic light stabilizers for greater protection, and to prevent pigment fading. But results depend on the application; some studies have even shown these fillers to be *more* effective than organic UVAs for retaining gloss and impact strength. Complicating matters is that some fillers may deactivate organic stabilizers or otherwise negatively interact with them [4-2, 4-21].

4.2.2 Organic UV absorbers

Various organic molecules absorb varying amounts of UV wavelength to different degrees, across the spectrum of UV radiation that reaches the surface of the earth. Organic UVAs are transformed by UV into excited species that manage the UV energy they absorb through proton/electron transfers and molecular (tautomeric) rearrangements. Electrons are moved by UV to create a tautomer of the absorbing molecule, where heat energy is released and the electrons transfer back to the original UV-absorbing form. Organic absorbers are effective but degrade over time, losing effectiveness. UVAs used in POs are based on several benzene-ring-based chemistries, including the following:

- benzophenones, which absorb UV from 230 to 390 nm and include products referred to in the industry as UVA-1;

- benzotriazoles (UVA-2 and UVA-3), a complicated-to-manufacture type of UVA which absorbs UV more strongly than benzophenones, especially from 280 to 390 nm;
- triazines (UVA-4), offering long-term UV stability especially when combined with HALS;
- phenyl or aryl esters (such as salicylates or benzoates), sometimes referred to as UVAs because they absorb UV at lower UV wavelengths.

The effectiveness of these UVAs can be gauged with the Lambert–Beer equation, $A = \varepsilon bc$, in which absorbance (A) is the product of the molecule's absorptivity (ε), the light's path length (b), and the UVA's concentration (c) [4-7, 4-21].

Trade-offs may be necessary when choosing a UVA. As with other organic additives, low-molecular-weight UVAs may be effective absorbers but have high volatility and can be lost during processing or later on. Other UVAs may have low volatility at high temperatures, but supply only marginal absorption—though they may provide good color retention (nonyellowing) [1-1, 3-5, 4-7].

4.3 QUENCHERS AND PEROXIDE DECOMPOSERS

Certain molecules help absorb UV energy indirectly by deactivating damaging molecules that are energized by UV light. Excited state quenchers transfer energy from activated chromophore carbonyl groups and convert it into heat or lower frequencies of light. These additives have traditionally been based on organic nickel complexes. They can however produce an unwanted color, and nickel-based quenchers have been used less as concerns about heavy metals in the environment have increased. Still, they can boost the effects of other UV stabilizers in the compound [3-2, 3-3].

Other secondary additives can be used to react with the hydroperoxides created in the UV-induced degradation cycle. Hydroperoxides create free radicals when exposed to light, resulting in unwanted changes in the polyolefin molecular skeleton. They are deactivated by agents referred to in Chapter 3 as secondary AOs—organophosphorous compounds that decompose hydroperoxides into harmless alcohols.

4.4 HALS: FREE-RADICAL SCAVENGERS

4.4.1 Overview of HALS

As with radical-scavenging AOs, HALS (or sometimes more concisely called hindered amine stabilizers, HAS) deactivate free radicals created by reactions with UV light. HALS has been a successful additive technology by any measure, enabling many outdoor PO applications that would otherwise be impossible. The HALS family ranges from low-molecular-weight, migrating HALS (MW < 1000) to less-volatile, higher-weight oligomeric HALS. (As with organic UVAs in industry nomenclature, common commercialized HALS molecules have been assigned simple designations, with HALS-1 through HALS-6 including more traditional, lower-molecular-weight molecules, and HALS-7 and above including heavier, nonmigrating, newer chemistries; see Table 4.1) [4-7].

HAS are relatively costly but, fortunately, are effective at low concentrations (<1%). This efficiency is due to a still not fully understood regenerative process cited by experts to explain HALS' UV stabilization abilities. In short, their mechanism depends on the initial oxidation of the HALS into a form that interferes with the propagation stage of degradation; it may be summarized as follows:

- A HALS molecule is oxidized by reacting with a hydroperoxide (produced from degradation), creating a nitroxyl radical (NO•).
- NO• reacts with ("scavenges") a polymer radical or other free radical (R•), deactivating it and forming an alkoxy amine (NOR).
- NOR reacts with a peroxy free radical (ROO•) to create a new nitroxyl radical that can be used again in the cycle.

This cyclic process, along with the fact that HALS are compatible with and relatively nonextractable from the resin, makes them valuable for imparting long-term UV resistance. They effectively delay the degradation of the properties of an exposed polyolefin, and a critical measure of their effectiveness is the speed with which a HALS compound is oxidized into its useful nitroxyl radical form. However, HALS can also react with other stabilizers, flame retardants, or other additives, as discussed in Section 4.4.2. These reactions can lead to color and property changes [1-1, 4-7, 4-12].

HALS molecules differ in terms of UV absorbance across the UV spectrum, migration rates, and interactivity with other additives, even though they are based on related tetramethyl piperidine chemistries. High- and low-molecular-weight HALS may be combined with each other into blended products that provide a balance of stabilizing properties. Or they may be combined with UVAs to prevent UV light from doing damage deep within the resin product [4-2].

A HALS molecule's active amine group is typically hydrogen (NH), alkyl (NR), or alkoxy (NOR) based. Traditional HALS are basic (nonacidic), and their effectiveness is reduced by acidic environments; thus less-basic, NOR-group HALS molecules have been developed as the latest generation of radical scavengers. Especially when used in combination with UVAs, for example, Ciba's Tinuvin XT 850 stabilizer is a NOR HALS that reportedly resists degradation and retains more gloss than other HALS. This reportedly has been shown in testing at extremely high UV exposures (9500 kJ/m^2) at a 0.2% HALS loading, in natural PP. Efforts toward developing this level of UV protection are driven by the desire of the automotive industry for more weatherable PP/TPO exterior parts (see Case 4.2 and Section 4.5.2) [3-2, 4-6, 4-7].

4.4.2 Interactions of HALS and other additives

Perhaps the most complicated factor in using a HALS is dealing with its chemical reactivity with other materials the additive encounters. (This interactivity is also the HALS issue that most recent relevant industry literature seems focused on.) A HALS might interact with AOs, TiO_2 (which itself has a catalyzing effect when exposed to UV), flame retardants, external materials, other light stabilizers, or any acidic additive, such as certain processing aids.

UVAs and other light stabilizers

It is important to understand how different light stabilizers used in combination support each other's effectiveness. Combinations of low- and high-molecular-weight HALS may provide overall better long-term oxidative stability to a product. Alternatively, forms of benzoate stabilizers, though consumed in oxidation reactions, are known to enhance the effects of HALS while providing long-term heat stabilization. And adding UVAs to HALS and AOs provides a fuller range of protection for pigmented or thick parts [4-7, 4-8].

AOs and heat stabilizers

Conventional phenolic primary AOs have also been shown to provide synergies with HAS, though color formation and gas fading may result from their interaction.

The acidic reaction products of thiosynergist secondary AOs can react with basic HALS, reducing stabilization effectiveness. (However, the product form may determine the interaction; for example, for fiber products in dry conditions, the blooming of DSTDP thiosynergist to the fiber surface may have a positive effect on the HALS' effectiveness.) It has been suggested that when a HALS interaction is a problem, a high-molecular-weight HALS can effectively replace the thiosynergist by acting both as a heat and light stabilizer (such as HALS-12). Moreover, alternatives such as NOR HALS and hydroxybenzoate stabilizers do not interact with thioesters, and benzoates are synergistic with HALS in offering long-term heat and light stabilization at low concentrations overall [3-9, 4-3, 4-7, 4-8].

Titanium dioxide and other pigments

TiO_2 pigment particles are known to provide sites for chemical reactions that can deactivate stabilizers. Thus, they can accelerate product discoloration from

UV-induced reactions with common phenolic AOs (with amines present), unless the pigment particle surface is chemically modified with a coating of alumina, silica, and/or a compatibilizing agent. Also addressing this issue, some HALS products are specifically designed to have no effect on the surface quality of white (TiO_2 pigmented) products; this has been reported for BASF's Uvinul 5050 H HALS with white TiO_2/LLDPE film, for example [3-31, 4-26].

Colored pigment performance can be affected by HALS, causing unwanted color shifts in the polyolefin product. These reactions usually decrease the strength of the color, but there is little consistency in the way different HALS products affect different colors in different resins. Lighter colorants that use TiO_2 may provide better property retention than dark colorants. But different degrees of color shifting may take place at different rates under UV weathering testing, depending on the stabilizer package used with the colorant. For instance, a certain HALS may prevent the fading of one organic pigment, but not another; another HALS may increase the color fading of the same pigments. Moreover, certain HALS products may interfere with pigment dispersion and cause agglomeration, weakening color strength. Here as in other cases where these complicated interactions between additives take place, expert advice states that a complete additive formulation may need to be adjusted when just one component is changed [4-9, 4-11, 4-13, 4-21].

Flame retardants

HALS with basic chemistries can be deactivated by acidic halogenated flame retardants; the acidified HALS is then not effective in radical-scavenging reactions. A less-basic HALS (e.g., HALS-4) is less affected [3-2, 3-5].

Processing aids

Especially at higher processing temperatures, melt-processing aids can interact with HALS. With metallocene LLDPE film, for example, fluoroelastomer internal lubricants (especially when used in combination with abrasive pigments) have been observed interacting with HALS. The interaction may require a higher lubricant concentration in compensation so that the die surface is sufficiently coated and melt fracture does not occur. A low-interacting HALS, such as BASF's oligomeric Uvinul 5050 H (HALS-11), has also been proposed as a solution [4-12, 9-31].

Acidic coatings or foreign materials

As with flame retardants, the basicity of a HALS overall can be a problem that prevents its use completely in certain cases. For example, when used in agricultural films, HALS can be deactivated by acidic agricultural chemicals (e.g., pesticides) or gases the film is exposed to. Similarly, highly basic HALS can react strongly with acid-cured coatings, such as those used in the painting of automotive TPOs; a NOR HALS that resists acidification has been proposed as a solution [4-7, 4-12].

Nanofillers

As more modified clays or other nanofillers are being used in POs, users are discovering their synergistic effects with stabilizers. With the right thermal stabilizer, compatibilizer, and UVA, the physical properties of a PO nanocomposite, such as impact strength, reportedly can be maintained over thousands of hours of extended weathering exposure. For example, stabilizers based on a "nanoparticle synergist" are said to increase UV protection by 20% compared to standard stabilizer masterbatches for POs, according to supplier Alok Masterbatches Ltd. [4-15, 4-16].

4.5 FACTORS DETERMINING STABILIZER SELECTION

Highly UV-stabilized POs may contain combinations of most or all of the ingredients mentioned above; the question then becomes: Which kinds of stabilizers are truly needed, and in what proportions?

4.5.1 General factors

Along with the interaction effects of HALS described above, general factors for choosing a UV stabilizer package include:

Part thickness

Thin films, sheets, fibers may be more susceptibly damaged by UV since a greater proportion of their resin bulk lies near the part surface. Accordingly, nonextractable, high-molecule-weight stabilizers are more useful in thin products. UVAs are less effective in thin sections, since they require a significant path length to be effective. Conversely, for thick sections, UVAs and fast-migrating, low-weight stabilizers are useful for protecting at the surface, where the effects of UV light are the greatest [4-3, 4-7].

Migration and extraction

Polar stabilizer molecules are not compatible with nonpolar POs, leading to the potential of migration and extraction losses, especially with low-molecular-weight monomeric stabilizers. However, for intense outdoor exposure applications, it might be desirable to use stabilizers that migrate toward the surface of the product. It is near the surface where their effects are most needed, but these low-weight molecules can bloom and be lost over time, or be absorbed or *adsorbed* by fillers such as calcium carbonate or talc. Thus, a more reactive but more extractable HALS such as HALS-1 may be less effective than a less-reactive but more soluble HALS, like HALS-2 [4-7].

Tested UV weatherability

Accelerated UV weatherability tests of anti-UV formulations use artificial sources of UV light, such as standardized xenon-arc lamp or sun lamp testing. However, this testing may provide different results from what is found in service with an actual part created with production-processing conditions. For example, the testing time it takes for an exposed sample to lose 50% of its elongation properties (a common measure of light stability) may differ greatly depending on the test. There is no perfect testing solution: outdoor testing (e.g., "Florida" exposure tests) is time-consuming, while accelerated testing may provide misleading conclusions about how a stabilizer system will actually work. Thus the most well-informed approach requires taking into account data that correlate accelerated weathering tests with actual outdoor field testing. One rough estimate suggests that about 16,000 hours (<2 years) of Weather-Ometer lamp testing is equivalent to about 12.5 years of outdoor exposure in Florida [4-2, 4-13, 4-19].

Food-contact use

Various light stabilizers are food-contact compliant, making them fit for food packaging materials (or for materials that may come into contact with materials that themselves must be compliant). Among organic UVAs, UVA-1, -3, -4, and -6 are FDA compliant for use in PP. Nonmigrating additives are more likely to be compliant with US FDA or European Union regulations; thus higher-molecular-weight HALS tend to be more compliant than migrating HALS. However, a monomeric low-weight HALS-3-based stabilizer (BASF's Uvinul 4050) is reportedly now FDA compliant for nonalcoholic food-contact use at up to 0.25% concentration in PP. Developments like this show that approval status can change over time and should be checked periodically [4-7, 4-10, 4-18].

4.5.2 Light stabilizers for specific PO applications

Fibers, tapes, and yarns

Fibers and related thin polyolefin products have high surface areas in relation to their volumes; thus they require nonmigrating, nonvolatile, high-molecular-weight stabilizers. These materials are also highly pigmented for aesthetic, colorful outdoor carpeting and upholstery, so they also require very effective stabilizers that do not interfere with pigment dispersion. Fiber manufacturing also requires high productivity, with stabilizers that do not increase melt flow variations or filter blocking. Slit tapes are used in more utilitarian ways: PP tapes for bags, sack, and bulk containers for chemicals or food, and HDPE tapes for tents and tarps. These uses require stabilization for maintaining physical properties [4-13, 4-15].

Moreover, for PP tape manufacturing with water bath quenching, the water-carryover effect can also be affected by choice of stabilizer (where the additive can change the surface tension of the tape and cause water to remain on the tape, causing production problems). Depending on processing haul-off speed requirements, trade-offs and compromise may be needed in the use of a HALS; for example, a high-efficiency HALS-7 reportedly has a higher water carryover than other HALS or HALS blends that attract water less, but which may be less effective as stabilizers. Optimized stabilizer blends for these applications include both low- and high-molecular-weight HALS for both heat and light stability, such as Ciba's Tinuvin 783 (for PP and HDPE) and 791 (for PP) [4-3, 4-12, 4-13].

Tapes or yarns for artificial grass sports fields require attributes of both pigmented textile fibers and woven tapes: long-term nonfading color and physical properties. This synthetic turf is popular because of its low maintenance costs, but the plastic must last several years under harsh use conditions for the high installation costs to pay themselves back as savings. Case 4.1 reviews such an application of PE turf [4-12, 4-14].

Exterior automotive moldings

In the drive toward lighter, less-costly cars, PP and TPO will be called on for more automotive exterior and interior moldings and panels. Current exterior applications are typically painted, and as mentioned above, less-acid-inhibited HALS are being developed to resist acidic paint-cured systems used in automotive. But there will be increasing pressure to remove this paint-processing cost and use pigmented PO compounds that are directly exposed

CASE 4.1 ARTIFICIAL TURF STABILIZATION [3-30, 4-14]

Problem: Artificial turf made from LDPE yarn has limited use in sunny, southern-latitude countries.

Objective: Better long-term color retention and mechanical properties.

Solution: A stabilization package that includes a UV absorber.

Common outdoor PO applications may have special needs, depending on the geographical region they are found in. Artificial turf for outdoor athletic fields, for example, are pigmented PE applications that are expected to survive heavy exposure to UV light, foreign substances, and physical abuse over 10 years or more—even in regions with strong sunlight exposure year-round.

Turf fields made from LDPE yarn used in southern or equatorial regions are special cases. Thus additive supplier Cytec Industries developed a new stabilizer package that includes a UV absorber to protect the color and physical properties of the yarn. Company researchers reportedly tested the formulation using both accelerated weathering and field weathering in Brazil.

Compared with PE yarn containing a stabilizer package used in European turf fields, the new stabilizer package is said to provide better color and property retention. This reportedly is apparent even after only one year of outdoor exposure. Researchers also confirmed the stabilizer package's superiority after exposing the turf to common field materials that might accelerate its degradation under sunlight, such as chlorine bleach used for disinfection and cushioning particles made from recycled-tire crumb rubber.

to the sun. Here, more UV performance will be needed for both interior and exterior unpainted parts, which receive enough UV exposure to cause substantial discoloration and gloss loss without the proper stabilization. A few representative automotive situations are discussed in Case 4.2 [4-17, 4-18].

Pipe

Although PO water and pressure pipes are often buried underground, most require at least some UV protection if they are stored above ground and exposed for certain periods. Other pipes that are used above ground obviously require long-term UV resistance. HALS may be used for colored pipe compounds, while white pipes or co-extrusions may use TiO_2 plus a HALS. For black pipe stabilization, carbon black is the cost-effective choice [4-19].

Carbon black has a long tradition of use for pipes. Grades specific to pipe applications ("P-type") have fine particle sizes for increased UV light absorption and weathering. High-purity grades such as Cabot's Elftex P100 reportedly reduce water absorption, which can cause surface defects and voids. Here, "high purity" means low levels of ash, toluene extract, and sulfur (<1000 ppm vs. 10,000 in a conventional black), as well as decreased odor and taste in the water transported by the pipe [4-20].

Even if carbon black does allow some surface oxidation, this damage may be permitted by a specification, as long as pressure resistance, elongation at break, and environmental stress cracking resistance (ESCR) are maintained.

CASE 4.2 UV-STABILIZED AUTOMOTIVE PP/TPO [4-17, 4-18]

Problem: Automotive POs are being called on to face rigorous weatherability and aesthetics requirements.

Objective: Adequate UV protection that does not interact with acidic automotive coatings or cause color fading or interior odors.

Solution: Less-basic and more effective stabilizers offering long-term UV stability.

A number of automotive application requirements have caused suppliers to rethink their approaches to stabilizing automotive PP and TPO. Ciba and BASF Corp., for example, have proposed two products that target current automotive demands:

- Painted TPO: Acid paint-curing systems used in automotive can interact with conventional, basic HALS. Ciba's less-basic Tinuvin XT 850 NOR HALS is said to allow good paint adhesion in acid-cured systems, allowing partially painted, two-toned bumpers. BASF's Uvinul 5050 reduced-basicity HALS is a more standard, high-molecular-weight product offered as a solution offering good paint adhesion.
- Molded-in-color PP: NOR HALS is also said to have improved color retention of color in the weathering of pigmented body panels. Alternatively, the 5050 HALS, combined with a UVA, reportedly offers good weatherability as a low-cost stabilizer for black or gray TPO parts, with more consistent processability (melt flow) as well.
- Interior applications: Although weatherability is less of a factor inside vehicles, other stabilizer issues stand out, such as volatility, surface blooming, and odor—particularly when migrating monomeric HALS products are used. BASF proposes Uvinul 4050 as a less-migratory monomeric HALS solution. The nonblooming NOR HALS, at low loadings, also reportedly prevents gas fade and odor.

To fully understand the effects of UV, the test methods for these properties should use samples with a vulnerable, UV-exposed surface [4-19].

Wood–plastic composites

Long-term sunlight exposure is common for construction materials, and it can be a particular challenge for WPCs which are uncoated. WPCs put into service often experience an initial color change, followed by relative stability. But given their high filler content, degradation of the polymer at the surface can cause fibers to become exposed, delaminated, and subject to fungal attack. Complicating the WPC stabilization situation is the fact that the wood fiber itself undergoes UV degradation via its own free-radical mechanism, leading to lightened or bleached fibers; this process may affect the polyolefin matrix as well. The fibers, however, do provide some UV screening for the sub-surface resin, and UVA and HALS additives in the formulation can significantly improve WPC performance—depending on the compound's wood fiber type, dispersion, fiber–matrix bonding, lubricants, colorants, and so on [4-21].

Film

Food packaging films with UV stabilizers allow the food they contain to retain more nutritional value. But outdoor construction films for wraps, bags, and pool covers require a great deal of UV and heat stability. In the form of agricultural films in particular, light-stabilized PO compounds face intense sunlight and acidic pesticides and agrichemicals—so chemical resistance is important in the choice of a stabilizer. Thinner films (given their higher surface area-to-volume ratios) demand higher concentrations of HALS to maintain long-term performance, whether the film is used for greenhouse coverings, or mulching films, or silage wraps (Table 4.2). Greenhouse-cover films in particular face high temperatures over years of use, requiring specialized stabilizer solutions that also provide good heat stability (see Case 4.3) [4-13, 4-24].

Table 4.2 Inverse Relationships Between Film Thickness, Stabilizer Concentration, and Stabilizer Effectiveness (LDPE Films and Tinuvin 622 (HALS-8) + Chimassorb 81 (UVA-1) Blend and Tinuvin 783 (HALS-7 + HALS-8) Blend; Atlas Weather-Ometer Testing)

Film Thickness (μm)	HALS-8 + UVA-1 Concentration (%)	Hours Until 50% Elongation	HALS-7 + -8 Blend Concentration (%)	Hours Until 50% Elongation
50	0.3 + 0.15	3000	0.3	5500
100	0.2 + 0.1	4000	0.2	7000
150	0.15 + 0.075	4500	0.15	7500

Source: Adapted from [4-13].

CASE 4.3 UV QUENCHERS IN AGRICULTURAL FILMS [4-22, 4-23]

Problem: Dusty nickel-based UV quenchers can be hazardous in the workplace.

Objective: Safer, easier-to-handle alternatives for UV synergists.

Solution: "No-dust blend" concentrates.

Nickel-based quenchers (designated as NiQ-1, etc.) have been useful synergistic agents for light stabilization in agricultural films. For example, a 1:1 blend of NiQ-1 and UVA-1 loaded at 1% can be effective for protecting greenhouse-cover films. But the dusty, heavy-metal-based material is generally an unwanted hazard in the workplace.

One way that has been explored toward improving the use and efficiency of nickel quenchers is to include it with other stabilizers blended together as NDBs from Great Lakes/Chemtura. NDBs are said to be more efficient ways to both handle and disperse quenchers. This is because the "alloying effect" of low-melting additives (such as UVA-1) packaged in the NDBs causes the entire blend to melt at a much lower temperature (under 100°C) than the powdered stand-alone quencher (260°C for NiQ-1).

Despite the safer handling, heavy-metal-based additives such as NiQs also have an unwanted environmental impact overall; thus HALS blends and other materials packaged as concentrates are likely to be the next step for "Ag" films.

Rotational moldings and other molded consumer products

UV protection is crucial in many rotationally molded products, given PE's use for rotomolded playground equipment, kayaks, waste receptacles, and other large thick-walled applications that spend most of their lifetimes exposed to outdoor light. Here, blends of low- and high-molecular-weight HALS, along with UVAs and phenol-free heat stabilizers, supply a combination of surface protection, color retention, and long-term heat stability. Alternatively, high-weight oligomeric HALS blends such as Ciba's Tinuvin 783 can reportedly be economical and also have indirect food-contact clearance at high loadings. Or Cyasorb THT stabilizer packages from Cytec are said to provide extremely long service lifetimes beyond those typically offered by HALS [4-13, 4-25].

CHAPTER 5

Flame-Retarding Additives

Heat that is high enough to initiate the burning of POs has become more of a concern as these materials have been used for more electrical and appliance applications. Fortunately, there are several additive options for suppressing the burning of plastics; unfortunately, as with stabilizers, there is no “magic bullet” additive solution for all situations. FR additives often negatively affect the performance of other additives, or the physical properties of the material.

This chapter overviews the various types of flame retardants that are added to POs. The chapter’s content is influenced by recent trends in FR use, and it often focuses more on PP, given the market’s needs for better FR solutions for this resin in particular. At the end of the chapter, a few case studies will illustrate recent developments in flame-suppressing additives.

This chapter will address the following questions:

- (5.1) Why are FR additives important for certain PO applications? By what mechanisms do POs burn?
- (5.2–5.4) What are the various families of FR additives, and how do they compare in the ways they suppress burning?
- (5.5) What real-world situations have complicated the decision-making process for choosing the best FR for a given PO?

5.1 OVERVIEW: THE NEED FOR FLAME-RETARDANT FORMULATIONS

5.1.1 Trends in flame-retarding additives

With more plastics being used in applications where they encounter potential ignition sources, it is not surprising to see that the demand for FR additives is steadily increasing. Overall, world demand for flame retardants is growing at nearly 5% per year, and is expected soon to exceed annually 2 million metric tons, valued at nearly $5 billion. The Asia/Pacific region's demand is increasing at over 7% per year, while the more mature FR market in the United States is rising at about 3% per year.

Markets for electronic consumer products, motor vehicles, and textiles remain the most prominent for processors of FR plastic compounds, according to year 2007 and 2008 market surveys. In terms of volume, FR use in PP and PE surpasses the volumes used in all noncommodity polymers, and it also exceeds (and is growing faster than) FR use in PVC as well. This stems from POs' use for wire and cable coverings, electrical/electronic devices, stadium seating, films and fibers, and various construction applications—particularly in market sectors that have seen increasingly more rigorous fire codes [5-1, 5-2, 5-3].

The reasons for the growth of flame-retardant PO compounds are not surprising: POs' affordability and properties make them appropriate choices for many applications where possible ignition threats exist. However, since POs could almost be thought of as being inherently flammable, high-molecular-weight waxes, it is not surprising that formulators have given so much attention to their FR additives. Accordingly, these additives can compose a major proportion and/or cost of an FR–PO formulation.

As discussed below, flame-retardant POs require additives that come from one or more of three basic families of materials: combustion-suppressing halogenated organic compounds; inorganic, mineral-based compounds; and intumescent, typically phosphorous-based, char-forming compounds. There have been concerns about the high-temperature products of halogenated (specifically bromine- or chlorine-based) compounds. These concerns have caused compounders and processors, especially those serving European markets, to shift toward halogen-free alternatives to enhance their company's image or meet local directives on halogen use.

This trend toward nonhalogenated FRs may continue as more market regions regulate halogen compounds' use. However, efforts to substitute certain FR additives with alternatives are complicated by the lower performance/higher costs of other FR systems. They are also affected by the way in which alternatives such as mineral FRs reduce certain mechanical properties or complicate compounding at the high loading levels required. Thus, FR formulation practice will likely remain an ever-developing story for each compounder or processor, depending on its applications and market [5-1].

5.1.2 Mechanisms of burning

The burning of polymers could be described simply as a kind of rapid, exothermic, oxygen-induced degradation. Somewhat like heat-induced processing oxidation and UV degradation, combustion is a free-radical-sustained process:

- Fire is initiated by high temperatures (typically >320 °C, for POs), which decompose the polymer into gaseous species that are combustible.
- Hydrogen radicals (H•) are pulled by heat from these decomposition products, and combine with oxygen molecules.
- This reaction creates further radicals (oxygen and hydroxy, O• and HO•), which react with carbon monoxide exothermically.
- This reaction creates heat and more H• radicals, propagating a chain reaction that causes additional burning, unless combustion is interrupted or interfered with by flame-retarding additives.

Accordingly, the mechanisms of flame-retarding additives are analogous to those of heat and light stabilizers: FRs stop runaway free-radical reactions, and/or suppress the production of chemical species that propagate this rapid oxidation. The different types of FRs described below use their own mechanisms to interfere with combustion. Various FR additives, especially when combined into one PO formulation, can be extremely effective in preventing ignition, combustion, or smoke production. This effectiveness is rated using a number of industry-standard tests, summarized in Table 5.1, and basic FR additives are summarized in Table 5.2 [1-1, 3-4].

5.2 HALOGEN-BASED FLAME RETARDANTS

Like heat and light stabilizers, flame retardants containing bromine or chlorine act as free-radical scavengers. They interrupt combustion essentially by replacing free hydrogen and hydroxyl radicals with halide (bromide or chloride) radicals that prevent the combustion reaction from continuing, according to a cyclic process (simplified here):

- At high temperatures, the halogen FRs (H-FRs) first must dissociate, separating the halogen radicals from the molecule's organic component.
- These halide radicals react with the PO to produce hydrogen halide molecules.
- The hydrogen halides neutralize combustion-fostering radicals H• and HO•, producing halide radicals that continue their combustion-interfering activities, following the same cycle.

This reaction cycle makes H-FRs highly effective for extinguishing or suppressing combustion. In particular, brominated compounds are favored because

Table 5.1 Flammability Tests Relevant to PO Applications [5-13, 5-14, 5-16, 5-17, 5-20, 5-21]

Test Standard	Classification/ Rating	Description	Notes
UL94	5VA	Surface burning stops within 60 seconds of five 5-second flame applications, with no burn-through; highest UL94 rating	Highest UL94 rating
UL94	5VB	Surface burning stops within 60 seconds of five 5-second flame applications; burn-through allowed	
UL94	V-0	Vertical burning stops within 10 seconds after two 10-second flame applications; no flaming drips allowed	Commonly required for unattended appliance applications
UL94	V-1	Vertical burning stops within 60 seconds after two 10-second flame applications; no flaming drips allowed	Commonly required for unattended appliance applications
UL94	V-2	Vertical burning stops within 60 seconds after two 10-second flame applications; flaming drips allowed	Commonly required for unattended appliance applications
UL94	H-B	Horizontal burning on 3-mm sample at less than 76 mm/minute, or for less than 127 mm length	For partial-duty, monitored appliances and decorative materials; material considered "self-extinguishing"
Glow wire flammability index (IEC 60695-2-12)	Temperature	Sample held against heated wire to determine temperature at which sample shows no flame or glowing 30 seconds after wire removal	Electrical applications
Glow wire ignition temperature (IEC 60695-2-13)	Temperature	Sample held against heated wire to determine temperature at which there is no flame ignition within 30 seconds	Electrical applications
FMVSS 302	Pass/fail	Horizontal sample exposed to gas flame inside test chamber and burning rate and distance measured	Automotive interior applications
DIN4102-1	B2	Vertical sample exposed to gas flame inside test chamber; flame spread and drips recorded	Building products

they dissociate more easily. However, the acidic products of H-FRs can interfere with the activity of basic HALS in the formulation, and often these FRs bloom to the surface of the polymer [1-1, 3-4, 5-13].

5.2.1 Composition of H-FRs

There are many FR compounds that fall under the category "halogenated" (a few of the most common are shown in Table 5.1). An H-FR compounds'

Table 5.2 Summary of Common Flame Retardants Most Relevant for PO Use [5-15]

Base FR Type	Compound	Example Commercial Product Names (and Suppliers)	PO Application Notes
Halogenated*	Decabromodiphenyl ether ("deca-BDE")	Saytex 102E (Albemarle) DE-83 RTM (Great Lakes/Chemtura) FR1210 (ICL Industrial Products)	PP fiber and film; PE and PP wire and cable coverings; poor blooming resistance but good color
Halogenated*	Tetrabromobisphenol A bis(2,3-dibromopropyl ether)	Saytex HP-800AG (Albemarle) PE-68 (Great Lakes/Chemtura) FR-720 (ICL Industrial Products)	Low loadings possible in PP; commonly for UL94 V-2 applications
Halogenated*	Chlorinated paraffin	Chlorez 700 (Dover Chemical) Hordaresin NP-70 (Dover Chemical)	For LDPE (other grades for PP); high thermal stability, high lubricity in electrical cable conduit applications; reduced Sb_2O_3 usage
Phosphorous	Ammonium polyphosphate and nitrogen synergists	Exolit AP-750 (Clariant)	For PE and PP extrusion and injection molding
Phosphorous	Pentaerythritol phosphate, melamine phosphate, silica quartz	CN-2616/Reogard 1000 (Great Lakes/Chemtura)	Halogen-free FR developed for PP
Mineral	Aluminum trihydrate (ATH; $Al(OH)_3$)	Multiple	Endothermic, inert decomposition; widely used at high loadings
Mineral	Magnesium hydroxide (MDH; $Mg(OH)_2$)	Multiple	High-enough decomposition temperature for most PP processing; high loadings (~60%) required

**Halogenated FR products typically contain some percentage of antimony trioxide synergist.*

effectiveness is essentially proportional to the amount of bromine (or chlorine) carried by each molecule. But many other properties differentiate an H-FR's performance when used in PO compounds, including blooming resistance, thermal stability, UV stability, and color formation. For example, ethylene bis(tetrabromophthalimide) allows better UV-light stability and resists blooming to the surface of the plastic much better than the commonly used decabromodiphenyl ether (often referred to a "deca-BDE"). But it may also create poor color stability when compared with deca-BDE or tetradecabromodiphenoxybenzene [5-15].

Inorganic compound synergists are typically added to an FR package to increase the halogens' radical-scavenging effectiveness. Specifically, antimony trioxide (Sb_2O_3) reacts with hydrogen halides to form new radical scavengers that assist in suppressing combustion. For example, in bromine-based FR formulations (in which flame-suppressing hydrogen bromide (HBr) is produced), antimony trioxide reacts with HBr, ultimately creating antimony halides and neutralizing free radicals through a series of reactions. Other additives added along with antimony trioxide reportedly can increase Sb_2O_3's synergistic effect or can replace it as lower-cost, Sb-free alternatives; these include ferric oxide, zinc borate, and barium metaborate. And because standard-sized Sb_2O_3 particles tend to make plastic articles opaque, colloidal-size antimony oxides have been proposed for creating translucent H-FR plastics. Sb_2O_3 with particle sizes of 0.8–1 μm behave as white pigments, but antimony pentoxide (Sb_2O_5) with particle sizes under 0.15 μm can be used to produce translucent FR–PP (see Case 5.2) [1-1, 5-5, 5-19].

As with heat stabilizers, color formation can be an issue in some H-FR/PO applications. Reducing color formation and black specks requires an H-FR with high thermal stability and low initial color. Chlorinated paraffin FRs from Dover Chemical Corp. have been proposed as a low-color approach for achieving UL94 V-0 flame retardance. These compounds are said to be less expensive than brominated FRs and reportedly inhibit production of corrosive byproducts. They also act as lubricants during processing, keeping processing temperatures low, and they create a slippery, low-wear surface in PE cable conduits, for example. Along with less color development, chloroparaffins are said to require lower amounts of antimony trioxide than with standard H-FRs [5-5].

5.2.2 Concerns about halogenated FRs

General concerns about halogenated FRs have made formulators look for alternatives, even before clear evidence of harm to the environment or human health has been found. Questions have been raised about halogens' persistence and effects when released into the environment, and about the harm of their decomposition products, which can be acidic, corrosive, and potentially toxic. Such questions are slowly being answered (while new ones are being proposed), with the answers rarely pleasing all stakeholders.

Often the regulatory arguments continue well after the "final" regulatory decisions are made. For example, certain halogenated diphenyl ethers have been found under certain conditions to create dioxins and furans—reactive, environmentally toxic, and potentially carcinogenic compounds. One such

FR compound under review is deca-BDE, a common FR that is heavily used in plastics for electrical applications (such as television sets) and in PP textile fibers and PO wire and cable coverings. However, in 2004, the European Union EU Risk Assessment on deca-BDE found "no identifiable risks" to human health or the environment and exempted this material from being banned. Many other questionable FR ingredients, including antimony trioxide, are currently undergoing the EU Risk Assessment process (which can take over 10 years to complete), as well as the European REACH chemical registration process [1-1, 3-4, 5-6, 5-15].

Given the attention on deca-BDE and other H-FRs, PO processors, especially PP fiber producers, are considering their halogen-free options. Spun textile fiber and other thin materials can burn easily and thus require high levels of FR. For these applications, nonhalogen FR alternatives often include phosphorous-based FRs, discussed in Section 5.4. One nonhalogen, melt-processable additive is Flamestab NOR116 from Ciba (discussed in detail in Case 5.1), which reportedly can provide protection at only about 1% loading. Rather than interfering with light stabilizers, this FR/HALS is said to help maintain long-term light stability in thin-section PP film and fibers, woven and nonwoven [5-9, 5-10].

Other FR packages minimize but do not altogether eliminate halogen content. The view here is that reducing halogens overall in a compound reduces

CASE 5.1 FR/HALS ALTERNATIVE [5-22, 5-23]

Problem: Halogenated (and some phosphorous) FR decomposition products are acidic and react with common hindered-amine UV-light stabilizers.

Objective: Develop a HALS/FR additive solution that avoids this acid/base interaction problem.

Solution: A nonbasic HALS additive with flame-retarding properties.

An obvious strategy for avoiding the acid/base reactions between acidic FR decomposition products and basic HALS is to choose a nonhalogen, nonacidic FR. However, researchers at Ciba Specialty Chemicals followed the reverse path, developing an NOR HALS light stabilizer that is nonbasic and provides some flame retardance as well to PP fiber.

The product Flamestab NOR116 is said to increase UV stability sharply in PP fibers containing 5% deca-BDE FR. By contrast, when a traditional HALS is used with deca-BDE instead of the NOR HALS, even higher additions of HALS were not shown to increase UV stability.

There is a particular caution the researchers note however: UV stability with the H-FR/NOR HALS PP cannot reach the level of a non-FR/HALS PP (even when it contains less HALS). This illustrates the power H-FR decomposition products have over HALS.

Interestingly, the NOR HALS by itself in PP with no FR has been shown to provide minimal flame retardance in a PP fiber, even passing the automotive industry's FMVSS 302 burn test at only 0.5% loading. Also, 1% NOR reportedly allowed a 200-μm PP film to pass DIN4102:B2 burn testing.

The researchers conclude that when added with aliphatic halogen FRs, NOR116 serves as an FR synergist, potentially allowing lower overall levels of halogen content in FR compositions. And it shows potentially good results in antimony-free H-FR systems, as well as synergies with nonhalogen FRs.

objectionable risk, without completely losing H-FR's efficient flame-retarding effectiveness. (More about these materials will be presented in Section 5.5.)

5.3 MINERAL-BASED FLAME RETARDANTS

5.3.1 ATH and MDH

In response to concerns about halogenated FRs, resin users have increased their use of mineral-based FRs, especially magnesium (di-)hydroxide ($Mg(OH)_2$; MDH) and less-costly, more widely used aluminum trihydrate (or aluminum hydroxide; $Al(OH)_3$; ATH). These can be used alone, together synergistically, or in combination with other fillers. Mineral FRs are used in PE and PP for wire and cable, and in flooring, roof tiles, conduits, sheets, film, and wall coverings, along with other construction and nonconstruction applications.

When heated through the range of 200°C–340°C (which overlaps with PO decomposition temperatures), these materials decompose, releasing water (which is over 25% of their mass), inert gases, and metal oxides. The reaction is endothermic and thus absorbs some heat of combustion; the water produced dilutes combustion gases and helps choke off the reaction; and the oxide products tend to create a fire-insulating, glassy char layer on the surface of the unburned polymer. Moreover, to a much greater degree than halogenated FRs, these additives suppress large volumes of harmful smoke from being produced during burning [1-1, 3-4, 5-7, 5-28].

Unfortunately, there are at least two major problems with these two inorganic FRs:

1. For best results, they must be added at extremely high loadings (commonly 60%), affecting cost, compounding, and mechanical performance. High loadings of MDH and ATH can reduce a plastic's impact resistance, and their formulation may require other additives to improve melt flow and processing. At reduced loadings, mineral FRs can still reduce smoke during fires, but lose their overall effectiveness.
2. Their low decomposition temperatures often overlap with maximum PO processing temperatures, depending on the processing window used. This issue can be addressed somewhat by the proper choice of an FR; compared with ATH's low decomposition temperature near 200°C, MDH decomposes at 280°C–340°C. This tends to make ATH more suitable for lower-temperature POs (like PE) and MDH more suitable for higher-temperature PP processing.

Mineral FRs can also dramatically reduce the LTHA performance of hindered-phenol and thiosynergist heat stabilizers [1-1, 3-4, 5-7].

Because of shear in processing, local melt temperatures may spike well above an FR's decomposition temperature, especially in high-viscosity polymer melts containing fillers. So another approach to avoiding the problems of low FR decomposition temperature is to minimize the overall average processing temperature of the compound. Various lubricating additives can be used to reduce processing temperatures (many are covered in Chapters 11 and 12). Or, for example, for both lowering processing temperatures and increasing flame retardancy, coupling agents based on vinyl-silane and titanate chemistries (titanium-based salts or esters) have been proposed as "synergists" for mineral FRs [5-4, 5-7].

Synergies of FR performance are also possible when a PO formulation contains a blend of MDH and ATH. In one case, Vertex MDH and Micral ATH from J.M. Huber Corp. were blended in a 1:2 ratio and loaded at 70% in PP. The combination was found to produce a higher limiting oxygen index (LOI, the lowest amount of oxygen in the atmosphere that will support combustion). As loadings of mineral FRs increase, LOI tends to increase sharply up from pure PP's base value of 19%. In testing, the 1:2 MDH/ATH blend's LOI was reported as 41%—higher than the LOIs of 70% MDH or 70% ATH alone (having LOIs of 37% and 40%, respectively). Moreover, the smoke generated by the 1:2 blend PP was also less than that of the 70% MDH-only PP, and similar to that of 70% ATH. Finally, the cost of the 1:2 formulation package was estimated to be only 78% of the cost of MDH alone [5-7].

5.3.2 Other mineral fillers' FR effects

Researchers have also been interested in how well other common mineral fillers (including those discussed in Chapter 7) can help make POs flame retardant. They have studied the advantages of replacing some of the MDH or ATH content with relatively less-expensive fillers such as calcium carbonate or talc. For example, testing has shown that replacing 10% of the 70% MDH in a PP compound with common mineral fillers gives "acceptable" UL-94 V-0 flame-retardant performance, although much more (up to 50%) smoke is generated during burning. Specifically, a 70% MDH PP was found to have a UL-94 afterflame time of 13 seconds, and this increased to 16 seconds with 60% MDH plus 10% kaolin clay filler, to 18 seconds with 10% $CaCO_3$, and to 22 seconds with 10% talc as a partial replacement filler. The 60/10% clay-filled PP also presented a slightly higher LOI (38%). And when using the 1:2 Vertex/Micral blend mentioned above for the 60% component, up to 30% reductions in filler cost can be gained with these mineral filler replacements, with little or no loss of FR performance. This is true as long as the now more complicated compound can be processed within the ATH's stability window (and the compounding operation is set up economically to handle multiple fillers) [5-7].

Other studies have attempted to replace MDH in FR–PP with even larger amounts of cheaper fillers, such as talc. In PP, one study replaced one-quarter of the 60% MDH content with Luzenac talc (from Rio Tinto Minerals). In testing, the lower-cost 45%/15% MDH/talc PP retained the LOI of MDH alone and upgraded the UL94 (3.2 mm sample) rating from “not classifiable” to V-1. In another PP formulation, 20% talc was used to reduce the levels of halogen/Sb_2O_3 FR that is needed to obtain a sample with improved V-0 performance, without creating chemical interactions with the brominated FR. The talc also reportedly inhibited the dripping of polymer during flame exposure, increased ignition times from 49 to 59 seconds, and nearly doubled the flexural modulus—at three-quarters the cost of the unfilled halogen/Sb_2O_3 PP [5-8].

The ultimate extreme is to replace the standard FR completely and simply rely on the flame-retarding properties of cheaper conventional fillers. This might be possible for some applications; for example, high levels of $CaCO_3$ reportedly can reduce the rate of heat release and suppress smoke. However, overall, common inert fillers simply do not supply nearly the same degree of flame-suppressing effects as ATH and MDH decomposition [5-28].

5.4 INTUMESCENT AND PHOSPHOROUS-BASED FLAME RETARDANTS

Phosphorous-based FR systems based on phosphate salts can be useful in flame-retardant POs. P-FRs decompose in heat to produce an expanding, intumescing foam char on the burning plastic’s surface, which isolates the underlying plastic from further combustion. Since the burning of PP is more of a surface-oxidation process than that of PE, intumescent FRs are much more suitable for PP than PE [3-4, 5-13].

These FR systems can be as effective as halogenated FR systems and thus are their major competitors. They suppress smoke better and do not have the corrosive byproduct and UV-stabilizer interference issues of H-FRs. Their flexibility has caused their formulators to focus on reducing their typical limitations, such as low decomposition temperature, high loading rates, and water extraction [3-4].

5.4.1 Mechanisms of phosphorous FRs

Phosphorous can take multiple oxidation states, making the mechanisms of various P-FR compounds difficult to summarize. Generally, these FRs become active as the polymer starts to decompose from heat, leading to reactions which form a foamed charred surface. By its thickness and insulating quality, the char blocks the release of smoke, heat, burning gases, and other off-gases. This intumescence is especially useful in electronics applications where nearby parts could be susceptible to burning or damage. Also, P-FRs do not interfere with HALS light stabilizers as halogenated FRs do [5-11, 5-13].

Various P-FRs are used in major polymers of commercial importance. For POs and other polymers, the char-initiating component is aided by synergists that promote foaming and cross-linking. The following three critical functionalities are typically required in each P-FR package:

- an acid source, often ammonium polyphosphate, to initiate charring over the surface of the polymer;
- a char promoter and cross-linker, often pentaerythritol;
- a blowing agent, often melamine or other nitrogen compounds, which expands the cellular char foam.

To further suppress combustion, a polyhydric alcohol (polyol) in the additive systems may be used to form water during decomposition [1-1, 5-11, 5-13].

P-FR loadings range from 20% to 35% for meeting UL94 V-0 or 5VA performance. Roughly 20% loading is the "critical mass" required for raising the UL94 flame resistance of PP above "nonclassifiable" to V-0. Sometimes the loading must be higher. For example, one P-FR used heavily in PP, ethyl diamine phosphate (EDAP), is required at loadings of 30%–40% for a UL94 V-0 vertical burn test rating. EDAP must be used at high-enough loading to prevent flaming drips during testing. A proper loading rate depends on part thickness, fillers, other additives, desired melt-flow properties, and other factors.

P-FRs have both negative chemical and mechanical effects in the resin, limiting their applications. For example, they are not usually used in thin applications, or in water-handling applications, because of their solubility and extraction tendencies. Moreover, as with mineral FRs, P-FRs tend to increase modulus and heat-deflection temperature (HDT), while lowering impact strength and other mechanicals [1-1, 5-11, 5-13].

5.4.2 Issues in improving phosphorous FRs

Because of its halogen-free, low-density nature, P-FR technology has undergone much development in recent years. Advancements have been made in increasing processing temperatures, lowering loading rates, and lowering water absorption and extraction of the FR.

For example, improvements in water resistance have been reported for intumescent P-FRs based on ammonium polyphosphate and nitrogen synergists, such as with Budit flame retardants from Budenheim. In particular, the Budit 3178 product is targeted for HDPE cables, tubes, and thin-wall pipes that are exposed to water—reportedly maintaining FR performance even after soaking in 70°C water. For UL94 V-0 performance, the product must be loaded at 25% in unfilled HDPE and at 23% in 40%-talc HDPE [5-12].

Efforts have also been made in improving the processing of PP/P-FR grades. For example, increased melt flow and reduced melt pressure and viscosity have been reported with the melt-blended CN-2616 (Reogard 1000) FR from Great Lakes Polymer Additives (Chemtura). The product is a combination of pentaerythritol phosphate alcohol, melamine phosphate, and silica quartz. Melt-flow rate increases by 35%–40% are reported when 20% of the additive is added to PP homopolymers. After repeated extrusion passes at below 220°C, melt pressure and burn times (less than 10 seconds in UL94 V-0 testing) are reportedly maintained [5-13, 5-15].

However, various modifiers and fillers in the resin reduce P-FR efficiency, according to testing with the Reogard product. Some impact modifiers cause UL94 test failures, while calcium carbonate tends to completely interfere with intumescence. PP grades with talc (added at 10% maximum) and glass fibers (10%–30%) are allowable, but they may require higher levels (30%) of P-FR to attain a V-0, nondripping classification. Likewise, PP copolymers generally require higher P-FR loadings than homopolymers [5-13, 5-15].

5.5 FACTORS DETERMINING THE SELECTION OF FR ADDITIVES

Although it is difficult to surpass the effectiveness of halogenated FR packages, the interest among compounders and processors in using nonhalogen alternatives requires them to face several trade-offs and compromises between properties, cost, and performance. Complicating their choices are the very different forms and chemical natures of the different flame-retarding systems. And underlying all their considerations is the fact that, unlike with stabilizers or mechanical-property-enhancing additives, any user of a flame-retardant resin hopes never to face a situation where the FR additive is actually needed. Thus the FR formulator works to meet a certain standard or rating (UL94, etc.), rather than to meet a regularly observable property required in service conditions. Certain amounts of heat or light exposure or mechanical stress or impact may be fundamental daily requirements faced by a product; flames should never be, but still must be planned for, to protect lives and property.

Thus the sections and case studies below illustrate a number of factors that are considered by formulators and end users of FR PO compounds. In summary, most can be briefly listed as questions:

- *Risk vs. performance*: Exactly what standard of flame retardance does the resin require in service? What is the risk or benefit of lower or higher amounts of FR, or of lower or higher levels of smoke suppression, for example?
- *Cost*: Can costs be reduced by lowering certain FR additives and adding more less-expensive inorganic fillers? Or by substituting higher-cost

additives at low concentrations for low-cost FRs at high concentrations?

- *Mechanical properties*: How do different FRs affect various mechanical properties?
- *Additive interactions*: How is the performance of an FR affected by fillers, reinforcements, or other additives needed in the formulation?
- *FR form*: Do smaller, submicron particle sizes of FRs or synergists permit lower FR loadings, or more cost-effective use in thin-gauge PO materials?
- *Density*: What are the trade-offs in different applications of using high-density, highly loaded mineral-based formulations and lower-density halogen or phosphorous FRs?
- *Aesthetics*: How does an FR affect a compounded resin product's color and color retention?
- *"Halogen-free" perceptions*: How important is it for a product, market, or a company's image to provide "halogen-free" FR formulations? If no regulations prevent the use of H-FRs, is it still important to consider the alternatives?

Table 5.3 is an attempt to compare the three FR families in these terms, and some examples and further ideas below are intended to stimulate discussion and development of new approaches for FRs.

Table 5.3 Qualitative Comparison of Fundamental Flame-Retardant Types in PO Compounds

Factor	Halogen-Based FRs (with Antimony Oxide)	Mineral-Based FRs	Phosphorous-Based FRs
Overall flame-retarding effectiveness, per unit mass of FR	High	Low	Medium to high
Smoke suppression	Low	High	Medium to high
Health/environmental impact and reputation	Poor	Good	Acceptable
Bulk cost	Medium	Low	High
Net cost in final compounded FR–PO	Low	Low to high	Low to high
Density/specific gravity of final FR–PO	Low to medium	High	Low
Interference with UV light stabilizers	High	Low	Low
Potential harm of decomposition products	High	Low	Medium

5.5.1 Cost, risk, and performance

To define the flame retardancy requirements for any product, material specification writers have only common standards to use as benchmarks (see Table 5.1 for the most regularly cited standards). Their overall decisions are based on the potential risk of harm to humans or product components if a resin is ignited. In this critical specification process, which is mostly far beyond the scope and authority of this book, they may face several fundamental questions:

- In how close contact with the product are potential ignition sources, and what temperatures do these sources reach?
- How exposed would people be to the potentially burning product?
- How much smoke would be tolerated from burning in the end-use situation?
- What is the risk of an ignited product damaging or propagating its burning to surrounding materials?
- And what are costs and penalties of providing each level of FR protection, in comparison with the risk of fire and damage to life and property?

Risk/benefit analyses may answer a specifier's questions, but once the commitment is made to meet a specific standard, formulators must be certain they meet it. A couple of key issues are discussed below.

Cost

Since very different FR formulations can meet the same standard in a PO, various kinds of costs invariably become factors that complicate performance comparisons. For example, brominated FRs can be cost-efficient and very effective for meeting UL94 standards at low loadings, but can carry penalties of high smoke production, light-stabilizer interference, and environmental sensitivity. By contrast, inert, inexpensive inorganic synergists and fillers may be able to replace some or all of the H-FR or P-FR that would otherwise be required to meet a standard. However, in other cases, a relatively expensive (per-kilogram) P-FR, at low loadings, may be more cost-effective than a dense, cheap mineral FR. The P-FR may reduce the overall mass of compounded material needed to fill out a component's dimensions. However, it is difficult for P-FRs to compete with H-FR packages directly on per-kilogram cost and FR efficiency terms [5-13].

A related approach for reducing the cost and amount of FR overall may be to consider the effectiveness of overmolding a nonFR material with a layer of FR resin, or to use other multilayer constructions, composed of both FR and nonFR-containing resins [5-28].

Smoke

Although much attention is given to flammability standards, the smoke produced by a burning plastic compound can be particularly harmful in an application, both directly and indirectly. Smoke can kill via inhalation, but it can also obscure the vision of people trying to escape from a fire, making smoke density an important factor in the choice of an FR formulation, and one that is somewhat independent of flammability. Thus both types of FR performance must often be weighed individually against each other. For example, a phosphorous-based FR (such as Chemtura's Reogard 1000) may produce about half the smoke density in ASTM E662 testing than a corresponding halogenated FR. However, a PP containing 60% MDH may produce even less smoke than a PP with 25% P-FR, even though the MDH PP may meet only a UL94 V-2 rating, in comparison with the P-FR's V-0 rating [5-13].

5.5.2 Property effects and co-additive interactions

The price for flame retardancy paid by POs can be high in other ways. Because FRs are not added in order to be part of a compound-strengthening system, and because they must often be used at high loadings, it is not surprising that they have unwanted effects on most mechanical properties. Table 5.4, for example, compiles data from researchers and suppliers and is intended to show the relative effects of different FR systems on PP mechanical properties. Even though FR additives may be of various types from various suppliers, certain general physical property changes commonly result from the use of FRs:

- High levels of FRs can increase flexural modulus and rigidity.
- High levels of FRs can reduce strength.
- High levels of FRs can reduce impact resistance, sometimes severely.

Table 5.4 Rough Mechanical Property Comparison of PP Containing Various Flame Retardants [5-8, 5-13, 5-19]

Material	Flexural Modulus (GPa)	Tensile Strength (MPa)	Notched Izod Impact (J/m)
PP (homopolymer, no FR)	1.2–1.4	33 (25*)	44–48
PP + 10% halogen FR (PE-68[1]; with 3% Sb_2O_3)	1.2	33	32
PP + 30% phosphorous FR (Exolit AP-750[1])	1.9	30	27
PP + 20% phosphorous FR (CN-2616[1])	1.9	30	37
PP + 50% MDH (Versamag UF[2])	n/a	n/a	38
PP + 60% MDH	3.7	22*	n/a
PP + 45% MDH + 15% talc	4.6	23*	n/a

Yield strength.

[1] *From Great Lakes/Chemtura.*

[2] *From Morton International.*

These interactions become important in even the most basic material selection cases for FR–PP.

The cost and usefulness of co-additives might be considered as counter-remedies for restoring properties. For example, 5% silicone modifier additions have been shown to nearly double notched Izod impact strength in PP compounds, potentially raising the impact of an FR–PP to near the level of neat PP. Or, given that PP copolymers require more phosphorous FR than homopolymers, a materials selector might choose a less-expensive, impact-modified homopolymer FR–PP instead. This attention to property interactions can save costs, as long as the FR is not interfered with by the chosen modifier [5-13, 5-19].

Another fundamental interaction issue is halogenated FRs' negative effect on UV stability. This especially affects POs formulated for outdoor use, which rely on light-stabilizing (HALS) additives for long-term UV resistance. Here, a nonhalogenated FR is the obvious solution, or, if possible, a more innovative approach described in Case 5.1.

5.5.3 FR density and form

Density differences of different FR compounds can be significant, and density affects how and where a compound can be used. Using a highly loaded, high-density mineral-based FR obviously creates a high-density PO compound (with specific gravity 1.5 or above), contradicting POs' usual selling point as the most lightweight of plastics. By contrast, formulations and low-density halogen FR packages, and most phosphorous FRs, maintain specific gravity near 1 or below. Only a few percent of halogen FR matches several percent of mineral FR for equivalent flame retardancy; thus a trade-off in between the extremes is possible [5-6, 5-13].

The physical form of a flame retardant also determines its practical use and effectiveness. In an age when it is better to be smaller, mineral FRs may provide increased effectiveness as their particle sizes are reduced to nano-size. Recent development has focused on improving the efficiency with which ATH and MDH release their decomposition products (water and absorbed heat), by extending their particle size distribution below 1 μm. The finely precipitated Martinal ATH and Magnifin MDH materials from Albemarle Corp., for example, have much higher surface areas than standard fillers that are well above 1 μm in size. The submicron materials' higher surface areas, up to 11 m^2/g, result in higher tensile strength, higher LOI, and higher melt viscosity (according to testing with a PO copolymer ethylene vinyl acetate blend). Moreover, the company's coated grades are said to improve char formation, produce less smoke, and increase time to ignition. Smaller particle sizes likewise make antimony oxide synergists used in H-FRs more effective,

CASE 5.2 PP FIBER AND H-FR COLOR ISSUES [5-25]

Problem: PP fiber requires high flame retardancy halogenated FR concentrates that generally contain an antimony trioxide synergist, which impacts translucency and color strength.

Objective: Develop an equivalent H-FR package that provides higher translucency.

Solution: Antimony pentoxide as a synergist, with 0.03-µm particle size rather than 1-µm antimony trioxide.

Halogenated FRs containing antimony trioxide (Sb_2O_3) synergists are commonly used in fine-denier PP fiber for carpeting and wall coverings. However, Sb_2O_3 formulations are typically not translucent, though translucency is often a desirable property. Thus researchers at Nyacol Nano Technologies Inc. turned their attention to developing an alternative antimony oxide, Sb_2O_5, which can be provided in colloidal-size, sub-0.1-µm particle sizes, compared with the minimum 0.8-µm trioxide size that is commercially available.

In flame testing with brominated FR concentrates, the company's ADP480 colloidal pentoxide compounds were rated consistently at UL94 V-2 at total FR loadings of 1%–12%. In comparison, standard Sb_2O_3 H-FRs containing the same brominated aromatic compound provided V-0 protection at 8%–12% loadings, V-2 at 2.5%–4%, and failed at 1% loading.

Notably, the pentoxide FR materials showed at least 38%–75% higher Izod notched impact readings than the trioxide compounds across all loading rates, and roughly the same tensile properties.

Moreover, the pentoxide compound samples (1/8 inch (3.2 mm thick)) were rated "translucent" for loading rates of 4% and below; the trioxide samples were all "opaque," except for the 1% loaded sample, which was rated "slightly translucent." The differences in opacity translate into large savings in colorant costs for the antimony pentoxide FR, the researchers conclude. The less-opaque PP produced with this additive reportedly requires only about one-quarter the amount of pigment to achieve a particular shade, and these savings increase even more for dark red and blue shades.

as discussed in Case 5.2. However, fine, high-dusting airborne powders create obvious hazards for shop personnel [5-24].

5.5.4 Halogen-free benefits (and costs)

As mentioned in Section 5.2.1, the issue of halogen-free flame retardants and additives hangs on the horizon for all plastics suppliers and processors, and is a current reality for those supplying the European product markets in the consumer electronics, wire and cable, automotive, and construction sectors. European Union directives restricting the use of some halogenated compounds in electrical applications, such as WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restriction on Hazardous Substances), have pressured some companies to change to nonhalogen FRs. And even outside of this regulatory activity, the automotive industry and other industries have become more interested in halogen-free POs because of the growing halogen sensitivity of the public [5-6].

Accordingly, a 2008 market survey indicates that most processors expect the use of nonhalogen FRs to grow in coming years (and of the companies surveyed, PP, PVC, and PE were the three most-used polymers in their FR applications). Moreover, these processors indicate it is their company's desired image or policy—not a particular regulatory directive—that is the biggest driver for

CASE 5.3 LOW-HALOGEN FRS [5-26]

Problem: PO processors lack FR alternatives for addressing concerns about halogenated FRs.

Objective: More low- or no-halogen FRs that offer equivalent performance to traditional H-FRs.

Solution: A low-bromine/phosphorous FR offering UL94 performance at low loadings.

Nonhalogen FRs that offer the same performance as standard H-FRs are limited in availability and/or costly. But compounders and processors who wish to display sensitivity to halogen concerns are gradually getting more choices. One approach is to use an FR compound with very low bromine content. To that end, developers at Italmatch Chemicals SpA commercialized a phosphorous/brominated system called Phoslite B631C. When used in a compound to achieve a UL94 V-2 rating, the net bromine content from the product is only about 0.1%. In PP homopolymer, the FR reportedly achieves V-2 performance in loadings of 1%, along with an LOI of 27%, glow wire flammability index of 960°C, and glow wire ignition temperature of 750°C for 3.2-mm samples (and 825°C for 1.6 mm samples).

Phoslite is said to be flexible in its applications. It can be used in films because of its small particle size; and for V-2 performance, it can be added to 30% glass-filled PP at 1% loading, in 20% talc-filled PP at 2% loading, in PP copolymer at 2%, and in TPO at 2.5%–3%.

change. Even for markets such as North America, where H-FRs may never be officially banned, image-conscious companies are still trying to understand which halogen-free FRs may serve as replacements with low-enough cost and equivalent performance—without causing major losses of mechanical properties and compounding difficulties [5-1].

For companies looking to replace H-FRs, ATH and phosphorous/nitrogen compounds are the main options of choice; nonhalogen options are included in Table 5.2. Regulatory status, market conditions, and the political climate may favor one or another of these options at any time. Alternatively, FRs with lower levels of halogens (as discussed in Case 5.3) might also be good compromises [5-1].

Complicating the halogen argument are concerns about if and how H-FR-containing plastics are handled and then recycled or disposed of at the end of their life cycles. The industry is being urged through directives like WEEE to recover and recycle brominated FR plastics, especially those in electronic devices. Since engineering and styrenic plastics are mainly used for electronic devices and televisions, this may be a less relevant issue for POs (except perhaps for the way new rules would affect the kinds of H-FRs that will be permitted in all plastics). More relevant to PO users perhaps is the European Voluntary Emissions Control Action Plan (VECAP), which requires textile producers to monitor the deca-BDE and other FRs in their fibers to minimize releases to the environment [5-6].

CHAPTER 6

Additives for Modifying Electrical Properties

POs stand to gain from the greater demand for inexpensive electronic devices and system hardware, and these applications require materials whose conductive properties can be easily and cheaply modified. Among the most nonconductive of the polymer families, POs can be compounded with an increasing variety of internal agents that change their electromagnetic properties. Some additives simply prevent excessive static charge build up on the plastic surface to prevent difficulties in processing and use. Others provide more complete electrostatic dissipation or discharge (ESD) for more static-sensitive applications, such as electronics packaging. And still other more conductive additives prevent electromagnetic interference (EMI) from disrupting the function of the electronic devices they contain or of other devices.

With opportunities for POs requiring increased conductivity only likely to grow, a basic understanding of the ways additives change these invisible properties is important; accordingly, this chapter will address these basic questions:

- (6.1) What are the various kinds of migrating/nonpermanent and nonmigrating/permanent antistatic and ESD additives commercially used in POs?
- (6.2) What are the benefits and drawbacks of conductive fillers and fibers used for EMI applications?
- (6.3) What are some specific situations that require antistat/ESD/EMI compounds, and how is the proper choice of additive made?

The antistatic/ESD/EMI additives that are most relevant to POs are summarized in Table 6.1. The following sections attempt to categorize specific additives, despite the sometimes overlapping categories.

6.1 ANTISTATIC AND ESD ADDITIVES

As insulators, POs and most polymers can accumulate a static electrical charge that can interfere with the processing or end use of the material in a variety of

Table 6.1 Summary of Key Approaches Used for Antistatic, Static-Dissipating, and EMI Shielding Purposes for POs

Additive Type	Chemical Compositions: Examples	Performance	Comments
Antistats (nonionic)	Glycerol esters (glycerol monostearate, GMS), lauric diethanolamide (LDA), ethoxylated amines	Migratory, nonpermanent	Non- or low-polar molecules bloom and attract surface moisture
Electrostatic-dissipative (ESD) polymer modifiers	Polyether block amides, ethylene ionomer	Permanent, nonmigratory	Lower surface resistivity possible for electrostatic dissipation (ESD)
Conductive fillers	Carbon black, carbon nanotubes and graphene, metal pigments/flake, conductive coated inorganic particles	Permanent, nonmigratory	Carbon black inexpensive, but subject to allowing rapid discharge; electromagnetic interference (EMI) shielding possible
Conductive fibers	Stainless steel fiber, carbon fiber, conductive coated fibers	Permanent, nonmigratory	Used for internal EMI shielding
External antistats	Ethoxylated sorbitan ester	Short term	Sprayed-on solution for dust-free packaging
External conductive coatings	Metallized coatings	Long-term surface conductivity	Costly; health and safety issues; consistency and durability issues

electrical and common, nonelectrical applications. Charge accumulation can cause static cling, dust accumulation, or shock discharge (potentially causing explosions) during the production and handling of films, fabrics, and electronic components. Various conductive agents, either applied externally to the plastic or incorporated internally as additives, prevent this electrostatic buildup by increasing conductivity and lowering the compound's bulk-volume resistivity (measured in ohms-cm) or surface resistivity (in ohms/sq). (Surface resistivity is the electrical resistance between two bar electrodes across a square unit area ("sq") of any size test material. The property relates to another important measure of an antistatic agent's effectiveness, the material's "static decay time"—the amount of time a sample requires to dissipate an applied 5-kV static charge.) [3-4, 6-1, 6-28].

Without antistatic agents, POs acquire static charge easily, sometimes only dissipating it through troublesome spark discharges, especially in dry environments, where surface moisture cannot serve as a conductive aid for dissipating charge. To be useful, an effective antistat should lower the plastic's surface resistivity from 10^{14} ohms/sq or higher of the base polymer, to 10^{13} or lower. (Lower than 10^{9} is often classified as an "ESD" level of resistivity, required to prevent the damage of sensitive electronics or spark discharge.)

The compound's static decay time should also be reduced to less than a few seconds. These properties depend on the test specification and requirement called out (such as the military specification MIL-B-81705 or the National Fire Protection Association (NFPA) 99 specification) [1-1, 6-1, 6-2, 6-28].

Internal antistatic agents include insoluble, migratory additives that after a brief period bloom on the plastic part's surface where they are effective. These molecules have a partially hydrophilic structure which attracts a film of surface water that lowers the resistivity of the part, allowing excess electrons to dissipate. However, these blooming agents can interfere with a part's surface aesthetics, food-use approval, adhesiveness, or processing (though they can serve as useful mold-release agents). And because they are only weakly bonded to the polymer's surface, they can become removed from the surface gradually, and so they cannot be considered "permanent" antistatic solutions. Tables 6.2 and 6.3 compare some representative property values for commercial antistats in various POs after several days of aging, during which time the antistats have had time to migrate to the surface [1-1, 3-4].

The various antistatic and ESD additives shown in Table 6.1 are covered in more detail in subsections below. Internal migratory chemical antistats can be separated into ionic (cationic or anionic) or nonionic agents, which are more often used in POs. Static-dissipating polymers can also be added to POs as nonmigratory, permanent agents; these compete more for applications that require long-term ESD levels of protection, as in electronics packaging, rather than with nonpermanent migrating antistats. Conductive fillers such as carbon black can also reduce resistivity in the PO down below 10^5 when used at high loadings, offering ESD and EMI shielding. And even though internal agents are the focus of this chapter, external antistats also have an appropriate use, though they may be rubbed off a plastic's surface relatively easily. Sprayed-on antistats in alcohol or water solutions help minimize dust accumulation on PO packaging such as medicine, cleaner, and cosmetics bottles [1-1, 6-1, 6-2, 6-4].

6.1.1 Migrating chemical antistats

Migrating antistats are time-sensitive in their use. Time is required for the additive to migrate to the surface of the PO product and to attract moisture from the air and minimize static buildup. This migration may delay its reaching optimum antistatic effectiveness by days or weeks, especially with a crystalline polymer like PP. Other factors affect the migration rate, such as the presence of other additives, insufficient concentration of the antistat, and temperature.

Conversely, the effectiveness of an agent is reduced in low-humidity environments, and its effects eventually decrease over time. As more antistat molecules

Table 6.2 Comparison of Representative Antistatic Additives for POs, with Data from Commercial Supplier PCC Chemax, Inc. (Note that the Surface Resistivity of all PE and PP Control Plaques Was Recorded as 10^{14} ohms/sq.) [6-1]

Polymer	Antistat Composition (Plus Form, and Supplier Designation)	Tested Antistat Loading Level (and Typical Loading Range)	Static Decay Time* (Seconds) After Various Aging Periods (Days)			Surface Resistivity* Exponent (10^x ohms/sq) After Various Aging Periods (Days)		
			3	**21**	**60**	**3**	**21**	**60**
LDPE	Ethoxylated amine (liquid, Chemstat 122)	0.1% (0.1%–0.4%)	0.01	0.01	0.01	9	9	9
LDPE	Ethoxylated amine (powder, Chemstat 122/60DC)	0.25% (0.15%–0.60%)	3.85	1.82	0.72	11	10	10
LDPE	Lauric diethanolamide (solid/pellet, Chemstat LD-100)	0.5% (0.15%–1.2%)	0.05	0.01	0.01	10	10	9
LDPE	Lauric diethanolamide (powder, Chemstat LD-100/60DC)	0.8% (0.25%–1.4%)	0.45	0.32	0.21	11	10	10
HDPE	Ethoxylated amine (liquid, Chemstat 122)	0.4% (0.1%–0.4%)	1	0.01	0.01	10	10	10
HDPE	Ethoxylated amine (powder, Chemstat 122/60DC)	0.4% (0.15%–0.60%)	n/a	0.12	0.13	12	10	10
HDPE	Lauric diethanolamide (solid/pellet, Chemstat LD-100)	0.8% (0.15%–1.2%)	5	0.02	0.02	10	10	10
HDPE	Lauric diethanolamide (powder, Chemstat LD-100/60DC)	(0.25%–1.4%)	1.2	0.60	0.32	11	10	10
PP	Ethoxylated amine (liquid, Chemstat 122)	0.8% (0.15%–0.80%)	3.50	0.09	0.03	12	11	10
PP	Ethoxylated amine (powder, Chemstat 122/60DC)	1.4% (0.25%–1.4%)	n/a	0.12	0.13	12	10	10
PP	Lauric diethanolamide (solid/pellet, Chemstat LD-100)	1% (0.25%–1.2%)	0.13	0.05	0.05	10	10	10
PP	Lauric diethanolamide (powder, Chemstat LD-100/60DC)	(0.25%–1.4%)	0.80	0.22	0.08	11	10	10

**Measured via NFPA 99, at 50% rel. humidity*

congregate to the surface, they may start to crystallize or bond with each other, hindering their hydrophilic properties. Or the antistat layer may eventually get washed or rubbed off the product. Despite their migratory and blooming nature, most of these materials generally have approvals for food packaging use, though sometimes only within certain limits in their concentration or application [3-4, 6-2, 6-6, 6-25].

Table 6.3 Comparison of Representative Commercial Antistats for Packaging POs, with Data from Supplier Danisco [6-7, 6-8, 6-9, 6-24]

PO Tested (and Typical Application)	Antistat Composition (Plus Form, and Supplier Designation)	Tested Loading Level (wt%)	Static Decay Time* (Seconds) After Various Aging Periods (Days)		
			1	28	112
LDPE (dust-free food packaging film)	Polyglycerol ester (paste, Grindsted PGE 308)	0.1%**	0.5	0.9	0.2
LDPE (dust-free food packaging film)	Polyglycerol ester (paste, Grindsted PGE 308)	0.4%**	0.7	0.5	0.3
LLDPE (low-humidity electronic packaging film)	Polyglycerol ester (paste, Grindsted PGE 308)	0.4%**,†	4.41	2.96	2.04
LLDPE (low-humidity electronic packaging film)	Polyglycerol ester (paste, Grindsted PGE 308)	0.8%**,†	4.81	2.02	1.02
PP random copolymer (dust-free injection-molded food packaging)	Monoglyceride (pellets or beads, Dimodan HS K-A)	0.1%	1.4	0.6	1.5
PP random copolymer (dust-free injection-molded food packaging)	Monoglyceride (pellets or beads, Dimodan HS K-A)	0.2%	0.3	0.2	0.6
PP random copolymer (dust-free injection-molded food packaging)	Monoglyceride (pellets or beads, Dimodan HS K-A)	0.3%	0.2	0.8	1.1
PP homopolymer (dust-free injection-molded food packaging)	Monoglyceride (pellets or beads, Dimodan HS K-A)	0.6%	6.0	0.8	0.6
PP impact copolymer (dust-free thin-wall injection-molded food packaging)	Monoglyceride (pellets, Dimodan HPL 70)	0.6%	0.3	0.1	0.1

**Test method not specified*
***In 50-μm blown film*
†Tested at 12% rel. humidity

Antistats for POs are typically waxy agents that are completely incompatible with the polymer, but hygroscopic when accumulated at the surface. Various organic agents are effective in POs at <2% loadings, such as stearates, amides, amines, and glycols. The most commonly used antistats referred to in industry literature are based on ethoxylated fatty acid amines (EA), lauric diethanolamide (LDA), and glycerol esters such as monoglycerides (glycerol monostearate (GMS)) or polyglycerol esters (PGE, polymerized glycerin esterified with fatty acids):

- *Amines (EAs):* Suited more than other migrating antistats for HDPE, EA grades come with different base fatty acid feedstock compositions that affect their migration rates in the polymer.
- *Amides (LDA):* Depending on feedstock composition, diethanolamides can be effective at low humidity, and especially with LDPE and LLDPE.

Amides reportedly do not react as much with polycarbonate parts as EAs, when the antistats are used in PO electronics packing.

- *GMS:* Usually used for short-term static resistance (less than 2 months), GMS is less efficient in POs than EA and LDA. Often used in processing operations to reduce static and dust on the product.
- *PGE:* Higher-molecular-weight, lower-volatility antistats designed to have a distribution of migration rates.

Other differences between these types are mentioned in Section 6.3 [6-1, 6-2, 6-25, 6-27].

Tables 6.2 and 6.3 compare the effectiveness of some common commercial antistats in POs from two suppliers over time. Even though antistat testing methods differ, and industry-provided data can show nonreproducible variations, the tables indicate some trends that make sense in terms of principles of polymer science:

- *Speed*: Surface resistivity and static decay values require time after processing to reach optimum values while the additives migrate to the surface. In some cases, more than a few days may be required for major improvements in properties.
- *Form*: An antistat in liquid form may provide more immediate and lower static decay and resistivity properties than the same chemical composition used in powder form, likely because of differences in migration rate or dispersion. PO film forms also matter; for instance, winding a film into a roll using high tension delays the migration of the antistat to the film surface, compared with an unwound film.
- *Concentration*: More antistat is not necessarily better; for optimum antistat properties, the best concentration may lie between extremes for a given PO or application. Thinner films usually require higher antistat concentrations than thicker films, so that enough antistat is available for migration to the surface from within the film.
- *PO crystallinity*: POs such as HDPE or PP homopolymer may require roughly double the concentration of antistat for equivalent performance, compared to less crystalline POs such as LDPE, LLDPE, or PP copolymers. This is because of the interference with antistat migration in crystallized domains.
- *Effectiveness over time*: Static decay times may start to increase several weeks after processing as antistats become consumed, removed from the surface, or otherwise deactivated. (Overall effectiveness also depends on having enough moisture in the air with which to form a thin surface layer of water.)

The note about relative humidity should be emphasized. Migratory antistats, in particular, require enough water available in the air for them to attract a thin water layer at the product's surface. In a dry electronics manufacturing environment or in the wintertime, this can be a difficult challenge and may result in unanticipated (poor) results. This humidity sensitivity also makes the testing and direct comparisons of migrating antistats more difficult [6-1, 6-2, 6-7, 6-8, 6-16, 6-25, 6-27, 6-28].

6.1.2 Nonmigrating polymers as permanent antistatic/ESD additives

Migrating antistats are satisfactory solutions in many cases, but inherently dissipating polymers (IDPs) or conductive polymers added to POs induce permanent antistatic/ESD properties. Two main advantages of these materials are usually cited in the literature: (1) IDPs are large molecules that are not consumed, so they provide stable antistat/ESD properties over time and (2) IDPs do not bloom to the surface, so they cannot be "wiped off" and do not affect other surface properties. They are also usually clear, thermally stable, and some are much less affected by humidity than migrating antistats. Permanent polymeric antistats are usually conductive block copolymers that form continuous conductive networks when added to a polymer matrix. Many IDPs are not compatible with POs; the ones discussed below are compatible [6-16, 6-20, 6-28].

Nonmigrating agents can be used across most if not all PO applications that require an antistat. For instance, the Entira ethylene ionomer from DuPont has been evaluated in film food packaging, pharmaceutical and cosmetics products, electrical products, and injection-molded and blow-molded packaging. Effective use requires a loading of 10%–20% of the Entira MK400 material, but in multilayered packaging film and bottles, for example, only the thin outer layer requires the IDP for product effectiveness. However, as with migrating antistats, resistivity depends on relative humidity, with resistivity with this additive dropping off into the ESD range only when RH is above 40% [6-16, 6-17].

Other permanent IDPs in electronics packaging provide charge dissipation that is neither too fast nor too slow. An excessively conductive surface (surface resistivity $<10^5$ ohms/sq) can damage electronic parts; too-slow restrictive ESD (resistivity $>10^{12}$) may cause dust accumulation and random discharging. One antistatic polymer family said to provide these in-between ESD properties are Pebax polyether block amides from Arkema. These materials are reportedly less affected by relative humidity than other antistats, and provide surface resistivity of around 10^9 ohms/sq. With melting points of about 150°C–200°C, they are dry-blended with POs at about 15%–25% loadings (typically also requiring a compatibilizing agent loaded at 3%–5%) [6-14, 6-15].

Permanent antistats developed by Ciba likewise reduce resistivity to ESD levels (10^9–10^{10} ohms/sq) without being significantly affected by low-humidity levels. In PE film packaging of industrial powders, pellets, or fluids, the company's Irgastat P additives prevent uncontrolled discharge at about 12%–15% loading. On blow-molded HDPE intermediate bulk containers, an outer PE layer containing the additive is said to provide safe handling of flammable substances. These containers can acquire static charges from the friction of being filled, potentially leading to accidental spark charges, unless an antistatic outer layer allows the charge to gradually dissipate when the container is grounded. Other reported uses of the additive include electronic parts packaging, as shown in Case 6.1 [6-19, 6-20, 6-21].

At the extreme end of permanent antistatic polymers are inherently conductive polymers (ICP), some of which are said to have recently overcome processing problems in their use. ICPs, including polyaniline, polypyrrole, and polythiophene, can reduce resistivity well into the ESD or conductive range ($<< 10^8$). Typically "doped" with a reducing or oxidizing agent, the ICP polymer chains provide a direct path for electron conduction at 10^4 ohms/sq resistivity. However, ICPs can cause a "hard," rapid discharge in use, as can carbon black and conductive fillers discussed below [6-4, 6-20].

6.1.3 Conductive fillers as antistatic/ESD additives

Inherently conductive filler particles, at high-enough concentration, create a stable network in the bulk volume of the polymer that allows electricity to flow or "percolate." Good conductivity requires that filler particles contact

CASE 6.1 STATIC-DISSIPATIVE AND COLORABLE LDPE BAGS FOR ELECTRONIC PARTS [6-22, 6-23]

Problem: Bags for handling electronic parts are subject to "hard" static discharges, damaging parts.

Objective: A "soft" discharging permanent antistatic additive alternative to migratory additives and carbon black.

Solution: A permanent antistat that allows coloration of the bags.

Uncontrolled discharge is a threat in all sensitive electronic component manufacturing operations. Thus the handling of these parts requires plastic packaging that dissipates charge relatively slowly over time.

For LDPE bags used to carry electronics parts, migratory antistats or external antistats can be wiped too easily from the surface of the bag and onto the parts, causing contamination or corrosion. Another antistatic additive option is carbon black, but it can allow rapid discharges of a charge built up in the bag, and it is not colorable (with coloration useful in electronics plants for identifying parts quickly).

These inexpensive antistatic solutions cannot be justified when the threat of costly part damage is high. Thus Ciba's Irgastat P series of permanent antistats have been proposed as a solution that allows coloration and slow, "soft" discharging as bags are moved around the plant with nongrounded transportation methods. Likewise for bags used in chemical plants, these soft ESD properties are said to be critical for reducing the risk of explosions.

each other in the resin, which requires adequate loading levels up to a threshold level (above which additional amounts do not significantly increase conductivity). Obviously, the filler material's conductivity is a key factor, as well as its shape. Fillers that are much longer than they are wide (in other words, having a high aspect ratio) are more likely to contact each other and thus they lower resistivity. These additives are typically flake-shaped metals or conductive fibers, which are most useful in higher-conductivity EMI shielding applications discussed in Section 6.2 [6-4].

Carbon black is a relatively standardized, inexpensive, and easily processable filler material that can provide ESD properties. Carbon blacks are formed by burning hydrocarbons in a limited oxygen environment, leaving a residual of 98% fine carbon particles.

A filler of flexible design, carbon black grades for ESD are available in various grades to meet various cost and compound performance criteria. As defined by supplier Cabot Corporation, these criteria are conductivity, dispersability, surface smoothness, flexural stiffness, and impact strength. High conductivity in the carbon black tends to depress the last three properties in this list. But, for example, Cabot's high-end carbon black (Vulcan XC605) reportedly optimizes all five criteria at once. Other grades maximize just one quality, such as conductivity, to its highest level, with the other properties being only equivalent to or worse than standard carbon black. With carbon black, however, the coloring options for the PO are limited, but resistivity can reach from antistat levels to even below what is typically required for ESD performance, down to near-conductive levels ($<10^4$ ohms/sq) [6-10, 6-11, 6-12].

Other, nanometer-scale forms of carbon, such as nanotubes and graphenes, have been proposed as ESD fillers, though their early use may be greater with engineering polymers. Carbon nanotubes (CNTs), in diameters of 10–100 nm, can induce the conductivity needed for electrostatically paintable plastic automotive body panels, for example. They are also said to be replacing carbon black and fiber in small, detailed electronics applications [6-5].

However, CNTs are still high-cost fillers, and they must be properly dispersed to obtain percolating ESD conductivity that is higher than compounds containing carbon black. Dispersion may be achieved through adding CNTs dispersed in a precompounded masterbatch, or, reportedly more effectively, direct mixing of CNTs using a specialized mixing process. A study by Stratek indicates that 3.5% CNTs dispersed in HDPE using a "Tek-Mix" process provides resistivity levels equal to those of a masterbatch-dispersed CNT loaded in HDPE at 7%. (The CNT in the study was Bayer MaterialScience's Baytubes C150P, supplied as 1- to 2-nm diameter CNTs agglomerated into 750-μm diameter particles.) The company estimates the lower usage translates into a potential savings of over \$5/lb (\$10/kg) of product produced [6-26].

Graphenes are thin carbon-based sheets or platelets 5 nm thick and up to 100 μm long. This gives them a higher surface area available for conduction than nanotubes have. According to manufacturer XS Sciences, graphene's percolation threshold is only 2–5 wt% in plastics, similar to that of high-conductivity carbon black but less than that of metal fillers and fibers. Graphene is also said to cost about as much as high-end carbon black and half as much as metal and carbon fibers, with better processing characteristics than other carbon fillers [6-5, 6-13].

6.2 EMI SHIELDING

EMI shielding applications of POs are not mentioned often, since most electronic devices use engineering polymers as enclosure materials. Yet one might expect more electronics applications in which low-cost PP would be called upon to enclose sensitive electronics. More and more of these devices require that the electromagnetic noise or radio frequencies they emit or are exposed to do not interfere with the operation of other devices or their own functioning. Consumers' interests and some government regulations will ensure that device makers will always be looking for better cost-effective ways of shielding devices from EMI, whether the electromagnetic energy comes from other devices, stray radio signals, or power lines [6-3].

For EMI shielding within a device's plastic enclosure material (rather than added on as conductive paint or metal foil), conductive fibers or fillers are usually proposed as internal agents. These additives typically must reduce surface resistivity below 10^4 ohms/sq to be considered effective. The most appropriate standard method for determining EMI shielding effectiveness (SE) of composite materials is ASTM D4935, which measures the transmission of electromagnetic waves of various frequencies [6-4].

6.2.1 Conductive fillers for EMI shielding

As mentioned above, additives such as carbon black or metal fillers offer various levels of conductivity in a resin. Researchers have reported various SE results with these fillers in PP. For example, testing has determined EMI conductivity loading thresholds of around 5 volume percent (20 wt%) for carbon black in PP, which provides similar SE values, at 30–35 dB, as 5–10 volume percent (20–40 wt%) aluminum flake in PP. Other researchers have mixed these two materials together in a resin for better results. However, at the high loadings required for EMI, the negative impact on mechanical properties can be significant [6-3].

Whether these fillers are used for ESD or EMI purposes, silane, titanate, or zirconate coupling agents are said to improve a conductive filler's effects without reducing mechanical properties. These coupling agents reportedly lower melt viscosity, de-agglomerating conductive particles, and increasing dispersion. Even forms of zirconate agents added alone, at 1% concentration, are said to facilitate transfer of electrons and create permanent antistat properties in olefins and other polymers [6-3, 6-18].

6.2.2 Conductive fibers for EMI shielding

Stainless steel fibers have aspect ratios of 500 or more, making them effective at only a few volume percent (10wt%–20wt%) loading. These fibers require gentler processing in molding operations, with higher temperatures and lower injection pressures needed to prevent fiber breakage and to optimize dispersion. *Carbon fibers* (nickel-coated or otherwise) in the resin also offer EMI conductivity and positive properties for a compound, though at some expense (as discussed in Chapter 7) [1-1, 6-4].

However, in comparison with external conductive metallization coatings for EMI shielding, these internal conductive fibers can be more cost-effective. For example, even though 15 wt% stainless steel fibers may add 50% to a compound's cost, the part's total costs should still be less than the costs of metallizing a nonconductive part in a secondary operation, because of the coating operation's fixturing, handling, inventory, and health and safety costs [6-4].

6.3 CHOOSING ANTISTAT/ESD/EMI ADDITIVES

6.3.1 Antistat selection factors

Obviously, cost and application requirements will determine the choice of an antistatic additive. Migrating antistats, for instance, have cost advantages, but also have usage limitations that industry observers have noted. Along with the pluses and minuses discussed in Section 6.1.1, there are other specific important factors to consider when using migrating antistats:

- *Consumption of antistats*: Thin PO products limit the extent to which antistats lost at the surface can be replaced by antistats migrating from within the bulk material. But thick products, such as wood–plastic composites, can be loaded with high amounts of antistats, allowing a steady supply at the surface over a long period [6-5].
- *Antistat performance variability*: A given antistat product may not perform the same in different PO applications. For example, a higher melt-flow-index or more crystalline PO may require a higher antistat loading. Or, higher-molecular-weight antistats may be needed when higher thermal stability is required. And as mentioned, the relative humidity of the final application is a dominant factor [6-1, 6-9].

CASE 6.2 UNRESTRICTED USE OF MIGRATORY ANTISTATS [6-6, 6-24, 6-25]

Problem: Limitations of ethoxylated amine and amide antistats used in PE food and electronics packaging.

Objective: A migratory antistat without use limitations or side effects.

Solution: An amine-free PGE antistat with no food-use restrictions or corrosive effects.

Ethoxylated amines have been used effectively in food and electronics packaging PE, yet some issues are connected with their use. EAs have concentration restrictions in food packaging, which limits their potential effectiveness. And in electronics packaging, EA-containing packaging causes stress cracking of polycarbonate used in electronic circuit boards and other components, when the two materials inevitably come into contact (and even some amide-based antistats are said to have enough amine content to cause problems).

So product developers at Danisco Emulsifiers tailored amine-free, fatty-acid-based polyglycerol esters for use as antistats. Being the company's main product of interest, PGE 308 reportedly carries no loading restrictions in food packaging such as 50-μm LDPE blown film, thus allowing adequate concentrations for effectiveness. In electronics manufacturing environments, PGE 308 is said to work in the very low relative humidity levels (<12%) that are common, without damaging polycarbonate components.

After processing, the PGE 308 takes about 2 weeks to develop good properties. It then sustains the properties over the long term, when used at the 0.25%–0.80% loadings recommended for electronic packaging. Moreover, the PGE's relatively high-molecular-weight also reduces its volatility.

Developers considered a number of factors when developing PGEs as antistats. First, there must be sufficient polarity in the molecule for it to function at the plastic's surface, even in dry environments. And when possible, the antistat's migration rate can be distributed over time and optimized through the combination of relatively fast and slow migrating components.

- *Reactivity with other additives*: Amine (EA) and amide (LDA) antistats can react with halogenated flame retardants and other acidic additives. They also compete for space at the surface of the polymer with other migrating additives, such as slip agents [6-27].
- *Clearance for food-contact use: Food use*: Some traditional antistats also face regulatory usage limits in food-contact packaging; current food safety regulations may limit their use to certain product forms. Many of the nonionic agents used heavily in POs meet basic US FDA approvals, although EU regulations prohibit phenolic antistats in food packaging. Some antistats face specific concentration restrictions in food use, such as LDA or ethoxylated amines in packaging film (by comparison, fatty-acid-based glycerol esters typically lack these restrictions; see Case 6.2). Achieving antistatic properties within food-contact concentration limits may even require combining different antistats at their maximum allowed concentrations, such as GMS and ethoxylated amine in a PP impact copolymer application [1-1, 6-1, 6-5, 6-9, 6-25].

6.3.2 Design considerations for EMI shielding

With internally shielded electronics enclosures, other nonmaterial issues, such as part design, need to be considered before the material or additive can be blamed when EMI problems occur. For example, thin-wall enclosure designs—though often preferred as a way of minimizing material costs—can reduce the shielding effectiveness of internal conductive fibers (as well as causing more fiber breakage). Or an enclosure design that has several holes or slots or leaves gaps between components can permit electromagnetic leakage, reducing overall shielding effectiveness.

In fact, leakage between mating surfaces or at joints is cited as the main factor that reduces an enclosure's shielding. These gaps break or cause resistance in an enclosure's internal electrical "circuit"—the continuity of electron current flow through the inherently conductive material. Moreover, molded-in "resin-rich" surfaces are favored by customers, so that fibers or large flakes are not visible on the product's surface. But a resin-rich surface isolates the conductive additives more, increasing resistance between mating surfaces. Fortunately, various joint designs or joining methods can mitigate these leakage problems [6-3, 6-4].

3

SECTION III

Mechanical Property Enhancement

CHAPTER 7

Overview of Fillers and Fibers

This chapter concerns the most commonly understood additives for plastics—and perhaps the most important ones for enhancing a compound's physical properties for designed uses. Fillers and fibers made from inorganic and (increasingly) organic materials are essentially foreign constituents added to the PO matrix. These "intentional contaminants" are themselves relatively chemically inert (except in the way they react with coupling agents to bond them to the polymer)—yet their mechanical property contributions can be critical for creating new PO applications.

There is somewhat of a contradiction of discussing fillers and fibers in the same chapter. Fibers and many fillers can increase properties in very specific, desired ways; yet the most common inexpensive fillers, such as calcium carbonate, are mostly used to displace the resin needed in a product to keep resin costs low (literally "filling out" or extending the volume of a product). In the first decade of the twenty-first century, when double-digit percentage increases in resin prices have been common, perhaps this use of fillers has become even more important.

However, this chapter is more focused on summarizing how different fillers and fibers affect PO properties. The next chapter will take on the burden of trying to relate these property-changing effects to actual end-use situations, to assist in the decision-making process for filled and reinforced POs (thus, all filler/fiber case studies are placed together in Chapter 8 rather than in this chapter). This chapter will limit itself to these questions:

- (7.1) Why are fillers and fibers used in POs?
- (7.2–7.4) What are the most used inorganic and organic fillers and impact modifiers, and how do they affect a PO compound's properties?
- (7.5) What are the most used fiber reinforcements, and how do their size, composition, and concentration enhance a resin system's properties?

7.1 IMPORTANCE OF FILLERS AND FIBERS FOR POs

PE and PP might always be placed into the category of "commodity resins" and set off from engineering resins by virtue of their relatively low tensile properties and service temperatures. However, this is oversimplifying in many cases; compounded POs can serve in many engineering-type applications by incorporating fibers and fillers to increase mechanical and other properties [7-1, 7-2].

Whether these useful property changes come from the most inexpensive inorganic fillers, or from highly engineered, long glass fibers requiring specific processing techniques and equipment, reinforcing additives turn PO compounds into composite systems with property vs. cost trade-offs, just as with chemical compound additives. Moreover, inexpensive fillers (whose costs are not directly tied to fossil-fuel feedstock prices) offer opportunities for saving materials costs by decreasing the percentage of relatively expensive polymer needed in a compound.

Although many kinds of fillers and fibers have been added to POs over the years, and new ones continue to be developed, the sections below cover the most used and most commercially important materials. These fillers and fibers continue to draw the greatest efforts from industry and academia for further development and improvement. Some newer kinds, such as nanofillers and plant-based fibers, are included here mainly because of their potential future importance. As in other chapters of this book, here the focus is more on materials that can be added in a typical compounding operation or "at the press"—rather than modifiers that are added more upstream by the resin producer, or hybrid combinations of materials, such as glass-mat composites or laminates, where the reinforcing material is not added during screw processing.

The next section will focus on relatively conventional fillers composed generally of particles above 1 µm. Section 7.3 will focus on nanofillers composed of sub-micron size particles; many of these materials are only just emerging into the commercial arena. Section 7.4 will cover impact-modifying materials added to POs during compounding. Section 7.5 will focus on fiber reinforcements and fillers whose particles' length is much longer than their diameter or width.

7.2 COMMON INORGANIC FILLERS

Inexpensive fillers are economically useful as "extenders" that displace more expensive resin needed in a resin system, without adversely affecting most properties. Indeed, processors often depend on increasing their use of such fillers during times of high polymer prices.

But most of these fillers can be seen as "functional" as well. Generally speaking, when properly dispersed in a polymer matrix, filler particles physically interfere with the continuity of polymer domains and thus also the way forces are transferred through the material system. Provided that the bulk filler is free of contamination, its particle size and shape is consistent, and its particles are well dispersed a filler will affect a compound's mechanical properties in predictable ways. Mineral fillers typically increase hardness and stiffness, usually at the expense of impact resistance. Mineral fillers also help maintain dimensional stability. For example, they counteract PP's tendency to distort and warp, a frustrating problem that has caused some processors to refer to PP using the unflattering nickname "polywarpylene." Dimensional stability, as well as the scratch resistance that some fillers enhance, will become even more important in engineering uses of PP for automotive applications and their fit and finish requirements [1-1, 3-4, 7-6].

7.2.1 Calcium carbonate

Along with talc, calcium carbonate ($CaCO_3$) is one of the most used fillers in POs. Calcium carbonate's reputation lies more in its role as a bulk extender used for displacing the relative amount of resin needed in an application. Producers of commodity HDPE bottles and packaging, for example, rely on these fillers for minimizing raw resin costs. However, fine particles of $CaCO_3$—loaded at 10%–60% and using the proper surface treatment or coupling agent to bond them to the polymer—also increase stiffness, hardness, and dimensional stability (while normally lowering tensile and impact strength properties, depending on the grade of $CaCO_3$ and its coating) [1-1].

Commercial calcium carbonate products typically contain 95%–98% $CaCO_3$, with the remainder being various metal oxides. The material is typically ground from limestone (such as dolomite) or chemically precipitated into fine, uniform particles with, unfortunately for processors, high moisture take-up. $CaCO_3$'s specific gravity is 2.7, and particle sizes may vary from 1 to 100 µm, with the median size usually being from 3 to 20 µm [7-5, 7-6].

Treating calcium carbonate particles allows maximum dispersion of the filler, easier processing of highly filled compounds, and higher-impact strengths than POs filled with untreated $CaCO_3$. Typical materials for coating $CaCO_3$ particles include fatty-acid-based stearic acids, which are molecules having carboxylate functional groups that anchor them to the filler surface. Stearic acid, however, has limited ability to bond or entangle with the polymer, limiting its effectiveness as a true coupling agent. In contrast, maleic-anhydride-grafted polymers do bond to the filler particle and the polymer for better coupling. But such formulations may require 5%–10% of the polymer, increasing viscosity and affecting mechanical properties. Alternatively, silane-based agents bond both to the filler and polymer, and at least one product (Solplus C800 from Lubrizol Advanced Materials) is said to bond effectively to the relatively inactive surface of $CaCO_3$. This product, loaded at about 1% in highly loaded $CaCO_3$/PP systems, reportedly results in higher strength and modulus properties, while better maintaining impact strength at levels above those of stearate-treated $CaCO_3$ grades and closer to the values of the unfilled polymer [7-4].

7.2.2 Talc

The other most used PO filler, talc, is a plentiful, naturally occurring hydrated magnesium silicate mineral (with composition $Mg_3Si_4O_{10}(OH)_2$). Relatively soft and slippery, talc has similar effects as calcium carbonate in a PO matrix, although talc typically increases modulus more and reduces impact strength more. Its mechanical effects are enhanced by its plate-like particles' high aspect ratio, which is the ratio of a particle's major dimension (length) to its minor dimension (width, thickness, or diameter). Talc greatly affects certain properties in both PE and PP, as shown in Table 7.1. In particular, in PP, talc is valuable for increasing HDT, and in PE films, it also provides anti-blocking properties (see Chapter 12) [1-1, 3-4, 7-6, 7-11].

Talc is typically used at up to 50% loading, in particle sizes of 1–100 μm. "General purpose," coarse talcs (used in WPCs, for example) have particle sizes above 5 μm, while "fine" talcs have median particle sizes between 2 and 4 μm and are particularly important for high-impact automotive TPO applications. In recent years, manufacturers have offered processing options for some

Table 7.1 Comparison of Mechanical Property Effects of Very Fine Talc in PE and PP (Luzenac and Jetfine 2-μm Median Size Talc from Rio Tinto)

		Talc Loading		
Polyolefin	**Property**	**0%**	**10%**	**20%**
HDPE	Flexural modulus, MPa	670	990	1480
HDPE	Tensile yield, MPa	25.0	26.5	26.2
HDPE	Elongation at yield, %	40.6	22.1	16.8
HDPE	Izod impact strength (at 23°C), kJ/m^2	27.4	23.4	18.2
HDPE	Heat deflection temperature (1.8 MPa), °C	39	40	44
PP copolymer	Flexural modulus, MPa	1255	1925	2800
PP copolymer	Notched Charpy impact strength (at 23°C), kJ/m^2	n/a	9.5	6
PP copolymer	Heat deflection temperature (1.8 MPa), °C	53	61	70

Source: Adapted from [8-10, 8-11].

talc grades that "compact" the bulk talc. This increases the bulk density of fine lamellar talc grades that have relatively low bulk density, reducing the amount of trapped air and improving handling and feeding in processing. Compacted talc has roughly 3 times the bulk density of standard fine talcs (0.9 g/cm^3 vs. 0.3 g/cm^3), allowing reportedly a 300% increase in output in the melt processing of a 30%-talc PP [7-8, 7-9].

More recently, higher-aspect-ratio "ultrafine" grades of talc have become available. These are particularly directed at improving the properties of PP and PP-based TPOs for automotive bumpers, body panels, dashboards, and interior trim. The production of these talc grades improves the quality of talc's layered structure, which is composed of weakly bonded layers of silica. The layers generally delaminate during talc milling operations, but only until particle sizes decrease to about 2 µm. At this point, milling starts to destroy the talc's useful platy lamellar structure rather than delaminating the layers; this reduces the stiffening and reinforcing effects of any sub-2-µm talc particles in the compound. However, improved milling processes from Rio Tinto Minerals, IMIFabi Spa, and other manufacturers create delaminated talcs that retain their platy structure and properties down to around 1-µm sizes. This is said to improve the resulting compound's stiffness/impact-toughness balance, especially at low temperatures [7-10, 7-11, 7-12].

With improved dispersion methods, these talcs, in compacted form, reportedly allow lower (3%–10%) loadings of talc to be used for the same properties of standard fine talc compounds at higher (~20%) loadings. This allows lighter PP and TPO parts, a priority of the automotive industry. Moreover, masterbatch concentrates with 50% ultrafine talc have been shown to provide dispersion with single-screw processing that is similar in quality to the dispersion of powdered talc with twin-screw extruders. The grades are also said to reduce permeability and shrinkage in HDPE blow molding [7-10, 7-11, 7-12].

Combining both talc and calcium carbonate in one compound combines some of the benefits of each filler (and helps hide their weaknesses). For example, adding the plate-like talc particles with calcium carbonate particles reportedly brings in the high stiffness of talc without losing as much impact strength as in talc-only PO compounds [7-6, 7-7].

7.2.3 Wollastonite

Wollastonite is a mineral composed of calcium and silicon oxides (a metasilicate, composition $CaSiO_3$). It is valuable as a filler in its form of acicular (needle-like) particles with aspect ratios from 5 to 20 and particle sizes (lengths) of 2 to 40 µm. It is often used at 10%–20% loadings as a reinforcing filler that increases a PO compound's tensile and flexural strength, as well as offering higher-dimensional stability and less mold shrinkage than talc or

$CaCO_3$ compounds. Wollastonite's fiber-like shape provides similar properties as those of the glass fibers discussed below, and also like glass, its abrasiveness can damage processing equipment. However, unlike other mineral fiber, asbestos, its particles are nonhazardous [1-1, 3-4, 7-6, 7-13, 7-15].

Overall, wollastonite has become a more common filler alternative to talc or glass fiber. Its properties have made it useful for reinforcing PE and especially PP, for applications such as automotive panels and housings, door handles, and appliances. For a PP copolymer used in a hard automotive trim component, for example, wollastonite at loadings of 5%–10% in PP provides similar mechanical properties as 15% talc-filled PP, according to data from major wollastonite supplier Nyco Minerals. And in a head-to-head comparison with a 7.5-μm 20% talc-filled PP copolymer, an 8-μm 20% wollastonite-filled grade provided about 30% higher tensile strength, 20% higher flexural strength, 60% higher flexural modulus, and 60% higher notched-Izod impact strength. Scratch and mar resistance is another important property for automotive use; one study showed that 20% wollastonite PP, especially when containing a lubricant/modifier additive, provides much less scratch visibility than 20% talc PP containing the same lubricant/modifier [7-13, 7-14].

As a partial glass-fiber replacement, 10% wollastonite plus 10% chopped glass fiber in PP reportedly provide equal HDT and nearly equal flex modulus and tensile strength as 20% glass fiber alone (though it does not provide the same Izod impact strength as does 20% glass) [7-13].

As with other silicate mineral products, the freshly milled surface of wollastonite particles attracts hydroxyl groups (from water), preventing the filler surface from fully coupling with the nonpolar polymer. However, surface treatment of the wollastonite particles with a silane-based coupling agent is said to improve dispersion and processing. It also improves impact resistance, surface gloss, dimensional stability, and scratch resistance properties. Silane coupling agents are also said to reduce dust in filler handling and increase filler flow and dispersion in processing [1-1, 7-6, 7-15].

7.2.4 Mica

Mica is a general term for other metal-hydrate silicates with plate-like particles having aspect ratios of 50–100. As a platy filler, it provides similar property enhancements as talc. In PP, high-aspect-ratio mica has been shown to increase modulus to levels 50%–100% higher than talc or $CaCO_3$ can at the same loading levels, with little or no reduction in impact strength. Adding mica or talc to glass-filled compounds helps control warpage, while mica by itself could be seen as an intermediate reinforcing filler option in between talc and glass fiber. Surface-modified mica has particular importance for providing "special effects" coloration to a compound, discussed more in Chapter 9 [1-1, 3-4, 7-6].

7.2.5 Silica

Silica (silicon dioxide) particles, synthetic or natural based, have commonly been used in various polymer systems. Silica has a low coefficient of thermal expansion and high stiffness, translating into increased modulus of the compounded polymer. However, silica filler particles are not flake or plate like as talc or mica particles are, and typically have low aspect ratios. This means that unless the particles are very small, a silica filler addition provides a relatively low surface area for contacting the polymer, and thus it reinforces the resin system less than platy fillers. Researchers have also noted that mica-filled PP, for instance, contains fewer voids than silica-filled PP, which helps explain the higher strengths of mica compounds at 20% filler loadings. This tendency to form voids or cavities increases as silica filler content increases [7-20, 7-21].

Diatomaceous earth (diatomite) is composed of fossilized silica-based shells of diatoms, single-celled marine organisms. Like synthetic silica, it is used mainly at low percentages for its anti-blocking properties in clear PE films (see Chapter 12). However, also like synthetic silica, diatomaceous earth absorbs water, which limits its shelf life [7-20].

7.2.6 Glass flour and spheres

In addition to its use as glass fiber (discussed in Section 7.5), glass is used in the form of low-aspect-ratio filler particles to provide useful properties and the economic advantages.

Glass flour has been proposed as a relatively inexpensive, environmentally responsible filler, since it is made from crushed recycled glass. However, this low-aspect-ratio form of glass has suffered from the poor quality and inconsistency of its recycled source material because of contaminants and inconsistent color and particle sizes; this has made its commercialization as a filler difficult. At least one supplier, Vitro Minerals, now provides amorphous glass flour (free of crystalline silica) that is made from a relatively high-quality post-industrial recycled fiberglass. Although conventional mineral fillers are still more cost-competitive, the lower "carbon footprint" of the recycled filler and its properties are said to make it a legitimate filler option. In particular, the supplier claims it offers better or favorable chemical resistance and abrasion resistance; lower oil absorption; and better clarity and colorability than calcium carbonate, talc, wollastonite, diatomaceous earth, or other conventional fillers [7-22].

Hollow glass microspheres can be added to POs as a way of stiffening the resin system while also reducing its density substantially. Microspheres that are used as plastics fillers have typically only about 0.6 g/cm^3 density, much lower than standard fillers (with densities of 2.7–2.9). The low density helps make the spheres more cost-effective on a volume basis, and translates into filled-PP densities as low as 0.8 g/cm^3 when loaded with 30% spheres (by volume).

Typically used in plastics at particle sizes around 16–30 μm in diameter, the glass spheres' "ball-bearing" effect is said to ease the melt flow and cooling of the compound, unlike other fillers which increase viscosity. The spheres also reportedly reduce cycle times (compared with talc-filled compounds), molding shrinkage, and coefficient of linear thermal expansion (CLTE), while increasing modulus and flexural strength. In an injection-molding study comparing a 20% (by weight) 16-μm microsphere black PP frame part with a 20% talc-filled PP, the density of the sphere-filled PP was nearly 19% lower, translating into 17% reduced part weight. Moreover, shrinkage of the microsphere-filled part was reduced in all directions, compared with a talc-filled part. And since the microspheres allowed the part to cool quicker, cycle time was reduced from 16.6 to 13.2 seconds [1-1, 7-16, 7-17].

An issue that has delayed microspheres' use in plastics has been their breakage under standard processing conditions. However, in recent years, manufacturing process improvements have created smaller 16-μm microspheres that are strong enough to resist the higher pressures and forces of plastics compounding or injection molding. Still, some precautions should be taken in processing, such as side-feeding the spheres farther downstream into the screw rather than with the resin in the hopper, and lower packing pressures during molding [7-16, 7-17].

The size of microspheres also affects mechanical properties; the 16-μm spheres reportedly provide higher notched-Izod impact and tensile strength than 30-μm spheres. And, like other inorganic fillers, silane coupling agents enhance the hydrophilic glass filler's bond to the polymer, improving impact and tensile strength by about 40% over untreated microsphere compounds. Coupling agents also reportedly increase elongation dramatically and reduces sphere breakage during processing [7-16].

7.2.7 Other microfillers

Various other functional fillers used in POs offer useful properties for particular applications. These include *metal flake pigments* (discussed more in Chapter 9). Used mainly to add aesthetic coloration or conductivity to a compound, they also affect mechanical properties. Metal fillers such as aluminum flakes slightly reduce tensile strength, even at low loadings (1%–5%) and small particle sizes (10–30 μm). And they are reported to reduce elongation substantially, by 20%–80%. However, unexpected relationships are also reported in the literature. For example, in an elastomer-modified PP, for example, aluminum flakes were found likewise to decrease elongation, although they did increase impact strength at 10-μm flake sizes [6-3].

Magnetite (Fe_3O_4), a common iron ore, adds density and magnetic properties to a resin for sound-dampening or anti-static/low-resistivity applications. The filler also absorbs microwave energy and resists visible scratches. Added at 60%–80% in 9-μm or higher particle sizes, magnetite reportedly can be processed with common equipment [7-18].

Other dense fillers are useful for sound-deadening purposes, such as *barium sulfate*. Likewise, *tungsten* and *bismuth* can be used in POs to increase density and create a metal-like heaviness in consumer products. This quality is said to be potentially useful for semi-durable products like cosmetics/personal-care packaging (lipstick tubes, etc.), where the density of metal suggests quality, but where it would be cost-prohibitive to produce the product in metal. Standard plastics processing can be used with these filler compounds, according to manufacturer Clariant Masterbatches [7-19].

7.3 NANOFILLERS

Up to this point, the fillers discussed are commonly used in the micrometer (10^{-6} m) range of particle sizes. Extending into the smallest possible, submicron range (10^{-9} m) of particle sizes are the technologies loosely grouped under the term *nanofillers*, which are dispersed into polymeric matrix materials to create *nanocomposites*. These materials have drawn great attention recently and have spurred a steady stream of journal articles and academic literature. Yet nanofiller materials comprise essentially just a sub-category of polymer fillers (though a potentially important one if early speculation proves true, and if early applications for nanofillers can become commercialized at larger scales).

Far from being extending bulk fillers added at high loadings to displace resin, nanofillers are functional reinforcements that enhance properties at low loadings. The optimum result of their development would be nanocomposite resin systems that can be easily processed with common compounding, extrusion, and molding equipment. But questions remain about whether their processability and economics will truly allow nanofiller-reinforced plastics to reach widespread use.

7.3.1 Potential of nanofillers

The growth of nanocomposites is predicted to outpace other plastics-related materials over the next one or two decades. The market-tracking firm Freedonia Group Inc. estimates nanocomposite demand to grow in the United States alone from 133 million pounds (60 million kg) in 2006 to 920 million pounds (420 million kg) in 2016. Early applications have predominantly been in packaging, but by 2016, the motor vehicle and electrical/electronics sectors are expected to be the largest users of nanocomposites, given the engineering properties nanofillers can provide. These engineering uses reflect nanocomposites' potentially high value in the market; consultants expect overall worldwide nanomaterial demand to increase from $1 billion in 2006 to $100 billion by 2025 [7-29, 7-30, 7-32].

There are some reasons for these optimistic growth predictions. As a filler particle's size is decreased to sub-micron dimensions, unusual and desirable property improvements appear in the resin composite. Although sub-micron silica and barium sulfate have been used as nanofillers, relatively inexpensive organically modified clay-based nanofillers provide the most notable properties because of their extremely high aspect ratios (above 1000, compared to 100 or less for common fillers). This high L/D ratio of the clay particles provides better dimensional stability than conventional microfillers, as well as higher stiffness at lower filler loadings (typically under 5%)—without typical losses of impact resistance or other desirable properties. Some nanofillers have been shown to enhance gas-transmission barrier properties, flame retardancy, and electrical static-charge dissipation properties. And the smallest nanoparticle fillers do not block visible-light frequencies, therefore allowing levels of translucency or transparency that are not possible with standard filled resin compounds of equivalent properties. POs, with their low properties, low cost, and easy processing, probably have the more to gain from nanofiller additions than engineering plastics [3-4].

Obstacles to greater nanofiller use remain, and just explaining these challenges requires a new set of terminology. The main issue is that nanofiller particles are difficult to disperse, meaning that actual nanocomposite properties may not reach their potential or theoretical properties. For example, for proper dispersal, sheet-like nanoclay platelets must be *exfoliated*, physically or chemically, to separate them into individual layers. This issue is probably the most discussed and most problematic obstacle impeding the full commercialization of nanocomposite compounds, since the full surface area of each separated sheet or platelet is what creates optimum properties [7-31, 7-32].

However, the same small size and high surface area quality that makes nanofillers useful have also called attention to their possible effects on the human body. This question has drawn calls for better health and safety standards specifying human exposure limits and handling practices. Conclusions about nanomaterials' health effects are limited, and regulatory and voluntary industrial standards are only in their early phases. (And considering the continuing negative public perceptions by the public about plastics in common use, industry would be wise to answer health questions about long-term nanofiller exposure well before large-scale nanocomposite commercialization accelerates.)

7.3.2 Platy nanoclays

Nanoclays potentially provide more significant property improvement at lower loadings than other fillers or reinforcements. The nanofiller that is most studied and commercialized is based on montmorillonite (MMT) clay, an abundant natural smectite clay material derived from bentonite ore. (Nanoclay products are typically modified with ammonium salts and are thus often called "organoclays.") Full nanoclay dispersal in the polymer is key to its effectiveness. For example, it has been estimated that just 2% of MMT nanoclay in a PO compound—when it is well exfoliated—provides equal reinforcement properties as a 10% micro-talc-filled compound. Thus, nanoclay fillers potentially provide an economical return in the form of enhanced properties; this is unlike nano-talc, for example, for which the costs required for size reduction do not result in significant-enough property enhancements in the polymer. The properties of nanoclay/PP materials have already allowed them to be used for lightweight, low-thermal-expansion automotive body moldings and high-gas-barrier packaging films [3-4, 7-31, 7-32].

Nanoclays are particularly difficult or impossible to fully disperse in the matrix during melt processing. To exfoliate MMT into layers of nanometer-range thickness in a polymer matrix, MMT particles are often surface-treated with charged quaternary ammonium compounds (quats) or other coupling agents (see Section 14.2.2). Yet even with sophisticated surface treatments that help separate clay layers and create a nonpolar environment that allows the polymer melt to intrude, platelets may still tend to remain stacked or layered, even in high-shear melt processing. As with any filler, without full dispersal, promised properties outside the laboratory are difficult to attain in real-world processing environments. (The large number of academic papers published each year on nanofillers and exfoliation shows the work researchers need to complete before more practical approaches to dispersion are available.) [3-5]

Still, some companies have offered nanoclay fillers in easy-to-handle, masterbatch pellet form. Nanocor, for example, is one company offering masterbatches with 40%–60% nanoclay content, in a variety of olefinic carrier resins. Let down at 8%–12% in PP, the company says the masterbatch improves flexural strength and modulus (by 50%–60%) and, in flame-retardant grades, improved UL94 ratings from V-1 to V-0, reducing the amount of mineral-filler flame retardant that would otherwise be needed [7-33].

Other similar "platy" clays are also being developed as nanofillers, including hectorite, a magnesium silicate. Hectorite is said to provide better high-temperature performance when loaded into PP than MMT/PP materials. For example, the manufacturer cites a hectorite nanocomposite's performance in exposure at 150 °C over 24 hours, where it did not degrade as the MMT/PP did [7-31].

7.3.3 Nanotubes

Nanotubes, both multiwalled (diameters 2–100 nm) and single-walled (diameter ~0.4 nm), have achieved high notoriety in the technological literature.

Hollow tubes extracted from the silica/alumina clay halloysite exist naturally as particles roughly 500 nm long, and they do not have the exfoliation issues of platy nanoclays. Thus, these nanofillers do not require the same specialized equipment and processing that nanoclays require for proper dispersal. As fillers, nanotubes provide high properties because of their very high aspect ratios.

Unfortunately, the high interest in these nanofillers matches their high costs from the difficulties in mining and separating the material (currently in the hundreds of US dollars per kg). Still, their annual growth rate is expected to be around 25%, according to industry analyst group Frost & Sullivan. But their commercialization requires that they are available in high volumes at more reasonable prices; this might require plant expansions or a technology breakthrough in producing nanotubes that could occur at any time [7-31, 7-32, 7-34].

Such developments will require new and improved halloysite extraction technologies, and there is steady progress toward this end. For example, in 2007, the “Pleximer” line of halloysite nanotube additives became available from NaturalNano Inc. These tubes have diameters typically less than 100 nm and lengths from 500 to 1200 nm. They have been demonstrated to nearly double the stiffness of PP, in loadings of 5%–13%, and increase tensile strength without losses of elongation. The company’s intention is to create a functional nanofiller that can be added to PP at the molding step, without special processing or equipment for dispersal [7-34, 7-35].

Carbon nanotubes offer similar potential property improvements. These are made from hexagonally bonded carbon atoms, like graphite, in single-wall or multiwall tube forms. They have high thermal and electrical conductivity, and this suits nanocomposites requiring electrostatic dispersion properties for applications such as fuel-handling parts and electrostatically painted automotive panels. The tubes also supply a char-forming, flame-retardancy effect. In terms of mechanical properties, Nanocyl, a company that produces the tubes, reports a near-doubling of tensile strength in PP (21–38 MPa) with a 5% loading of nanotubes. Here, modulus also increased while Charpy notched impact strength was reportedly unchanged, although there was a loss of elongation at break (from 114% to 11%). Nanocyl does report that carbon nanotube dispersal is a challenge, because it requires disentangling aggregates of the extremely long, thin, tangled tubes in the polymer melt [7-36].

7.3.4 POSS nanomaterials

Polyhedral oligomeric silsesquioxane (POSS) has been described as a three-dimensional “cage-shaped” molecule composed of a silicon–oxygen framework bonded to organic groups that make it compatible with a polymer matrix. Unlike conventional nanofillers that must be dispersed and exfoliated to be useful, POSS molecules formulated in the resin are induced by shear to “self-assemble” throughout the matrix into particles of 25–200 nm size. In a nanocomposite, POSS reportedly can provide as much as a 70% modulus improvement, 30% tensile strength improvement, and improved dimensional stability. In POs, nucleating agents are said to be useful for initiating the self-assembly of the POSS nanoparticles and providing the full property enhancements. With the relative lack of recent reports in polymer publications about POSS (relative to the amount published about other nanomaterials), it is still unknown if or when these interesting materials might become commercially important [7-52, 7-53].

7.4 IMPACT MODIFIERS AND TPOs

In most applications, impact resistance is usually a necessary quality; however, most inorganic fillers have a tendency to reduce a compounded resin's impact strength. By providing the opposite effect and increasing impact strength, elastomeric (rubbery) polymers added to POs could, in this context, be thought of as alternative functional fillers.

These impact modifiers soften and toughen POs for a number of enhanced uses in which standard thermoset rubbers or engineering resins were formerly used, including tubing and hoses, wire coverings, various seals, tear-resistant packaging, "soft-touch" products, and lightweight automotive trim. They have made certain products and properties possible that were never before possible with POs, such as PO films modified for higher tear or puncture resistance. Impact modifiers are cost-effectively integrated with the main polymer within polymerization reactors, and sold by major suppliers in large volumes; however, when added via screw processing they can also be used more flexibly as additives that increase impact toughness.

Compared with PE and random copolymer PP, PP homopolymers are brittle, and accordingly, they have the most to gain from impact modification. Their otherwise relatively high heat resistance and overall strength make impact modification a commercially important addition to their favorable properties, allowing them to be used in more engineering-type applications. Thus PP homopolymer modification will tend to be the main focus of this section, though other POs can also be toughened.

Unfortunately, the definition of "impact-modified PO" is sometimes obscured by commercial terminology. For example, the term *thermoplastic polyolefin* or *thermoplastic olefin* (TPO) covers a range of materials which are typically immiscible blends or compounds of PP, a stiffening filler, and a rubber impact modifier. These resin systems are sold as finished, ready-to-process pelletized materials, or are sometimes created at the final processing stage. Sometimes the distinction between TPOs and PP impact copolymers is not clear, since both depend on a finely dispersed rubbery phase for their properties (with impact copolymers generally including elastomers at lower loadings than TPOs).

TPOs are commonly made via reactor methods or compounding, depending on the product, properties desired, and manufacturer. Compounded TPO demand is forecasted to grow at an average rate of about 4.5%, per year, largely because of its importance in the automotive sector. TPO formulations typically include talc as a stiffening filler, so that the resulting parts are relatively stiff but still do not shatter on impact. Thus, commercially available TPO compounds target low-temperature, high-impact applications, such as automotive bumper fascia, panels, and trim. Given the broad range of TPO products and their growing importance in automotive, an entire book would be required to cover this class of materials. Some people in the automotive industry even speak of TPO as if it were a separate polymer family of its own [7-26].

However, the objective here is to focus on ways in which rubber modifiers can be added downstream of the reactor to improve impact strength, not to compare the various forms of materials sold as "TPOs." Dry blends of rubbery modifiers can greatly improve PP impact properties or LLDPE film properties, even when the modifiers are added at the injection-molding or extrusion screw-processing stage. (So even when the term *TPO* is used below, it generally indicates a PO modified with an elastomer in some way by a compounder or processor.) [7-23, 7-24, 7-25]

Elastomeric constituents used for impact modification create roughly the opposite physical properties of those created by standard inorganic fillers. They also differ from standard fillers in that they are perhaps more properly discussed as dispersed phases within a PO matrix, rather than as isolated filler particles having distinct boundary interfaces with the resin. Still, as with inorganic fillers, impact modifiers bring specific properties to the resin that depend on their type, loading, and dispersal.

7.4.1 Impact modification for thick products

Impact modification of POs had once meant simply adding ethylene–propylene–diene monomer (EPDM) rubber or other basic elastomers to PO. The PO then takes on some of the flexibility and impact toughness of the rubber but still retains melt-processability in injection molding and other processes. High rubber additions were used in successful, well-known thermoplastic compounds such as Santoprene. In the 1990s, the development of single-site metallocene catalysts for PO polymerization allowed new options in PO elastomer (POE) modifiers, such as *plastomers*—low-density ethylene-α-olefin copolymers with both plastic and elastomeric properties. POE development has led to strong, tough, and inexpensive TPO materials for physically rigorous applications [7-25, 7-26].

Ethylene–propylene rubber (EPR) and EPDM are traditional random copolymers used for impact modification. In PP, the elastomer content separates as a distinct phase, and it is this dispersion that tends to determine the compound's properties. The phase morphology and phase-particle size are affected by the qualities of the rubber and by the screw-processing or even by molding conditions. So it is no easy task to incorporate impact modifiers into processing, compared with the use of basic mineral fillers. Rubber particles can grow or coalesce during processing, especially when the viscosity ratio of the rubber's viscosity to the matrix resin's viscosity is high ($\gg 1$). This reduces the impact modifier's effectiveness [3-4].

In *thermoplastic vulcanizate (TPV)* modified compounds, the unsaturated (double-bond-containing) monomer branch in EPDM or another rubber modifier is crosslinked by sulfur, peroxide chemicals, or other curing agents. This is done "dynamically" during screw processing while the rubber is blended with the PO matrix. Crosslinking provides properties to the resin system that standard TPOs cannot provide—such as lower compression set and better mechanical properties at elevated temperatures. Thus, TPVs mimic thermoset rubbers and can compete with them because of their lower processing costs. These products have become commonly known by their trade names, such as Santoprene (from ExxonMobil) and Sarlink (DSM), though other specialty compounders offer effective products as well. It has been suggested that the expertise to create effective TPVs limits the number of compounders supplying it [3-4].

POEs or metallocene plastomers in pellet form are easier to handle and process than standard rubbers. They have displaced about 70% of the traditional EPDM modifiers used in TPOs, though EPDM-modified materials still have advantages for low-temperature impact applications. Still, metallocene/POE technology is probably the most important impact-enhancing technology developed over the last 20 years.

Plastomers are α-olefin copolymers of consistent structure, very low density ($<0.9\,\mathrm{g/cm^3}$), low crystallinity, and low molecular weight, allowing them to be processed as free-flowing pellets of predictable melt-processing behavior. Blended with homopolymer PP in twin-screw extruders at 20%–30% loadings, the resulting injection-molded parts have shown radical notched-Izod impact-energy improvements in tests at room temperature, down to −40°C. In testing reported by ExxonMobil Chemicals, this impact resistance reportedly increases even more when lower-density ($0.86\,\mathrm{g/cm^3}$) ethylene–octene copolymer plastomers are used in place of ethylene–butene plastomers. The octene-based materials are also softer (Shore "A" 50–80) [7-25, 7-26].

7.4.2 Impact modification for film and sheet

Impact modifiers for POs are not all based on olefinic chemistries, nor are they only used for "TPO"-type, injection-moldable automotive materials. In the area of packaging film, for example, thin PE and PP films suffer from poor tear and puncture resistance, properties analogous to impact resistance in thicker products. Here too, impact modifiers added in relatively low amounts (under 10%) reportedly can offer much improved properties. The octene-based POE modifiers mentioned above, for instance, reportedly also offer improved heat-sealing properties and optical clarity in PE or PP flexible packaging and films [7-25, 7-26].

In common practice, films are toughened by adding a variant olefinic form of the base PO resin. For example, PE cling films have been toughened by adding very low-density PE; LDPE films by ethylene vinyl acetate copolymer; and PP films by PP-based elastomer modifiers. But these impact modifiers are often required at high loadings, which lowers a film's other desirable mechanical properties. And they are not useful for toughening already-tough films made from metallocene LLDPE, which itself is used as an LDPE impact modifier. For extreme toughness, possible solutions include alternative elastomeric modifiers from outside the PO family, such as styrenic block copolymers, discussed in Case 8.4 [7-24].

A final word in this short summary of impact modification concerns the amount of imagination compounders and polymer scientists continue to invest in the development of rubber-modified compounds. Efforts are being made to decrease their compounding costs, to enhance their paintability, and to formulate them to replace more competing materials such as ABS, thermoset rubber, and PVC—thereby allowing more recyclable, "all-olefin" automotive interiors, for example. Recent efforts have even been made to incorporate ground vehicle tire rubber or other "ultrafine" rubber particles into PP to create vulcanized elastomeric thermoplastics that cost less than half as much as standard TPVs. Similar concepts will continue to push impact-modified POs into new applications [7-26, 7-27, 7-28].

7.5 FIBER REINFORCEMENT

Since it is silica-based, glass fiber for polymer reinforcement could be thought of as a cousin to mineral fillers. But glass fiber is more carefully produced in controlled, uniform, and symmetrical shapes with extremely high aspect ratios, with particle dimensions that are (usually) visible to the human eye. Glass-fiber reinforcement is probably the most cost-effective and most proven way of reinforcing polymers to increase tensile and flexural modulus and strength.

But glass fiber is not the only fibrous material used as a polymer reinforcement. Fibers made from plants and even other polymers have been used to make the PO system environmentally friendly as well as to lighten products, reduce brittleness, or improve wear qualities. Section 7.5.3 will cover alternative fibers, including wood and other plant-based fibers, that have made the most penetration into the commercial arena. Along with glass, various kinds of fiber reinforcement, more than any other type of additive, have allowed POs and other polymers to penetrate into automotive, construction, and other structural applications.

7.5.1 Short glass fibers

Glass fiber is the most common fiber reinforcement for polymers, given the consistent way in which it increases a polymer's strength and stiffness properties. Glass fiber also effectively addresses another critical limitation of POs that keeps them from being considered "engineering materials"—heat resistance. For example, glass fiber can increase hard deflection temperature radically; in the case of PP with 40% glass, the HDT at 1.82 MPa can increase from 60 °C (for unfilled PP) to 150 °C.

Although glass fiber is widely used, glass-fiber compounds are not easy to process. Because of the high aspect ratios of fibers, mechanical properties in different directions can be affected radically by fiber length and by fiber orientation that is induced by the flow of the melted resin. These fiber-dependent property differences are magnified by longer glass-fiber lengths, and designers must take them into account, as well as the corresponding irregular dimensional shrinkage or warpage that may occur in molded fiber-filled materials. And glass fibers' abrasiveness can damage tooling and processing equipment surfaces; conversely, the glass fibers themselves may be damaged or shortened by inappropriate screw design and processing [1-1, 3-4, 2-5].

Chopped-strand glass fibers have been used for decades for reinforcing polymers. Compounds with short fibers (typically 0.2–1 mm long) are commonly processable in standard molding operations and provide predictable properties and performance. When bonded properly to the resin matrix with a coupling agent on the fiber, short fibers stiffen the compound and still allow it to be easily molded. Most fiber used in plastics is "E-glass" (an electrical, lime–borosilicate grade), which for optimum effect requires titanate or silane coatings and maleic anhydride or acrylic acid coupling agents to bond fiber with resin (discussed more in Chapter 14) [1-1, 3-4].

Despite the established use of glass-fiber-filled resins, several factors that account for their strengthening effects are still being studied. For strengthening a resin, it is not simply that "more glass is better"; rather the fiber loading, length, aspect ratio, and orientation distribution, as well as other fiber–matrix interactions, all affect the resulting part's properties. Fibers must not be too short; research has shown that the strengthening effects of glass fiber are not optimized for fibers less than 0.5 mm in length (and these strengthening effects begin to increase dramatically as fibers are lengthened above 1 mm, as with the long glass fibers discussed in Section 7.5.2) [7-37].

Recent research has also focused on creating complex models that accurately predict the orientation of the fibers in the plastic melt and part. This knowledge is useful in molding-simulation programs to design parts better, so that fibers are aligned in critical areas, providing optimal mechanical properties. For example, studies have focused on mathematically modeling "the domains of interest" that surround every glass fiber, domains which combine to determine the total net reinforcing effect of the fibers in the plastic part. In a study on the orientation of 0.5-mm fibers in PP, researchers found that reinforcement depends on both steady-state and transient flow properties of the melt. These short fibers can be modeled as rigid rods, allowing their orientation to be predicted (unlike fibers 12 mm long, which tend to act as flexible "bundles") [7-54, 7-55].

7.5.2 Long glass fibers

As short-glass compounds have matured and now see relatively routine use in a variety of polymer systems, long glass fibers as reinforcements for PP in particular have drawn growing interest, with double-digit annual percentage growth rates. Maximizing a glass fiber's property contributions, the addition of fibers with initial lengths of 25 mm or even longer has allowed long-fiber PP (LF-PP) to become a common engineering material that behaves like a true fiber composite in automotive and other applications.

The effects of long glass fibers in the resin are analogous to the loading of resins with high-aspect-ratio fillers or nanoclays: The higher mechanical properties of LF-PP come from adding relatively long fibers rather than chopped, low-aspect-ratio glass. Thus, even when loaded at a similar weight percentage levels as short-glass, LF-PP moldings show strength and impact resistance that improve with fiber length. When comparing short and long fiber in a 30% glass-filled PP, for example, testing has shown that tensile yield strength increases by a factor of 1.5, and notched Charpy impact strength doubles (see Figure 7.1). Moreover, falling dart puncture impact (ISO 6603) increases by 3 or 4 times; even though glass is an essentially brittle material, it is thought that the long fibers help a PP composite absorb this extra impact energy simply because of the additional raw tensile strength they provide. Research indicates that gains of tensile strength attributable to long fibers translate directly into even greater gains in impact strength [7-37, 7-39].

These properties have allowed LF-PP composites to replace heavier and more expensive engineering resins and even metals. Automotive applications include front-end carrier modules, instrument panels, door modules, bumper structures, and battery trays (another recent application is shown in Figure 7.2). These uses are expanding, given the industry's interest in reducing vehicle weight. LF-PP has also been used as clothes-washer gears and gear transmissions.

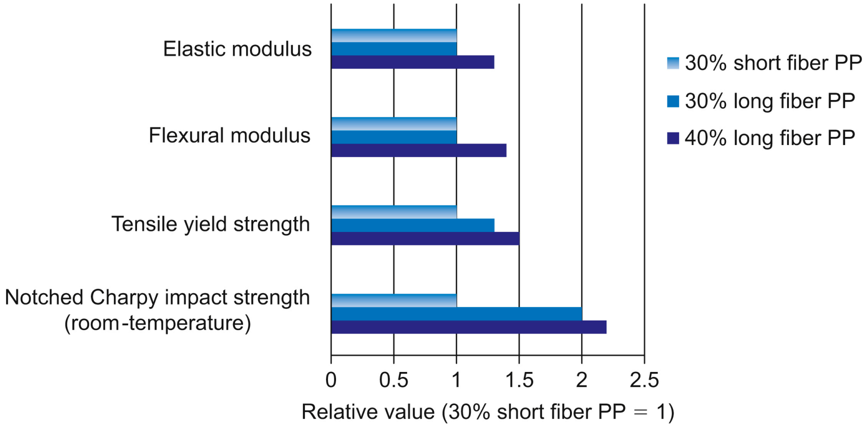

FIGURE 7.1

Glass-fiber length effects on properties. *Longer glass fibers in PP supply significant gains in impact and tensile strength, relative to standard glass-filled PP.* ***Source****: Adapted from [7-39].*

FIGURE 7.2

Long-glass-fiber-molded PP. *This large injection-molded part is made from long-glass-fiber-reinforced PP from SABIC. The molded-in-color part is the structural inner panel of the liftgate of the Ford Kuga compact crossover vehicle. The part reportedly reduced weight by 40% compared with an alternative steel design, and enabled molded-in parts integration to reduce assembly costs. (Photo courtesy of the Society of Plastics Engineers.)*

Annual growth estimates in the use of LF thermoplastics range from 10% in North America to 25% in Asia, and most of these applications use PP as the base resin [7-38, 7-39, 7-42].

Glass-mat thermoplastics (GMT), which incorporate PP into a mat made from strands of glass, were historically the first PP materials that contained long (in this case, continuous) glass. These stiff, lightweight materials quickly became particularly important for automotive applications. While not an "additive formulation" of the type covered in this book, compression-moldable GMT material is an alternative for relatively tough and flat load-bearing panels. Low-density GMT materials have become popular for vehicle headliner supports and underbody shields, replacing traditional higher-density GMT. Other forms of related LF-PP composites are likely to grow in automotive for relatively flat panels. These include sandwich constructions composed of outer skins of PP with 60%–80% unidirectional continuous glass fibers, laminated to an inner core of LF-PP [7-41, 7-57].

Molding LF-PP part applications: Current arguments about LF-PP no longer concern whether its properties are valuable. Rather they concern which process is the most efficient and cost-effective method for incorporating long glass into the polymer, and then molding the composite into a three-dimensional product. Compounded pellets or masterbatches, or various compounding/molding arrangements may be used.

In the production of raw LF pellets for standard screw-processing and molding processes, long continuous fibers are pulled (pultruded) into extruded pellets and cut into 10–30 mm in length. Depending on the manufacturer, such pellets contain a core of longitudinal continuous glass surrounded by a layer of resin, or have the glass fibers impregnated with resin for easier molding. Various compounders and large material suppliers have developed pelletized masterbatches containing over 60% glass, which can be let down with resin and molded into contoured products with detailed features. Some fiber breakage occurs during extrusion pelletizing, and subsequent screw processing of the pellets additionally reduce fiber lengths substantially to well below 10 mm. This is unwanted, since a 10-mm fiber length or above is typically desired for optimizing the composite's strength, modulus, and impact properties [7-37, 7-57].

Fiber size and its bonding to the matrix determine the potential of each fiber to carry a load on the composite before breaking or being pulled out of the matrix. Fiber orientation also determines the maximum reinforcing effect, with fibers in the longitudinal/flow direction providing maximum reinforcement. Long-fiber orientation does play a large but sometimes misleading role in determining reported LF-PP properties. A compound sample may show stiffness in the flow direction that is twice the compound's isotropic modulus value and multiple times higher than its cross-flow (perpendicular) direction stiffness, which more closely matches the modulus of the base PP resin. Moreover, the quoted or theoretically calculated modulus of an

LF-PP material may be different from the actual stiffness of the final molded part, depending on the degree to which screw processing and molding have reduced the average fiber length and distribution [7-37].

Direct extrusion or compounding of long-fiber thermoplastics (D-LFT), also referred to as in-line compounding (ILC), is an equipment-intensive alternative to pelletized long glass. D-LFT allows flexible control of the material composition in a continuous process, from compounding to molding. The process starts with the adding of resin, additives, and glass rovings into a twin-screw extruder—cutting the glass fibers to length and wetting them with resin—and then feeding the melt directly to a compression or injection-molding press at the end of the process. With D-LFT, glass-fiber percentage and length can be adjusted "on the fly." Overall material cost-savings are said to result from this method, and the heat history on the PP is reduced, since the compounded pellet stage is bypassed. However, equipment investment is high and D-LFT requires significant skill and a commitment to the technology by the compounder/molder.

The use of D-LFT is growing, but industry observers have commented on whether financing for D-LFT equipment will be feasible for many processors in the long term. Thus D-LFT also competes with improved pelletized forms of LF-PP from large compounders. For example, suppliers such as RTP, Dow, and Ticona offer LF-PP as precompounded LF pellets up to 30 mm long. Suppliers likewise "long cut" additive masterbatches that are designed to blend easily with the LF pellets, adding color, static dissipation, stabilization, or other properties to the LF-PP [7-38, 7-39, 7-40, 7-41, 7-42].

7.5.3 Plant-based fibers

Lately, given the overall interest in more sustainable, bio-based products, various plant (cellulose-based) fibers have been incorporated with POs with differing degrees of success. In laboratory environments, researchers are investigating plant fibers that supply similar properties as glass fibers, but which are lighter in weight and consume less energy in their production. At the high-volume end of the industry are the multiple producers that profitably provide tons of WPCs. These highly filled compounds of scrap wood fibers can be formed into aesthetically appropriate, long-lasting building materials. (The importance of these producers for providing products made from recycled plastics and wood often goes underreported in a world that still sees plastics as inferior structural materials and throwaway items.)

Of all polymers, POs are one of the families well suited for natural-fiber reinforcement, because their processing temperatures are low enough to allow fibers to survive intact. Unfortunately, POs' nonpolar nature prevents good bonding with natural fibers, making coupling agent strategies important, as discussed below and in Chapter 14. The hydrophilic nature of natural fibers also complicates their use.

Wood-reinforced PO materials include WPCs and other materials reinforced with wood fiber (generally having aspect ratios >10) or fine wood flour (aspect ratios <10). Wood has been used as a fine filler in POs for injection molding, but of most commercial importance are relatively coarse fiber-filled WPC products for fencing, railings, flooring, and decking. Since the year 2000, the importance of WPCs in construction applications has grown remarkably. Such applications allow the reuse of scrap wood (sawdust) and recycled POs. Moreover, wood can be viewed as an extending, low-density, cost-reducing additive, given that its costs are around $0.35/lb, roughly half that of HDPE or PP, and it can be used at high loading rates of 35%–80% [2-5, 7-3, 2-5, 7-46].

Although WPCs do help satisfy the market's interest in durable "green" products, as a reinforcement, wood fiber has much less strength than glass fiber. Thus, along with its relatively low aspect ratio, it usually fails to increase a compound's strength much (or reduces it), though it can lend some stiffness and hardness to PO compounds. WPC products can be made to resemble wood and, sufficiently UV-stabilized, are generally more resilient to outdoor conditions than natural softwoods. Some staining and minor cracking issues in extreme and/or wet environments have been encountered, and these problems are gradually being resolved [7-46].

Wood is an extremely cheap filler/fiber, but its handling invites stray costs that complicate its processing:

- Low-temperature stability prohibits wood fiber/flour's use in many applications. Wood's processing temperature is limited to 210°C, meaning that PE is often the WPC matrix material of choice.
- Most of the high moisture content of wood (typically 5%–12%) must be removed before processing, using predrying equipment or in the screw.
- Best results in WPCs usually require a strong coupling of wood fibers to the matrix (discussed more in Chapter 14), using maleic-anhydride-grafted resins or other coupling agents.
- Wood is not abrasive to equipment like inorganic fillers/fibers, but certain desired properties can only be obtained with additions of mineral fillers such as talc (for lubricity and strength), calcium carbonate, calcium oxide, alumina, wollastonite (for scratch and wear resistance), or even Portland cement, as a reactive filler supplying strength and fire retardancy.

Given all the potential ingredients and high loadings, highly filled WPCs (to a greater extent than long-glass-fiber PP compounds) are commonly processed with direct extrusion/in-line compounding operations to reduce compounding steps and energy costs [3-4, 7-3, 7-6, 7-47, 7-49].

Developers of better wood–plastic systems have focused heavily on improved fiber coupling, since chemically bonding the cellulose fiber and the polymer matrix improves strength and reduces water absorption. This typically requires additions of POs grafted with functional maleic anhydride monomer groups, which contain hydroxyl groups that bond to the wood. This increases properties in proportion to their loading, and higher amounts of anhydride can be obtained in reactor-produced ethylene/anhydride copolymers. The surface of cellulose fibers themselves can also be chemically or physically modified [7-48, 7-50].

Nonwood plant fibers made from various plants have been proposed as reinforcements for polymer systems. Some of these plant fibers offer advantages over wood, especially in the way they increase tensile strength similarly to higher-density, less-environmentally-friendly glass fiber. But many plant fiber reinforcements remain in the research and development phase until problems with moisture absorption, low processing temperatures, and economies of scale (and other cost issues) are resolved.

Rather than the construction focus of WPCs, future applications with these reinforcements will likely include more lightweight automotive parts (an industry in which wood and plant fibers have already had a long, spotty history of use with various polymers). Below are some of the more recent developments for these fibers in POs reported in the technical publications; a steady stream of these developments is likely to continue, being reported on at major conferences:

- The fibrous plants *sisal*, *jute*, and *curauá* have been studied as reinforcements, and optimum reinforcing properties have been at 30%–40% loadings in PP, using masterbatches containing 70% fiber. In regions such as Latin America, for example, grades reinforced with these types of plant fibers may be competitive wood-replacement materials in construction or furniture. Leaf fiber from the Brazilian curauá plant has also been proposed for automotive plastics, offering higher strength than sisal or jute and twice their modulus.
- *Hemp* and *kenaf* are fast-growing plants, making them practical sources of fiber; in particular, kenaf fibers (taken from the middle of the plant's stalk) show high tensile strength (261 MPa) and modulus (20 GPa).
- *Bamboo* fiber has been commercialized as a reinforcement for injection-molding grade PP. Netherlands-based Transmare Compounding, for example, produces a 30% bamboo-fiber-reinforced PP with density of 1.01 g/cm^3 and melt flow index of 1.8 g/10 minutes (measured

at 190 °C to avoid fiber degradation). The company reports the compound as having 3 GPa flexural modulus, 31 MPa tensile strength, 3.3% elongation at yield, and 8 kJ/m^2 Charpy impact strength at room temperature.

- *Abaca* fiber from waste banana plant husks have been used as a filler/reinforcement for PP in at least one automotive application, a spare-wheel cover in 2005. Here, the abaca fiber was integrated with PP as continuous fibers and then was compression molded. It is said to require 60% less energy to produce than glass fiber cut from rovings, is less harmful to handle than glass, and eliminates 7% of the weight from the glass-filled version of the part.
- The *agave* plant grown mainly in Mexico, used to make tequila and sweetener (and related to sisal), also supplies a waste fiber that has been used in PP at 55% loading. It is said to increase tensile modulus, and like other plant fibers, requires PP grafted with maleic anhydride for fiber/matrix coupling.
- *Pure cellulose fiber* (stripped of the lignin and hemicellulose contained in wood and other plant fibers) has been studied as an enhanced, high-aspect-ratio fiber alternative that costs less than glass fiber (roughly < $2/kg). This fiber has chemical resistance, heat resistance (up to 260 °C), and it can be produced at nanometer-scale fiber widths to provide improved properties as a reinforcement in various modified forms.

These and other natural fibers may be slowly commercialized, depending on market demands for bio-based, renewable, low-carbon-footprint material content in plastics [7-44, 7-45, 7-46, 7-50, 7-56].

7.5.4 Other kinds of fiber reinforcement

Other fibers may be used in POs, though some of these may be chosen more for their special properties. *Basalt* mineral fibers or *Kevlar* can provide extreme reinforcement for ballistics applications; other fibers include *metal fibers* for electromagnetic shielding purposes (discussed in Chapter 6). However, as in the case of stainless steel fibers, just because an additive is in fiber form does not necessarily mean it provides meaningful mechanical property reinforcement, but it may provide the opposite of what is wanted [6-4, 7-57].

Increasingly in the future, more kinds of polymers will use *carbon fiber* as a reinforcement—since it is a stronger, lighter alternative to glass fiber, though currently it is prohibitively expensive for most reinforced applications. The modulus of carbon fiber is about 50 GPa, its tensile strength is around 3000 MPa, and its CLTE is essentially zero. It also provides electromagnetic interference and radio frequency shielding. Thus carbon fiber is already used in thermoset composites in aerospace and high-end applications. Industry experts have proposed using continuous carbon fiber for reinforcing PP and semicrystalline engineering thermoplastics, in sheet form, for thermoforming stiff, high-end parts. Cost reductions in carbon fiber may eventually extend its use in this type of common PO application [1-1, 7-44].

Polyvinyl alcohol (PVOH or PVA), in a high-modulus, thin-fiber form, has been proposed for reinforcing POs and other polymers. PVOH filament fiber producer Kuraray America Inc. proposes it not as a replacement for glass fiber, but as an enhancing fiber reinforcement. The company specifies PVOH as having a higher Young's modulus, tenacity, and elongation at break than glass fiber, as well as a lower specific gravity (1.30 vs. 2.54). Alternatively, the company has reported similar strength advantages and a doubled Charpy impact strength for a 10% PVOH fiber plus 14% mica PP compound, in comparison with a 20% glass-fiber PP [7-52].

Self-reinforced PP is an intriguing avenue for creating a more recyclable, single-polymer, reinforced material. Such a composite system is reinforced by oriented, drawn PP fibers within a PP matrix, or as part of a laminated system. However, current cost disadvantages have limited their use [7-42].

CHAPTER 8

Factors Determining the Selection of Fillers and Fibers

Understanding conceptually how various fillers and reinforcements affect a resin compound's properties is relatively straightforward, in comparison with the difficulties of making practical decisions about their use in application-driven situations. To aid in this task, this chapter contains a number of case studies having to do with actual uses of fillers and fibers. These stories are linked to a number of major points about the use of these additives and essential issues encountered when combining fillers and fibers with resin and other additives. Since PP tends to be reinforced more often than PE for engineered uses, the discussion is weighted more toward PP and TPO.

When one considers all the possible purposes for which fillers and fibers are used in POs, this chapter could be expected to be quite long. Instead, some essential points are covered concisely, with the acknowledgement that certain points may already sound very familiar to some users of these compounds, and other good points may be missing. New situations and opportunities arise over time, constantly altering the economics of polymers and fillers.

The arguments presented in this chapter try not to neglect one key point: that choices about fillers and fibers depend not just on the properties they supply, but also on how easily they can be processed, how they interact with the resin and other additives, and how cost-effectively they can be supplied and added to the resin. (Table 8.1 shows generally some of these basic filler/fiber/resin relationships.) Also, the chapter will attempt to address the following questions:

- (8.1) How can low-cost fillers be used effectively as extending or functional fillers to cut resin costs or improve properties?
- (8.2) What are some complications of using impact-modified POs?
- (8.3) What are the most dramatic ways in which reinforcing additives are used to improve mechanical properties?
- (8.4) What are some difficulties of handling fillers and fibers and processing the compounds they are used in?

Table 8.1 Simplified Cost and Mechanical Property Comparison of Generic Filled and Reinforced POs

Resin System	Cost Impact	Mechanical Property Effects	Potential Reductions in Product Thickness
Resin with mineral fillers	Reduced when inexpensive fillers displace more expensive resin	Typically higher stiffness but lower-impact strength	Thinner products possible if reduced impact strength not a factor
Impact-modified	Increased	Higher-impact strength in lower-modulus part	Thinner products possible if reduced stiffness not a factor
Impact-modified plus mineral filler	Increased, though mineral filler displaces resin	Higher impact plus retained stiffness	Thinner products possible
Short-glass-fiber reinforcement	Increased	Higher stiffness and strength	Thinner products possible
Long-glass-fiber reinforcement	Increased, depending on fiber length and processing technology	Very high stiffness and strength and higher impact strength	Optimally thin products possible in structural applications
Nanocomposite	Increased, though potentially cost-effective	Higher stiffness, strength, and impact, depending on dispersion	Thinner products possible

- (8.5) What questions remain for compounders and end users to consider when weighing the full costs and benefits of various filler–resin/fiber–resin combinations?

8.1 CUTTING COSTS AND IMPROVING PROPERTIES WITH FILLERS

Combining low-cost mineral fillers in a PO compound is a well-known way of displacing resin in a product, thus reducing overall material costs, especially during periods of high resin prices. Calcium carbonate is a common choice for this kind of low-cost extender role for various products in which engineering properties are a secondary concern.

When properties are more of a concern, lower-cost fillers also can act as extenders that displace not resin, but rather higher-cost reinforcing additives. For example, wollastonite can sometimes partially or fully replace more expensive, milled glass filler, or partially replace chopped glass fibers, while providing similar mechanical properties [7-6, 7-13].

In other situations, the form and average particle size of a stiffening filler like talc can be specifically tailored to fit an application's mechanical property needs.

CASE 8.1 COARSE TALC STIFFENS PO PIPE [8-9]

Problem: A lack of options for reducing the wall thickness of extruded PP pipe.

Objective: Determine how functional mineral fillers can create stiffer and thinner PP pipe.

Solution: 20-μm talc at 20%–30% loadings supplies properties that allow downgauging.

As POs for plastic pipe have grown in use to occupy about 40% of the market, opportunities have started to appear for functional mineral fillers to be tailored more specifically for the application. To this end, Rio Tinto Minerals did studies with copolymer pipe PP with different loadings of the company's Luzenac 20-μm talc. Initial work showed that the flexural modulus and pipe ring stiffness of the copolymer PP were doubled with 30% talc loading. Heat deflection temperature was also increased from 53°C to 63°C, CLTE was reduced by about 40%, and shrinkage was cut in half. However, the talc reduced Charpy impact strength from 12 to 8 kJ/m^2 at –20°C, and from 46 to 17 kJ/m^2 at 23°C.

Given the negative effects on impact strength by the high talc loading, the company focused on studying 110-mm diameter copolymer pipes loaded with only 20% talc. The 20% talc pipe still provided 75% greater ring stiffness than unfilled resin pipes of similar (6.5- to 6.9-mm) wall thickness. The researchers also observed that at a downgauged 5.4-mm wall thickness, the 20% talc PP provided equivalent stiffness as a 6.5-mm thick neat PP pipe.

CASE 8.2 FINE TALC ALLOWS THINNER PE PACKAGING [8-10]

Problem: Competitive pressures and high resin prices create a need for lighter-weight packaging for consumer goods.

Objective: Use alternative forms of stiffening fillers to allow reductions in wall thickness, weight, and resin.

Solution: Very fine micro-talc allows thinner/lighter HDPE bottles that are equally rigid in service.

Rio Tinto has also looked at how very fine lamellar talcs allow thin-wall blow-molded HDPE bottles and packaging. Here, extra fine 1- to 2-μm Luzenac talc reportedly stiffens and strengthens the resin efficiently without excessively reducing impact strength—allowing thinner, lighter bottles containing less resin.

In tests of extrusion blow-molded HDPE bottles, the optimum talc loading was found to be about 5%–10%, depending on how much impact resistance could be sacrificed. Drop impact failure height (ASTM D2463) was reduced by nearly half with the 10% talc. But the filler did allow 15% thinner and 10% lighter bottles to be produced with top-load cylinder strengths that were equal to the strength of unfilled HDPE bottles. The talc also reportedly makes the bottles less permeable to oxygen.

In thick, high-volume PO applications such as extruded pipe, standard (20-μm) talcs provide effective stiffness. But finer talc grades may allow reduced resin use by allowing thinner parts with equivalent beam stiffness. Reduced talc particle sizes (near 1 μm), for instance, can create a better balance of properties in thinner parts to help justify increased filler cost that results from the use of very fine talcs. Lower talc loadings may also be possible; the newest high-aspect-ratio talcs are said to create the same mechanical properties at 3%–7% loadings in PP than in PP compounds loaded with 20% standard talc. Cases 8.1 and 8.2 cover applications in which different talcs supply these different functional needs [7-10].

Finally, creative combinations of low-cost fillers in various forms allow reduced resin content without reducing desired properties. Blends of small and large particles of the same filler material, or blends of plate-like filler particles and coarse filler, help limit the filler's most extreme, unwanted effects on stiffness, strength, or impact behavior. For example, platy talc, mica, or kaolin clay in a PO provides stiffness enhancement, which complements the strength properties provided by fiber-shaped wollastonite or the more forgiving impact properties of spherical calcium carbonate particles [7-6].

8.2 IMPACT MODIFICATION: BALANCING STIFFNESS WITH TOUGHNESS

Nonetheless, impact strength often must be sacrificed by additions of low-cost fillers. Mineral fillers usually tend to stiffen PO compounds but also lower their toughness. Thus, increasing these filler loadings without considering effects on impact, tear, or puncture resistance could be a recipe for failed resin products.

It is often important for a PO material to have a specific, consistent impact resistance, preferably without reduced stiffness. Applications have driven the need for PP impact copolymers and rubber-modified PP, as well as for low-density PE made with metallocene catalyst reactor technology, all of which provide high toughness at various temperatures. But for practically all common POs, toughness can be increased via additions of impact modifiers by the compounder or processor. When considering the use of an impact-modified compound, a few questions should be reflected on:

What are the costs and risks of processing impact-modified compounds? Unlike in some PO resin situations, major suppliers of impact-modified POs capitalize on years of experience, economies of scale, and their large equipment investments to produce reasonably priced high-impact compounds. Since impact modification is often not a straightforward process, using a specialty supplier may ultimately minimize costs for processors with limited access to specialized compounding equipment or expertise.

Alternatively, if a processor chooses not to use a certified grade of impact-modified PO from a specialist, but rather is modifying resin independently, the company may need to introduce extra testing to verify the compound's properties, such as notched impact testing at extreme temperatures. Testing is particularly important for rubber-modified materials, because variations in processing can change the morphology of rubber in the polymer matrix, affecting the properties of the final product. In this case, the risk of inadequate testing is catastrophic brittle fracture of a part in service, an occurrence which also fractures the reputation of the processor [7-26].

Do we need to become a specialist in processing impact-modified POs? There is nothing easy about understanding and handling high-impact materials. Indeed, in the automotive industry, entire conferences are devoted to TPO issues alone. Companies accustomed to using standard POs must enter a world that uses terminology from the rubber/elastomer industry. They must fulfill mechanical requirements that are much more extreme than in standard PO applications. They must also decipher various, complicated property and additive relationships to produce the right balance of stiffness and impact toughness—properties that are essentially inversely related. And they must face head-on the pressure from industry to create toughened parts that are thinner and stiffer. Success requires higher-flow impact-modified materials, and compounders and processors who have become experts in evaluating the relative efficiency of alternative impact modifiers (consider Case 8.3) [8-6].

Are impact modifiers too difficult to process? Impact modifiers are being supplied in easier-to-process forms. Development work with masterbatch concentrates, which are more user-friendly for the nonspecialist compounder/molder, have shown that well-dispersed talc and rubber in a masterbatch can be used to create TPOs with equivalent properties as with TPOs from traditional direct compounding. Other, "at-the-press" methods for creating TPOs or for modifying PE film are becoming possible (see Case 8.4) [7-12].

How much low-temperature impact performance is needed? In automotive applications, parts are often specified to resist violent impacts at −20° to −40°C without shattering into pieces. These impact requirements mean that specialized commercial grades of compounded TPO or reactor-modified TPO may

CASE 8.3 ALTERNATIVES FOR TOUGHENING LLDPE FILM [7-24]

Problem: Even metallocene catalyst reactor grades of LLDPE may not provide adequate tear or puncture resistance for some applications.

Objective: Efficient impact modification of mLLDPE film.

Solution: New modifiers based on a nonolefinic elastomer.

The properties obtainable from PO film created with metallocene catalyst technology can result in consistent film materials with high toughness. Yet impact-modification strategies can still be used to enhance the tear and puncture resistance of these films. And these impact modifiers do not themselves need to be based on olefinic chemistries.

Styrene–butadiene–styrene (SBS) block copolymers have been proposed as modifiers for 50-μm mLLDPE high-performance film. Styroflex elastomers from BASF, for example, are reported to be compatible with mLLDPE when dispersed at extremely fine particle sizes in the nanometer range. This reportedly has resulted in 10%–27% greater tear resistance and 15%–24% greater puncture resistance, at low 2.5%–5% modifier loadings.

Researchers also note that mLLDPE's high-shear melt processing allows the SBS to be much better dispersed than it would be in standard low-density PE resulting in very small (120-nm) particles. This characteristic reportedly allows it to effectively prevent crack propagation in mLLDPE, while not affecting the stiffness of the film.

CASE 8.4 CREATING TPOs AT THE MOLDING PRESS [8-7]

Problem: Given the rise of TPOs in automobiles, TPO molders seek options for reducing processing costs or increasing their flexibility.

Objective: A practical method for molders to create their own TPOs without a full compounding step.

Solution: Equipment that feeds and mixes the three key ingredients of TPOs at the molding press.

TPO molders generally rely on compounding operations for combining PP, elastomer, talc, and other additives. But this is a high-cost step that would be lucrative to eliminate, if possible, by combining these materials right at the molding press. So researchers at Dow Automotive developed an "At-Press TPO" methodology for creating TPOs by blending a functional talc masterbatch, PP, and elastomer via distributive conveyors and gravimetric blending equipment at the screw hopper.

This setup allows more control of the molded material by the molder, either through using a two-component system that blends reactor-impact-modified PP and talc, or a three-component system that combines PP, elastomer, and talc. Depending on the approach, the molder can adjust the talc and/or elastomer content of the TPO in order to adjust properties such as CLTE, shrinkage, stiffness, low-temperature ductility, and HDT.

This "compounding-on-demand" approach reportedly reduces inventories and allows flexibility to meet changing needs. Ideally, the TPO formulation could be quickly adjusted to meet the various property combinations for various automotive TPO parts such as fascia, hard interior trim, and instrument panels. Dow researchers also say that the TPO compounds produced at the press provide the same TPO quality as precompounded TPOs, including consistent rubber and talc dispersion and multiple-shot repeatability in molding. It is also compatible with cost-effective bulk shipping methods for supplying the individual ingredients.

be needed for many parts. High-quality talc is particularly needed to maintain stiffness without losing cold toughness (see Figure 8.1), because the automotive market's two biggest interests in TPO by far are its flexural modulus and impact resistance for rigid TPO parts like bumper fascia. Low-temperature toughness has often been beyond the capabilities of POE plastomer modifiers and may require traditional EPR or EPDM modifiers (though with newer POE "Engage" grades from Dow or other products, this may become less of a concern) [7-26, 8-6, 8-8].

8.3 MECHANICAL REINFORCEMENT: PROPERTIES CREATE OPPORTUNITIES

In engineering applications, the mechanical properties of a reinforced PO compound need to be weighed against the higher costs of the compound and its processing, and against the costs of the part if it were made from engineering resins or nonpolymeric materials. It is in these borderline metal/plastic applications where PP in particular has been exploited as a cheap, moldable, and adequately strong matrix material for high-strength reinforcing fibers. (Reinforced PP also supports efforts toward all-PO plastics in cars, ultimately simplifying recycling.)

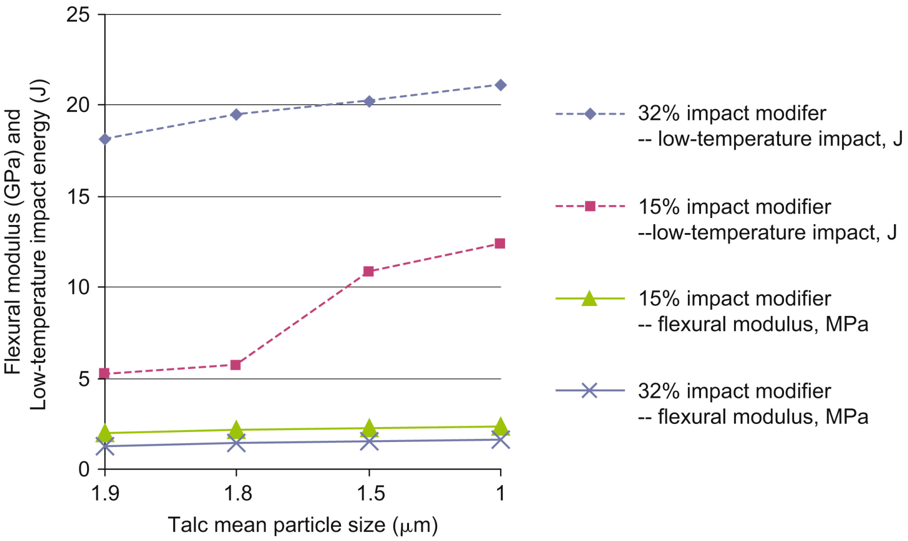

FIGURE 8.1

Effects of talc and impact modifier in TPO. *Data show influence of talc particle size (at 15% talc loading) and impact-modifier content in homopolymer-PP TPO. Finer talc sizes increase impact resistance and flexural modulus; higher impact-modifier loading increases impact while reducing modulus.*

Source: *Adapted from [8-8].*

And just as an inexpensive filler can allow the amount of resin in a product to be reduced, fiber reinforcement can be used to minimize a product's thickness and weight. Lightness is an advantage PP's low density already provides, in comparison with engineering materials. Conventional fillers may allow thinner products of relatively high beam stiffness and strength, while reinforcements such as long glass fiber maximize PP's engineering use in new automotive applications, as shown in Case 8.5.

With the advent of *nanocomposites*, notions about how to cost-effectively reinforce resins may change. As with fiber-filled PP, the issues of stiffness and strength vs. weight and cost could be key questions for nanocomposites, which require only low loadings (3%–5%) of nanofillers to maximize properties. Since resin makes up most of the balance of these composite systems, a cost-conscious user of a PP nanocomposite would likely seek to minimize product thickness. Otherwise, other value-adding properties of a nanofiller (such as charge dissipation, flame retardancy, or barrier properties) may also help it to compensate for its extra material and processing costs [8-12].

However, questions remain about the best processing methods required by nanocomposites in production situations, allowing proper nanofiller exfoliation and dispersion. Questions also have been raised about whether nanocomposites

CASE 8.5 SHORT- AND LONG-GLASS-FIBER PP COMPOUNDS STIFFEN VEHICLE APPLICATIONS [8-1, 8-2, 8-3]

Problem: Multi-part vehicle structures are too heavy and costly for an automobile manufacturing market that demands lightweight, fuel-efficient vehicles and simplified, modular vehicle assembly methods.

Objective: Strong, lightweight, and moldable materials for automotive structural trim and supports, allowing integrated, molded-in features.

Solution: Short- and long-glass-fiber-reinforced PP for both structural and visible-trim applications.

One of the greatest recent advancements of PO-based materials has been reinforced PP's increasingly important role as an engineering material for load-carrying vehicle structures. Glass-fiber PP has been used for a widening array of vehicle structures since 2000; recent innovations in production vehicles show this importance. A few representative examples are covered here.

- For new kinds of door-module trim, PP containing 40% short glass fibers has provided low-gloss, "Class A" surface aesthetics and high strength. One system was developed in 2007 by Delphi Interiors and Closures for Freightliner heavy truck doors, at a volume of 40,000 trucks per year. The door system using the material weighs 9 lb (4 kg) less than the previous design, supports a 300 lb (140 kg) vertical load, and has injection-molded-in features for latch, electrical, and window glass attachments. The design has also reduced part and labor costs, and reduced the number of fasteners by half, Delphi reports.
- A notable use of long-glass-fiber-reinforced PP has been for front-end carrier modules, which have multiple mounting points for attaching parts such as radiator components, headlamps, and the washer tank. Front-end carriers have been made of metal castings or assemblies, but more manufacturers have taken advantage of LF-PP's high stiffness-to-weight ratio, crash-worthy toughness, and its low creep, warpage, and thermal expansion. Ticona in particular supplies its Celstran 40% long-glass-filled compound for the application (reportedly meeting Ford Motor Company's WSB-M4D865-A3 specification).
- Another development combines both the strength of LF-PP with interior surface aesthetics. The overhead console or the 2009 Ford Flex is made from a Ticona 20% long-glass PP molded by Grupo Antolin, North America. The molded-in-color part has a light "stipple" grain surface, and the company says it was chosen because of its resistance to high temperatures, compared with TPO and PC/ABS. The part showed that even long-fiber materials can be molded to have a PP-rich surface layer, which prevents fibers from being visible on the show surface.

supply the same property enhancements when they are processed outside of controlled laboratory environments. Without more satisfactory answers to these questions, improved high-aspect-ratio micro-talc PO compounds may remain stiff competitors of nanocomposites for auto applications, for providing positive improvements in properties such as long-term heat aging, heat deflection temperature, impact strength, CLTE, and melt flow index [8-11].

8.4 PROCESSING PITFALLS AND HIDDEN COSTS

Often technical and marketing literature focuses on the huge material property gains from new additive/resin combinations, sometimes neglecting processing issues that arise during their use. Reflecting on the difficulties of using filled/reinforced compounds, this section attempts to relate the "cons" with the "pros" of filled PO use. These "pitfalls" (and there are many others not listed here) may apply to compounding operations, molding shops, or other processing operations. They hopefully can be used as points for discussion.

Pitfall: Premature screw and tooling wear caused by abrasive fillers and glass fibers in filled compounds.

The low cost of POs means that even highly reinforced POs are often preferred over less-filled engineering resins. However, depending on volumes and the run length of given products, plans should be made to anticipate the future tooling reinvestment needed because of the damage that glass fiber, in particular, can do to metal surfaces. Screws, runners, and molds may benefit from wear-resistant coatings or harder materials, though these solutions require higher investments and mold-making costs. Alternative, less-abrasive reinforcement materials, such as plant fibers, softer minerals like mica, or nanofillers, provide longer tool lifetimes. Unfortunately, no "soft" reinforcements currently provide the cost-effective performance of glass fiber, and no newer alternatives have its long history of reliable performance in widespread applications.

Pitfall: Underestimating the extra handling and mixing challenges of adding fillers and fibers to resin.

Compounders understand well the difficulties of creating well-dispersed compounded materials that are ready for final screw processing—challenges that some processors may never have to deal with. Filler and fiber storage, drying, pretreating, handling, and mixing invite potential problems affecting consistency and worker exposure to hazardous materials. For processors not wanting to build their own compounding operations, the only common cost savings alternative to buying precompounded pellets is to buy neat unfilled resin and highly filled masterbatches independently, and mix them near the final conversion operation.

Enhanced process flexibility is one advantage for processors who mix masterbatches and resin "at the press." Masterbatch and concentrate products are designed to be safe and easy to handle, and cost-efficient when they contain multiple additives, including colorants and UV stabilizers. Using PO-compatible materials as their additive carrier resin, masterbatches suit standard screw processing. Yet these products can themselves be costly, so there is continuing argument about their true cost benefits. Arguments often take into account an operation's size, required operational flexibility, material volumes, and product types and requirements (although, not surprisingly, the argument is sometime shifted toward the personal interests of the expert making the argument!).

Pitfall: Hazards to workers when fillers and fibers are handled.

To be most effective in a resin, fillers and fibers are inherently fine-particle materials, which unfortunately can easily become dispersed throughout an operation. Exposures to workers' skin and lungs are constant concerns. Glass fibers can be hazardous or at least an extremely unpleasant irritant, and the potential lung problems from inhaled fine mineral powders are obvious. These threats can be reduced or essentially eliminated by the use of dust-free concentrates, masterbatches, or fully compounded pellets.

But each new generation of filler brings its own special handling requirements or exposure limits. For example, nanofillers and their possible health effects are only beginning to be investigated and approved. Some nanofillers, such as Bayer MaterialScience's Baytubes C150P carbon nanotubes, have gained approvals of agencies like the US Environmental Protection Agency. But for many nanomaterials, just the current health and safety paperwork required for their use or acquisition can be overwhelming [7-55, 8-15].

Pitfall: Potential losses of material properties after processing, or inconsistent properties across the final part, depending on the rigors of the molding/forming process.

Predictable, verifiable material property data about a compounded material are typically available from the compounder or resin supplier. These documented test results from molded plaques may help justify a material's suitability, yet it is the properties of the final product that matter to the customer and the long-term reputation of the molder. With highly reinforced resins, questions may remain about local variations in a molded part's final mechanical properties (and gaining answers to these questions by waiting for part failures is not a solution most customers would accept).

Processing may produce various unwanted changes. Unanticipated glass-fiber breakage might occur during molding, reducing strength in certain areas of a part. Or a filler might not have been dispersed evenly during compounding or processing, causing unwanted dimensional changes. It is exactly because POs are not inherently strong materials without reinforcement that these problems could be disastrous. Monitoring them may require special part testing fixtures and/or detailed examination of the molded part, at least during part, material, or process development.

Pitfall: Additional quality checks and testing to control and verify material properties, especially when adding filler/reinforcement to resin in-house, near the final part processing stage.

Depending on customer requirements, constant verification of a filled material's properties may be required. This responsibility may to some extent be reduced by the use of customer-certified precompounded materials from approved suppliers. Otherwise, particularly when fillers are added to resin near the press, in-house testing may require trained support staff using standardized, certified testing equipment and methods, and additional quality certification procedures.

Pitfall: Misjudging the potential costs or benefits of in-line/in-house compounding vs. off-line/outsourced compounding.

Processors of various sizes may ask themselves about the degree to which they can add fillers to resin themselves, compared with relying on compounding specialists. The practical arguments about this are mentioned above, but there may be additional cost issues, volumes, and market forces that do or do not justify the additional equipment required.

For example, as shown in Case 8.6 about the in-line compounding of LF-PP, large parts-making operations have chosen to invest in processes that combine compounding and molding in one continuous process. This eliminates processing steps and inventory, key tenets of "lean manufacturing." It is also said by some (though disputed by others) to reduce material costs and allow more flexibility for controlling the properties of the reinforced material. Yet in a world of tighter credit for financing new equipment, the large investments required for D-LFT equipment may be difficult to make, preventing more molders from becoming their own compounders. On the positive side, if the market remains hungry for highly reinforced materials, it may lead to larger capacities (and lower costs) of specialty-compounded LF-PP pellets [7-42].

CASE 8.6 DIRECT IN-LINE COMPOUNDING OF LONG-GLASS-FIBER PP [8-4, 8-5]

Problem: Progress toward more affordable long-glass-fiber thermoplastic applications is limited by conventional compounding/molding practices.

Objective: Develop "leaner" processes for compounding and molding LF-PP.

Solution: Establish ILC/D-LFT processes to eliminate intermediate compounding steps.

Given greater interest in LF-PP parts for automotive front-end carriers and other parts (as in Case 8.5), ILC and molding processes have been developed, mainly in Europe, by KraussMaffei, AKsys, Coperion, and other equipment manufacturers. The processes are said to reduce material costs and provide more flexible process control for 40% long-glass-fiber-filled PP.

The ILC/D-LFT process starts with continuous glass rovings, PP, and other additives and feeds them into a twin-screw compounding extruder. The glass becomes cut during processing into long (usually 8–25 mm) lengths, and the hot LF-PP material is directly fed to a compression molding press or, increasingly, an injection molding press. Compression molding, a low-pressure process, allows optimum fiber positioning for high-strength parts; in comparison, injection-molded parts require no rework, but have lower mechanical properties, reports KraussMaffei.

The process is being used to create more diverse kinds of auto parts. The "assist step" component on model-year 2007 General Motors sport utility vehicles is made from a 40% LF-PP made with ILC and injection molding. This structural part supports each passenger's weight as they step into the vehicle, using molded-in stiffening ribs and brackets. Molding with ILC reportedly allowed a cost savings of $19 per vehicle, and the part reduced mass by 50%, compared with the previous five-piece metal/plastic design, according to GM and molder Magna International.

Pitfall: Difficulties in properly dispersing fine fillers in the polymer matrix.

Fillers that are not properly dispersed in a production operation likely will not supply the same property effects as in compounds created with laboratory-scale extruders. Dispersion may require significant screw torque and special screw designs (see Chapter 18) for introducing and breaking up filler particle agglomerates in the resin. Good dispersion practice allows large amounts of cheap extending fillers to be used in the resin, better overall properties contributed by functional fillers (which can be used more efficiently), and lower melt viscosity for the compounded material. Effective dispersion also requires some knowledge of coupling agents (discussed more in Chapter 14). These agents react with both the filler and the PO matrix, reducing the "thermodynamic drive" of the fillers to reaggregate by reducing the surface energy of the filler particles [8-14].

Pitfall: Unanticipated interactions between fillers and other additives.

Although interactions of fillers with other formulation ingredients can sometimes be productive, other interactions are not. In the case of calcium carbonate added with talc in PP, the resulting balance of properties can be harmonious, as mentioned in the previous chapter. However, talc may deactivate certain stabilizers, leading to product degradation and failures later on. Relatively unfamiliar nanofillers interact with conventional and unconventional additives in useful and nonuseful ways, as shown in Cases 8.7 and 8.8.

8.5 QUESTIONS WHEN CHOOSING FILLERS AND FIBERS

In materials-selection situations for PO compounds, numerous questions may arise. A number of questions offered below indicate the real-world challenges of selecting and using these materials profitably while addressing external concerns of the customer and the outside world.

Should a DoE, simulation, or related methodology be used to determine an optimum formulation and processing parameters? Working off suppliers' material property data sheets when choosing a compound may be adequate for some applications, but more analysis may provide the best recipe for an application in processing. Processors have used DoE to determine the optimum percentage of fiber or impact modifier that will allow a part to meet certain requirements, by varying the formulation and processing parameters and recording the changes in part properties. Or they have used molding simulation to predict if a resin system can be cost-effectively molded into a part with the required properties. These efforts can answer specific questions, for example: Will a slightly higher filler loading increase scratch resistance without affecting cycle time or impact strength? Or will a filler or fiber harm gloss or surface appearance

CASE 8.7 NANOCLAY AND TITANIUM DIOXIDE IN CAST-FILM LLDPE [8-12]

Problem: Greater nanocomposite use is delayed by gaps in the research about their interactions with commercial compound ingredients.

Objective: Verify nanoclay's compatibility with a common pigment in LLDPE film.

Solution: Titanium dioxide and nanoclay can be used together, creating slight property changes, compared with the addition of nanofiller alone.

With growth rates of up to 25% per year estimated for nanocomposites overall and 100 million pounds (45 million kg) of these materials expected in packaging applications by 2011, there is pressure to determine how nanofillers interact with common compound ingredients. Extruded cast-film LLDPE will be one of the key packaging nanocomposite materials, with nanofillers being used to enhance gas-barrier properties and mechanical properties. Yet the nanofillers will also need to work with the most common of white pigments for packaging, titanium dioxide. Their possible interaction was a focus of investigators from compounder RheTech, Inc. and nanofiller supplier Nanocor.

In the film study, MMT nanoclay exfoliated in a masterbatch was let down to 3% clay loading in 20 and 50 melt-index LLDPE resins. A second batch of these materials was each loaded with 2% titanium dioxide, added via a 20% TiO_2 masterbatch. The materials were extruded through a slit die and cast to 2-mil (50-μm) nominal thickness.

Even at 3% loading, which is equivalent to only a 1% volume fraction in LLDPE, the exfoliated nanofiller particles provide a "tortuous path" for oxygen molecules to navigate through the nanocomposite. This results in low oxygen transmission rates (OTR) for the nanocomposite film, values of which increase with the nanofiller's average aspect ratio. (Relative permeability is reduced by about half by using 3% nanoclay with an aspect ratio of 200, but is reduced only about 25% by an aspect ratio of 80.) The nanoclay also doubles tear strength and increases modulus and strength without affecting elongation, the researchers note.

Adding 2% TiO_2 supplied a "neutral to modest enhancing effect on barrier or physical properties" of the nanocomposite. Relative permeability ranged from 0.47 to 0.56, depending mostly on the calculated aspect ratio of each formulation. For the 20 melt-index LLDPE, tear strength increased in the transverse film direction, elongation increased in both directions, and tensile strength and modulus was held to within about 10% of unpigmented film values. These effects appeared to be similar or less pronounced in the 50 melt-index LLDPE film.

CASE 8.8 STABILIZATION SYSTEM FOR PP NANOCOMPOSITES [8-13]

Problem: Nanoclay fillers interact negatively with standard heat stabilizers.

Objective: Develop a stabilization system for nanocomposites.

Solution: A stabilizer that reduces the yellowing and improves the weathering of PP nanocomposites.

The organically modified nanoclays used in POs interact with standard antioxidant additives, reducing their effectiveness, according to researchers at Ciba. Thus the company developed the Irgatec NC 66 stabilizer specifically to reduce discoloration during processing and to reduce the odors that are emitted by the nanocomposite's organic modifiers when they degrade.

In the Ciba research behind the development of the stabilizer, a PP nanocomposite with a standard heat stabilizer became embrittled during long-term thermal aging tests at 135°C in less than half the time as unfilled stabilized PP. With the NC 66 stabilizer loaded at 1.0% in the nanocomposite, embrittlement time was increased to the level of unfilled PP, 40 days. Moreover, data from outdoor weathering tests show that the impact strength of the nanocomposite loaded with 0.5% NC 66 (and 0.4% light stabilizer) is maintained 1000–2000 hours longer than when 0.5% of a standard heat stabilizer is used with the same UV stabilization (in which impact strength was completely lost at 2500 hours).

at its current loading, or can it be replaced or reduced? Finding answers to such questions at an early stage, rather than during production or tooling development, can save money and project delays.

How recyclable is the formulation? In many cases, a compound simply may not be easily recyclable using the current material-recovery infrastructure, even for parts that are well labeled with the codes that identify their mineral or fiber content. Fossil-fuel cost pressures and environmental pressures are only starting to provide the necessary impetus for the greater recovery of filled or reinforced plastic products when their lifetimes are complete. Fortunately for POs, a basic recycling infrastructure already exists, and these materials comprise a family of plastics that is readily and heavily recycled into other products. This makes the filler/fiber content a less complicating factor for recovering POs from automotive shredder residue or consumer recyclate.

That said, perhaps the best general rule to be followed is, when it is feasible: Use the more common fillers and reinforcements that would be most compatible with the current recycling infrastructure. Other rules about material life-cycle costs and long-term environmental costs of a particular filler or fiber would likewise apply. Unfortunately, these "rules" will only likely become more complicated, vague, and contradictory. For example, as more natural-fiber compounds are used for thermoplastic parts, questions will arise as to whether the low "carbon footprint" of the natural-fiber reinforcement is preferred over the difficulties in establishing new sorting techniques to recover these plastics. Moreover, there are limitations in reheating and reprocessing compounds containing these degradable fibers, which are much more heat and moisture sensitive than glass fibers.

How critical is the product's appearance, and what in the formulation affects aesthetics? Customer tastes tend toward plastic products that simply do not look "plastic." Moreover, the materials must be durable and scratch resistant, a challenge for soft POs that mineral fillers such as talc can sometimes help overcome (see Chapter 17).

Does an additive needed in the compound for another purpose also influence properties like a conventional filler or fiber? Particulate additives used to enhance other properties discussed in separate chapters in this book (for flame retardancy, electrostatic discharge, pigmentation, etc.) also might change physical properties significantly, like standard fillers or fibers. Flame-retarding mineral fillers such as aluminum trihydrate and magnesium dihydroxide, for instance, often must be used at very high loadings, affecting properties. Or pigments such as carbon black or titanium dioxide are sometimes spoken of as "fillers" because they can influence strength properties. Frequently these additives will simply reduce mechanical properties, so care should be taken to understand which properties a flame-retarding filler affects at high loadings, for instance.

Alternatively, as discussed in Chapter 7, fillers such as nanofillers can provide multiple desirable properties at low loadings, offering profitable options when both mechanical and nonmechanical property enhancements are needed.

Are the characteristics of filled resins worth the cost savings from filler use? The whole idea behind extending fillers is to reduce resin use and reduce costs in commodity applications. Yet if the filler increases the part's density by 10% or more, and it does not provide high enough properties to allow less material volume to be used in the overall product, is its use justifiable? After all, a nonoptimized filled PO product may feel heavier, look less attractive, and be more subject to tearing or cracking.

Of course, filled POs for engineered uses do not usually encounter this contradiction. With low-density micro-talc-filled compounds or nanocomposites, thin walling is more possible and desirable (though potentially accompanied by higher costs). Likewise, fiber-reinforced PP for structural applications is specifically designed with minimum wall thickness. And this optimizing approach is being used more for consumer and commodity extruded compounds as well, as shown in Cases 8.1–8.3 [7-10, 8-9, 8-10].

4

SECTION IV

Appearance Enhancement

Colorants

Colorants can make relatively cheap commodity materials such as POs appear to be (superficially at least) more than just the sum of their parts. POs have relied on their colorability to make products more aesthetically pleasing to use, or simply to draw more visual attention toward a product. Product differentiation is perhaps the main reason POs are colored, whether for short-lived packaging or for color-matched, durable, multi-material assemblies such as automobiles and playground equipment.

One factor that makes an overview of colorants difficult is the large number of new pigments and colorant products—many of which can only be verified as effective through use in production-processing environments and application conditions. Moreover, coloring plastics can be more art than science, and the "properties" of a colorant are often best measured only by the human eye rather than by test equipment.

Even though coloration comprises a large subfield of plastics, this chapter will attempt to address these questions concisely:

- (9.1) What different kinds of organic, inorganic, metallic, and special-effects colorants are of greatest commercial importance for POs?
- (9.2) What are the different forms in which colorants are handled for cost-effective blending with the resin?
- (9.3) What are some key factors to consider when making decisions on how to color a product, given all the requirements of the product in service?

9.1 COLORING STRATEGIES

There are several options for inducing varieties of colors into an otherwise naturally colorless or translucent PO resin product. Colorants are normally used in the form of solid pigments: submicron-scale organic or inorganic particles dispersed throughout the resin. But unique forms of the pigments can attract the eye more by mimicking metals or by reflecting or re-emitting light in interesting ways.

Formulating for color depends heavily on answering questions about whether the PO will be used for a long-lasting durable application or for a relatively short-term packaging application. Should the color be bright and glossy to draw consumer attention? Or should it be subtle and low gloss, as in automotive interiors, where attention might not want to be drawn to the material's "plastic" identity? Will the color hold up under the worst possible conditions of use, such as trash containers or car panels in the sunlight? And will it be resilient to high surface temperatures, moisture, and pollutants over a long period [9-5]?

9.1.1 White colorants

White pigments such as titanium dioxide (or titania) reflect and scatter all visible light wavelengths, making a pigmented product white and opaque. As the most used inorganic pigment by far and the most used colorant overall, titanium dioxide creates a dense whiteness in polymers at low cost, when used in its rutile mineral form at optimum 0.25-μm average particle size. TiO_2 used in UV-exposed applications is commonly surface treated so that it is not reactive in the degradation processes of the polymer or with phenolic-based antioxidant additives. A coating may be composed of a layer of silica covered with a layer of alumina, which aids in dispersion and handling and is itself covered with an organic surface treatment creating wettability with the polymer. The silica in the coating helps suppress TiO_2's catalyzing tendency in the production of free radicals when it is exposed to UV light. Moreover, by absorbing the near-UV-light spectrum and blocking some UV radiation, titanium dioxide also imparts a degree of UV protection to the polymer [1-1, 9-5, 9-6, 9-10].

Alternatively, other white pigments reflect some or all UV light; these include zinc sulfide (which absorbs some UV light) and barium sulfate (barytes or "blanc fixe," which absorbs no UV light). These two pigments have lower refractive indices than rutile TiO_2 (1.64, 2.37, and 2.75, respectively); this allows some flexibility for adjusting the shading or transparency of white resins. Moreover, ZnS, with its low Mohs hardness, is less damaging to glass fibers when used for pigmenting glass-fiber-reinforced resins, in comparison with harder, abrasive TiO_2. (Other white pigments include antimony oxide (refractive index of 2.1–2.3), zinc oxide (index of 2.02), and the anatase form of TiO_2 (2.55).) [9-1, 9-5, 9-6, 9-10]

Alternative pigments can be used to enhance TiO_2's effectiveness or to replace it. Barium sulfate can serve as an extender or "spacer" in TiO_2-filled materials, separating pigment TiO_2 particles to optimal distribution so that the pigment is 100% effective at its lowest possible loading. Zinc sulfide has been shown to help heat-stabilize and protect the color and strength properties of POs over long periods at elevated temperatures, and ZnS also produces brighter, blue/violet-tinted whites [9-5, 9-6].

Despite these alternatives and TiO_2's long history of use, improvements continue to be made in TiO_2 grades to help processors who rely on it. New grades often carry higher material costs, but open potential opportunities for lower overall handling and processing costs. For example, low-dusting, less-agglomerated materials such as Huntsman Pigments' DELTIO grades are said to help masterbatch producers handle and dose the pigment, reportedly allowing easier flow from feed hoppers; less caking, bridging, and binding from compaction; and faster changeovers and output rates. Similarly, new Ampacet TiO_2 masterbatches containing 75% pigment loads in LDPE carrier resins are reportedly designed to reduce die buildup and dispersion for downstream processors. Overall, titanium dioxide's mining and extraction processes are becoming more efficient, ensuring that it will remain relatively low in cost [9-7, 9-8, 9-9].

9.1.2 Black colorants

Absorbing essentially all visible wavelengths, carbon black is the most important black pigment for durable outdoor PO articles. Carbon black particles (especially around 0.02 μm in size) can also be used to enhance the weatherability of the product by limiting the resin's exposure to damaging UV light (however, it does absorb infrared radiation, heating the product). Larger particle size grades, though less expensive, provide "low jet" black pigmentation.

While furnace-type carbon blacks (produced from petroleum) may be adequate for non-weatherable, non-food applications, outdoor products or deeper shades may require finer channel-type carbon blacks (produced from incomplete natural-gas combustion). Channel blacks are several times more expensive, but generally meet US FDA food-contact standards. However, some furnace blacks, such as high-purity grades from Cabot, reportedly can meet food-contact standards, because like channel blacks, they have low levels of aromatic hydrocarbon and benzo(α)pyrene impurities [1-1, 9-1, 9-5, 9-11].

Synthetic mixed metal oxides such as copper chromate can also be used as black colorants [9-1, 9-5].

9.1.3 Full-spectrum colorants

For creating colors across the visible-light spectrum, pigment particles must be insoluble and non-migrating in plastics, and properly dispersed for well-distributed coloration. As with white pigments, when the refractive index of a color pigment particle is different from that of the polymer, light scattering will produce opaque coloration. Conversely, some pigments or colorants such as dyes selectively absorb certain wavelengths of light to create coloration, but do not scatter light as much, and thus most of a material's transparency is maintained. (As alternatives to pigments, dyes are usable with many polymers but are generally incompatible with POs, in which they bloom at the surface.)

Inorganic pigments have generally been based on inert metal-based compounds, and they produce acceptable colors with generally high thermal stability and UV resistance. Particle sizes are typically less than 1 μm for best results. Heavy-metal pigments are particularly durable and heat-stable; unfortunately, cadmium-, lead-, and nickel-based compounds face regulatory restrictions in the processing workplace and of course in food- or human-contact applications. In durable outdoor applications, they may be allowed and are particularly more effective than organic pigments. Some specific colors possible with common inorganic compounds include the following (also shown in Table 9.1):

- *Red and brown:* Iron oxide provides a dull red or brown pigmentation, depending on the iron's oxidation state. Cadmium/selenium compounds are also used for reds.
- *Yellow and orange:* Cadmium sulfide produces orange-yellow or similar shades when combined with zinc or selenium, but it contains the problematic heavy metal and is mainly used in engineering applications. Lead chromate produces bright yellows, but is light-sensitive and must be treated. Lead chromate, sulfite, and molybdate combined can create a stable orange color. Newer non-toxic compounds based on rare earth elements, such as cerium sulfide, reportedly offer the same shades as toxic chromates.
- *Green:* Oxides of the heavy-metal chromium produce a weak, low-strength green pigmentation, most suitable for weatherable outdoor applications.
- *Blue:* Ultramarine blue pigments are sodium/aluminum sulfide–silicate complexes. They are used in PP and HDPE, but they have poor resistance to acidic and alkaline outdoor environments. "Cobalt blue" (cobalt aluminate) is a higher-cost, more weatherable alternative. Ferric ammonium ferrocyanide "iron blue" has been used in LDPE bags, for example.

This information is given as a summary, and safer or at least less-controversial alternatives to some of the pigments above do exist (though they can be expensive) [1-1, 9-1, 9-4, 9-5].

Organic pigments are typically stronger and less opaque than inorganic pigments, but are not as light- or heat-stable. They have smaller particle sizes

Table 9.1 Overview and Examples of Relevant Organic and Inorganic Colorants [9-1, 9-4, 9-5, 9-6]

Color	Type	Chemical Base	Common Pigment Designations	Application Notes
White	Inorganic	Titanium dioxide	White 6	Most common pigment, in rutile form; some UV absorption
White	Inorganic	Zinc sulfide	White 7	Brighter, bluer whites; non-abrasive to glass fibers
Black	Inorganic	Carbon black	Black 7	Channel blacks purer and more expensive than furnace blacks, plus greater weatherability
Red	Inorganic	Iron oxides	Red 101	Inexpensive; dull reds and browns
Red	Organic, classical/ high performance	Azo/diazo	Red 177 and 220	Food-use approvals (US FDA); expensive but effective
Red	Organic, high performance	Quinacridone	Red 202 and 122	Good light stability and chemical resistance; expensive but effective
Orange	Inorganic	Cadmium sulfoselenide	Orange 20	Heavy-metal content; expensive but extremely heat-stable
Yellow	Inorganic	Cadmium sulfide	Yellow 35 and 37	Heavy-metal content; expensive but extremely heat-stable
Yellow	Organic, classical/ high performance	Azo/diazo	Yellow 93 and 95	Weatherable
Green	Inorganic	Chrome (III) oxide	Green 17	Weak greens; excellent weatherability at low cost
Green	Organic, classical	Phthalocyanine green	Green 7 and 36	Inexpensive, stable, bright, and transparent
Blue	Inorganic	Cobalt aluminate	Blue 28	Excellent weatherability and high cost, compared with ultramarine blue
Blue	Organic, classical	Phthalocyanine blue	Blue 15	Inexpensive, stable, bright, and transparent; food approvals (US FDA)
Violet	Inorganic	Ultramarine violet	Violet 15	Limited weatherability; poor acid/ base resistance
Violet	Organic, high performance	Quinacridone	Violet 19	Fair stability; food-use approvals (US FDA)
Metallic	Inorganic	Aluminum flake, brass	“Silver,” “gold-bronze,” etc.	Aggressive shear in processing can damage flakes and effects
Pearlescent	Inorganic	Coated mica flakes	Special-effect pigments	Aggressive shear in processing can damage flakes and effects

(0.05 μm) than inorganics, and, per-kilogram, are more expensive. But they provide brighter coloring, which lowers their net expense, allowing them to be feasible replacements for heavy-metal pigments. There is a large array of organic pigments available with various, complex chemical structures; only some notable ones are summarized below and in Table 9.1:

- *Yellow, orange, red, and violet organic pigments* tend to contain multiple azo (double-bonded nitrogen–nitrogen) groups. These groups serve as chromophores for the pigment molecule, chromophores being the agents of coloration (chemical groups that absorb certain wavelengths of visible light, while transmitting or reflecting others). Azo pigments are among the "classical" organic pigments referred to in the literature. Red and violet shades can also be created with slight changes to the polycyclic molecule quinacridone (QA). Though used for decades, QA pigments are considered "high-performance" because of their relatively good light stability and chemical resistance. Isoindolinone (for yellow, red, and orange) and dioxazine violet pigments are likewise used mainly in high-performance applications. Orange and red diaryl pyrrolopyrrole (DPP) and perylene pigments also provide bright shades.
- *Blue and green* organic pigment molecules have complicated, non-azo polycyclic structures, or are complexes with metals such as copper. Blue phthalocyanine, for example, is a classical pigment that is relatively low cost, bright, transparent, food-friendly, and heat- and weather-stable. Different crystal forms of "phthalo" provide different shades of green or blue.

Blends of these pigments may be necessary to reach proper custom color intensities and values [1-1, 9-1, 9-4, 9-5].

Pigments and dyes for transparent coloration: Dyes are used in many polymers as soluble agents that absorb specific wavelengths of light without scattering light like pigments. But traditional dyes are incompatible with POs and have a tendency to migrate and bleed out of the resin. Dyes would be useful in transparent PO applications, where they could supply a tint of color that creates extra product differentiation for packaging—a market segment that already is relying more on transparent plastics.

For example, hot-fillable clarified PP (cPP) containers are growing in use, and cPP relies on clarifying agents to reduce the haze of its naturally milky appearance. It is difficult to tint with pigments, which tend to reduce clarity. Extensive studies have been done on coloring cPP using various organic and inorganic pigments of different particle sizes and shapes, with various positive results (see Case 9.1) [9-12, 9-13].

CASE STUDY 9.1 PIGMENTS AND cPP [9-12, 9-13]

Problem: cPP is difficult to color with standard colorants.

Objective: Determine which pigments and factors produce the best low-haze coloration of cPP.

Solution: Pigments with particular chemistries, particle sizes, and particle shapes provide best results.

Becoming more popular for hot-filled food containers and other packaging applications, cPP that is also tinted provides some additional eye-catching qualities. To understand better how to pigment this material, researchers at BASF's GPU Performance Chemicals compared the performance of dozens of standard pigments molded in cPP in 2-mm plaques, measuring the samples' haze, clarity, and color quality. They noted a number of trends and conclusions:

- Pigment particle size: One important measure of visual quality is haze, the cloudiness and loss of contrast measured as the percentage of incident light that is scattered when passing through a translucent sample. The researchers found generally that pigments with larger particle sizes increase haze and hurt transparency. Inorganic pigments perform particularly poorly, given their relatively large mean particle sizes (generally greater than 500 nm). However, small pigment particle sizes do not translate automatically into low-haze values if particles are agglomerated and hard to disperse, or added as powders rather than pre-dispersed in carrier resins.
- Particle shape: Pigment particle shape can affect transparency even more than particle size. For example, two forms of an organic yellow pigment were compared; the form with long (1300 nm) needle-shaped particles gave haze measurements similar to those with shorter pigment particles with half the average length. These findings were explained by the fact that the average minor dimensions (diameters) of the pigment particles were similar.
- Pigment chemistry: Other parts of the investigation included comparisons of pigment chemistry and the effect of pigment concentration. Briefly stated, phthalocyanine pigments with low particle sizes (300–500 nm) provide low haze; isoindoline pigments with roughly the same particle size range provide much higher haze; and inorganic pigments with particle size of 500–1200 nm provide the greatest haze of all. Higher pigment concentrations generally increase haze, except for certain pigments that, even at higher concentrations, provided haze values nearly as low as those of natural cPP.

Interest in coloring cPP has also led to the development of PP-compatible, non-migrating polymeric dyes. One result is Milliken & Company's ClearTint functionalized polyether dye; another is the GemTone polyester-amide-based dye from DayGlo Color Corporation. Though commercialized, these colorants are still being studied. For example, one study found that at high loadings of the ester-amide dye, haze can be produced, which reportedly can be reduced with the addition of various waxes [9-5, 9-12, 9-13, 9-14].

9.1.4 Metallic colorants

In some situations, it may always be true that plastic products that look "plastic" will never be preferred by consumers over products that resemble metals. A metallic sheen projects value, durability, and strength; thus plastics are often designed to imitate the look of metals, using pigments or other metal-mimicking coloration strategies. Soft, pleasing metallic colors can be created using fine metal powders as pigments, without solid metal's weight and cost.

Popular metal pigments include aluminum flake, which, along with its relatively low specific gravity (2.7), provides various shiny colorations when used in plastics at 5–650 μm particle sizes. Aluminum pigments are used in PE agricultural film to reflect light, in containers to provide a metallic sparkle, and in automotive moldings to resemble metallic paint. Brass pigments produce a gold-bronze color, and have a much higher SG of 8.5. Another metal pigment/filler is stainless steel (SG of 8.0), highlighted in Chapter 6 because of its electrical conduction properties. Metal pigments mixed with color pigments also produce good results; for example, a metallic gold effect can be produced by combining lens-shaped aluminum flakes and red and yellow pigments. Gold-colored mica flakes plus aluminum achieve a similar effect.

Metal pigments (mostly) resist PO-processing conditions. However, metal flakes can become bent or broken by high shear forces in melt processing. And aluminum can easily become oxidized; to protect aluminum flakes from oxidation, they are commonly coated with alumina or fatty acids after being ball-milled into flakes or other shapes. During molding, thin pigment particles tend to orient themselves in the flow direction, which can be a problem when their continuity is broken along flow or weld lines. In injection molding in particular, streaks or lines result when the proper flake orientation is lost at regions of disrupted or inconsistent melt flow in the mold [6-3, 9-15, 9-16, 9-17].

For aluminum pigments, an unusual relationship has been observed between cost, concentration, particle size, and color brightness (or brilliance). With small aluminum particles, maximum brilliance is reached at relatively low loadings and costs, above which there is no increase in brilliance. Larger pigment flakes require higher loadings (and costs) to reach a much higher maximum brilliance. Opacity is increased by the greater reflective surface area of multiple small particles with a wide size distribution. Conversely, large metal flakes in a narrow size distribution supply an attractive, irregular, internal sparkling effect.

Thus, with adjustments to size, size distribution, and shape, aluminum pigments can be used to create various kinds of "sparkle" effects. Pigment supplier Silberline categorizes five different kinds of aluminum flake effects [9-15]:

1. *Liquid metal*: a bright brushed-metal appearance, created using pigment grades with particles of roughly 8–20 μm median size with "cornflake," "silver dollar," or lenticular (lens) shapes.
2. *Metallescent effects*: produces diffuse, pearlescent-like light reflection using small pigment particles (11–24 μm) at low loadings.
3. *Pinpoint sparkle*: uses spherical pigment particles of 30–45 μm median size to produce random light reflections from particles beneath the plastic surface.
4. *High sparkle*: uses large pigment flakes up to 250 μm in size that provide distinct, bright surface reflections and a metallic sheen.

5. *Glitter effect*: uses very coarse aluminum grains (up to 600 μm) that emphasize the transparency and depth of transparent objects containing the suspended flakes.

The next section covers other kinds of "special effects" for enhancing or manipulating coloration.

9.1.5 Pearlescent colorants and color-enhancing additives

As with pigments that create a metallic surface appearance, other additives supply additional visual effects meant to draw the human eye to a product and differentiate it from competing products. This may involve simply enhancing the color strength of a colorant, or another colorant may be used to add a deep pearl-like shine to a colored product. Ironically, with the right special-effects colorant or additive, a product made from the most inexpensive of plastics may take on a more high-end visual character.

Pearlescent additives are usually various forms of flaked mica or highly polished aluminum flakes, both of which reflect light in a diffuse, iridescent, brilliant way. The flakes must be oriented in the plastic in layers parallel to the surface to achieve this effect. Smaller flakes create a soft sheen; incorporating larger particles provides a glitter effect. Mica and aluminum flakes may be combined to provide an opaque, metallic luster in the resin product. Pearlescent additives can also be combined with other pigments to create various color shades and opacity levels, and are often packaged in various color concentrates. Only low concentrations (<1%) of effects-pigment products are added to transparent materials, to help preserve their transparency; higher loadings (>1%) are required in opaque resins. In processing, these flake materials can be difficult to disperse without defects, and they are sensitive to the high-shear stages of screw processing [1-1, 9-17, 9-18, 9-25].

Mica flakes may be coated to provide extra properties or effects. For relatively long-term performance in molded items such as cosmetics containers, jars, and decorative items, surface treatments on pearlescent additives have been used to provide stabilizing, anti-yellowing properties. To create the effect of changing colors as a product is viewed from different angles (a "flip-flop" effect), a titanium dioxide coating is applied to the pearlescent mica particles. These effects can be applied to plastic toys, housewares, and office accessories, as well as to packaging (however, pearlescents are not always appropriate in food-contact products). Components with complex contours and sharp angles may make most dramatic use of this color-shifting effect [9-18, 9-22].

Fluorescent whitening agents (or optical brighteners) add a glowing effect to the pigments in the resin, since they convert the UV light they absorb into visible, blue-shifted wavelengths of light. Fluorescing colorants are often simply dyes attached to a carrier molecule to make them compatible for use in PE or PP. Their effects brighten whites or colors, and they can mask any natural yellowing of the product. One commercial brightening agent offered for POs and other polymers is of the thiophenediyl benzoxazole family, designated UVITEX OB by Ciba. Its effects are not light-stable and UV-light absorbers reportedly can interfere with its effectiveness; but even if these factors necessitate higher loadings, effective concentrations in POs still may lie well under 1% [9-1, 9-24].

Phosphorescent effects additives are similar in mechanism to fluorescent agents, except that the yellow-green glow they emit continues in the dark, after the light source is removed. Replacing the radioactive phosphorescent additives that were once used, copper-doped anhydrous zinc sulfide has become a common additive that produces phosphorescence. This pigment may require high loading rates to be effective, but metal oxide alternatives have been developed that are said to be effective at much lower loadings [1-1, 3-5].

Granite and similar speckled surface effects use a combination of pigments and large, reflective (often colored) mica flakes, up to or over 2000 μm in size, depending on how coarse of a grain is desired. Granite powder itself reportedly has been used in LDPE to create rotationally molded fencing that resembles stacked stones [1-1, 9-23].

Wood-grain effects colorants for wood–plastic composites have been commercialized, with recently improved formulations reported by Americhem. These formulations are said to produce deep wood-grain effects for more natural-looking building products, serving as a durable, low-cost alternative to surface embossed graining or laminated films [9-39].

Laser-marking additives, though not technically colorants, allow lasers to permanently, selectively discolor and mark PO products. These additives or pigments make a polymer surface receptive to the effects of laser beam energy, creating a local color change. Laser marking allows tracking numbers, promotional decorations, or even barcodes to be written on otherwise hard-to-decorate PO surfaces. Molded caps and closures in particular are target applications for the additives, for use in automated laser-marking systems [9-17, 9-38].

9.2 COLORANT DELIVERY AND PROCESSING

9.2.1 Colorant delivery

Compounders and converters of resin pellets typically use colorants in forms that are becoming increasingly flexible to use, including:

- concentrates or masterbatches, in which pigments are highly loaded in easy to handle pellets;

- "liquid color," where pigments are dispersed in non-volatile liquids;
- dry powder pigments, which are used more rarely, given their inherent handling difficulties;
- pre-colored resins, an inflexible and expensive solution for commodity POs (though this approach is still of some interest for reinforced or highly filled PPs for automotive use, for example, where specialty compounders offer pellets with consistent color in one ready-to-mold form).

The proper choice of colorant is dictated by health and safety concerns, handling ease, volumes of use of certain colors, as well as by obvious color quality issues, such as color-matching accuracy. Table 9.2 gives a rough comparison of the above colorant forms [9-15].

About 70% of colorants used worldwide for plastics are in the form of concentrates, with white and color concentrates sharing roughly equally the majority of that volume. For POs in particular, color concentrates are by far the leading form in which colorants are added directly to resin. Concentrates come in different free-flowing pellet or bead shapes, allowing easy integration with resin pellets using automatic metering equipment during melt processing. The typical carrier resin used in concentrates for coloring all POs is typically LDPE, specified with a melt-flow rate that roughly matches that of the matrix resin (though high-performance PP applications benefit from carrier resins that are also PP). Pigments pre-dispersed with other additives in standard masterbatch pellets also offer opportunities for simplifying handling and improving dispersion [1-1, 9-2].

Normal pigment loadings in concentrates are 20%–25%. But "superconcentrates" loaded with up to 80% pigment have become cost-effective alternatives to standard products, because they require less concentrate for

Table 9.2 Basic Comparison of Colorant Delivery Forms

Factor	Concentrate	Liquid Color	Dry Pigment	Pre-colored Resin
Cost	1–2	2	3	1
Ease of handling	2	1–2	1	3
Inventory burden	1–2	2	3	1
Dispersion	2–3	2–3	1	3
Dosing control	3	3	2	1
Ease of color changes	2	3	1	2–3

Source: Adapted from [1-1]. 3 = good; 2 = medium; 1 = poor.

equivalent coloring levels. Highly loaded concentrates in the form of round "mini-beads," a few millimeters in size, are said to blend with resin more efficiently. These products may also include a UV stabilizer for outdoor applications, such as construction products. Even smaller super-concentrate beads are available, such as Teknor's "Color Spheres" which are less than 1 mm in size. These products carry a cost premium, but they can be added at let-down ratios of 100:1 (or higher for thick molded parts), rather than the conventional 25:1. This reportedly allows potential cost savings overall, along with higher production rates because of the products' easier blending with the resin [9-19, 9-20, 9-26, 9-29].

Liquid colors contain pigments in carrier liquids with high pigment loadings of around 80%. As a liquid, this form requires specific equipment for automatic metering and pumping the colorant into the processing machine's hopper throat. The liquid carrier allows good dispersion of pigment, but can affect some processing properties, and of course carries the threat of messy mishandling. However, handling equipment that allows liquid concentrates to be piped cleanly through a plant has improved over the years. These include centralized liquid-color delivery systems (from Colors For Plastics, Inc., for example), which reportedly can supply color from a materials-handling area to multiple molding machines dozens of meters away [1-1, 9-27].

Dry powder pigments may be the most cost-effective colorants to purchase. But they require careful weighing and batch-blending, which complicates their use, as well as wetting agents that allow their dispersion into the resin. As powders, they can easily contaminate the surrounding operation and invite regulatory headaches. Moreover, dry pigments such as aluminum can become explosive if suspended as dust in the air, meaning that a binder or carrier resin is critical for their safe handling in the form of free-flowing micropellets or granule concentrates [1-1, 6-3].

9.2.2 Processing issues with colorants

Each type of individual plastic-processing method has its own difficulties, dangers, or advantages when handling pigmented resins. A few processing notes are briefly provided below:

- In *compounding* or screw processing that incorporates additives separately rather than in the form of masterbatches or concentrates, the order in which colorants are added to the resin can be important. For example, adding pigments and metal flakes together can produce poor results: pigments require shear to break up their agglomerates of particles, yet this same shear can damage aluminum flakes. Thus, as when adding sensitive glass fibers, flakes would be more appropriately added into the screw downstream, via a side feeder.

- In the *co-extrusion of multilayer films*, opaque pigments in the outer layers provide not only aesthetics but also an opportunity to conceal off-color recycled material used in the inner layers.
- With *blown film*, only very small metal pigments are appropriate, at loadings under 1%, to avoid film damage. These tend to align themselves in parallel for effective reflectivity.
- The *blow-molding* of containers may require the use of color masterbatches for good dispersion.
- In *thermoforming* extruded sheet, one advantage is that proper color match and pigment distribution can be verified before the final forming operation.
- In *injection molding*, warpage from differential shrinkage can become a problem when a molder uses certain pigments, such as blue and green phthalocyanine organic pigments. Fillers such as talc and calcium carbonate can help control warpage, as can nucleating agents for PE and PP, which raise crystallization temperature and encourage isotropic shrinkage.
- And finally, *rotational molding*, primarily of PE, consumes large amounts of pigment per part because of its suitability for producing colorful and large outdoor items. Rotomolding seems like it should be particularly friendly to metal pigments, since it is a low-pressure process that puts little stress on pigment flakes. However, rotomolding raw materials are typically pre-colored resins ground into powder, a process which damages flake pigments. One alternative to this size-reduction process is to add pigmentation via compounded "micropellets" of under 1-mm size to obtain pigment uniformity in rotomolding.

These and other processing factors should be anticipated and built into the planning of converting resin into colored products [6-3, 9-16, 9-28].

9.3 FACTORS THAT AFFECT THE CHOICE OF COLORANT

9.3.1 General factors

Colorant experts have noted a wide variety of issues processors and compounders encounter when they attempt to match the color requirements for an application in a consistent, controllable manner. A handful of the main issues are explored briefly in paragraphs below, with as much specific attention to POs as possible. Then the following two subsections address more detailed issues with POs and colorants:

Evaluating the color of the final product: As everyone familiar with the science of color agrees, color is subjective, and no two people will equally perceive the color of a final product. Even a single person's perception may be inconsistent over time. Spectrophotometers can help provide objective, repeatable Delta-E comparisons of shade and hue, and allow processors and users to decide exactly "how close" a color should be to matching a standard. But a contoured colored product may still frustrate expectations that were based on a flat colored plaque or standard chip. The product and standard may also differ in terms of material, process, finish (matte vs. glossy), or even the samples' physical dimensions; all of these affect the reliability of making comparisons and judging a color match (by either a human being or spectrophotometer's computer).

Moreover, judging coloration also depends on *metamerism*, a phenomenon in which the color of an object shifts depending on the kind and/or angle of incident light. Two samples may appear to be the same color under one light source, but not under another; or shifting the angle of view of a sample surface may change the apparent color (a characteristic which or may not be desired, depending on the application). Thus a colored product sample should always be tested with the light source and conditions under which the product is most likely to be viewed [9-3].

Organic vs. inorganic pigments: As regulatory changes tend to encourage users to steer away from heavy-metal-based inorganic pigments, more users encounter the limitations of organic pigment alternatives. Organic pigments provide stronger colors but can be less dispersible than inorganics in the resin. In particular, phthalocyanine green pigment particles can act as nucleators and cause uncontrolled resin crystallization, shrinkage, and warpage. Classical organic pigments can also be more susceptible to weathering than inorganics and are less opaque (which may or may not be a desired property). Moreover, some organics are thermally stable only up to 200°C, limiting their use to blown film, compared with well above 200°C for inorganic pigments [9-1, 9-14].

Still, pigment specialists are making progress in removing these limitations on organic pigments, while improving dispersion and loading levels with "superconcentrates." These pigment forms make organics more cost-competitive with inorganics, especially since organic pigments can provide brighter colors at overall lower loading levels [9-19, 9-20].

Pigment vs. filler/fiber: A common, inexpensive, and low-refractive-index filler such as calcium carbonate, for example, can affect the shade of a pigmented article. Generally high levels of these mineral fillers dull the brightness of colors or prevent deep dark colors from being possible. Glass fibers used for mechanical reinforcement likewise scatter light and darken colors, and thus these compounds may also require higher pigment loadings than neat resins.

But higher loadings can reduce mechanical properties, and hard, abrasive inorganic pigment particles such as titanium dioxide can damage the reinforcing glass fibers [9-1, 9-37].

Pigments vs. properties: Despite their necessity, pigments have been spoken of in the industry as "dirt" in the resin, because of their usually negative effects on material properties. As with fillers, pigment agglomerates must be broken up by shear forces during processing to provide effective coloration; the more dispersed the pigment is, the less it will tend to reduce the mechanical properties of the compound. Along with causing an uneven colored surface, large pigment agglomerates can cause brittleness by acting as stress concentrators, and also lower impact strength and other properties. Thus, unexpected property reductions can occur simply when "upping" the concentration of a pigment to create a brighter color in the product, by adding more "contamination" to the resin [9-37].

And changing colorants during processing without changing processing speeds and other parameters may change a product's shrinkage behavior, pushing product dimensions out of tolerance. "Color-leveling" additives are said to solve these possible warpage problems by causing the same degree of shrinkage for all colors at the same process settings. (Ampacet's ProBlend is an additive that is said to work particularly well with PP closures, tubs, and containers.) [9-40].

Pigment particle size: Depending on the refractive index of the pigment, varying the particle size of a pigment can allow a compounder to adjust the tint of the material and the amount of light that is scattered. For opaque materials, the optimum particle size that scatters the most light is proportional to the difference between the refractive index of the pigment and the polymer. Extremely fine particles that are too small to scatter light waves decrease the resin's opacity, and a wide distribution of particle sizes may produce color undertones [9-5, 9-6, 9-10].

Gloss: Unlike paint, most internal colorants are limited in how much they can affect the gloss of a colored surface. Gloss is the inverse of surface roughness, and multiple, non-colorant factors can have major effects on gloss (potentially requiring a massive DoE to understand a given application). These factors may include the resin grade, filler content, tooling surface quality, and processing parameters, which determine, for example, whether a clear, glossy layer of resin can be concentrated at the surface of a molding. However, certain colorant additives can enhance the gloss of generally low-gloss POs such as HDPE without significantly affecting material properties (see Case 9.2).

Outdoor use and weatherability: UV light can ruin pigmentation; for example, in testing of pigmented HDPE, lighter colors (red, orange, and yellow) tend to

CASE 9.2 IMPROVED GLOSS OF INHERENTLY LOW-GLOSS HDPE [9-34, 9-35, 9-36]

Problem: PE is an inherently low-gloss material, diminishing the visual impact of colored PE packaging, relative to high-gloss PET.

Objective: A gloss-enhancing additive solution for colored HDPE packaging that does not affect mechanical properties.

Solution: A masterbatch that increases the gloss of colored HDPE parts by over 200%.

Although high-gloss-colored PET and homopolymer PP bottles and packaging are common, PE does not naturally permit high gloss for molded products, and thus PE usually cannot compete visually with the other materials in these terms. One alternative for increasing HDPE gloss (without reducing mechanical properties) is to incorporate gloss enhancers into the color masterbatch, an option reportedly commercialized by Ampacet Corporation.

The company's "POP" color masterbatch is said to improve HDPE gloss by 200%, allowing opaque HDPE to compete with PET in more container applications. Compounds with the POP colors reportedly show improved stiffness and melt strength, allowing its use in monolayer bottles. This is unlike with other high-gloss PE compounds, in which a loss of melt strength and crush strength restricts the high-gloss material to the outer layer of a product. Along with its use in mono- and multilayer cosmetics and personal-care containers, the POP masterbatch has US FDA food-contact approvals.

show faster and greater Delta-E color change during weathering than darker colors (blue, teal, and green). To prevent color changes from degrading in sunlight, surface treatment of the pigment particles may be required. And stabilizers may be needed that do not interact negatively with the pigment, in order to prevent yellowing and shifts in the desired color (see Section 9.3.2). On the other hand, carbon black and some pigments act as UV-light screeners, preventing damage to the polymer itself [9-4].

Supplier variations: For other additives, changes in suppliers may not result in noticeable product differences, but with colorants, a change in supplier may be visually obvious to the customer, despite what the resin documentation may indicate. Similarly, the sourcing of the uncolored resin itself can be a color factor; for example, post-consumer-recycled material mixed in with virgin PE can create a "gray cast" in the resin color that may require strong colorants to overcome [9-21].

Product thickness influences: Changes in product thickness may change the level of opacity that was initially desired, requiring adjustments to pigment concentration or type. Similarly, multilayer films or bottles also complicate the decision about how much colorant is needed in which layer for adequate coloring. However, multilayered products do expand the possibilities for combining variously colored layers or special-effects layers, for example, to produce unique looking products.

Regulatory restrictions: Ideally, colorant suppliers seek regulatory approvals that allow their products to have the widest use in a broad range of applications.

In reality, each colorant's suitability and compliance should be verified before use; some colorants specifically advertise their suitability for certain uses, such as biocompatible medical products. And it almost goes without saying that pigments based on cadmium, chromium, lead, or other heavy metals—though they are effective—are restricted in multiple cases, and processors wishing to retain a perfect "green" image should simply avoid these pigments.

9.3.2 Additive/colorant interactions

As with all additives, colorants may weaken or enhance the effects of other ingredients in the compound, thus requiring other colorants or different additives in compensation. Colorants may also weaken the resin's properties; for example, a low-purity grade of blue phthalocyanine may cause premature aging of PP fibers, which could be avoided using a high-purity (low copper) form of the pigment. Or the pigment isoindoline reportedly causes darker colors at high processing temperatures, when combined with an antistatic agent and alkaline metal soap. Antistatic agents and lubricants in general, since they concentrate themselves at the part's surface, tend to scatter light, changing the effect of the colorant. Likewise, flame retardants, impact modifiers, fillers, and fibers can all affect light scattering and thus the brightness or shade of the color, as mentioned above [9-31, 9-37].

Discoloration from additive interactions has been a concern of LLDPE film processors, for example. As discussed in Chapter 3, phenolic-based and phosphite antioxidants can cause color changes that interfere with the film's intended color over the short and long term. If a stable combination of additives and blend ratios cannot be found, the phenolic stabilizer may need to be changed to a non-phenolic product. In the hunt for a non-coloring combination of stabilizers, factors such as melt-flow rate retention, the effect of multiple extrusion passes, mechanical property changes, gas fade aging, and heat aging performance also need to be evaluated. Another factor is the extent to which titanium dioxide in the material tends to increase discoloration over time (or not), and whether the coating on the TiO_2 prevents these effects [9-32].

Great interest has also been focused on how HALS interact with pigments to produce color shifts. These color changes reportedly are usually more extreme in pigmented HALS POs than they are in colored non-HALS POs or in unpigmented HALS POs. Thus experts have concluded that HALS additives do interact with colorants, though the exact mechanism is unclear. Since various HALS chemistries have been shown to correlate with specific color changes, questions linger about whether color-matching is as affected by the choice of HALS as it is by pigment choice and loading. So although one HALS will not work in every coloring situation, a specific HALS can work well for a specific colorant/resin formulation [9-30].

9.3.3 External coatings vs. internal colorants

Paints and coatings are generally incompatible with non-polar POs, unless energetic or chemical surface pre-treatment is performed to activate the plastic surface to accept paint. Painting may be needed for color-matching on automotive moldings, for example, if the molded colored part is not close enough to the color specification. Still, the environmental hazards of painting (such as emissions of VOC solvent), the wastage of paint (20% or more), and the plant infrastructure required for painting operations create constant pressure for improving other approaches for coloring plastics. Thus molded-in-color pigmentation is favored as a one-step, lower-cost solution, when possible, especially when there is a great threat of chipping a coated part in service [9-33].

But along with final color-matching, coatings have other aesthetic advantages over internal pigmentation in molded parts. First a uniform coating can hide all weld and flow lines. And in coatings with metallic flakes, the flakes align themselves relatively flat on the surface as the paint solvent evaporates, maximizing their reflectivity (this surface orientation effect is much less prevalent with molded-in metallic resin parts). For the most extreme effects, the highest reflectivity is gained (at high cost) by vacuum metallizing the part, which produces a mirror-like finish [6-3].

Thin colored films or decorative foils, coated with paint pigment or internally colored, are used as alternatives to painting or internally coloring an entire part. Uncolored or lightly colored resins can be molded or formed behind these films, producing a colored part with a "Class A" finish. Years of development have gradually made colored films more feasible for automotive parts in particular, since they often require durable, high-gloss, and consistent color-matched surfaces that may be beyond the abilities of molded-in pigments and mold tooling. Interior automotive parts, by contrast, have used thicker skins or sheets of low-gloss colored resins over PP/TPO substrates, allowing specific textures and grains on the part surface, as well as color.

In particular, molded products covered with metallized films can be highly reflective and lack the flow- and weld-line inconsistencies in metal pigment distribution that can be found in internally pigmented moldings. The films are usually more durable than paint, with lower system costs and a lower environmental footprint as well. However, part compatibility depends on the process and pressures required to form the part and apply the film [6-3].

A final word: The coloring of plastics is a field of study with subtleties that extend far beyond the scope of this chapter. Ultimately, experts with decades of experience with colorants are the best sources about this art/science. For more details, readers might turn to full-length reference texts such as *Coloring Technology for Plastics* by Ronald M. Harris or *Coloring of Plastics: Fundamentals* by Robert A. Charvat, as well as other texts and annual conferences.

CHAPTER 10

Nucleation and Clarity

Recently, supplier announcements about new nucleating and clarifying agents have become among the most frequent of any additives used for POs. Directing their attention mainly at PP, makers of clarifying agents in particular have been trying to open up new packaging applications that allow low-cost cPP to compete directly with PET, especially for hot-filled food and beverage containers. Yet nucleating agents, of which clarifying agents are just a subcategory, offer multiple property improvements in POs by promoting the fast, controlled formation of fine spherulite crystal regions throughout the volume of the resin product.

This chapter will tend to focus on PP, since its crystallization rate is slow enough to allow nucleating agents to significantly affect its crystallization properties. However, the idea of using nucleating agents for improving fast-crystallizing PE has drawn increasing attention as well.

This chapter will first cover the general value of nucleating agents, and then the specific value of clarifying agents, along with factors and alternatives to consider when a clear or nucleated PO material is needed. The chapter is guided by these questions:

- (10.1) What is the overall value of nucleating agents, how do they affect resin properties and processing, and which are most often used in POs?
- (10.1.2) What are some important clarifying agents, and how do they work?
- (10.2) What are some key issues encountered when using nucleators/clarifiers, and how can these issues be addressed?

10.1 NUCLEATING AGENTS: OVERVIEW

Nucleating agents thermodynamically encourage the initiation of spherical, radiating crystalline regions (spherulites) at multiple, well-distributed sites throughout a polymer matrix. Added to the resin usually right after the polymerization reactor stage, these agents have been described as "foreign phases" creating "artificial defects" in the polymer, providing the surfaces on which crystals can begin their growth. Nucleators allow crystallization temperatures to be increased by as much as 20°C or more for PP (and 2°C–5°C for PE, whose crystallization can only be minimally enhanced by a nucleator). By effectively raising the crystallization temperature and increasing the possible sites and rates of crystallization, nucleating agents are used for creating more dimensionally stable parts, higher mechanical properties, quicker processing (solidification) times, and often higher clarity. The ultimate number and size of the spherulites and total fraction of crystallization in the matrix ultimately determine how much the resin's properties and processing are affected by the agent [10-5, 10-19].

Nucleating agents may simply be used to enhance physical properties and processing, but the industry has also created *clarifying agents* as a class of nucleating agents that specifically affect optical properties. These agents create spherulites that are smaller than the wavelengths of visible light (400–700 nm); thus light is not scattered by the crystal regions, and there is little opacity in the resin product. Experts have also categorized nucleators as being melt-insensitive (where the agent does not melt with the resin) and melt-sensitive (when the agent's melting point is near that of the resin). Melt-insensitive agents are metal organic salts, and, some are clarifiers; melt-sensitive agents tend to be fully organic and are usually clarifiers. Some of these distinctions are summarized in Table 10.1, and they are useful to make in the following sections [3-4].

10.1.1 Nucleating agent effects on processing and properties

As particles distributed within a matrix, nonmelting nucleating agents create single-point nucleation sites. Traditional agents include aromatic carboxylic acid salts such as sodium benzoate, which is mainly used for enhancing physical properties, and metal salts of phosphate esters, which both clarify the resin and enhance properties. The amount of clarity gained is dependent on the number of nucleation sites created, the size of the nucleator particles, and the amount of dispersion that occurs when the agent is mixed with the polymer. Finer particle sizes generally make for more effective nucleators, and even the particle shape has been said to determine nucleation effectiveness. Oriented, "needle-like" crystal shapes produced by traditional agents are considered inferior to "plate-like" shapes for encouraging isotropic shrinkage [3-4, 10-1, 10-3, 10-4, 10-27].

Nucleating agents provide processing advantages. In injection molding, they allow parts to be removed from the mold at higher temperatures, resulting in shorter cycle times (see Figure 10.1).

Table 10.1 Summary of Nucleating and Clarifying Agents Discussed in this chapter

Primary Purpose	Chemistry	Commercial Product Names (Examples)	Common Materials/ Application	Application Notes
Nucleation	Carboxylic acid salts	Milliken HPN-68	PP	Traditional and fast nucleators enhance physical properties and productivity and reduce warpage
Nucleation	Organophosphate salts/esters	ADK NA-11 and NA-21	PP	Fast nucleation
Nucleation	Fine talc	Rio Tinto Luzenac and Jetfine	PP	Increased stiffness and crystallization temperature (short cycle times)
Nucleation and clarification	Trisamide	Ciba XT 386	PP	Low haze at 1/10th the concentration of sorbitol clarifiers; cycle-time reduction
Nucleation and clarification	Carboxylic acid salt	Milliken HPN-20E; Ingenia IP1810	LLDPE film	Haze reduction and higher gloss and physical properties
Clarification	DBS and MDBS (trad. sorbitols)	Multiple	PP	DBS: plate-out limitations; MDBS: organoleptic (taste/ odor) limitations
Clarification	DMDBS (“third-gen.” sorbitol)	Milliken Millad 3988	PP	Most used clarifier; overcomes most previous sorbitol limitations
Clarification	Nonitol	Milliken NX8000	PP	Higher levels of “water white” clarity possible
Clarification	Non-sorbitol	RiKA PC1	PP	No plate-out; wide processing window; not affected by peroxides

The agents also generally allow molded parts to shrink more evenly (isotropically) and thus warp less. However, fast-acting nucleators are said to have a tendency to freeze stresses into a part, which later could be released as dimensional instability, or conceivably they may allow parts to shrink so fast in the mold that part ejection is difficult. Nonetheless, nucleating agents can be an effective means to compensate for or override the warping/anisotropic shrinkage caused by pigments such as blue and green phthalocyanine. Nucleators packaged in masterbatch form are available for reducing warpage specifically in situations where a part molded in different colors displays shrinkage that is changed radically by different pigments, or simply where part cycle times and warpage are considered to be excessive (see Case 10.1) [1-1, 10-1, 10-3, 10-10, 10-11].

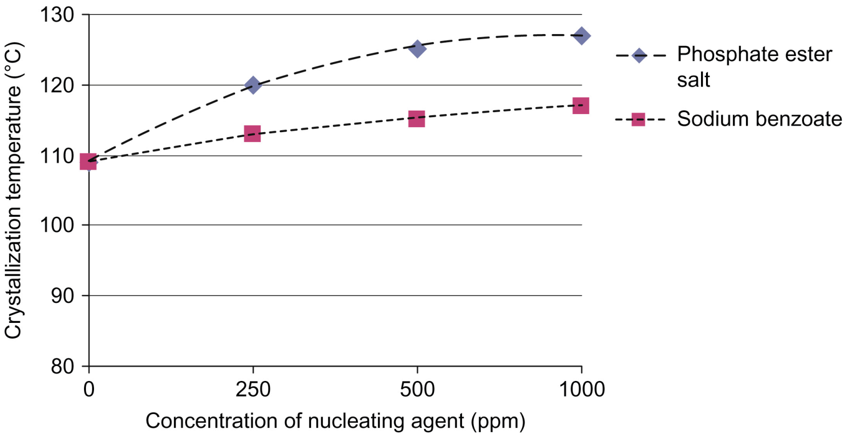

FIGURE 10.1

Crystallization effects of nucleating agent. *Nucleating agents increase the temperature at which the polymer crystallizes, allowing shorter cycle times. Above are data for PP homopolymer with a standard sodium benzoate and with Ciba's Irgastab NA 11 nucleating agent.*

Source: *Adapted from [10-4].*

CASE 10.1 NUCLEATING AGENTS DECREASE MOLDING CYCLE TIMES AND WARPAGE [10-11]

Problem: Warping and slow cycles when molding PP toilet seats.

Objective: A quick and easy adjustment for faster cycles and more stable parts.

Solution: A masterbatch concentrate containing a fast nucleating agent.

One might be forgiven for not thinking of the lowly PP toilet seat as being a high-volume product that is not easy to injection mold in fast cycles without inviting warpage. Such was the situation for South African injection molder Braymould Plastics, which would sometimes receive orders for as many as 10,000 of the ringed seats at a time.

The molder considered the original cycle time for molding the seats to be too high, at around 40 seconds. Plus, the seats were prone to warping and bending. So the company tried a masterbatch containing a nucleating agent—specifically a PropaForm concentrate from Plastamid, which contained Milliken's HPN-68L nucleator.

Let down at 1%–2% in PP, the nucleator reportedly eliminated warping and reduced cycle times to 32 seconds—translating into 22 hours for a 10,000-seat order.

For fulfilling a part's service requirements, nucleating agents increase strength, stiffness, and heat-deflection (HDT) properties; for example, flexural modulus may increase 10%–20%. Some agents may reduce impact strength slightly, though others maintain this property (see Figure 10.2). New "hyper-nucleating" agent formulations are said to increase HDT by 15°C–20°C. Since these nucleating agents increase critical mechanical properties without much effect

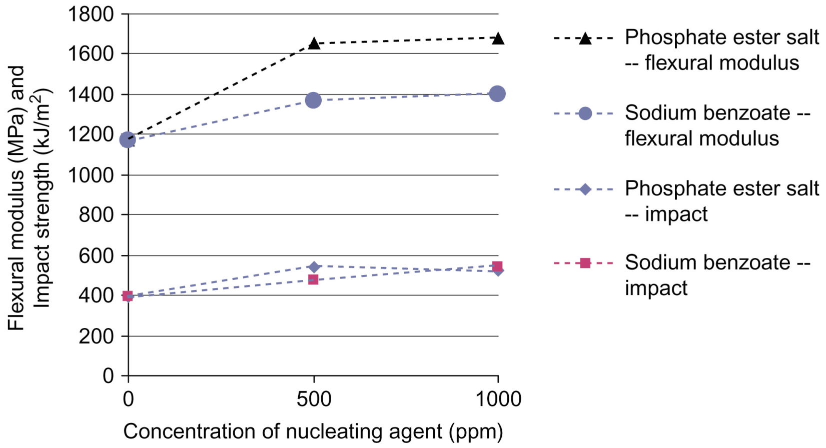

FIGURE 10.2

Mechanical property effects of nucleating agents. *Nucleating agents can increase modulus without losses of impact strength. Above shows data for PP homopolymer with a standard sodium benzoate and with Ciba's Irgastab NA 11 nucleating agent.*
Source: *Adapted from [10-4].*

on impact strength, the nucleating agent's strengthening effects alone may justify its use. For instance, nucleators are said to be invaluable in molding thin-wall automotive bumper fascia with sufficient stiffness [1-1, 10-1, 10-4].

Newly commercialized nucleating agents are being publicized regularly; these agents may become common, and then later serve as a basis for even more advanced technologies:

- High-speed nucleators include the phosphate esters NA-11 and NA-21 from Asahi-Denka Kogyo (ADK, or Amfine Chemical in the USA) and Irgastab NA 11 UH from Ciba, and Milliken Chemical's HPN-68, a norborane carboxylic acid salt approved for food contact (by the US FDA) [10-4, 10-10].
- Commercial nucleators generally induce the formation of PP crystals in their "α" crystal form, though some effort has been made to market nucleators that produce "β" crystal forms, which are said to increase impact strength and thermoformability [10-2, 10-26].
- Agents based on trisamide chemistries are said to reduce warpage, with some increase of crystallization temperature and clarifying effects [10-18, 10-25].

Nucleating fillers such as talc or calcium carbonate at low loading have also been shown to increase crystallization temperature in PP homopolymer. The increase is a few degrees, in the case of 1% $CaCO_3$, to over 10 °C, for 1% fine talc. Talc in particular is suited for nucleation given that one of its main crystal axes matches well with the spacing and angles between atoms in the PP polymer chain. Thus talc offers a compatible surface on which the polymer can begin crystallization. A talc product specifically designed for nucleation, of 1–5 μm median particle size and loaded as high as 2%, can speed crystallization to nearly the level of a standard phosphate salt agent, while allowing less shrinkage and providing similar mechanical properties. Such products are also said to be alternatives to phosphate salts in the way they overcome the variable shrinkage effects of various pigments. Talcs can also be combined with sorbitol clarifying agents, discussed below, to enhance clarity and reduce haze [10-8, 10-9].

10.1.2 Clarifying nucleating agents

Clarifiers are usually melt-sensitive nucleators that require between 220 °C and 270 °C to melt during processing. They are often acetal sorbitol-based agents which form a continuous, fibrous "gel network" that promotes nucleation throughout the resin. This fine network creates a great deal of surface area on which very fine spherulites form. The spherulites that are created are small enough to allow light waves to pass without scattering them, bringing transparency to a semicrystalline material like PP (shown for example in Figure 10.3). Ideally, an agent producing the highest possible clarity is only limited by the haze caused by the clarifier itself, or from its nonuniform distribution. Sorbitol agents used at what are considered high concentrations (0.2%–0.3%) in PP create clarity for food packaging or personal-care product packaging, or allow products to be more effectively colored [3-4, 10-4, 10-10, 10-18].

Many suppliers define their newest clarifiers against the standard of the most commonly used sorbitol clarifier for cPP—1,2,3,4-di-meta, para-methylbenzylidene sorbitol (DMDBS)—or its predecessors dibenzylidene sorbitol (DBS) and 1,2,3,4-di-para-methylbenzylidene sorbitol (MDBS). Each of these generations of clarifiers show particular limitations of sorbitol-based agents; for example, DBS presents significant plate-out problems from its thermal decomposition, while higher-melting, more efficient MDBS creates taste and odor (organoleptic) problems, which DMDBS reduces. In the past decade, the DMDBS agent designated Millad 3988, introduced by Milliken Chemical as an alternative to the other benzylidene sorbitols, has quickly become heavily used for cPP. Along with its better organoleptics, it can be used at higher injection-molding temperatures [10-10, 10-11, 10-12, 10-13, 10-19, 10-23].

DMDBS alternatives: A review of clarifier alternatives below from major suppliers illustrates their evolving emphases on solving the problems of traditional clarifiers. (Unfortunately, suppliers are sometimes reluctant to reveal the chemistries

FIGURE 10.3

Effect of clarifier. *Ciba's XT 386 nonsorbitol clarifier is said to provide low haze (right) at low loadings, evident when compared with unclarified PP (left). Photo reproduced by permission of Ciba Corp.*

behind their newest proprietary alternatives to DMDBS/MDBS/DBS, but rather only stress their advantages over these materials.)

- A recent Milliken clarifier with a novel chemistry is based on dibenzylidene nonitol (DBN; nonitol being a polyol alternative to sorbitol). Designated Millad NX8000, it is said to reduce haze in PP by half, in comparison with DMDBS. This higher clarifying ability is needed for creating thick-walled injection-molded cPP products from resins with high melt flow rates (>35). The clarifier is said to provide the "water white" clarity of inherently clear polymers such as polystyrene, polycarbonate, PET, and acrylic. In testing, the DBN was shown to allow only 20% haze in 2.9-mm molded plaques (using 4000 ppm of the DBN). When loaded at 2000 ppm, the DBN only roughly matches the haze produced by DMDBS at 2000 ppm. But DBN's reported advantage is that even though it requires 4000 ppm concentration to reach minimum haze, this haze is about 40% less than the lowest possible haze of DMDBS at these higher concentrations. Moreover, the 4000-ppm DBN also provides faster crystallization, faster cycles, and higher or equal flexural modulus and impact strength than DMDBS. And it produces less taste, allowing the supplier to seek regulatory food-contact clearances [10-18, 10-24].
- Ciba's Irgaclear XT 386 "high-efficiency clarifier" is a nonsorbitol, trisamide-based potential replacement for DMDBS. It is less migratory, meaning little or no plate-out and fewer organoleptic odor issues

in use, thus allowing food-use approvals (e.g., US FDA approval up to 210 ppm). At 150 ppm concentration, it is said to be as effective as DMDBS at 1800 ppm. And unlike DMDBS, which is prone to degradation, the XT 386 reportedly maintains its haze properties in regrind/scrap material after repeated extrusion passes (not including the haze produced from the ground-up EVOH barrier layer and other constituents in the recycled packaging material). Thus, it is said to allow more recycled cPP to be used as inner layers of new packaging [10-15, 10-16, 10-17, 10-25].

- Another nonsorbitol product introduced in 2007 is from RiKA International. In random copolymer PP, the "PC1" clarifier is reportedly effective for haze reduction starting above 1000 ppm concentration in thin 0.5- to 1-mm test plaques. The agent provides a wide processing window from 1000 to 2000 ppm with no plate-out, and higher heat distortion temperatures than DMDBS. In PP homopolymer with peroxide additives in high-flow, rheology-controlled materials, the PC1 (at 2000 ppm) reportedly allows significantly less haze to develop than DMDBS [10-19].

Other clarifying nucleators: Some nucleators that are not always spoken of as clarifiers do clarify PP; these include phosphate esters or salts. For example, ADK's NA-21 organophosphate product reportedly supplies clarity to random copolymer PP that equals that of Millad 3988. Moreover, NA-21 is not extractable, which is said to make it useful for medical syringes, for example. The material does not cause plate-out, though it is reportedly difficult to disperse in high-flow PP [10-10].

It is not easy to choose among products such as these; some factors determining their selection are given in Case 10.2.

10.2 FACTORS IN CHOOSING NUCLEATING/CLARIFYING AGENTS

10.2.1 Applications and resins

Not all POs in all processed forms can benefit equally from nucleating/clarifying agents. Suppliers sometimes only report optimum results under optimal processing conditions; clarifying agents may only be expected to provide reasonable improvements in the applications targeted by suppliers, and perhaps no measurable improvements in others. Much has already been said about nucleating/clarifying PP in general; below touches on some other materials issues and converter situations.

CASE 10.2 EVALUATING NEW CLARIFYING AGENTS [10-15, 10-17, 10-18, 10-19, 10-20]

Problem: Evaluating and selecting from a large number of possible clarifiers that could be used for a cPP application.

Objective: Understand which properties are most affected by clarifiers and how to compare them.

Solution: A list of benchmark testing and properties needed to determine clarifier type and concentration.

Given the evolving state of clarifiers for PP, it is sometimes difficult to see past the hype of each new product announcement to determine if a new agent really would be appropriate, useful, or cost-effective. Product developers typically consider several kinds of property comparisons, some of which are more relevant to one application than to others. Below is a compendium of the properties and tests the literature emphasizes as most important for making clarifier/nucleator comparisons:

- Optical properties: Clarity measured as a haze value is an obvious critical attribute, though haze values should be compared only for a specific sample thickness and for a specific resin rheology (e.g., melt flow rate). Optical measurements may also include molded plaque gloss or internal gloss, for containers.
- Crystallization temperature and rate: Especially important for nucleating agents in general, T_C and the time until 50% of crystallization is achieved may indicate possible cycle-time reductions.
- Organoleptics (taste and odor): The relative sensory effect of aldehydes emanating from sorbitol-clarified material, for example, can be rated by human test subjects.
- Processing temperature window: Thermogravimetric analysis (TGA) can determine if a clarifier thermally decomposes within the expected processing temperature window for the PP grade.
- Plate-out: Equipment surfaces, such as cast rolls and die surfaces, can be checked for residue after material trials.
- Impact resistance: Particularly relevant for PO packaging are Gardner (falling dart) impact, drop impact strength for containers, and tear strength for films.
- Strength and modulus: Fundamental tests for strength and stiffness, along with HDT testing, reveal to what extent a clarifier also serves as a useful nucleating agent.
- Barrier effects: Oxygen and moisture vapor transmission rates can be affected by some clarifiers.
- Recycling/regrind performance: Multiple extrusion passes determine whether haze or yellowness index increases as the clarifier experiences repeated melt processing.

A user may only be interested in a few of these properties for a given application. But these tests, performed at various clarifying agent concentrations in the resins of interest, provide an overall profile of a clarifying nucleator's effectiveness.

PP resin structure and polymerization: Usually, traditional PP random copolymers have lower haze values than homopolymers, though copolymers composed of phases having different refractive indices (i.e., heterophasic impact copolymers) cannot be clarified. Ziegler–Natta-catalyzed PP random copolymers usually have higher haze values than metallocene-catalyzed homopolymers that contain sorbitol-based clarifiers [10-10].

Injection vs. extrusion/blow-molding: For clarity, processing factors go hand-in-hand with the choice of a clarifier. Relatively thick-walled, injection-molded cPP homopolymer or random copolymer parts have limits on the clarity they can achieve, perhaps down to 7%–10% haze. Only thin extruded or injection-stretch blow-molded (ISBM) cPP may achieve lower haze levels (1%–2%) that allow it to compete with PET. For one-stage ISBM of random copolymer PP, for example, newer clarifiers may work better than sorbitol-based agents for clarifying the high-molecular-weight/low-melt-flow resin used in the process [10-10, 10-14].

PE blown film: As mentioned above, PE crystallization can be enhanced by nucleating agents, offering a relatively new alternative approach for improving clarity and mechanical properties. For example, commercialized in 2006, Milliken's Hyperform HPN-20E carboxylic acid salt-based agent reportedly provides a reduction in haze and improved gloss when used at 1000 ppm in LLDPE flexible packaging film, possibly because the agent tends to reduce surface roughness. The agent's optical effect is said to be similar to the effect of blending LDPE with the LLDPE, except that the agent does not reduce tear strength as LDPE does. The agent also reportedly allowed 5%–20% faster line speeds during trials, and slowed moisture and oxygen vapor transmission rates by about 40%. (The agent has also been used for blow-molded HDPE bottles to reduce warpage and decrease cycle times.) Ingenia Polymers' IP1810 masterbatch loaded at 2% is said to be a similar clarifying alternative to 20% LDPE additions in LLDPE [10-5, 10-7, 10-11, 10-23].

PP blown film: Clarifying agents also reportedly allow PP blown film to become a more stable process, offering high surface aesthetics for flexible packaging. In the past, BOPP film was laminated onto multilayer structures to provide the desired surface gloss for packaging. Milliken's popular Millad 3988 clarifier is said to produce co-extruded blown PP film with equivalent aesthetics, at 15% lower cost. In comparison with BOPP, blown PP film with the agent also reportedly provides equal or improved haze values, gloss, stiffness, and moisture transmission rates [10-11].

PP/TPO extruded sheet: In PP or TPO sheet extrusion and thermoforming, nucleating agents promote crystallinity and improve surface quality, flatness, and dimensional stability—and can speed up processing due to the faster solidification. Moreover, nucleating agents that encourage the formation of β crystalline forms reportedly improve impact strength and thermoformability, and enable the production of unusual products such as microporous films [10-6, 10-26].

10.2.2 Practical use factors

A number of other issues are being addressed by new generations of clarifying and nucleating agents. Some of the issues below have hindered cPP from directly competing with PET in packaging applications, for example.

Cost: Traditional nucleators may cost anywhere from \$2/kg (US) to over \$30/kg for advanced nucleators or clarifiers. Fortunately, their required concentrations are usually under 0.5%, conventional nucleators such as organophosphate salts and new hyper-nucleating agents may be effective at even lower levels (<200 ppm). Thus a nucleating agent can add a cost premium of a few cents per kg in the compound—but a cost that can be recovered through increased productivity and reduced scrap from warpage. For example, an overall cost savings of around 7% has been estimated from the use of a Milliken nucleator which added \$0.05/kg of material cost to the resin, because of reduced cycle times and scrap rate [10-10, 10-27].

Organoleptic side effects: Traditional acetal sorbitol agents can hydrolyze and decompose to produce aldehydes that have an unwanted "cherry-like" odor, or, particularly with MDBS, an "almond" odor. Yet their effectiveness and lower costs may still suit applications in which odor is not important [3-4, 10-19, 10-23].

Processing side effects: As mentioned, sorbitol-based clarifiers have weak solubility in PP and may gradually plate-out on equipment surfaces and dies, building up over time. Glycerol monostearate may be added as a processing additive to limit this, notwithstanding a complete change to an organophosphate nucleator/clarifier, if justified [3-4, 10-10, 10-23].

Interactions with other additives: Some nucleators or clarifiers may interact with other additives in the compound. Sodium benzoate, for example, is reactive with calcium stearate, which is used as a lubricant and acid scavenger—though not with hydrotalcite-based acid scavengers. Or haze may be increased by the peroxides used in controlled-rheology PP for viscosity-breaking and improved melt flow. Different clarifiers reportedly can limit this haze increase, such as RiKA's nonsorbitol PC1 product [10-4, 10-19].

Other additives' effects on clarity: Apart from clarifiers and colorants specifically used to alter the transparency of PO materials, other common additives, carefully chosen, may allow higher levels of clarity to be maintained than others. For instance, Ingenia Polymers supplies the high-clarity "1091" antiblock masterbatch for PE film that is said to create lower haze than conventional diatomaceous earth antiblocks commonly used for blown film. The company's trials showed that the 1091 maintained haze from 8.5% (the neat PE level) to 13.5%, at loadings from 1500 to 15,000 ppm—compared to haze levels of 9%–19% for diatomaceous earth across the same loading range [10-21].

Impact-modifying additives designed to increase the drop impact resistance of rigid PP containers, for example, may also be chosen for how they affect clarity. PO bottles require low-temperature drop-impact properties in particular, which can be enhanced with additions of metallocene plastomer modifiers. However, these modifiers can create haze if they have shown large enough differences in refractive index with the base resin. Specifically, in tests of HDPE bottles, plastomers with lower densities (~0.900) were found to affect clarity very little (20%–24% haze), whereas a 0.910-density plastomer produced "noticeable" haze (37%) [10-22].

Regrind/recycling reuse: Recycled cPP may be desired in the inner layers of new packaging, but sorbitol-based clarifiers like DMDBS are prone to thermal degradation and hydrolysis, so they tend to lose their clarifying abilities when reprocessed in recycled material. Alternative clarifiers, such as Ciba's Irgaclear XT 386, are said to maintain cPP haze properties even after repeated extrusion passes. Nucleating agents in general can help level-out inconsistencies in processing and shrinkage created by the inclusion of recycled resin [10-15, 10-16, 10-17, 10-27].

This list could continue, since nucleators and clarifiers affect some of the same properties as other additives groups. All additives can affect processing parameters or inherent characteristics of the PO itself. This nexus of competing effects often means that a compound's physical and optical properties will not be clear until the final product is created and evaluated.

5

SECTION V

Processing Aids

CHAPTER 11

Processing Aids for Molding

Processing aids for closed-mold processes are sometimes the key additives that make a molded product both possible and profitable. In injection molding particularly, melted resin must flow quickly from screw to mold, and parts must release from the mold quickly and cleanly. And these things must happen with compounds that may be highly filled, viscous when melted, or fast-shrinking when solidifying.

Although many processing aids are used in both injection molding and extrusion, this chapter will focus on answering questions of interest to most injection molders of POs (as well as rotational and blow molders, to some extent):

- (11.1) What is the value of common internal lubricants and other additives for increasing injection-molding productivity?
- (11.1) What are some kinds of mold releases and flow modifiers?
- (11.2) How can processing aids improve the molding of different difficult-to-mold products?

This chapter (and the next) will take a relatively narrow view of the additives that are called “processing aids,” because many additives can improve the processing of POs, though this may not be their primary purpose.

11.1 MELT-FLOW MODIFICATION AND MOLD RELEASE

The overarching reason for using processing-aid additives usually has more to do with reducing overall processing times and costs than with enhancing properties of the compound. Even though POs are relatively easy to process, molding operations still can benefit from processing aids that decrease the viscosity of the melt by lubricating the polymer internally, or by simplifying demolding by lubricating the surface of the resin. Thus processing aids are essentially tools that reduce the time and energy to plasticate the melt, completely fill the mold, and expediently allow a part to be extracted. Such tools are also helpful for solving processing problems that can reduce an operation's productivity. (Table 11.1 summarizes the types and uses of processing aids discussed in this chapter.) [11-1]

11.1.1 Melt-flow-enhancing lubricants and modifiers

Internal processing lubricants are somewhat soluble in the polymer and allow polymer chains in the melt to slide against one another with minimal friction. This lubrication decreases melt viscosity and reduces the screw torque and processing

Table 11.1 Overview of Processing Aids for PO Molding Processes

Processing-Aid Purpose	Most Common Chemistries	Primary Advantages	Possible Disadvantages
Internal melt lubrication	Metal stearates; fatty amides, ester, acids, or alcohols; polymeric agents	Increased output Reduced melt viscosity and temperature Process energy savings and reduced torque Improved mold-filling	Part-surface contamination possible (and reduced printability) Lower physical properties (or higher, depending on the processing aid)
Rheology control (for PP)	Peroxides	Extreme viscosity reduction Improved throughput and mold filling Narrower molecular weight distribution	Interference or interaction with antioxidants
Mold release	Hydrocarbon waxes; fatty amides or acids or low-molecular-weight esters (GMS)	Easy part release Reduced scrap Elimination of external spray-release agent	Excessive part-surface accumulation and contamination May not provide any melt lubrication effect
Dispersion of fillers, pigments, fibers	Various additive packages	Improved processability of highly filled compounds Similar productivity advantages of internal lubricants Improved property-enhancing effects of filler	Selection and use of processing-aid package complicated to determine

energy required for mixing and plastication. Lubrication also assists in the complete filling of mold cavities (though sometimes lubricants may affect the physical properties in the molded part). Some lubricants are also effective at the polymer surface, where they enhance mold release (discussed more in the next section).

A number of internal lubricants can be effective at loading levels below where they start to significantly lower the molded resin's properties. These processing aids, typically used as proprietary blended formulations, are effective at <2% concentrations when added during compounding, or even when added as pellet concentrates to dried resin right before injection molding. Some basic families of flow-enhancing aid chemistries include:

- metal stearates (stearic acid salts or soaps), which are common internal lubricants that modify viscosity and neutralize catalysts, but which can accumulate on the part's surface, interfering with surface treatments;
- erucamide, oleamide, and ethylene bis-stearamide (EBS), amides which provide both internal flow enhancement as well as lubrication at the resin's surface for mold release;
- esters such as GMS and vegetable oils, which at high molecular weights can provide internal lubrication (and at lower molecular weight, provide surface lubrication);
- other fatty acids or alcohols, which enhance resin flow at lower temperatures and injection pressures, preventing the need to increase melt temperatures to levels that might degrade the resin;
- polymeric additives, such as silicones, fluoropolymers (e.g., PTFE), or metallocene-catalyzed PO plastomers or oligomers; these are relatively expensive internal lubricants, but they tend to be heat-resistant, tend to resist migrating after processing, and tend not to reduce impact strength or other properties as much as other processing aids (and they may even improve the physical properties of the resin).

Experts have noted the benefits of lower melt temperatures and pressures made possible by these additives in molding. Along with cycle-time reductions, lower pressures may allow a smaller injection-molding machine to be used for a job. Part quality may also be improved (with fewer flow lines and stronger knit lines), with less molded-in stress. (And by no means are most of these additives limited to molding processes; Chapter 12 addresses their use in extrusion, where they have analogous benefits.) [11-3, 11-4, 11-9, 11-14]

In injection molding, advanced processing aids show the extent to which additives can improve flow and reduce processing costs. Sometimes suppliers' evaluations of their additives' effectiveness are performed under optimal conditions, providing maximum results. But often they present various data from different, real production situations, or present what the range of expected improvement could be for a given material and process. An example of the kinds of reportable benefits from processing aids is from Axel Plastics Research Laboratories. The company's fatty amide/modified-polymer INTE-41FPE blend is said to reduce HDPE melt viscosity by 12%–20% at 1% loading (see also Case 11.1 for other examples of process gains) [11-8].

Alternative processing-aid chemistries have the toughest arguments to make for their use, since they have less history of use than standard lubricants. For example, silicone-based processing aids, such as the Genioplast materials from Wacker Chemie, are said to reduce to screw torque substantially and increase the melt-flow rate of both unfilled and filled PO compounds. These pelletized aids are composed of an ultra-high-molecular-weight siloxane polymer in a fumed-silica carrier that is compatible with thermoplastics. In trials

CASE 11.1 EFFECTS OF PROCESSING AIDS IN MOLDING [11-2, 11-12, 11-14, 11-23]

Problem: A lack of information about how processing aids actually improve productivity.

Objective: To choose the right additive for a specific, real-world situation.

Solution: Evaluate uses of processing aids in real molding situations.

The supplier literature is sprinkled with stories about the effects of processing aids in various molding situations. Although some of these stories may sound anecdotal or seem to be based on idealized processing situations, they do indicate the types of processing improvements that may be possible from small additions of processing aids. A few are summarized from the literature below:

Basic injection molding: Struktol has reported how its TR016 fatty acid metal soap/amide-blended lubricant allowed an injection molder to reduce cycle times by 2% when molding coat hangers from a recycled PO resin. Although this does not sound like much, the cycle-time savings increased the molder's capacity by 50,000 parts per year, and translated into reduced manufacturing costs that offset the cost of the additive.

Talc-filled PP: Fine Organics has reported on the effect of its Plastaid-T multifunctional processing aid on 40% talc-filled PP and other highly filled PO compounds. In the talc–PP compound, a 0.5% additive loading is said to improve injection-molded spiral-flow test lengths by 7.5% over the compound without the additive, while increasing notched-Izod impact strength by 25%, reducing mold shrinkage uniformly by 19%, and holding strength, modulus, and hardness values to within 5% of the values of the compound without the additive. The additive also reportedly decreases viscosity in this compound more than an equal loading of calcium stearate, across shear rates from 0.1 to 1/second.

Mold release of automotive TPO: Axel has reported part-ejection-force reductions resulting from both its MoldWiz INT-33LCA and INT-33PA additives, when each is used at 0.3% in an automotive TPO containing 10% talc. The additives enabled a 9% reduction in ejection force for test parts in a single-cavity cup mold on a 90-ton injection-molding press. Moreover, in the molding of actual TPO instrument panels, the company's INT-33CRS additive reportedly helped reduce mold pressure by 23%, reducing the cracking (and high scrap rates) that resulted when excessive force was required to extract parts from the mold.

in compounded resin at 1% loading, the product reportedly reduced torque by 71%, 49%, and 82% for LDPE, PP, and PP with 40% $CaCO_3$, respectively. Moreover, the silicone additive improves Charpy notched impact strength of filled POs, especially when loaded at 1%–5% [11-5, 11-9, 11-10].

Another alternative processing aid is the Excerex metallocene olefin oligomer from Mitsui Chemicals. This low-melting product reportedly helps speed up resin melting and output when dry-blended with PO pellets, reducing screw torque, barrel temperature, and cycle time. In HDPE injection molding, for instance, 3% of the oligomer reportedly allowed the reduction of cylinder temperatures from 200 °C to 180 °C, reducing scorching. In PP bottle blow molding, 2% of the product allowed the cylinder temperature to be lowered from 190 °C to 170 °C, reducing cooling time from 25 to 22 seconds and thus increasing productivity by 14%. The product is said to have a narrow molecular weight distribution (around 4000), resulting in less stickiness and less bleed-out from the resin than conventional low-weight processing aids, such as olefin waxes. A side benefit of the torque reduction is that less energy is needed per kilogram of output resin [11-6, 11-7, 11-22].

Controlled rheology PP: Peroxide additives are another kind of melt-flow enhancer used for creating "controlled rheology" PP resins, particularly important for injection-molding applications that require high-flow PP. These viscosity-lowering (vis-breaking) additives create free radicals by cleaving or "cracking" the longest polymer chains to reduce average molecular weight. This also creates a narrower molecular weight distribution and improved melt-flow rate (the increase in MFR is roughly linear with increasing peroxide concentration, up to 1000 ppm). Peroxides have essentially the opposite effect of antioxidants in the resin, but in small amounts, they can provide significant processing improvements. Still, peroxides are tricky to use, since they interact with the antioxidant and can cause color changes [3-4, 11-17, 11-21].

Used properly, peroxides supplied in free-flowing concentrates ultimately can reduce processing temperatures and cycle times for PP molding. In one cited case, PP melt temperature was reduced by about 20 °C, translating into 32% decreased cycle time and 50% more molded parts per hour. Their changes to melt rheology also permit a resin to fill thinner mold sections or multi-cavity molds. Moreover, in random copolymer PP in particular, the narrower molecular weight distribution created by peroxides reportedly also improves surface appearance by reducing surface roughness [11-18, 11-21].

11.1.2 Mold-release additives

Mold-release additives supply external, surface lubrication to the polymer part. Being generally incompatible with the polymer, they accumulate at the surface of the cooling part and prevent it from sticking to the mold or to other surfaces. They also lower the release force of semi-crystalline resin parts that tend to shrink and bind in the mold, and they often eliminate the need for external sprayed-on mold releases.

Given the low surface friction characteristics they impart, mold-release additives are related to slip additives used in extrusion, discussed in the next chapter. Some overlap with the migratory flow-enhancing lubricants mentioned above. Mold-release agents are typically based on one or more of the following chemistries:

- hydrocarbon microcrystalline waxes and partially oxidized PE, which, though effective, may excessively pollute a part's surface;
- fatty acids or low-molecular-weight esters, such as GMS (also used as an antistatic additive);
- amides such as erucamide and oleamide, which provide both internal polymer lubrication as well as lubrication at the resin's surface.

Adding other internal lubricating aids to the amides may also provide adequate mold release for a given molding situation [11-3, 11-14, 11-15].

However, dedicated mold-release aids are completely insoluble in the polymer, and migrate from within the polymer to the surface (and thus they do not enhance melt flow). Molders usually seek to use a balance of soluble, flow-enhancing lubricants and insoluble mold-release lubricants to enhance both melt flow and mold release. These commercial processing-aid products for molders are formulated by suppliers to be multi-functional at low loadings (often $<1\%$). These blends contain soluble and insoluble lubricants appropriate for specific molding situations. They are typically supplied as a powder or as pellet blends, or in a masterbatch for feeding at the throat of the molding machine.

Evaluating the effectiveness of a mold release requires somewhat less standardized test methods than the rheological methods available for evaluating the flow enhancement of a processing aid. At best, part-ejection force can be quantified and compared for a specific trial and mold. The part-ejection force required for demolding a part without any mold release is quantified and compared to the force values of parts with varying amounts or type of mold release to find the least-force formulation. A mold-release aid might be expected to provide anywhere from a 10% to 40% reduction on mold-release force, depending on the test situation. Such an evaluation, though difficult to set up, may be essential for operations that rely on automation for part demolding, especially where there are concerns about a part's consistent release from the mold, and the automation's reliability in dealing with any inconsistency [11-15, 11-16].

Optimum additive loading rates to achieve large ejection-force reductions vary according to loading, pigment or filler content, and release aid composition.

Loadings for commercial aids typically fall between 0.1% and 1%, with test trials required to find the loading supplying the optimum combination of release force, processing screw output, and melt temperature. PO type also determines effectiveness. For example, the "high-purity" 90%-monoglyceride (GMS) Dimodan HS K-A additive from Danisco is recommended at loadings of 0.1%–0.25% in random copolymer PP, 0.2%–0.4% for homopolymers, and 0.3%–0.5% for impact copolymers. The aid's dense composition reportedly allows it to be used at 30%–50% lower loadings to provide the same release force as less-concentrated GMS additives [11-13, 11-16].

Post-molding benefits of lubricants at the part surface have been observed, although these benefits are sometimes overlooked in the literature. For example, a thin lubricant layer allows small parts to slide against one another and thus increases their packing efficiency in boxes. A low-friction surface may allow parts to be more easily used by the consumer (as when opening bottle closures). Or they may allow parts to be easily assembled by the manufacturer; for instance, Croda Polymer Additives cites a case where its IncroMold S lubricant package reduced the assembly force of a PP/HDPE assembly by 30%. Low-friction surfaces also reduce the noise of parts moving against other surfaces, and resist scratches and abrasion more [11-24].

External mold releases, sprayed onto the mold and not added to the compound itself, can still be valuable tools. These solutions are water- or solvent-based, and when applied condense into a semi-durable, heat-resistant film on the hot mold that may allow dozens of part releases or more before having to be reapplied. However, if an external agent has to be used repeatedly during a production run, it can interfere with productivity, making a mold-release lubricant added to the resin itself the more cost-effective approach [11-3, 11-13].

11.2 SPECIAL CASES FOR PROCESSING AIDS IN MOLDING

11.2.1 Aids for molding highly filled compounds

Processing aids are useful when high filler content in a resin reduces its melt flow. Some aids enhance filler dispersion in the matrix, as well as internally lubricating the compound. Fillers that impede melt flow include titanium dioxide and other pigments; talc, mica, glass fiber, and calcium carbonate at high loadings; and nonhalogen inorganic flame retardants such as ATH.

However, given their slippery nature, processing aids such as fatty esters or stearic acid may weaken the bond between filler and matrix, thus reducing mechanical properties of the filled compound. And conventional lubricants such as calcium stearate may only provide less-than-optimal increases in melt-flow rate for filled compounds.

But other specialized processing additives are nonblooming, multifunctional blends composed of molecules that help connect polar filler groups to nonpolar polymer groups. Along with improving the coupling of filler and polymer, they still can reduce torque and improve mold release like regular lubricants. These processing aids could be described as filler synergists—improving melt flow while also improving mechanical properties of a filled compound; a few examples are given below:

- BYK's P 4101 coated-silicon dioxide compatibilizer reportedly increases the mechanical properties of 40% talc-filled PP homopolymer, for example, while still reducing screw torque and pressure [11-11].
- Croda Polymer Additives' IncroMold additives provide internal filler and glass-fiber lubrication and mold release; in one case, 0.45% additive in a 30%-glass-fiber, carbon-black-pigmented PP automotive molding reportedly increased output by 20% and eliminated the need for a silicone spray-on mold release [11-24].
- Wacker Chemie's silicone-based torque-reducing aids (also mentioned in Section 11.1.1) have also been shown to be effective for improving the impact strength, elongation, and abrasion resistance of PE and PP compounds that are highly filled with $CaCO_3$, talc, or ATH (see Table 11.2) [11-9].
- For EPDM rubber blended in PP (i.e., TPOs), calcium stearate and multifunctional aids such as Plastaid masterbatches from Fine Organics reportedly reduce viscosity during processing and may even enhance certain mechanical properties such as impact strength [11-12].
- Dispersion aids and compatibilizers based on reactive phosphato-titanate chemistries are also said to reduce viscosity of filled compounds. They are compatible with nonpolar polymers such as POs, and are available in masterbatch form (more is said about these compatibilizers in Chapter 14) [11-1].

11.2.2 Aids for ISBM

Given the interest in using clarified PP for injection stretch blow-molded containers, every possible factor is being scrutinized that could speed up the PP-ISBM process to make it more cost-competitive with PET ISBM. Indeed, the longer process times for molding the thicker walls required in PP containers is one thing that is tending to delay their greater use. Clarifying nucleators, which themselves could be categorized as processing aids, have significant effects in increasing stiffness (allowing reduced wall thickness), hastening solidification, and thus speeding up cPP molding cycles.

Table 11.2 Performance Comparison of Filled and Unfilled Compounds With and Without a Silicone Processing Aid (Wacker Genioplast Pellet S)

PO System	Required % of Maximum Torque		Melt-Flow Rate Increase, %		Charpy Notched Impact, kJ/m^2	
	Without Additive	With 1.0% Additive	Without Additive	With 1.0% Additive	Without Additive	With 1.0% Additive
PP	25	13	0	n/a	n/a	n/a
PP + 40% $CaCO_3$	96	17	0	89	3	4
LDPE	63	18	0	n/a	n/a	n/a
LDPE + 60% ATH	60	43	0	37	17	23

Source: Adapted from [11-9].

In the injection-molding phase of ISBM in particular, the right additive can bring processing times closer to those of PET. As reported by Milliken & Company, the newest clarifiers for cPP can reduce preform molding cycle times by about one-third, depending on preform thickness. These nucleators increase crystallization temperature and shorten solidification time, while providing clarity [10-10, 11-20].

11.2.3 Aids for rotational molding

As one of the least-used molding processes, rotomolding is often neglected in the literature. Yet the process is essential for producing the largest plastic products, and rotomolders depend on PEs far more than any other polymer family. However, the times required for sintering, densification, and cooling in the process limit it to relatively low-volume parts—although the long cycle times mean that even small-percentage gains from processing aids can add up into several minutes cut from each part cycle, and significant cost savings.

Mold-release aids based on saturated primary amide chemistry, for example, bloom to the surface of rotomoldings to create an invisible lubricating layer on the part. However, other additives, such as stabilizer systems containing nonphenol (nonyellowing) antioxidants, are said to speed up densification times by expediting the removal of bubbles from the densifying polymer. This not only reduces cycle times, but lowers peak internal air temperatures and saves heat energy that would be required for longer solidification cycles, according to Ciba researchers [11-2, 11-19].

CHAPTER 12

Processing Aids for Extrusion

It is impossible to imagine how thin PO films could be commercialized without processing aids. These aids lower their surface friction, allowing the film to be rapidly extruded and then shipped or stored in rolls. Or they allow resin to be converted easily in blown-film processes or in thermoforming processes. Other extruded POs likewise benefit from the friction-reducing properties of slip agents, antiblocking agents, and other processing aids, whether they are added to resin by the resin producer or by the converters themselves.

Although some of the additive chemistries covered in this chapter were already mentioned in the previous chapter on molding aids, this chapter will cover processing aids in the context of extrusion, with particular attention on cast and blown films. Some basic questions will be addressed, such as:

- (12.1) What are the particular needs of extrusion processes?
- (12.2–12.4) How are these needs addressed by slip agents, antiblocking agents, and aids that prevent melt fracture?
- (12.5) What are some of the unique extrusion situations that require special attention in the choice of processing aid?

12.1 REQUIREMENTS OF EXTRUSION-BASED PROCESSES

Various processing aids serve the needs of cast- and blown-film converters and other extrusion operations, including the following:

- *High line speeds*: The attractiveness of film and sheet products depends on their low costs, which is determined partly by line speeds. Processing aids can allow higher line speeds without their own costs negating the overall process savings that are gained.

- *More efficient conversion operations downstream*: Films must slide easily against process equipment, and rolled films must unroll easily without sticking.
- *Printability and adhesion*: The additives used to decrease the friction of film and sheet ideally should not interfere with printing or adhesion on the plastic surface, if it is required.
- *Process cleanliness*: Excess additives or fragments from the melt or solidifying resin must not build up on screen packs, dies, or processing equipment.
- *Process flexibility*: When problems with film processing occur, converters who can flexibly adjust their processing-aid type or concentration stand to benefit.
- *Low scrap*: Given that 80% of a film's cost may be tied to resin costs, a successful operation must use resin efficiently, minimizing waste or off-spec materials.

Many of the processing aids discussed in this channel address more than one of these needs, although some also have negative side effects such as additive buildup or high cost. Thus the most complicated issue is to sort through the products offered by industry to find the right additive solution [12-17].

12.2 SLIP AGENTS

Slip agents lower the sliding coefficient of friction (CoF) between a film and processing equipment or other surfaces (including the film itself). Similar in function to antistatic agents and mold-release agents, slip agents must be incompatible with the resin and migrate to the surface of the film to be useful. Various slip-agent chemistries have been used for PO films, but the most used are migratory *fatty-acid primary amides* such as erucamide, oleamide, stearamide (in order of effectiveness in LDPE film), and EBS, which is more thermally stable [3-4, 12-1, 12-4].

The effectiveness of slip agents in reducing CoF have been classified as low slip (0.5–0.8 CoF), medium slip (0.2–0.5), and high slip (0.05–0.2). These typically correlate with the concentration of slip agent in the resin: 100–400 ppm for low effectiveness, 500–600 ppm for medium slip, and 700–1000 ppm for high slip. Levels of slip agents at the higher end of concentration may be particularly necessary for reducing the CoF for amorphous or tacky POs such as metallocene LLDPE.

But many factors determine the right concentration for a film. If anything, slip agents are often added at too high a concentration. This causes an excessive accumulation of agent on the film surface that can cause equipment contamination and “wet blocking,” or the sticking of layers of film to one another. Specifically, excessive slip agent at the surface can be caused by adding too much agent to thick films so that they contain much more total agent than they require, and all of that agent migrates to the surface. Inversely, resins for thin films may require higher concentrations to build up an adequate surface layer. And higher melt-index resins may not reach the same low CoF as low-flow resin using the same agent and concentration. Thus, experts encourage converters to use masterbatches that contain only slip agents, so that they can easily adjust their slip levels [12-1, 12-2, 12-4].

A major factor that affects the choice of a slip agent is the time frame in which the agent’s effectiveness is needed. Some situations include the following:

- If the film requires a low CoF surface immediately, such as in bag conversion, slip agents based on unsaturated molecules are useful, such as unsaturated erucamide or oleamide. At high concentrations, these migrate within minutes to the polymer surface (where their effect then dissipates over several days or weeks).
- For a film that requires an anti-friction surface for later conversion processes after being rolled and stored, a larger, slower-migrating slip molecule can be used.
- Ideally a slip agent should also fit the timing of printing or corona treatments on the film, which are affected negatively by migrated slip agents on the film surface.
- A slip agent can be specifically chosen for how it migrates through different POs in a multilayer film; for example, a secondary amide such as stearyl erucamide will migrate through a PP copolymer layer but not through a homopolymer layer.

Generally, amide slip agents migrate more slowly through higher-crystalline POs such as HDPE and especially PP. Thermal stability is higher for larger, saturated slip-agent molecules. Although these reduce CoF less than unsaturated amides, they have fewer tendencies toward oxidation, discoloration, odor development, blocking, and volatility at higher processing temperatures [3-4, 12-1, 12-2, 12-3, 12-4].

Other additives may slow the expected migration rate of slip agents. And surface-acting agents such as anti-stats or anti-fogging agents may also interfere with the effects of slip agents (or be interfered with by them), since they all require exposed surface area to function [12-1, 12-2].

Secondary amides such as stearyl erucamide or stearyl stearamide provide more stability and more medium slip control for PO films that must be stacked without excessive sliding, for instance. This medium slip level is difficult to obtain and control with primary amides because the extremely low concentrations that are required increase process variability. This leads to high scrap costs that are said to outweigh the costs of the higher concentrations of secondary amide agents (typically 1000–1500 ppm) [12-26].

Nonmigrating slip agents have also been added in the outer layers of multilayer films to minimize their expense. These are high-molecular-weight organic or siloxane-based molecules that do not require time to bloom at the surface, but still create a medium slip CoF level. They are generally reserved for high-temperature or specialty applications, and often add other useful properties to the film material. Cyclic-olefinic copolymers (COCs) are a class of nonmigratory additives that are used to reduce slip as well as enhance film barrier properties, stiffness, heat resistance, printability, and clarity. Added at 5% or higher in LDPE, for instance, a COC serving as a low-glass-transition-temperature component and reportedly reduces the CoF of cast films to 0.4 or lower [12-1, 12-2, 12-5].

12.3 ANTIBLOCKING AGENTS

Similar to and sometimes overlapping with the functions of slip agents, antiblocking agents prevent layers of smooth PO film forced into close contact from sticking to one another. Antiblocks include both organic and inorganic additives. Inorganic mineral antiblocks are typically diatomaceous earth (DE), synthetic silica, or talc, which tend to create surface roughness on the film to disrupt polymer-to-polymer contact. Organic antiblocks include saturated primary amides and other migratory chemistries of the type used for decreasing CoF.

Blocking force is typically measured as film-to-film adhesion using an ASTM test method (D-3354). Other tests include 180° peel-off strength and film-to-film CoF (ASTM D-1894). "Induced reblock" tests measure blocking force after films have been pulled apart and then compressed against each other again for 24 hours at higher temperatures (40 °C–60 °C), and then tested for blocking force. Haze, clarity, and gloss tests may also be useful for evaluating antiblocks (ASTM D-1003, D-1746, and D2457/60), since some antiblocks affect film optics [7-20, 12-4, 12-6, 12-7, 12-30].

12.3.1 Inorganic antiblocks

Various mineral fillers are used to add roughness or "bumps" to the film surface to prevent blocking, though they can reduce the clarity of films. For these nonmigratory antiblocks, particle shape, size, and size distribution are factors determining their effectiveness. Their antiblocking effects must be balanced with their negative effects on film haze, clarity, and gloss. Thus, large, irregular particles are better for antiblocking, but worse for clarity, a quality greatly desired in shrink films and flexible food packaging. The median particle size for common antiblocks usually falls between 4 and 8 μm. Unfortunately, the size distribution of a grade of DE, for example, may include particles larger than the thickness of the film itself. Moreover, some of these additives, such as talc and silica, may absorb antioxidants, other processing aids, or other additives. And some have an iron oxide content that is high enough to catalyze the degradation of organic slip or antistatic agents in the resin. But inorganic antiblocks are generally inexpensive materials, and a few of the most commercially important ones are compared and contrasted below [7-20, 12-2, 12-7, 12-30].

Talc, in specific forms, has become the most widely used inorganic antiblock. Its low hardness also wears tooling less than other inorganic antiblocks such as silica. Some talc grades are available in treated forms for improving dispersion, lowering odor, or improving polymer/talc adhesion. There are also low-haze and low-additive-interaction forms for both PE and PP, where the "top-size" (maximum) talc particle size is about 10–12 μm, half that of standard talc antiblocks. These smaller maximum particle sizes and the low price of talc allow it to compete with higher-priced DE or silica antiblocks commonly used in high-clarity LLDPE films [7-20, 12-2, 12-8].

DE, diatomite or "natural silica," provides strong antiblocking at low concentrations and is the next-most-used inorganic antiblock, though its use is probably declining. This form of silica is composed of irregularly shaped remains of diatom microorganisms. The blocking force of DE in PE film has been shown to be lower than that of talc when they are each used at concentrations below 0.5% (though their antiblocking effect is roughly equal above this concentration). Compared with other inorganic antiblocks, DE creates little haze in thin films, since its refractive index (1.5) is similar to that of PE. Neither does DE tend to absorb other additives as much as other inorganic antiblocks, though it does absorb moisture. DE is expensive, and DE grades usually contain low levels of crystalline silica dust, a known respiratory hazard [7-20, 12-1, 12-2, 12-8, 12-30].

Synthetic silica is another high-clarity antiblock, but as with DE, it has the highest hardness of these additives and thus can easily damage metal tool surfaces. It also tends to absorb slip agents and can be hard to disperse, and, like DE, it absorbs moisture and is expensive [7-20].

Other inorganic antiblocking fillers such as calcium carbonate, alumina-silicate ceramic spheres, zeolite, kaolin clay, feldspar, and mica have also been used as antiblocks. In PE film, calcium carbonate can provide the low blocking force of talc and DE, but only when loaded at 2–3 times their concentration (or higher), reducing clarity of the film, and increasing its density [12-1, 12-22, 12-30].

In judging the suitability of a common filler such as $CaCO_3$ as an antiblock in PO film applications, researchers have noted complicated relationships between the mineral and PO type. In a study by Heritage Plastics, for example, LLDPE with 5%, 1-μm size calcium carbonate showed blocking forces near those of talc and DE. The $CaCO_3$ also raised the surface energy of the LLDPE, making it more suitable for printing. Higher levels of calcium carbonate, as high as 20%, reduced friction and blocking force even more for tacky metallocene-catalyzed PE. But in high-molecular-weight HDPE bags, calcium carbonate tended to *increase* CoF (which can actually be an advantage in situations where the bags are stacked and must not slide over each other) [12-22].

Head-to-head comparisons of the most common inorganic antiblocks are heavily dependent on the testing situation, the grade of antiblock and PO, and of course the points the tester is trying to emphasize by performing the tests. For example, Specialty Minerals and Rio Tinto provide data (see Tables 12.1 and 12.2) comparing the properties of some of the inorganic antiblocks mentioned above in various PO resins. Table 12.1 compares two grades of antiblock talcs with DE, showing that talc can be used as a drop-in replacement for the more expensive DE.

Table 12.2 compares 25-μm metallocene-LLDPE films containing 2500 ppm of each antiblock (except for synthetic silica, loaded at 1500 ppm). The resulting blocking force and clarity data are similar, but some differences stand out. Synthetic silica provides the lowest haze (5.5% vs. 9%–9.5% of the other additives), highest clarity (72% vs. 60%–61%), and highest gloss (68% vs. 53%–62%). But it and DE also showed the highest reblocking force (23–27 g vs. 12–17 g) and highest CoF (0.33–0.46 vs. 0.15–0.18). Overall, talc grades for antiblocking are best positioned to provide a good balance of these properties and processability, at low cost [12-7, 12-8].

12.3.2 Organic antiblocks

Organic antiblocks allow a PO film to retain its clarity—or to enhance its clarity, when the organic agent is used to reduce the amount of inorganic antiblock. Generally, the migratory amide chemistries used as slip agents, discussed above, also provide antiblocking properties. Saturated fatty amides such as behenamide and stearamide in particular provide superior antiblocking for POs, especially at higher temperatures, compared to erucamide and oleamide. However, when comparing various organic antiblocks, blocking force results can be greatly affected by minor changes in test temperature, PO crystallinity, and melt index, so it is often difficult to give clear answers about which organic agent is "best" for a material or processing situation (e.g., see Table 12.3 for blocking-force comparisons from Fine Organics). Although organic agents provide better slip and metal-release qualities than inorganics, they are several times more expensive, confining them more to specialty extruded applications [12-1, 12-4, 12-30].

Table 12.1 Some Data on Talc and Diatomaceous Earth (DE) Antiblock Performance in 25-µm PE Blown Film

Antiblock	**LLDPE, 2 Melt Index**			**LLDPE, 1 Melt Index**			**LDPE, 2 Melt Index**			**LDPE, 0.8 Melt Index**		
	40°C Reblock Force (g)	**CoF**	**Haze (%)**	**60°C Reblock Force (g)**	**CoF**	**Haze (%)**	**40°C Reblock Force (g)**	**CoF**	**Haze (%)**	**60°C Reblock Force (g)**	**CoF**	**Haze (%)**
DE	41	0.14	9	156	0.16	10.6	44	0.21	5	27	0.13	8.9
Antiblock talc*	45	0.13	9	n/a	n/a	n/a	36	0.12	5	n/a	n/a	n/a
High-clarity antiblock talc†	n/a	n/a	n/a	151	0.13	9.1	n/a	n/a	n/a	32	0.08	8.1
Antiblock/slip concentration	5000 ppm/1000 ppm			6000 ppm/1500 ppm			1500 ppm/ 750 ppm			5000 ppm/1000 ppm		

Source: Adapted from [12-8].
**Specialty Minerals' Polybloc.*
†Specialty Minerals' Optibloc 25.

Table 12.2 Antiblocking and Clarity Data for Common Inorganic Antiblocks in 25-μm m-LLDPE Film

Antiblock and Concentration	Reblocking Force (g)	Coefficient of Friction (Static/Dynamic)	Haze (%)	Clarity (%)	Gloss (%)
No antiblock (neat resin)	37	1.44/1.35	13.5	46	62
Talc, high-clarity, compacted, 2500 ppm	12	0.15/0.16	9.5	60	62
Calcined clay, 2500 ppm	17	0.18/0.18	9	61	53
Natural silica (DE), 2500 ppm	27	0.33/0.33	9.5	61	60
Synthetic silica, 1500 ppm	23	0.42/0.46	5.5	72	68

Source: Adapted from [12-7].

Table 12.3 Comparisons of Antiblocking Performance in Various PO Films Containing 1000 ppm of Selected Organic Antiblocks

Antiblock	LLDPE, Blocking Force (g/16 in^2) at 50°C		LDPE, 6.5 Melt Index, Blocking Force (g/16 in^2)		PP, 8.0 Melt Index, Blocking Force (g/16 in^2)
	1.0 Melt Index	2.0 Melt Index	At 50°C	At 60°C	At 50°C
Control	45	123	63	113	76
Stearamide*	16	46	15	32	10
Behenamide**	20	56	15	29	9
Erucamide†	23	71	15	88	19

Source: Adapted from [12-4].
**Fine Organics' Finawax-S.*
***Finawax-B.*
†Finawax-E.

12.3.3 Clarity/slip antiblocks

"Clarity antiblocks" or "high-clarity slip antiblocks" are recent formulations that combine a mineral antiblocking ingredient with a slip and/or clarifying agent. The mineral particles in high-clarity products have spherical shapes of uniform size distribution to minimize light scattering. These blends help negate the haze created by the mineral agent, and the synergism of the inorganic/organic antiblock combinations minimize the total amount of antiblock required in a film. For LLDPE film, for example, these formulations allow processors to reduce the amount of LDPE that is typically blended with

Table 12.4 Runs Used for a Statistical DOE for Predicting LLDPE Blown-Film Properties

Run	Talc Antiblock Mean Particle Size (µm)	Talc Antiblock Concentration, ppm	Erucamide Slip Agent Concentration, ppm	Film Thickness, mils (µm)
A	1.0	1000	1000	0.8 (20)
B	1.0	1000	2000	1.6 (40)
C	1.0	6000	1000	1.6 (40)
D	1.0	6000	2000	0.8 (20)
“center point”	2.5	3500	1500	1.2 (30)
E	4.0	1000	1000	1.6 (40)
F	4.0	1000	2000	0.8 (20)
G	4.0	6000	1000	0.8 (20)
H	4.0	6000	2000	1.6 (40)

Source: Adapted from [12-6].

the LLDPE to enhance clarity. In blown film, 1%–3% of Ampacet’s 102286 product reportedly reduced the haze of LLDPE by itself. Ingenia Polymers’ IP1092 product is another high-clarity, low-loading antiblock masterbatch [12-1, 12-2, 12-10].

However, finding the right combination and concentration of organic/inorganic slip/antiblock agent for an application requires sifting through several competing factors. This task at first may seem overwhelming. Statistical DoE methodology may help narrow down and weigh the key factors; for example, a study on LLDPE blown film performed by Specialty Minerals focused on four factors: median talc antiblock particle size (1–4 µm), talc antiblock loading (2000–6000 ppm), erucamide slip/antiblock loading (1000–2000 ppm), and film thickness (0.8-1.6 mils (20–40 µm)). This pared-down DoE study efficiently determined which and how much these four variables affect blocking, CoF, and clarity. The DoE only required eight test runs to combine the “high” and “low” variables, plus a “center point” formulation used to estimate error (shown in Table 12.4). The researchers then used software to predict the results of other untried combinations [12-6].

12.4 ADDITIVES FOR REDUCING MELT FRACTURE AND DIE BUILDUP

Processing aids are often called on to solve problems having to do with poor melt stability (“shark-skinning”) or with stray material buildup on extruder surfaces, which causes excessively long start-up times or downtimes.

12.4.1 Fluoropolymer processing aids

Fluoropolymer process aids are commonly used to create smooth die surfaces, thus reducing die buildup and melt fracture (shark-skin surfaces). Like other processing aids, they also often increase throughput, reduce operating pressures, improve film clarity and surface finish (gloss), and in some cases, allow faster color changeovers. Fluoropolymer aids are immiscible in POs and tend to build up on metal die surfaces, where they form a slippery coating extending from the die entrance to the die exit. This increases the flow stability of the melted resin, which flows easily against the Teflon-like coating. These aids also prevent oxidized molecules from accumulating on the die wall and then being released into the melt as gels.

These additives allow a process to stabilize quickly after a short period of processing or conditioning time (as little as 10 minutes), during which the die coating forms. This relatively short period is potentially several minutes less than the start-up time that would otherwise be required without the additive, for stabilizing the process and eliminating melt fracture. To be effective, the aid must be added at a threshold concentration level, typically at around 500–1000 ppm. However, as discussed in Case 12.1, new additive packages allow reduced concentrations to be used [12-11, 12-13].

CASE 12.1 HIGH-EFFICIENCY PROCESSING AIDS TO REDUCE MELT FRACTURE [12-11]

Problem: Processing aids can cut costs, though some still lack the effectiveness and efficiency desired in blown-film bag production.

Objective: Processing aids that are more effective at lower concentrations.

Solution: Next-generation fluoropolymer processing aids that clear melt fracture faster, at lower loadings.

Since the conditioning time required to clear melt fracture in a blown-film line essentially equals lost bags and lost value, any improvement is welcome. Thus Ampacet has proposed new fluoropolymer processing aids that clear melt fracture faster than “first-generation” additives.

In trials of blown LLDPE film, the company reports that its 102725 product was much more effective than its 10919 product, at much lower concentrations of 300–400 ppm. With metallocene-catalyzed hexene LLDPE, the newer product cleared melt fracture in about one-third the time of the other product, at about one-third lower loading. With Ziegler–Natta octene LLDPE, the proportional improvements were about one-quarter for each parameter.

Productivity also reportedly remained high with the new additive. In monolayer bag extrusion runs with LLDPE/LDPE blends, a 65% reduction in processing aid, using the 102725 product, still allowed a 150 in/minute line speed and 900 lb/hour output from a 22-in die. In co-extrusion, a 6-in die outputted 470 lb/hour, with the additive loaded at 80% less than the other product.

Another next-generation product, designated 102823, reportedly produced similar results, along with less frequent die cleaning. One blown-film producer reported that using the 102823 at about one-third the concentration of standard aid reduced the time to clear melt fracture from 1 hour to 10 minutes. Loaded via a masterbatch at 1.5%, the additive also is said to reduce die cleaning frequency from every 12 hours to every 100 hours or more, in HDPE blown-film operations.

Along with increasing flow stability and reducing conditioning time, fluoropolymer processing aids also allow higher screw speeds to be used before melt fracture starts to occur. For example, Solef and Technoflon aids from Solvay Solexis are said to maintain stable melt flow at higher screw RPM and higher mass throughput (about 20% higher, with only 200 ppm loading) [12-13].

Recently, processing aids based on viscous fluoroelastomers have been used to reduce the time required for building up the die coating that makes them effective. Work by DuPont Performance Elastomers showed that fluoroelastomer aids with particle sizes of 5–6 μm generate die coatings faster than smaller particles. The larger particles can be formed by limiting the dispersion of high-viscosity fluoroelastomer in the PE, a practice that must be done in balance with the resulting flowability problems. Still another new additive approach being discussed is the use of polydimethyl-siloxane (PDMS) grafted to a PO carrier and blended with LLDPE to reduce melt fracture and die/melt friction [12-12, 12-19].

12.4.2 Reducing die and screen-pack fouling

Other processing aids serve extruders by limiting the accumulation of degraded resin materials inside the equipment. For example, as in molding processes (Chapter 11), inexpensive process lubricants such as *metal stearates* (typically calcium or zinc stearate for POs) have great value as acid scavengers and catalyst neutralizers (covered in Chapters 3 and 4). Widely produced from natural fatty-acid sources, but particularly effective in synthetic forms, metal stearates lubricate and filter the polymer melt, reducing screen-pack back-pressure and the number of screen-pack changes needed. Common stearate products tend to become discolored from heat exposure, but more thermally stable grades are available [12-15, 12-16].

Alternatively, by preventing thermal degradation, *heat stabilizers* also have the effect of keeping die surfaces clean, increasing throughput, and maximizing film properties, such as tear and puncture resistance. Cel-Span 306P is a 6% stabilizer concentrate offered for this purpose from Phoenix Plastics, for use in HDPE, LDPE, and LLDPE film [12-14].

12.5 PROCESSING AIDS FOR SPECIFIC EXTRUSION SITUATIONS

A number of studies and examples have shown the various ways different processing aids can be effective in extrusion processes; a selected few are summarized below.

12.5.1 High-throughput extrusion

As in injection molding, processing aids used in extrusion can increase throughput simply by decreasing the viscosity of the melt. Along with the basic fatty amides, fatty-acid soaps, and olefin wax lubricants mentioned previously, aids such as Mitsui's Excerex olefin oligomer discussed in Chapter 11 can provide significant decreases in screw torque, temperatures, and energy use, for greater productivity in extrusion. Various improvements have been reported with the additive by the company. These include:

- doubled extrusion volumes and 20 °C lower cylinder set-temperatures (with lower scorching) for 0.5-mm thick PP sheet extrusion (loaded with 3% of the product);
- 20% increased volume in biaxial PP film processing (with 1% Excerex);
- 16% greater output in HDPE blown-film extrusion (with 0.5% of the additive) [11-6, 11-7].

12.5.2 LLDPE blown-film stability

LLDPE has become a key PO for blown film, but not without some difficulties in establishing methods for maintaining bubble stability and gauge consistency. Typically, LDPE is blended with the LLDPE to increase melt strength and bubble stability, but this can reduce tensile, tear, and dart-impact strengths. Alternatively, process developers have turned their attention to a melt-strength additive (MSA) developed by DuPont Canada in the 1980s particularly for when bubble stability is a problem.

The MSA is added before extrusion at 1%–3% loading, and reportedly can provide the necessary melt strength for blown film, improving output by 10%–50%. It also reduces draw-thinning and gauge variability, thus allowing downgauging opportunities. The MSA acts as a chain-branch extender, increasing viscosity at low shear rates but not at high shear rates. It does not reduce most physical properties to the same degree as LDPE (except for clarity and tear strength, which are said to be moderately reduced). In terms of cost, a DuPont researcher suggests that the MSA is cost-effective when used at 2%, provided that it increases output by 10% and allows 2% downgauging. This estimate is based on a line operating at full capacity that is also powerful enough to run neat LLDPE, with specific output and pressure limitations, and with the film sold on an area basis rather than a weight basis. Though not a processing lubricant itself, the MSA can be used with other processing aids [12-18].

12.5.3 Oriented PP slit tape fibrillation

The production of oriented PP slit tapes is complicated by the tape's tendency to split or fibrillate randomly into tiny fibrils, damaging the quality of the final woven tape product. Typically, HDPE or calcium carbonate additions are used to fight random fibrillation, but these can change the resin rheology and/or reduce the "hand feel" quality of the woven tape. One additive specifically created for controlling this tendency to fibrillate is the Cel-Span 435 product from Phoenix Plastics. When added at 2%–4% in PP homopolymers at the extruder, the additive is said to produce a better hand feel in the final tape product than the other additive solutions, with no fraying during weaving, and less dusting and less friction with processing equipment. A related additive, the "Entira Strong" modifier from DuPont, is also said to reduce tape splitting and dusting while allowing stretch ratios to be increased by 20%–30%, creating stronger tapes [12-20, 12-22].

12.5.4 Thin PP fibers

In PP fiber applications, major increases in melt-flow index (above 400 MFR) can allow the production of thinner fibers, improving productivity and the fiber's insulation, absorption, or filtration qualities in nonwoven fiber products. As used in injection molding, peroxides reduce the longest polymer chain lengths, reducing viscosity and increasing melt flow. For example, Polyvel's peroxide granular concentrates, mixed with granular or powder PP, are said to increase PP melt-flow rate dramatically, resulting in much finer fibers. MFR was increased from 400 to 2600 when the PP was loaded with 0.5% of the company's CR20PX 20%-peroxide concentrate, and a larger gain to 3900 MFR was seen using 0.75% of the concentrate [12-25].

12.5.5 Highly filled masterbatch production

Masterbatch processing is the extreme situation for processing aids, where very high loadings of fillers or pigments must be efficiently incorporated with a resin carrier. In particular, masterbatch compounders are challenged when integrating high percentages of titanium dioxide, carbon black, phthalocyanine blue pigment, or other difficult-to-disperse fillers. Yet end users expect masterbatch products with these high loadings completely wetted out by the carrier resin. Here, additives such as PE waxes or Fine Organics' Plastaid multifunctional aids are said to reduce viscosity and increase melt flow when creating pigment masterbatches, even when dispersing 75% TiO_2 in LLDPE carrier resin [11-12].

12.5.6 Wood–plastic composites

WPCs have been extruded at high volumes since the 1990s. WPC products for construction are only likely to become better and more popular as alternatives to wood, although the extrusion productivity challenges seem enormous: demanding a twin-screw extruder to incorporate 60% wood flour or fiber into a PO matrix to produce a high-quality product down the line. Here, processing aids are valuable tools for dispersing fiber into resin and providing an extruded surface free from fracture and mottling (irregular coloration).

Processing aids for WPCs can include mixtures of metal stearate and specialty amides such as EBS for improving fiber-wetting and dispersion, along with coupling agents (see Chapter 14). Like aids for standard extrusion, these aids can help maximize output, reduce processing temperature, increase modulus of rupture (MOR), and reduce water uptake, a particular problem for absorbent wood fillers. Concluding this chapter, some effects of various processing aids in WPCs are explained more in Case 12.2 [12-23, 12-24, 12-27].

CASE 12.2 PROCESSING AIDS FOR WPCs [12-27, 12-28]

Problem: Questions about how different processing aids affect the properties of WPCs.

Objective: Data from trials that show the effects of different additive ingredients.

Solution: Conclusions about PP WPCs containing various processing aids.

As the processing of WPCs becomes more of a science than an art, systematic studies are needed to understand the possible benefits of processing aids. These benefits will be needed if WPC product manufacturers are able to lower their costs enough to compete better with conventional construction materials.

One viscosity/processability study on 40% and 60% wood-flour PP composites was taken on by Struktol. The study focused on the company's TR016 and TR251 processing lubricant formulations, loaded at 1% or 2% individually and combined together (and also loaded at 1% with 0.1% of a 60% peroxide concentrate). The company developed a series of conclusions from the study.

The basic final conclusion confirmed that the processing aids do deliver viscosity reductions, especially when the peroxide concentrate was added. This reportedly showed that a WPC compound is feasible that has a processing viscosity equivalent to that of neat resin (an important quality for creating thin-walled WPC parts).

Another conclusion stems from the processing aids' dispersal qualities: The flexural modulus was actually lower in the processing aid formulations than in the wood–PP control formulation. This is likely because the additives dispersed the filler completely, creating a more continuous PP matrix phase.

Based on this kind of research, the company provides several suggestions to consider when evaluating processing lubricants in WPCs; in short:

- Different processing lubricant systems respond differently to the same processing conditions and machine settings (thus process settings must be optimized for each lubricant package).
- Some lubricant systems allow faster screw speeds to be used to improve extrudate surface quality.
- Lubricant systems containing metal soaps (calcium stearate) can interfere with coupling agents used to bond wood to polymer.
- Processing lubricant performance can be affected by wood filler particle size or even by the species of tree the wood is from.

6

SECTION VI

Other Modifications of Form and Function

CHAPTER 13

Reducing Density: Polyolefin Foams

Reducing the mass of a PO or plastic part is helpful in efforts to "lightweight" various applications and for reducing resin content as well. Making products thinner is just one approach for reducing mass; foaming is another option for light part designs with high property-to-mass ratios. And foaming is useful for creating insulating or shock-absorbing properties that solid resin parts cannot supply. These properties have already made POs useful in the automotive sector, for example. Also in this sector, the foaming of already low-density PO materials will likely grow as an important approach for creating a new generation truly lightweight, fuel-conserving automobiles [13-1].

Many other PO applications benefit from foaming, including the most common packaging and consumer goods, since foaming allows significant raw material savings without major losses of aesthetics or key properties. Given that additives play a large role in PO foaming, this chapter will be guided by the following questions:

- (13.1) How are PO foams made, and what blowing agents are used?
- (13.2) What kinds of advantages do foams bring in specific product sectors?
- (13.3) What factors and additives improve foam quality or control foam cell size?

13.1 BLOWING FOAMS: EXTERNAL AGENTS vs. INTERNAL AGENTS

Not all types and grades of POs foam easily or with the same kinds of bubble or blown-cell sizes and structures. This variability is an advantage in a way, since it allows different kinds of PO foams to be blown for different purposes. Open-cell, sponge-like foams are useful in shock-absorbing applications, for example, while a closed foam cell structure is effective for pipe and cable insulation [3-3].

Highly branched, high-melt strength, amorphous POs are generally easier to foam than high-flow, crystalline POs. LDPE in particular can be foamed to reduce density to extremely low levels, with reductions from 0.92 g/ml for unfoamed LDPE to 0.03 g/ml in highly foamed extrusions. These light foams provide heat and sound insulation, shock-dampening, and water-buoyancy for protective packaging, building, and consumer products. Often, foamed PE materials are crosslinked with peroxide agents or electron-beam treatments to increase their strength. More dense and more rigid foams made from stiffer POs offer strength and stiffness in thick but low-weight parts. However, crystalline PP can be more difficult to foam because the nucleation and formation of its crystalline regions occurs at the same time as bubble nucleation. This inhibits its foam cell formation, and makes the choice of foam-blowing additives and process conditions critical [13-2, 13-7, 13-16].

Blowing agents, or materials that cause foaming in a plastic, can be added to the polymer as an internal additive (chemical blowing agents) or injected as gases or liquid during melt processing with special equipment (physical blowing agents). These agents create and expand bubbles throughout the polymer matrix, forming an internal cellular network of open or closed cells. Chemical agents decompose from the heat of processing into gases that nucleate and expand the cells, while physical foaming processes expand cells by using the energy of an injected agent. Physical blowing energy comes from the expanding compressed gas that is injected into the melt, or from a volatile injected liquid agent that creates cells when it expands into a gaseous state (these liquids have been based typically on various chlorofluorocarbon chemistries that have been controversial over the years because of their effects on the earth's ozone layer).

13.1.1 Physical blowing agents

While not being true additives in the context of this book, physical blowing agents and their processes have some advantages for operations whose production volumes justify the investment in the necessary foaming equipment or retrofits. The process equipment can be sophisticated, though the blowing agent often is not (nitrogen, pentane, butane, or carbon dioxide). Traditionally, physical blowing produces foamed products with relatively coarse cell structures and surfaces, but improved equipment and processes such as Trexel's MuCell process have produced finer foam structures. This process reportedly is even being used to produce lighter-weight, long-glass fiber-reinforced PP composites. Improvements in physical blowing methods are cost-driven, and also driven somewhat by interests to substitute chemical blowing agents, which are seen as less environmentally appropriate [1-1, 13-2, 13-6, 13-11].

Still, in physical blowing processes, chemical additives do serve as nucleating agents to produce finer cells, or to reduce the amount of physical blowing agent that is needed. Chemical blowing agents (discussed below), especially endothermic agents, are often added as nucleating agents to produce finer cell sizes in direct-gas extrusion. In one example, the effects of these nucleating/blowing agents in sheet packaging extrusion have been reported as allowing a 20% reduction in physical blowing agent, as well as 20% higher throughout. Exothermic organic blowing agents such as azodicarbonamide (ADCA) have also been used with physical blowing processes to produce even smaller cells than talc or silica nucleators provide. ADCA releases both gas and heat when it decomposes, creating local areas of reduced viscosity and surface tension, encouraging the formation of more and smaller cells. This results in lower foam densities than could otherwise be obtained [13-2, 13-3, 13-5, 13-8].

13.1.2 Chemical blowing agents

As the main focus of this chapter, chemical blowing agents include both inorganic and organic additives that decompose into gas at high temperatures. Their selection must be matched to the processing temperature of the polymer, and their reaction temperature can be lowered if necessary with additional activating additives, or "kickers." (Processors using chemical blowing agents also typically require a screw, barrel, and die design that controls foaming so that foaming does not begin prematurely.)

Inorganic blowing agents generally are endothermic, requiring heat to transform into a gas; organic agents are generally exothermic, releasing heat during their decomposition reaction. Sometimes these agents are combined in one compound to capitalize on both the finer cell structures made possible with an endothermic agent and the high gas volumes of an exothermic agent. Chemical agents and their blends are available in the same multiple product forms as other additives, and they can be added to resin in multiple ways as well, with masterbatches becoming more popular relative to powders [1-1, 13-2].

Exothermic organic chemical blowing agents include azide-, azine-, azole-, and other azo-based chemistries from which nitrogen is evolved at high temperatures. These agents decompose at processing temperatures from about 150 °C to over 200 °C. ADCA is widely used because of the combination of high gas yield and fine cell structures it produces. Estimates put ADCA's proportion of global chemical foaming agent volume near 90%. However, ADCA can cause yellowing, and it is no longer food-use compliant with European Commission regulations because of concerns about toxic decomposition products. Thus its use will likely decrease. Another popular organic agent is 4,4 oxybis-benzene sulfonyl hydrazide (OBSH) [1-1, 13-2].

Endothermic and inorganic chemical blowing agents have included materials that degrade into carbon dioxide when heated, such as sodium bicarbonate. Sodium bicarbonate's low decomposition temperature (100 °C–140 °C) suits its use with POs, though it can decompose rapidly, forming open-cell structures. Other endothermic agents include citric acid, sodium borohydride, and polycarbonic acid. These agents are now used for only a small percentage of foamed plastics, compared with exothermic organic agents. But given the fine cells they can produce and their less environmentally questionable nature, they are expected to grow in use at a greater rate than exothermic organics [1-1, 13-2, 13-12].

Microcapsule foams are a currently more expensive alternative to chemical and physical blowing agents. These small thermoplastic bubbles added into the melt do not release gas, but rather expand to an optimum size as they are heated, through the expansion of the hydrocarbon gas inside them [13-12].

13.2 PRODUCT SECTORS REQUIRING CHEMICAL BLOWING AGENTS

13.2.1 Molded packaging and consumer products

In foamed products, the blown-cell volume displaces resin to make consumer products less costly and less wasteful when discarded. A foam's shock-absorbing, heat-insulating, and compression properties are key added benefits for certain packaging applications (see Case 13.1).

Blowing agents added at low percentages can also be used to fill out an injection-molded part and eliminate sink marks or warping. For example, Foamazol agents from Bergen International are said to remove sink marks without creating “swirling” on the surface of the part; instead the filled moldings still retain a “Class A” surface. However, as with all foaming processes, control of feed and compression zone temperatures and injection rate (and other parameters) are needed for controlling foaming and surface appearance [13-3].

CASE 13.1 PO FOAM WINE-BOTTLE CORKS [13-10]

Problem: Natural wine-bottle corks have become increasingly expensive.

Objective: A plastic-based cork design with the unique characteristics of natural cork.

Solution: Foamed POs.

One of the most intriguing foamed packaging applications of recent years is the foamed PO wine cork, an alternative to more expensive natural corks. Initially thought of as a “cheap” artificial solution not befitting quality wines, plastic corks nonetheless now have widespread use, and some wine drinkers may consider their toughness to be a preferable quality over natural corks.

The highest-quality synthetic corks are made with metallocene catalyst-produced POs, which provide a soft texture and, because of foaming, a satisfying consumer experience when a bottle is opened. Underneath the smooth resin skin are foamed cells created during injection molding using an endothermic blowing agent certified for direct food-contact use.

For cork molding, Adeka-Palmarole supplies its BA.M7.E blowing agent in a 70% masterbatch, with a carrier resin that is compatible with PO cork materials. The agent has a processing temperature of around 180°C, in the processing range of most POs. A related masterbatch with 50% blowing agent is also offered for processes that have less accurate feeding equipment, the company reports.

Other molding processes benefit from foaming. In low-pressure structural foam molding, large rigid parts can be created with 10%–40% less mass than unfoamed resin, and relatively high strength-to-weight ratios. Often a physical agent is employed for foaming, with a chemical blowing agent added to provide nucleation and cycle time reduction. Alternatively, in co-injection molding, resin containing a foaming agent is injected into the core of a sandwich-structure molding, inside an outer skin of unfoamed, aesthetically appealing resin. In blow-molding, foaming is also useful, though in intermittent parison-extrusion processes, premature foaming may occur when the melt is not held under pressure. As with co-injection, multilayer blow-molding using dual extruders can be used to form a structure with a solid skin and foamed inner layer, resulting in attractive, lightweight parts [13-3, 13-8].

13.2.2 Automotive moldings

Especially for automotive PP and TPO resins, foaming has been useful in the interior of vehicles as impact-resistant moldings or sheet coverings for dashboards, door panels, and other trim. Overall, molded interior parts have multiple, sometimes conflicting needs for impact and scratch resistance and softness and stiffness. Here, foamed parts with skin-core constructions can be useful. Foamed interior POs also provide the weight savings that automakers desire. Moreover, foamed POs can be molded into parts with equivalent section stiffness as unfoamed parts, but which weigh up to 30% less. (One requirement in all foam molding processes, however, is careful control of the molding process. The press clamp or mold core must be opened the right amount at the right time, to allow the part to foam in the cavity, expand, and cool after injection.) [13-9]

Although PP/TPO compounds have so many preferred properties for auto interior parts, injection-molded PP often has inadequate melt strength and melt surface tension to form sturdy, intact foam cells. Instead, broken cells and surface swirl marks are the result, caused by blowing-agent gas escaping the matrix and moving to the surface. The rubber constituent in TPO and filler particles in particular can reduce this melt tension. Research on reducing swirl marks has resulted in some success in using a PP/TPO formulation that includes a highly crystalline PP, an ethylene–styrene copolymer rubber, and an ethylene-α-olefin rubber. Research on chemical blowing agents has also produced improved results for foamed TPOs with consistent cell structure and high stiffness. Here, a blowing agent added at 2%–3% reportedly can reduce part weight by 25% [13-9, 13-12].

Perhaps the ultimate low-weight use of foamed POs in vehicles comes in the form of expanded polypropylene (EPP) bead materials, which can be molded into cushioning materials for sound-dampening, seating, storage systems, energy absorption, and occupant protection. A couple of recent uses of EPP are covered in Case 13.2.

CASE 13.2 EXPANDED PP FOR AUTOMOTIVE WEIGHT SAVINGS AND SAFETY [13-13, 13-14]

Problem: Automakers need more options for reducing vehicle mass and increasing occupant safety.

Objective: Lightweight, impact-resistant, PO-compatible (and recyclable) materials.

Solution: Moldable EPP bead foams.

EPP bead foams are already heavily used in vehicles for a variety of applications, given EPP's energy absorption, moldability, and extremely low density. Automakers at BMW and Ford have recently adapted the material into innovative uses.

In the BMW X5, EPP is used to reduce mass by eliminating the need for a secondary steel floor pan under the rear seat. The company adopted an unconventional design that uses just a thin steel bracket for supporting a thick but light molded EPP seat riser. This reportedly reduced weight by almost 4 kg (45%) compared with the previous design. The seat riser even includes foam access panels through which the vehicle's electronics and fuel system can be serviced. The EPP design also reportedly reduced steel panel tooling and welding equipment costs by nearly US$3 million.

In the Ford vehicle application, an insert molded from EPP is used in the front seat's head-restraint assembly. A low-cost and low-weight redesign with EPP allowed better compliance with US safety standards (FMVSS-202A). Development of the insert allowed the automaker to improve its head-impact ratings to "good" on several 2007 and 2008 vehicles. The EPP insert is also molded into a shape that allows "snap-on" installation onto the metal head-restraint support, without fasteners.

13.2.3 Extruded construction products

Manufactures of WPCs and extruded construction trim moldings benefit from the resin savings foamed materials offer. Foamed POs also allow lighter handling weights of long construction products and easier building with the materials, using conventional building tools and fasteners.

PO WPCs are processed at lower temperatures than other PO applications to prevent wood fiber deterioration. They typically require blends of endothermic and exothermic blowing agents, with endothermic agents providing faster extrusion rates and consistent, small cell structures, and the exothermics providing higher blowing pressures for these highly filled compounds [13-2].

Other common extruded PO products benefit from foaming, such as wire and cable insulation. And for protective or decorative packaging or insulation, industrial film and sheet can be foamed for reduced density and weight. For example, an LDPE film with 3% of an endothermic blowing agent (IP1890 from Ingenia Polymers) reportedly showed reduced density, below 0.6 g/cm^3, and 10% increased elongation (tensile strain) [13-4].

13.2.4 Foaming in rotational molding

Given the large dimensions of many rotomolded parts, it is not surprising that foaming is being used to reduce part mass and raw material consumption. Offering higher stiffness-to-weight ratios, foaming may allow future potential growth opportunities in this sector. For example, better blowing agents are said to be making rotomolded foamed PE more competitive with two-component polyurethane foams. Moreover, rotomolded parts often do not always need to satisfy high engineering property requirements of technical applications; thus foaming's negative effects on these properties may not be a limitation [13-17].

Rotomolders have used ADCA in powder form in their formulations to create foamed products. However, micropellet masterbatches are reportedly becoming more popular and offer improved foam quality. As in other processes, process control is important in rotomolding foams, since premature decomposition of the blowing agent can result in gas escaping from between the particles of unconsolidated resin during molding [13-2, 13-8].

13.3 FACTORS IN BLOWING BETTER FOAMS

Foaming introduces unique factors to monitor, since it is a process in which part quality is determined heavily by radical internal changes in the part. Various factors and additives can influence foam cell size, consistency, or quality. Other economic factors determine whether foaming may even be appropriate for an application.

Cost: Especially when resin prices are high, a blowing agent's cost theoretically can pay for itself from the savings in raw resin costs. Reductions of only 5% in part weight may be enough to recover a blowing agent's cost. A chemical blowing agent can also reduce cycle times and increase throughput, due to its lubricating effects which allows reduced processing temperatures. In particular, the carbon dioxide produced by endothermic agents can dissolve in the melt, improving melt flow and mold filling [13-2].

Particle size of blowing agent: The particle size of an ADCA-based agent, for example, affects the size and structure of the foam cells produced. It also affects the temperature at which the blowing agent decomposes, with smaller particle sizes ($\sim 2\ \mu m$) decomposing at lower temperatures [1-1].

Cell-modifying additives: Like the nucleating additives mentioned in Section 13.1.1, other additives can enhance foam structure by reducing the size or variation of cell size or limiting the blowing of open cells. Cell size is important, because finer cell sizes allow higher tensile strength and elongation (and better surface appearance), while larger cells support impact strength.

For example, the "*in situ*, repolymerizing," catalyzing effects of zirconate and titanate coupling agents in plastics are said to strengthen cell bubble walls and allow more strain (elongation), resulting in fewer blown-open cells. In a PE foamed with ADCA, the coupling agents reportedly reduced cell size variation and size from 6–48 μm to 9–15 μm [13-15].

Modified nanoclays have also been used to improve foaming, particularly in PP. Dispersed nanoclay fillers reportedly have been observed increasing cell nucleation and/or increasing the melt strength and strain-hardening of PP, allowing smaller foam cells to be blown without breaking. In an extrusion study comparing treated-organoclay PP materials with neat PP, the foaming of the nanocomposites with ADCA reportedly had a much higher proportion of closed cells, and lower densities, than neat PP. This was especially true for a nanocomposite having a lower crystallization rate, which allowed more cells to form before crystallization [13-16].

Coupling, Compatibilizing, Recycling, and Biodegradability

The modification of PO resins with additives is not straightforward; the PO matrix itself is often resistant to interacting with additives or the environment in the ways desired by the formulator or end user. After all, POs are relatively inert and nonpolar and tend to repel many additives, and other polymers. They also tend to resist degradation in places—such as landfills—where end users would prefer that they decompose.

Thus this chapter unites various modifiers whose specific purposes are to make POs interact better with other materials or conditions they are exposed to. The chapter is organized by making distinctions between functions of the additives. The first section covers coupling agents that promote the adhesion of fillers or fibers with the PO matrix; the second section covers compatibilizing agents that allow commingled recycled and virgin polymers to be blended more effectively together; and the third section covers additives that are intended to promote the biodegradation of POs. The following questions are addressed:

- (14.1) What additives are effective for coupling POs with fillers or reinforcements?
- (14.2) How can compatibilizing additives allow the more efficient use of regrind and recycled PO content?
- (14.3) Which additives reportedly allow POs to biodegrade more efficiently when their product life cycle is complete?

14.1 COUPLING FILLERS AND FIBERS WITH THE PO MATRIX

Since most common fillers have no inherent reactivity with inert, nonpolar POs, reactive dispersion aids and coupling agents are essential. Without proper dispersion and bonding to the matrix, fillers and fibers added to POs are greatly limited in improving a compound's properties—or they may even degrade essential properties, acting simply as contaminants in the polymer. Many of these dispersants and coupling agents have been mentioned in the previous chapters on fillers, fibers, colorants, and processing aids, but this section will put more focus on their mechanisms and effects.

To be effective, coupling agents must essentially surround each filler particle and link the particle to the polymer. Typically, filler and fiber suppliers precoat their products with coupling agents, somewhat making the coupling agent's important role less obvious to the end user. They may also be added when mixing or extruding the filled-polymer compound. Here, they may help increase throughput (like processing aid lubricants) while also improving the dispersion of high pigment or filler loads. The selection of a coupling agent can have an important effect on how well the filler is dispersed and bonded to the matrix, and on how easily the compound processes [14-1].

14.1.1 Traditional coupling agents

One traditional approach for coupling glass fiber or wood cellulose fibers to POs uses maleic anhydride grafted to a polymer or copolymer (g-MAH) and mixed with the resin. This coupling agent is made with a two-step process: a base polymer (such as PO) is created in a reactor, and then MAH monomers are grafted onto its polymer backbone. When the g-MAH polymer is added to the compound at just a few percent loading, the polar functional groups of the MAH bond with hydroxyl groups on the fiber or filler surface. Grafted MAH coupling agents increase the physical properties of fiber-filled compounds, such as the bending elasticity and density of HDPE WPCs. The improvement in properties is usually proportional to both the g-MAH concentration in compound and the concentration of MAH that is grafted onto its polymer carrier [7-49, 14-3].

Grafted MAH coupling agents have also been effectively used for bonding long glass fiber to PP in LF-PP composites loaded with 30%–50% glass. Here, the coupling agent concentration, glass content, melt flow of the PP, and processing factors create complicated relationships with the resulting mechanical properties, as discussed in Case 14.1 [14-7].

Organosilane coupling agents have also been heavily used, especially for bonding nonorganic siliceous fillers and fibers (such as talc, clay, and glass), metals, and metal oxides to the PO matrix. Along with chemically coupling the outer surface of the filler particles with the PO, silanes act as filler dispersants, preventing filler agglomeration and allowing higher filler loadings and properties. The silicon atoms in silanes are bonded to "head" functional (alkoxy) groups that bond (or adsorb) onto the filler particle's surface chemistry. The silane's silicon is also bonded to a "tail" organic (alkyl) group that is compatible with

CASE 14.1 COUPLING AGENTS IN LONG-GLASS-FIBER PP [14-7]

Problem: Some new LF-PP formulations are not yet optimized for costs and properties.

Objective: Determine how to minimize the costs of the expensive components in LF-PP, such as the g-MAH coupling agent.

Solution: New grades of glass fiber allow reduced coupling agent use.

Given the rapid growth of long-glass-fiber PP composites for structural applications in automotive and other areas, there is interest in maximizing the influence of glass on mechanical properties of the composite. Since the g-MAH coupling agent is one of the most expensive components of LF-PP, one goal is to maximize the effects of the glass while minimizing the amount of coupling agent required. Thus researchers from glass-supplier PPG industries studied various factors based on the coupling agent and glass fiber in LF-PP, including key systems' characteristics, such as melt flow of the PP resin and processing method.

The PPG researchers compared various compositions of LF-PP. They contrasted homo-PP resins with MFI values from 5 to 100 and glass percentages of 30%–50% (added as 17-μm glass rovings pultruded with the PP and cut into pellets 12-mm long). They compared different grades of glass fiber and also varied the coupling agent concentration from 0.5% to 3% in the study. The resulting injection-molded samples were then evaluated with a variety of mechanical tests.

The study revealed expected (and unexpected) trends:

- At high glass loadings, an increased concentration of coupling agent increases tensile strength, as expected, but the properties are not increased above a plateau "saturation" concentration of g-MAH (at which point the glass-fiber surfaces are completely covered with coupling agent).
- Heat deflection temperature increases with increased MFI: This perhaps "counterintuitive" trend may be explained by the greater impregnation and wet-out of the glass by the high-flow PP. (This wetting-out is said to reduce voids, allowing better load transfer between resin and fiber, as well as greater retention of the original fiber length, which is typically reduced by fiber breakage during molding.)
- Modulus is not significantly affected by the coupling agent, but rather is controlled by fiber content (and is ideally predicted by the traditional "rule of mixtures" law, in which the composite modulus is simply a weighted volume average of the moduli of the composite's matrix and reinforcement).
- Higher MAH content in the coupling agent can increase composite properties, enabling perhaps less overall use of coupling agent and thus less cost.
- Glass-fiber grades with modified chemistries (such as PPG's TufRov 4576) allow higher composite properties—and thus potentially require lower amounts of coupling agent.

the polymer. Linking filler and polymer, this structure lowers the filler's surface energy, improving its compatibility and wetting with the low-energy PO. It also creates a barrier that prevents a filler particle from bonding with other filler particles. These mechanisms help the silane serve as a coupling agent with high surface-energy fillers such as (from the most effective coupling to least effective): silica/glass fiber, mica, kaolin, wollastonite, ATH, talc, titanium dioxide, calcium carbonate, and carbon black [8-14, 14-1].

14.1.2 Alternative coupling agents

Since silane agents are less effective with coupling lower-energy carbon black and $CaCO_3$, other agents may be tried. For coupling these fillers, organometallic complexes based on "neoalkoxy" titanates and zirconates have been used as coupling agents. These complexes contain oxygen groups that are reactive with surface protons (H^+) found on most common fillers, unlike silanes which require hydroxyl (OH^-) groups on a filler's surface and the presence of water (under 100 °C) to be most effective. These agents are molecular complexes whose Ti–O or Zr–O bonds and other catalytic functional groups are said to have a strengthening, "repolymerizing" effect on the polymer (to be discussed more in the next section). The agents are said to improve properties in compounds such as talc-filled PP, where a titanate coupling agent was found to decrease melt viscosity, improve dispersion, and improve mechanical properties. Or, in a highly filled 60% ATH flame-retardant compound, a titanate reportedly was found to increase flow and impact strength. The Ti/Zr coupling agents can be coated on filler particles, or are available in masterbatch or other forms that match the resin's form, for proper mixing with the polymer [14-2].

For WPC processing, improved coupling agent technologies focus on strengthening the connection between the PO and wood or natural cellulose fiber, providing stronger products for the construction industry. For example, Clariant offers a coupling agent (Licocene PP MA 6452 TP) composed of a metallocene-catalyzed PP wax grafted with MAH, which reportedly is a more precisely controlled product offering better performance. Other alternatives to traditional g-MAH agents are said to improve dispersion, resulting in higher strength properties and lower absorption. DuPont offers a reactor-produced ethylene/MAH copolymer, which contains higher levels of anhydride than in g-MAH. The product, designated Fusabond W PC-576D, is said to increase bending modulus of elasticity (MOE) and density more than an LLDPE-g-MAH, when added in HDPE board with 60% pine fiber and 5% untreated talc. Water absorption with the product is also noticeably less than with g-MAH (at 2% loadings and higher), reducing the potential of rot or mold growth [7-49, 14-3, 14-4, 14-5].

Even more complex recipes for coupling fibers in WPCs have been studied. For example, in one study, MAH grafted onto a styrene–ethylene–butylene–styrene block copolymer (SEBS-g-MAH) was added at 1%, along with 2% PP-g-MAH, in a WPC system. This reportedly doubled the impact strength over PP-g-MAH alone, though it reduced the modulus. However, when researchers used a WPC that was also loaded with nanoclay (1%–5%), the SEBS-g-MAH likewise increased impact strength, but the nanoclay helped support the modulus value [14-6].

With nanocomposites, there is likewise a drive to determine coupling agents that best exfoliate and disperse nanoclays, thus increasing their properties and expanding these materials into new applications. Exfoliation is often done with surfactants like charged quaternary ammonium compounds (quats). Nanoclay is typically exfoliated in a water slurry with a high percentage of an ammonium quat before incorporation with the polymer. However, the high percentage of ammonium quat required for exfoliation reportedly creates compatibility problems with POs. Alternatively, research from Kenrich Petrochemicals argues that instead of ammonium quats, a much lower percentage of a titanate quat coupling agent should be used in the wet slurry or in the polymer system. This effectively exfoliates nanoclay by creating a monolayer on each clay nanoparticle. It does not create PO compatibility problems, but instead is said to enhance many polymer properties through its catalytic effects on the polymer [14-8].

14.2 COMPATIBILIZERS FOR INTEGRATING REGRIND AND RECYCLED MATERIALS

For most operations that handle POs, the maximum reprocessing of in-house scrap material is a "no-brainer," when it is permitted by the application. Recycling regrind keeps costs as low as possible, as well as allowing a company to consider itself more environmentally sustainable. Purchasing and reusing postindustrial or postconsumer POs can be a more difficult matter.

There is usually no shortage of recycled material. Among all the resins that recyclers buy and sell, POs, including HDPE, PP, LLDPE, and LDPE, have the largest shares. And postconsumer POs, particularly HDPE, are flooding the marketplace (with over 40% of all bottles that are recycled being made from HDPE, even though less than 40% of all bottles produced are HDPE). Also, the highest rate of postconsumer plastic bottles collected for recycling are for bottles made from HDPE, ahead of PET. But the costs to collect and reprocess postconsumer materials are high, and the overall prices and quality of these external recycled materials are unstable, sometimes making their reuse hard to justify [14-9, 14-10, 14-26].

Whether using scrap produced internally or recycled material from outside the operation, integrating recycled material with virgin material and creating a quality output is not easy, for several reasons:

- Though all grouped under the generic term "commodity POs," PE, LDPE, and other POs typically are somewhat immiscible with one another and do not always process efficiently as blends.
- Even when the PO families and colors match, and the recyclate is free of contamination, the molecular weight distribution and MFI of different lots can vary wildly. Additives such as peroxides in masterbatch form have been proposed as means for making the melt properties of mixed PO recyclate streams more homogenous.
- Different levels of copolymers, modifiers, or other additives in the recycled material can frustrate those who try to combine various sources of scrap and produce a quality product.

- Because the recycled material may have partially degraded after going through repeated processing cycles and heat histories, the allowed recycled content is typically limited to 30% or less in visually sensitive, functional products. Even when different polymers or grades can be blended or used in different layers of a multilayer product, maximizing the recycled content of a product may require changing the gauge thickness or part design to accommodate for the reduced mechanical properties of the blend.
- Moreover, certain additives that were originally added to the regrind material may have since been consumed or lost (especially heat stabilizers or migratory agents like antistats or processing lubricants); thus, higher additions of these additives in the virgin/recyclate blend may be needed in compensation.

In other words, regrind or recycled material might often be thought of as an additive that unpredictably degrades the properties of virgin material, rather than enhancing them. But such obstacles are being overcome to allow more recycled content in more PO applications, including durable automotive parts (see Case 14.2) [3-4, 14-12, 14-27].

For PE in particular, the characteristics of recycled off-spec or wide-spec grade materials that are available may vary greatly. These materials are often difficult

CASE 14.2 RECYCLED TPO IN AUTOMOTIVE MOLDINGS [14-16, 14-17]

Problem: More recycled plastic content is desired in automotive components.

Objective: Determine how to cost-effectively increase the recycled content in durable moldings.

Solution: Automotive panels made from TPO recycled from discarded moldings or postconsumer PP.

For cutting costs while improving their "green" image, automakers are seeking new ways of incorporating recycled plastic content in new vehicles. In a recent application, General Motors, resin supplier MRC Polymers Inc., and molder NylonCraft Inc. determined how they could use TPO from recycled bumper fascias in the new air-intake (cowl) molding for GMT360 sport utility vehicles. (This molding is the long black part located between the hood and the windshield.)

One of the keys to the application is a process that removes paint from the scrap fascia moldings, so that it does not contaminate the cowl molding. MRC uses a proprietary water-based process to remove the paint, and even boxes the removed paint and sells it as a filler material.

The recycled TPO meets color and weatherability requirements, and can be molded using the same tooling as virgin TPO. It also creates minor cost savings, along with saving hundreds of thousands of kilograms of fascia TPO that would otherwise end up in landfills.

In another recent development, postconsumer recycled PP is being used in the TPO underbody moldings of the 2009 Ford Flex vehicle. Supplier Flex-n-Gate supplies about 9 kg of the material per vehicle for use in splash shields, spoilers, and radiator air deflectors. The material must be compounded with additives to offer and improve its UV stability and impact strength. However, because the recycled material's cost is not tied to raw petroleum prices, the supplier says that significant cost savings are possible, in comparison with virgin material.

to fit into the relatively narrow processing windows of extrusion, blow-molding, or injection molding. Extrusion and blow-molding processes require PE with melt indices from 0.05 to 1, typically, while injection and rotational molding require 5–100 melt index PE. Recycled materials may be identified by melt index and density, but unfortunately, the melt index may be stated inaccurately by the source, and the material may contain unknown fillers or colorants that affect its modulus and processing. All these issues increase the potential for downtime and increased scrap, thus reducing the motivation for using scrap at all [14-11].

But additives that compatibilize different components in a blend can make recycling more efficient. Coupling agents can improve melt flow, processing, and final properties. These additives offer converters more flexibility and options for controlling and reusing material, rather than relying on outside brokers or recyclers to provide the right grade of material at the right time. (And as recent history shows, these businesses themselves are subject to economic cycles and radical swings in resin prices, which vary the amount of high-quality scrap they can provide.)

When used as compatibilizers in PO regrind blends, MAH-grafted polymer coupling agents and other modifiers chemically unite ingredients in the blend, producing higher properties and allowing more recyclate to be included. Compatibilizers can improve the properties of recycled feedstreams that contain common ingredients normally found in PE. These "contaminants" may include zinc stearate lubricants, EVOH packaging barrier resin, and water. Some compatibilizing modifiers are effective at low loadings for improving properties of these blends and for reducing die buildup. For example, DuPont's Fusabond E EC-603D copolymer modifier is said to improve notched-Izod impact strength at 0.5% loading in PE containing 2% zinc stearate, 9% EVOH, and moisture [14-14].

PP and PE have been successfully blended together into materials with high properties, despite their rheological differences. Work by Dow Chemical has shown that olefin block copolymers added as compatibilizers can "stitch" together PP and PE polymer phases. The soft block segment of the copolymer is said to be miscible and compatible with the PP, and the hard segment is miscible with HDPE. In this study, a random ethylene–octene copolymer, Dow's Affinity 8842, was used as the compatibilizer at 7% net loading in a 63% PP/30% HDPE blend. The tensile strength in the compatibilized blend reportedly more than doubled and the elongation increased by over 6 times, compared with the uncompatibilized blend [14-13].

Titanate and zirconate coupling agents have also been used to compatibilize PP and PE to create useful products that contain more recyclate. For example, a titanate reportedly created a useful 80% LDPE, 20% PP regrind blend, enhanced by the catalytic "repolymerizing" effect of the additive. And in a HDPE blow-molded toy application, 0.2% loading of a zirconate agent, added within a color concentrate, allowed the amount of regrind in the product to increase from 50%–80%, while reducing cycle time, process temperature, and part weight [13-15, 14-2].

Other additives for recycling are not compatibilizers, but rather allow mixed scrap downstream to be more easily sorted, and thus more easily reused. For example, Eriez Magnetics' "PolyMag" system is said to simplify the sorting of mixed polymer streams using an additive that changes the magnetic properties of one of the streams of material, making it identifiable by specialized automated sorting equipment. Such an approach may be useful for operations that produce multilayer or overmolded parts with streams of multiple grades of material, which inevitably cross-contaminate when they become scrap. For example, in a pulverized stream of scrap from a multilayer HDPE blow-molding operation, the system reportedly has separated EVOH barrier resin containing the magnetic additive from the HDPE regrind [14-15].

14.3 ADDITIVES THAT PROMOTE PO BIODEGRADABILITY

Besides improving recyclability, another "green" issue related to additives is biodegradability, a desirable quality for disposable packaging. Yet POs are useful specifically because they are stable, inert, and do not degrade easily; thus the question of whether they can be formulated to truly degrade in a reasonable time remains controversial. Even when called "biodegradable," a PO product may actually require many years to degrade in real disposal situations, especially if it contains antioxidants that interfere with degradation. Nonetheless, there are a number of suppliers and converters who claim to supply PO compounds or additives that encourage their degradation after disposal. However, any claim that a compound or product can truly be called "biodegradable" may be questioned unless it is well supported within the framework of the industry's biodegradation guidelines and testing standards, such as ASTM D6400 or D6954 [14-18, 14-19, 14-22].

Since POs and most plastics resist biodegradation, a number of proprietary additives are offered as promoters of polymer degradation under various conditions. Most additives encourage the degradation and shortening of polymer chains in some way. These may be designed to initiate a chain reaction of chemical changes that reduce the polymer into a more degradable species, by reacting with the surrounding light, air, and soil. Some additives require the plastic to be exposed to moist composting conditions, at which point the additive initiates the hydrolysis and degradation of the polymer. Others help "oxo"-biodegrade a partially oxidized polymer in aerobic, outdoor conditions, chemically turning it into a form that is more digestible by microorganisms. These have found some use in agricultural mulch films designed to degrade each growing season, for example [3-3, 14-20].

Oxo-biodegradability additives may use cobalt as an oxidizing agent, but this is a restricted or regulated material in many countries. Other additives based on cornstarch require high loadings of up to 25% in POs, and the effectiveness of these compositions has been questioned. Efforts are also directed toward non-starch compounds that require lower loadings. A few examples of formulations below are said to be alternatives for encouraging biodegradation in POs:

- The PDQ-H masterbatch from Willow Ridge Plastics is specified for use at 1%–3% in POs, and reportedly can be used in clear food-contact film applications.
- Phoenix Plastics' Cel-Span 480 concentrate is said to use sunlight, air, and heat to encourage the degradation of extruded PE film (used at 2%–4% loadings).
- The "d2w" additive of Symphony Environmental Technologies reportedly is based on a metal salt that, after a designed time interval, catalyzes the cleavage of C–C bonds in POs, lowering molecular weight and encouraging biodegradation. As the molecular weight decreases below 40,000, water, oxygen, and microorganisms can more efficiently attack the material (1%–3% is needed in film extrusion).

But again, claims about such products are susceptible to industry scrutiny and independent test verification [3-3, 14-19, 14-21, 14-23, 14-24, 14-25].

Crosslinking

With the help of crosslinking agents, polyethylene in particular makes a remarkable transformation from commodity thermoplastic to useful engineering material. Crosslinking is often an unwanted result of free-radical degradation processes. But in medical, foam, pipe, wire/cable, and other PE applications, only controlled crosslinking provides the higher physical properties that are needed. This chapter will cover additives that cause crosslinking and discuss related issues, addressing:

- (15.1) What is the value of crosslinking PE?
- (15.2) What are the main types of agents and other methods that cause crosslinking?
- (15.3) How do these different agents and methods compare?

15.1 CROSSLINKED PE: ADVANTAGES AND APPLICATIONS

The crosslinking of polyethylene typically occurs during the degradation of the polymer, but PE crosslinked in a controlled way has useful properties. Methods for intentionally crosslinking extruded and molded PE have created an important niche of applications; crosslinked polyethylene (XLPE or PEX) is used for more resilient foams, tubing, film, sheet, cable coverings, and rotational moldings.

Crosslinking agents tie together carbon atoms from different chains of the polymer, transforming what were once viscous linear segments into an insoluble gel network that no longer melts or flows like a typical thermoplastic. The degree of crosslinking that occurs is determined by the percentage of polymer chains that are interconnected in this network, or in other words, the density of the gel component. Higher crosslink density is the result of more linkages per length of polymer chain, resulting in larger property changes.

Because crosslinking prevents molecules from slipping by each other in the amorphous regions of the resin, it especially affects temperature-dependent properties, giving the XLPE more thermoset-like qualities, including:

- higher long-term service temperatures, including better heat and dimensional stability (and as little as 1% the creep of the noncrosslinked polymer);
- improved impact resistance and environmental stress-cracking resistance (ESCR);
- higher tensile strength and stiffness properties, especially at high temperatures;
- better "shape memory" or "memory effect," in which a heated and deformed XL material holds its shape when cooled, and then returns to its original shape when reheated;
- improved cell formation in foams (stronger cell walls limit the cell-size distribution and prevent cells from blowing open);
- improved solvent resistance (though some solvents cause the XL material to swell);
- better electrical resistance and dielectric properties;
- and in some cases, improved weatherability.

Other properties may also be improved, depending on the degree of crosslinking in the polymer, the crosslinking agent or process, and the initial properties of the PO [3-3, 15-2, 15-4].

These properties make XLPE useful especially for extruded hot-water pipe, foam insulation, large containment tanks, and wire and cable coverings. For power-cable coverings or insulation, XLPE withstands higher temperatures from electrical overloads and short circuits than alternative materials such as PVC. Its memory effect can also be exploited for joining together components in these applications. Crosslinking properties are also used for more durable, multilayer silane-crosslinked PE pipe, which is becoming more competitive with copper pipe for water and fluid transport [15-2, 15-5].

However, there are at least two general caveats about crosslink-induced properties. One penalty for the property improvements is that crosslinked materials no longer truly melt at high temperatures, limiting their recyclability. And excessive crosslinking initiated in the melted polymer can result in brittle materials that lack crystalline regions—regions that also contribute to valuable mechanical properties. Thus ASTM pipe specifications (F 876-93) limit the degree of crosslinking in XLPE pipes to between 65% and 89% [3-3, 15-5].

15.2 CROSSLINKING AGENTS

The main commercially useful methods for crosslinking use agents whose sole purpose is to promote free-radical processes that essentially initiate polyethylene degradation. This ultimately creates bonds directly between carbon atoms on adjacent polymer chains. Some crosslinking agents, such as silanes, integrate themselves between polymers to form intermediate "bridging" links that connect one chain to another.

15.2.1 Peroxide-based agents

Organic peroxide agents are the most common agents used to initiate free radicals and thus controlled crosslinking in PE. The peroxides (ROOR) decompose in the heat of processing into peroxy radicals (RO•) that abstract (remove) hydrogen atoms from the polymer chain. This creates a free radical on the chain that can bond with a carbon radical on another chain (though the radicals can also react undesirably with other species in the compound). A number of competing mechanisms and factors can affect the efficiency of this crosslinking process:

- Shorter, low-molecular-weight polymer chains have less statistical chance of crosslinking with other chains.
- Crosslinking agents have no effect within the crystalline regions of a polymer.
- Because crosslinking encourages a mechanism of polymer degradation, effective processes must suppress unwanted oxidative degeneration of the polymer (by keeping oxygen out of the resin and process).
- Less-branched polymers and polymers with methyl groups (such as PP) tend to be more susceptible to degradation from unwanted chain-scission (breakage), rather than crosslinking.
- Primary antioxidant radical scavengers in a compound, otherwise useful as heat stabilizers, can suppress the desired crosslinking mechanism.

And perhaps most importantly is the timing of the crosslinking in the process: Fast-acting peroxides that decompose at lower temperatures may initiate crosslinking prematurely in the process—before the resin is fully formed into its final shape by extrusion or molding. Thus a peroxide must be chosen that fits the temperature and speed of the process. For high-voltage XLPE cable coverings, for example, peroxide crosslinkers are specifically chosen to fit the production rates of high-output "continuous vulcanizing" processes, which include a curing chamber several meters long [3-3, 15-2].

The appropriateness of a peroxide for a process can be determined by its "half-life," or the time required for half of its mass to decompose at processing temperatures. A dicumyl peroxide crosslinking initiator, for example, degrades relatively quickly compared with other peroxides, requiring only a few minutes for half of its mass to decompose at common PE processing temperatures. Other peroxides with longer half-lives take more time for decomposition/initiation. Typically, a processing rate is timed to allow a certain number of half-life periods to pass before the polymer is considered to be sufficiently crosslinked [3-3, 15-1].

15.2.2 Silane-based agents

Silane agents composed of silicon bonded to oxygen and various carbon (R) groups use a multi-step mechanism to form crosslinked networks between polymer chains. They first must be grafted onto a polymer's backbone radical (created with peroxides). They are then available to form "siloxane bridges" (–Si–O–Si–) by combining with grafted agents on other polymer chains, through hydrolysis/condensation reactions.

Silane-XLPE is commonly used for low-voltage cable insulation, and it also can be used for thick products. Improved crosslinking processes and properties, along with new metallocene POs, have reportedly allowed its use in more rigorous applications, such as under-the-floor hot-water heating pipes and better foams [15-2, 15-4].

Traditional silane-XLPE processes used by various manufacturers can differ, but most share the following basic steps in common. First a preliminary mixing and compounding process is required to graft vinyl silane onto PE, creating a pelletized copolymer (which must be kept dry to prevent premature crosslinking). In melt-processing by the end user, this grafted material is mixed with a pelletized PE masterbatch that contains a crosslinking catalyst to speed up curing. This blend is processed into the final product shape, which is crosslinked typically in a process using steam or hot water (or it may be allowed to cure simply using ambient conditions and weeks of time) [3-3, 15-2, 15-4].

Alternatively, as in Wacker Chemie's MONOSIL process, the extrusion steps can be combined into a one-step process for creating a readily crosslinkable compound. Other suppliers such as Dow Corning have also tried to make one-step crosslinking easier for processors by offering preblended formulations that contain the crosslinking catalyst, peroxide, and silane agent in one PE compound [15-3, 15-4].

Outside Europe and North America, a one-step "infusion" process is reportedly becoming more popular for lower-cost silane crosslinking of cable coverings. This process uses a crosslinkable PO compound that already incorporates a crosslinking catalyst. The complete formulation is mixed in a separate machine near or in-line with the cable extruder, where the grafting occurs. The approach reportedly saves around 10% in costs, and, like the MONOSIL process, offers more flexibility for adjusting crosslinked properties by the cable manufacturer [15-2].

15.2.3 Radiation-induced crosslinking

High-energy electron beams (e-beams) and UV radiation can also be used to form free radicals and initiate crosslinking, in continuous processes. Requiring no crosslinking additives, high-energy e-beams abstract hydrogen atoms from the polymer backbone, just as peroxides do. UV crosslinking requires photo-initiator additives, or sensitizers, and crosslinking bridge molecules in the compound for efficient, controlled crosslinking. However, both approaches depend on the penetration of the electrons or light into the resin for uniform crosslinking. Thus this radiation-induced crosslinking is typically limited to thin, unfilled or low-density resin applications, such as film, thin tubes, fibers, wire insulation, and foam. Greater-penetrating X-rays and gamma radiation have also been used to initiate crosslinking [3-3, 13-7].

E-beam crosslinking does provide some advantages over chemical crosslinking agents, however. In extruded pipe, researchers have found that radiation-crosslinked PE has equal or better burst resistance at high temperatures than silane-XLPE. And for rotomolded LLDPE gas tanks, e-beam crosslinking reportedly enhances low-temperature impact strength and ESCR. Moreover, e-beam crosslinking requires no additional chemical agents and has fewer process variables to control. However e-beam equipment is extremely costly, making contract service companies the only option for many processors wanting to use it [15-7].

15.3 FACTORS IN CHOOSING CROSSLINKING AGENTS

Given the differences in methods and materials mentioned above, various factors influence the choice of crosslinking approach:

- *Costs*: In terms of costs, crosslinking is often more of an "equipment issue" than an "additives issue." For example, considering the equipment required and processing steps, silane-XLPE processing is more limited to manufacturers who supply or use high volumes of grafted-silane material. But more silane-crosslinkable materials are being provided by these companies that can be processed by the end user on standard extrusion equipment. For continuous processes, irradiation processes for crosslinking can be cost-effective—but only if the large initial investment for the equipment can be justified and recovered. But despite its own costs, crosslinking can help offset some raw material costs; considering that crosslinking increases a resin's mechanical properties, the gauge or wall thickness of a product may be reduced relative to its noncrosslinked design, reducing raw material usage.

- *Scrap reuse*: Scrap XLPE coming from the extruder may be recyclable only if it is reused before crosslinking has progressed significantly. Thus, slower-curing, silane-based crosslinking and in-line, radiation-induced crosslinking offer more opportunities for scrap reuse. Recycling after crosslinking is difficult if not impossible, though at least one process has been developed for using supercritical alcohol in an extruder to decompose Si–O–Si crosslinks in silane-crosslinked PE. This reportedly allows the XLPE to be reprocessed and reused for wire and cable insulation.
- *Processing flexibility*: Overall, continuous processes such as extrusion, or slow molding processes such as rotational molding, are more suited to crosslinking. High-volume, continuous processes are more suited to peroxide and radiation crosslinking. For easier handling and dosing, peroxides and other agents are available as free-flowing masterbatches.
- *Part design*: Radiation-induced crosslinking is more limited to unfilled, thinner products than chemical crosslinking. But all part designs and crosslinking methods—for both thick and thin products—must ensure that crosslinking is not simply limited to the surface of the part.

Other factors may be more specific to the particular needs of wire and cable, foam, rotational molding, or other industries that depend on XLPE [3-3, 15-1, 15-2, 15-6].

CHAPTER 16

Sterilization and Radiation Resistance

The growing importance of medical plastics has allowed POs to step outside their traditional low-cost roles and serve in life-and-death situations. However, their use in medical components is complicated by the degree to which they can resist various sterilization methods, including those that use damaging radiation. At the same time, more heat-sterilizable food packaging also requires POs that resist hot retort treatments.

A couple of key questions addressed in this brief chapter include:

- (16.1) How do POs and additives respond to sterilizing radiation and chemicals?
- (16.2) What are some additives that are helpful in sterilization applications?

16.1 STERILIZATION EFFECTS ON PO PRODUCTS

Plastics for medical applications will likely to grow in use, especially for pouches, bottles, trays, wrap, syringes, and other sterile closures or packaging. The annual growth of medical packaging in the United States has been estimated at 6%, and POs are particularly positioned as the materials of choice for the lower-cost applications [16-1].

Medical parts and packages are typically sterilized using ionizing radiation (e-beams, X-rays, or gamma radiation), ethylene oxide (EtO) gas exposure, and autoclave steam sterilization. Each has its advantages, as well as potential damaging effects on the polymer, especially if the PO is exposed to multiple treatments.

16.1.1 Effects of irradiation sterilization

Common irradiation treatments use ionizing gamma radiation bombardment or (more recently) X-rays, which can deeply penetrate plastic parts. In comparison, e-beams sterilization treatments have about one-fifth the penetration power, and thus may require higher overall doses of radiation. These types of energy effectively kill microorganisms, but, similar to ultraviolet light, they also initiate free-radical degradation in the polymer structure, leading to molecular chain-scission (breakage) or crosslinking. Multiple doses of radiation accumulate the damaging effects from free-radical degradation initiated in the polymer, causing degradation and embrittlement—although this damage can be limited to some extent using extra antioxidants or stabilizers in the formulation.

Different POs respond differently to radiation treatments. PEs (particularly LDPE) can withstand higher total doses of radiation than PPs and many other polymers. A PE's strength and impact properties may even increase from the crosslinking mechanism initiated by the radiation. By contrast, homopolymer PP must be sufficiently stabilized to prevent chain-scission and losses in tensile properties, if it is to be used in articles such as syringes. Fortunately, POs, which are more often used for disposable, one-time-use items, often only need to withstand one or two irradiation treatments during their short lifetimes [3-4, 16-2, 16-3, 16-4, 16-5].

Various factors have been proposed as increasing the impact of gamma radiation, X-ray, or e-beam treatments on PO products:

- Low-molecular-weight resins or compounds with low antioxidant content are likely to be more negatively affected by radiation treatments.
- Thin products or fibers are more affected, especially if exposed to oxygen during irradiation, increasing oxidative degradation.
- Residual molded-in stresses in a component may serve as sites for chain-scission initiated by irradiation.
- Crystalline PP products are particularly susceptible to irradiation, because it initiates oxidative aging processes that limit product shelf-lives, gradually causing embrittlement or color changes (specifically, radiation accelerates the yellowing caused by phenolic antioxidants).
- The type and rate of radiation also affects how properties are changed; surface oxidation may be made worse by low dosing rates of gamma radiation, while ductility is reduced the most from X-rays and the least from e-beams.

Along with the above, other unpredictable property changes may also be observed in testing. Crosslinking and chain-scission processes may exchange their dominant roles, causing initial increases in elongation after a number of treatments, followed by dramatic embrittlement at higher dosages [3-4, 16-3, 16-4, 16-5].

16.1.2 Effects of EtO sterilization

EtO gas sterilization has declined in use because of its overall toxicity to operators, and polymers' reactivity with (and surface adsorption of) the EtO gas. Testing has shown negative property changes in POs from EtO treatments. For example, repeated treatments have produced a 50% reduction in HDPE tensile modulus, lower dart-impact resistance, and lower ultimate tensile elongation. In similar testing with PP, tensile yield modulus was reduced by 78% after only two EtO exposures [16-3].

16.1.3 Effects of high-temperature sterilization

Heat is the natural enemy not only of microorganisms, but also of POs. Heat sterilization stimulates free-radical degradation processes, though not necessarily to the same extent as irradiation sterilization. But its negative effects can still be significant in a PO product that has previously been gamma-ray-sterilized, stored for weeks or months, and then heat-sterilized. Steam autoclaving, performed in a pressurized chamber at 121°C–132°C for several minutes, may also cause stress relaxation or warping of the resin, acting as a kind of annealing treatment. Autoclaving can also reduce properties such as clarity; for example, PP bottles containing clarifying agents have shown increased haze after autoclaving. Low-temperature POs like PE are limited only to lower exposure temperatures and/or times. Medical applications may also use dry-heat sterilization treatments at over 165°C, essentially beyond the range of POs [3-4, 16-2, 16-3, 10-14].

Other kinds of heat-based sterilization are used in food applications. For instance, retortable packaging is typically exposed to 120°C for 30 minutes or more in retort sterilization treatments that cook the food inside the package. Used for hotels, restaurants, and the military, retortable pouches are made from multilayer films combining layers of POs and other polymers (see Case 16.1) [16-6].

16.2 ADDITIVE SOLUTIONS FOR STERILIZATION-RESISTANT POs

As mentioned above, extra stabilization is needed in some POs, particularly PP, to prevent induced oxidation and aging from sterilization treatments. Radiation-stabilized materials require a careful mix of primary and secondary antioxidants for optimum stabilization. However, given the multiple factors affecting sterilization degradation and the compounds' specialized nature, suppliers often conceal their stabilization formulations as proprietary information.

But some alternative stabilization strategies have been reported. For example, as alternatives to standard phenolic and phosphite antioxidants, non-yellowing HALS have been used for stabilizing PP for high-energy radiation

CASE 16.1 IMPROVED OLEFIN FILM LAYERS FOR HEAT-STERILIZED FOOD PACKAGING [2-28, 16-6]

Problem: Retortable food packaging is becoming more popular, but shelf-life, barrier properties, and heat resistance are limited.

Objective: An enhanced olefin-based film that can better resist the heat of retort sterilization.

Solution: COCs blended in the PO film layer.

For POs that undergo heat-sterilization methods, higher heat resistance without loss of properties is always desirable. With retortable food pouches, for example, there is more interest in multilayer film packaging systems that can better resist 120°C or higher retort sterilization treatments. These multilayer films must also serve as strong barriers to oxygen and moisture over weeks (or years) of food storage, especially when preserving food for military MREs ("meals, ready to eat"), for example.

One approach to enhancing the PO layer's properties in the pouches has been proposed by TOPS Advanced Polymers. It involves blending amorphous COCs in the PO film layer. (COCs are composed of ethylene linkages interspersed with norbornene cyclic hydrocarbons; these bridged ring elements are said to enhance stiffness, heat resistance, and barrier properties.)

Various film compositions of COC added to PP, HDPE, and LLDPE were tested by the company under retort conditions. Researchers found that the COC improved pouch seal strength and vapor transmission rate, with only slight losses in tear resistance. And after retort treatments, the COC content reportedly improved film stiffness, without causing other negative changes to properties or appearance.

treatments. ExxonMobil, for example, is one supplier that has developed (proprietary) HALS formulations for protecting sterilized PP. Reported research has also shown that radicals produced by radiation can be terminated or deactivated more effectively with the help of a "mobilizing" agent, such as hydrocarbon oil [3-4, 16-7].

Product developers have also increased PP formulations' resistance to radiation damage by blending in small amounts of single-site-catalyzed ethylene-based plastomers. Just 3% ethylene in copolymer PP reportedly has been found to help the compound resist the damaging effects of radiation more than more highly crystalline PP homopolymer, allowing more properties to be retained. For instance, an ExxonMobil patent calls out a proprietary PP formulation containing 5%–15% ethylene copolymer, 0.02%–0.25% HALS, 0.02%–0.25% phosphite secondary antioxidant, 0.1%–0.4% clarifying nucleator, and 0.05%–0.15% acid scavenger neutralizer. The researchers report that the higher the ethylene content is, the better the compound's resistance to embrittlement will be after radiation treatments. However, the higher ethylene content also tends to decrease the modulus, chemical resistance, and HDT of the PP [3-4, 16-8].

CHAPTER 17

Aesthetics Enhancement and Surface Modification

POs have become crucial materials not only for low-cost packaging, but also for durable and semi-durable automotive and medical components. The surface aesthetics of these molded or extruded PO products are attractive and consumer-friendly in a number of uses. But these products' aesthetic qualities can be harmed by abrasive handling, moisture, or microscopic organisms. Even the odor coming from a PO product's surface might need to be modified for its end use.

Although most interest in plastics focuses on their standard physical properties, the sensory external qualities of POs help these relatively low-strength materials take applications from more expensive, rigid engineering resins. Other chapters have touched on sensory characteristics as well (e.g., colorants and clarifiers), but this chapter will focus on additional issues of most current interest in the industry, including:

- (17.1) How can PO surfaces be both soft to the touch and scratch-resistant?
- (17.2) How do antifog additives prevent excessive condensation on PO surfaces?
- (17.3) What antimicrobial agents are useful for reducing microorganisms on PO surfaces?
- (17.4) How can the odors emitted from POs be modified to create a positive consumer experience?

Generally, the additives discussed in this chapter concern these superficial, harder-to-evaluate external properties. These organoleptic properties relate to the senses of sight, smell, taste, or touch, which help determine a consumer's full experience of a product. Additives can even address issues related to sound, as with anti-squeak additives that prevent noise that may result when expanded PO foam parts rub against other parts in vibrating automobiles, for example [17-25].

17.1 ANTI-SCRATCH ADDITIVES

POs are by nature soft materials, but they are more and more being asked to serve in durable products that require scratch-resistant surfaces. There is an apparent contradiction between asking a plastic to be both soft to the touch and also hard or tough enough to resist marring and surface damage from everyday use. Yet this is exactly what automobile manufacturers are demanding from PP/talc and TPO parts: grained surfaces that are attractive and durable but without the brittle, artificial feel of traditional rigid plastics.

By incorporating rubbery impact-modifying polymers into their formulations, PP-based TPOs already can supply a fair degree of tactile softness to automobile surfaces. But given their exposure to various “soft-touch” plastic products made from elastomers, consumers are likely to expect even softer TPOs. And since automobiles are not limited-use, throwaway consumer products, there is an additional need for these soft plastic surfaces to remain mar-free and scratch-resistant—both during energetic car-manufacturing processes and over years of consumer use. This need applies to the parts the driver normally touches, such as instrument panels and inner door trim with grained surfaces. It also applies to exterior parts such as bumper fascia, which face abrasive road materials [17-1, 17-4].

17.1.1 Conventional anti-scratch approaches

Industry experts point to several approaches that have been used to improve scratch and mar resistance. Their focus is particularly on TPOs and other POs that contain talc, which, despite its useful stiffening properties, worsens the appearance of scratch damage. These approaches usually lower the coefficient of surface friction of the material, reducing the amount of stress and damage experienced by the surface; or they otherwise toughen the surface. To avoid using relatively expensive coatings and laminates (such as paint films), many of these solutions rely on additives that make the surface more slippery or durable. Additive approaches include the use of lubricating migratory amide slip agents, polysiloxane (silicone oil) lubricants (such as PDMS), grafted polymer agents, and special fillers such as wollastonite and nanoclays, which have also shown some value. But each has drawbacks; for example:

- Migratory slip agents, though inexpensive, accumulate at the product’s surface, creating a stickiness on the surface when they degrade; or they can be washed off the surface completely.
- Silicone oil can be costly and can reduce the adhesion and paintability of the surface.

- Grafted-agent additives can reduce impact resistance.
- Some fillers may be difficult or expensive to incorporate effectively into the polymer mix.

Suppliers have also been busy developing special anti-scratch additives, or new combinations of additives, which do not have these disadvantages; this is because additives are potentially the lowest-cost approach for providing scratch resistance. (*Note*: Some of these additives have proprietary compositions, but the section below will present useful details about their composition when possible) [17-2, 17-3, 17-6, 17-8].

17.1.2 Evaluating anti-scratch additives

Product developers use several methods to determine the effectiveness of an anti-scratch solution. Scratch-testing methods that are popular in the automotive industry include the Ford Five-Finger Scratch Test, which, as its name implies, simulates various kinds of scratches possible from everyday use conditions. Visual ratings (1—best to 5—worst) of the sample after testing indicate the level of scratch resistance, according to how wide a scratch is visible and how much whitening results from the scratch. A related test method uses the Erichsen scratch tester, which applies a grid of scratches to a sample at different forces (typically 10 N for automotive manufacturing). In addition, crock meter tests evaluate the mar resistance of a surface by abrading it with abrasive media under load and then measuring the gloss change caused by testing. Complicating this testing and development is the fact that the PO grade, talc filler type, the decorative grain of the part surface, and even pigments can affect the measurable scratch resistance of a material [17-2, 17-4].

17.1.3 Alternative anti-scratch additives

Formulation developers have reported positive results from these tests when evaluating POs containing various additives or co-additives. These additive approaches could be seen as alternative to the approaches described above; a few are summarized below:

- *Co-additives that improve the performance of standard slip agents*: Migratory anti-scratch additives are easily wiped from the surface of nonpolar POs. However, co-additives that make the resin more polar have been proposed as a means for keeping the slip agents on the product surface. Polar additive combinations such as ethylene vinyl acetate copolymer (EVA) with amide slip agents reportedly have improved the scratch resistance of TPO. Also, “functionalized” POs grafted with a polar copolymer tend to reduce the blooming and loss of a slip agent. And inorganic filler particles such as silica can adsorb slip agent on their surfaces; this reportedly lowers friction more than with the slip agent alone and increases scratch resistance immediately (rather than after a migration period) [17-3].

- *Improved nonmigrating siloxane agents*: Agents such as the Tegomer organo-modified siloxane slip enhancer from Evonik are said to be long-lasting. The siloxane "backbone" of this material is molecularly anchored to the surface of the polymer. The additive, at 2%–3% loading in talc-filled PP, is said to create less scratch whitening in talc compounds than fatty amide, silicone oil, or grafted PO slip agents [17-4, 17-6].
- *Compounds with more finely micronized talc* particles show less tendency to be visibly scratched than compounds with standard, coarser talcs. Talc particles can also be surface-treated to improve a compound's scratch resistance. Both of these factors can also improve the performance of anti-scratch additives [17-6].
- *Alternative slip agents optimized for common TPOs*: For example, compared with erucamide agents, Ciba's Irgasurf SR 100 reportedly improves scratch performance and impact resistance, when used optimally at about 1%–3% loading in TPO compositions containing 20%–30% elastomer content and 10%–20% talc [17-5].
- *Advanced reactor polymerization processes*: Single-site metallocene catalyzed POs reportedly can produce PP with a fine, homogeneous dispersion of rubber regions and a soft, scratch-resistant surface. For example, LyondellBasell's Catalloy process and its Softell PP is said to provide improved scratch resistance and lower gloss, compared with standard TPO, and it can be compounded with glass fiber rather than talc [17-7].

17.2 ANTIFOGGING AGENTS

For multiple PO uses in food packaging and elsewhere, condensation and water buildup on the plastic surface can interfere with a consumer's view of a package's contents, or simply can be a nuisance. Surface-modifying agents that fight this fogging overlap with the migrating antistatic additives discussed in Chapter 6. Both antistatic and antifogging agents migrate to the surface and reduce surface tension, so that a thin, continuous, transparent film of water is formed rather than visible droplets. A variety of antifogging agents are effective for both short-term PE food-packaging film and long-term agricultural film use. These surfactants are usually simple migrating glycerol esters such as glycerol monostearate (GMS), glycerol mono-oleate (GMO), and more complex PGEs based on unsaturated fatty acids [17-12].

An antifog additive's effectiveness is usually measured with hot fog and cold fog tests. In testing, a beaker of room-temperature water is covered with polymer film containing the additive. After different time spans in hot (60 °C) or cold (4 °C–5 °C) temperatures, the type and size of condensation droplets on the film are observed and rated. Ratings can vary from "A," where the film is densely fogged with droplets, to "E," where the film is completely transparent. Repeated over a long time span of days or weeks, the tests indicate how quickly the migrating additives reach the film surface and become effective, and how long that effectiveness continues [6-1, 17-12].

With PE, the key performance criterion pursued by suppliers seems to be the speed with which these agents begin to work at the film's surface. However, the situation is more challenging for PP, which has higher crystallinity than PE and thus slows the migration of the antifog to the surface. For example, 0.3% of a standard PGE (Danisco's PGE O 80) in 50-µm LDPE blown film reportedly provides excellent ("E") antifog performance, but even 2% of the same PGE in PP film provides poorer "C" and "D" ratings, even after several days of migration time after production [17-10, 17-11, 17-12].

If higher loadings of glycerol esters are not adequate for PP, then smaller, faster-migrating agent molecules may have to be the solution. Accordingly, more antifogs are being improved for PP packaging. For example, testing has reportedly shown that 1% of an alternative PGE additive—Danisco's PGE 907—can provide "E" ratings in the 50-µm PP film mentioned above. Alternatively, Ampacet's Hydroclear antifog masterbatches are said to provide clarity for rigorous antifog applications such as PP films for precut salad bags or for foods that are packaged warm and then cooled. The agent in the masterbatch reduces the contact angle of water droplets on the surface. And cold fog tests with 5% of this masterbatch in 30-µm extruded film reportedly prevented droplets from forming within 15 minutes [17-9, 17-12].

As with other migratory additives, the thinner a multilayer film's gauge, the higher the concentration the antifog must be for good performance. And obviously, FDA or other food-contact approvals should be verified for each additive and concentration level as necessary; although PE antifogs are commonly approved, antifogs for PP have reportedly had trouble attaining unconditional food-use approval [17-12, 17-13].

17.3 ANTIMICROBIALS AND BIOCIDES

Especially in medical applications, microorganisms on a polymer product can be a threat to human health, if not also to the polymer itself. Fortunately for POs, and unlike other polymers, microbes generally do not eat PO molecules or typical PO additives (as they do with PVC's plasticizers). So the main issue here is to limit microbial growth on POs to keep their surfaces clean. Various organisms may affect the product's appearance or color, generate odors, or trap water, making the product unhygienic or limiting its shelf-life. Therefore, manufacturers that use POs for medical products, building products (such as WPCs), kitchen utensils, bathroom products, garbage bins, and electronic devices are seeking more fast-acting additives for killing bacteria and fungi (including mold and mildew) [3-30, 17-15, 17-17].

Antimicrobial agents or biocides can be used in the resin to control germ or fungus growth. To be useful, they must be present at the surface of the product. Various agents are effective, with various limitations; some may migrate excessively out of the plastic; others may allow microbes to mutate and become immune to the biocide. But overall, their use is expected to continue growing worldwide, and especially rapidly in Asia. Plasticized PVC is the biggest user of biocides, but POs reportedly consume about 20% of the market. As with all these additives, regulatory approvals are required for medical-device use, but use in consumer products has already begun. New regulatory directives such as the European Union's 2008 Biocidal Product Directive may affect both the quality of new additives and the speed with which they become available, with food and medical uses requiring special approvals [3-30, 17-15, 17-17].

Antimicrobial additives are based on an "alphabet soup" of complicated organic molecules, or increasingly on silver-ion-based inorganic compounds. For POs, organic fungicide compounds are based on 3-iodo-2-propynyl butyl carbamate (IPBC). Alternatively, a product such as Phoenix Plastics' Shield 5P is said to be based on "citrus extracts," which are said to retard bacteria, fungus, and algae growth in molded parts [17-15, 17-16].

Several producers provide silver-ion biocides (or copper-ion fungicides). In these, active metal ions are slowly released over long periods from an inert ceramic or glass carrier matrix. When released, the ions interfere with the cell's DNA and life processes. With AgION Technologies' silver antimicrobials, for example, the silver ions are pulled by moisture from a zeolite carrier incorporated as an additive in a coating. These are said to prevent the surface growth of microbes, making them useful for any human-contact product that also contacts potentially contaminated air or food or other materials. For preventing the spread of disease-causing bacteria and viruses on medical products, for example, high loadings of silver may be required. These products are available in PO masterbatches for easy use [17-15, 17-17, 17-18, 17-19].

Alternatively, a permanent, nonleaching antimicrobial introduced by Biosafe Inc. is said to "mechanically" puncture microbial cell walls (rather than simply act as a poison to microbes). This polymeric quaternary ammonium compound reportedly kills 99% of all bacteria in a few hours in PO fibers, well within the 24-hour industry standard for silver-based antimicrobials. The supplier recommends loadings of 0.2%–0.5% levels, which it says translate into one US dollar per kilogram of plastic or less. This is said to be less than with silver-based antimicrobials, which, required at higher loadings, can add up to twice as much cost [3-30, 17-14, 17-18].

Other additives are designed to repel not microbes, but rather larger damaging pests. For repelling damaging termites that attack plastics or wood fibers, an additive such as C-Tech's Termirepel is a heavy-metal-free additive. Or the company's Rodrepel additive is said to repel larger animals, such as mice which attack wire and cable coverings. Likewise, PolyOne's OnCap pest-control masterbatch is said to prevent rodents or termites from attacking cables alongside railroad tracks, for example, without killing the pests or polluting the environment [17-20, 17-24].

17.4 ODOR-MODIFYING ADDITIVES

Often in industry literature, references are made about the sometimes objectionable odors created by certain additives in plastics. Considering the importance of POs in applications that are meant to attract a consumer's (positive) attention, such as packaging, odor is indeed a critical "surface" characteristic. Thus certain additives have been commercialized to create specific odors coming from a product or the inside of an automobile—or at least to cover up unwanted odors from PO compounds.

Various tastes and odors might come from a number of polymer additives discussed in this book. With colorants, residual chlorine or sulfur might cause odors. Or slip agents produced from animal fatty acid sources can cause more odors than vegetable-based agents. In general, migratory additive molecules that contain functional groups with noncarbon atoms are said to be the most likely to cause objectionable tastes and odors. Additives and masterbatches can also degrade when stored, causing odors later when they are used in the resin. And excessive processing temperatures or sterilization treatments can cause odors [17-1, 17-22].

There are a number of odor-modifying additive approaches, when there are no alternatives to the compound ingredients that cause the odors. Antimicrobials or stripping agents may prevent certain odors, while encapsulated fragrance additives can help the PO product mimic aromas from nature or food. Stripping agents added during PO processing help remove the volatile agents (VOCs) that are developed during typical compounding and which can create odors after processing. Odor-neutralizing, -absorbing, and -modifying ingredients can be added to PO garbage bags, water-bottle caps, or even toothbrush handles.

And scent additives in packaging materials can be used to improve the sales of certain products. Scented masterbatches are provided by Polyvel, International Flavors & Fragrances Inc., and other suppliers. Their encapsulated odors are particularly more compatible for POs rather than with higher-temperature polymers, in which the odors might volatilize and be lost during processing. The science of scented additives may be just emerging [2-27, 17-1, 17-21, 17-25].

SECTION VII

Conclusion: Incorporating Additives

CHAPTER 18

Adding Additives to Resin

The conclusion of this book concerns another topic that by itself is suitable for book-length treatment—the physical integration of additives with resin. For the multiple situations faced by compounders and converters of POs, the issue is mainly an economic one, but there are engineering issues as well; for without proper blending and dispersion, many additives are simply not worth using in the first place.

Most additives have their own characteristics in handling and mixing with resin. And most additives have their own safety issues because they are fine particles or chemicals that can potentially affect the health of anyone exposed to them in an improperly protected operation. However, the industry is continually supplying more additives in better packaged forms—adding value to them at earlier stages in the production process, rather than only supplying additives in cheaper forms that can result in extra costs or problems down the line. Likewise, improved mixing and feeding systems provide more options for compounders and converters.

Thus the following relevant questions will guide this chapter:

- (18.1) What are some issues connected with handling additives in various forms (including health and safety issues)?
- (18.2) What are some improved screw-processing technologies for mixing additives with resin?
- (18.3) What are some equipment trends for "at-the-press" blending and feeding?
- (18.4) What are some key operational issues to consider when choosing among the various physical forms of additives?

18.1 HANDLING ADDITIVES

Whether in powder, paste, liquid, granule, flake, concentrate, or pelletized forms, the form in which an additive is handled and fed should suit an operation's equipment and practices; the end-product's processing and volumes; the sensitivity of the additive to storage conditions, spillage, and contamination; and last but most important, the health and safety of workers.

18.1.1 Practical handling issues

To a large extent, the form of an additive is simply related to the amount of upstream, value-added mixing and processing it undergoes. Raw powder or liquid additives come in bulk directly from their suppliers' raw processing lines; they require expert handling and extra distribution and mixing equipment to disperse properly into resin. At the other extreme, masterbatches with high additive loadings are produced with a great deal of attention toward additive dispersion and uniformity in a carrier resin so that the masterbatch pellet can be easily let down and mixed with resin during screw processing. The most economical choices for a large compounder may lie at one extreme; the best choice for an injection molder may lie at the other.

Intermediate additive forms between these extremes may also be useful. These combine advantages of flexibility, safe handling, cleanliness, and cost-effectiveness, while minimizing disadvantages of worker hazards, messy handling, additive loss, and clumping and bridging during feeding. Low-dusting additives in granular or flake forms are often easier to handle; or liquid concentrates may be easier to use, for operations having the proper equipment. Or, for example, "no-dust blends", developed by Great Lakes Chemical (Chemtura), were created as an easier-to-handle, safer option for packaging various additives together in small dry pellets. NDBs can preblend additives such as antioxidants, fillers, stearate lubricants, UV light absorbers, and nucleating agents into more processable forms for screw processing. Rather than using an inert carrier polymer like a masterbatch, the additives in each NDB are bound together using the lowest-melting additive as a binder for all the components. NDBs are said to allow faster melting at one low-melting point, better flow (for accurate dosing), and better additive dispersion in the resin (for higher properties). Overall cost benefits of NDBs have been identified for wire and cable, HDPE extrusion, and pipe extrusion, for example [4-23, 18-2].

18.1.2 Health and safety issues

Masterbatches, concentrates, and the NDB example also address worker health and safety, a major concern when handling polymer additives. In their raw forms, for example, some light stabilizers and antacids can be skin irritants, while fine particulates from common additives can create respiratory problems or the risk of explosion. Using non-combustible, non-dusting versions of these additives is just one approach, along with adequate ventilation, fume-extraction, dust-collection, static-dissipation, and other common factory protections, procedures, and policies. Additive feeders designed to fully enclose potentially hazardous additives are also helpful. However, the trend toward smaller particle fillers—particularly nanofillers—will undoubtedly complicate safe-handling issues as these fillers become more popular (and the possible negative health effects of nanofiller exposure are still not fully determined) [18-2, 18-3].

18.2 MIXING AND DISPERSING ADDITIVES INTO RESIN

18.2.1 Screw-processing developments

The technique of additive mixing performed by compounders is a sophisticated science that can only be summarized here. The value compounders add through the conveying, melting, mixing, dispersing, degassing, and pelletizing of resin compounds is essential for the plastics industry. Their work typically requires batch or continuous mixers with co-rotating rotors to supply the mixing power for formulations that are then sent to pelletizing extruders. Twin-screw extruders knead and disperse compound constituents using intermeshing screw flights of different pitches, shapes, and sizes to apply the necessary shear mixing and conveying of the melt. Gear pumps are often added to supply the necessary pressure to pelletize the melt stream when the screw extruder cannot [3-4].

Co-rotating twin-screw extruders in particular have undergone multiple design changes over the years. These changes have allowed them to supply increased throughputs of 75 tons/hour or more in PE compounding, for example. Screw profile designs that improve the “wiping” at the screw/screw interface have been optimized to improve shear and flow. Extruder designs have also been optimized for incorporating new PO fillers, such as glass spheres. Here, the compounding process must not destroy the hollow spheres, which are incorporated carefully downstream before a gear pump, used to increase pressure without damaging the spheres [18-4].

Single-screw extruders are also being improved. Here, barrier-type or Maddock mixing screws cause distributive and dispersive mixing by forcing melt constituents over carefully designed screw flights as the screw turns. Alternatively, a “CRD”-type screw uses slots in its slanted flights. This reportedly allows “elongational mixing,” which is said to provide better mixing of foamed or highly filled or colored resins, at lower melt temperatures. Technologies like these have reportedly been integrated into single-screw compounding units for running highly filled PO compounds. This would allow potentially lower purchasing and operating costs than with twin-screw extrusion, and better pressure generation (without a melt pump), making possible the direct extrusion of pipe, sheet, or profiles [18-5].

Also, various kinds of mixers placed inline with the extruder provide extra distributive and dispersive mixing, with low heat and low shear. These mixers break up filler and pigment agglomerates, without degrading fillers such as wood fiber. Both static mixers and mixers with rotor designs are used inline in compounding, extrusion, or injection molding. They reportedly are designed to create more homogeneous melts, equalizing both the melt flow rate and melt temperature profiles and distributing additives in the melt, preventing color streaks, flow lines, and other product inconsistencies [18-7, 18-8].

18.2.2 "Lean" compounding

Despite these options, the jobs of compounders and other processors of additives and POs are complicated by the wide range of additives available for allowing increasingly diverse PO applications. Even compounders of high-volume PO materials can benefit from a "leaner" flexibility to respond to market and customer changes.

Industry experts have suggested that compounders can follow lean manufacturing principles to help supply this flexibility. Following these principles minimizes wasted effort, scrap material, excessive inventories, process bottlenecks or delays, cleaning and changeover times, and the inefficient use of equipment. One approach requires the use of intermediate bulk containers (IBCs) to move additives and materials around an operation. This is said to make more efficient use of automation and human effort, ensuring a traceable, steady material flow between processes. For example, by using IBCs to insert a flexible preblending (formulation) step before batch mixing, an IBC approach can reportedly allow the near-100% use of the mixing equipment. Modular IBCs can also be used to feed mixed material directly into the extruder [18.1].

18.3 BLENDING AND FEEDING ADDITIVES

One of the more important advancements for handling additives are machine-mounted blending and feeding systems that consistently dose colorants or other additives into the resin. Whether used in injection or blow molding or other screw-processing operations, these systems allow a processor to automatically control the level of additives easily, allowing quicker adjustments or changeovers. Rather than volumetric blending methods or non-automated, off-line batch procedures, the newest blenders typically use sensitive mass scales or load cells for weight-based, gravimetric dosing of additives at the desired weight percentage.

A steady stream of new feeders, vacuum loaders, and blenders are announced by the trade press; the most recent models often include a number of features, such as:

- a wide range of mass throughputs to allow ingredients to be added at extremely high and extremely low levels;
- removable hoppers that allow quick material or color changes;
- stainless steel construction for all parts that contact the feed material;
- clear, see-through elements that allow visual confirmation of material flow;
- smooth internal walls to prevent bridging or sticking of flowing material;
- different material-discharge positions to allow variations for mounting multiple feeders on one machine;
- graphical touch-screen user interfaces for selecting preprogrammed recipes;
- electronics for monitoring throughput and recording quality data;
- programming that makes automatic adjustments to variations in multiple flows of additives or regrind;
- easy internal access for cleaning.

Sorting through all these options, users may find either that more expensive units pay for themselves through increased productivity and consistency, or that less-expensive blenders are perfectly adequate for a job [18-7, 18-9, 18-10, 18-11, 18-12].

PO processing using higher ranges of additive loadings places particular demands on both mixing and feeding equipment. For example, feeders and twin-screw extruders are being tested by the processing of wood-filled composite compounds (see Case 18.1).

18.4 CHOOSING THE BEST FORM OF AN ADDITIVE

Many of the factors that are considered when choosing the physical form of an additive have been mentioned above. Here, “physical form” simply refers to the means by which an additive is integrated into the final product. Thus the ideal physical form of an additive might be in a precompounded pellet that consistently matches the exact resin formulation needed for a product, supplied in flexible volumes by a large resin provider or compounder. More realistically, the form might be a compounded resin with a similar composition as the formulation that is needed, but which still requires adjustment or extra additives added at the press. These additive forms might be a masterbatch or

CASE 18.1 BLENDING ADDITIVES FOR WPCS [2-41, 18-4, 18-13, 18-14]

Problem: WPCs require extremely high loadings of additives that are difficult to blend with resin.

Objective: Options for handling and blending wood fiber and other WPC additives.

Solution: Exploring different options for arranging feeding equipment.

Given the high, 60%+ loadings of wood fiber demanded in WPCs, feeding and mixing equipment and systems must be robust. But at the same time, the systems must take into account the fibers' sensitivity to heat and moisture.

Whether in pelletizing or in direct-WPC-extrusion into boards or other forms, processors must make special accommodations for the wood. For example, overheating wood filler during processing can lead to a "burnt wood" smell, a sign of degradation. Complicating matters is the moisture content of the wood fiber (roughly 8% or more); this moisture level must be reduced through predrying and/or with venting from the screw during processing. Varying moisture content also can make accurate mass-based metering of the wood component percentage difficult, while predried wood filler carries an explosion risk.

Mixing the wood and resin in twin-screw extruders requires deep screw channels for low-shear distributive mixing. However, WPC compounds typically also include colorants, stabilizers, coupling agents, biocides, processing aids, and other additives, the mixing of which is challenged by the high wood content.

Fortunately, there is some flexibility in the way blenders and feeders can be mounted for WPC processing. Depending on the product/process constraints, the wood, additives and resin may be blended and fed together into the screw, or via separate feeders along the length of the extruder barrel. The wood might also be added downstream from the resin hopper to avoid overheating it. Simplifying matters somewhat in blending the additives are resin masterbatches formulated with the necessary additives for WPCs.

concentrate containing one or more additives in a compatible carrier pellet for easy integration with resin. Or the physical form might be a single-additive concentrate, raw dust or liquid, or other bulk additive added in a large twin-screw compounding operation.

The issues summarized below are just a few that are considered when choices are made about how to integrate additives with processing operation. There is no doubt that equipment improvements and larger market trends will make some of these issues more or less important for a given operation in the future.

Process flexibility and control: The concentrations or chemistries of many additives, such as colorants or processing aids, may often require adjustment during processing. This flexibility allows the processor to respond to part color-match problems, dimensional changes, shifting property requirements, excessive scrap, or other processing issues. Purchasing a heavily precompounded resin from a large supplier or compounder may not offer this flexibility; thus relevant questions here become: How much control over the resin's composition is needed at the conversion stage, which types of additives will likely require frequent adjustment, and which additives in the composition can be assumed to remain stable in the bulk resin?

Compounding vs. masterbatch/concentrates: Along with process flexibility, the choice of additive form may depend simply on the number of additives needed in a formulation. How many raw ingredients or concentrates need to be added to the neat resin? Can one or a few masterbatches be purchased that include all required additives, or is a compounder needed to integrate some, most, or all of the additives? Or can one "off-the-shelf" resin compound satisfy all requirements?

Transportation and logistics: Transportation costs and material availability will always vary according to global economic changes (e.g., the price of oil) or changes at suppliers, either local companies or those that are half-way around the world. Some widely available additives are easy to purchase and readily available; other, specialty additives may not be cost-effective to purchase or transport at the desired bulk quantities. Circumstances and costs thus may require the use of cheaper additives at higher loadings rather than more efficient, advanced additives. However, the cheapest additive forms to purchase or transport (such as glass-fiber rovings) may in turn require the highest equipment investment and sophistication (such as inline/direct compounding) to integrate them into a resin product.

Volumes and inventory: A lean manufacturing operation carries minimum inventories and creates minimum waste. Additives in concentrates or other forms, though they may be relatively inexpensive when initially purchased, are simply one more purchased product to stock on a shelf. Moreover, they are bulk products that may only be used slowly over time. They may also have limited shelf lives, acquiring moisture over time or otherwise degrading, causing odors or slowly or unpredictably transforming into useless material.

Health and safety regulations and concerns: As discussed in Section 18.1.2, dusty or liquid additive forms may create another layer of plant cost burden required for protecting worker health and safety. This begs the questions: Must an additive be handled in-house in a problematic form, or can a non-dusting or safer form of it be used? Or should the material's main compounding be done by another facility set up to handle the additive safely?

Blending and handling equipment investment: Likewise, blending and feeding additives require extra equipment in the conversion process for handling the additive and metering it accurately into the resin. How much of this equipment investment can be justified by the need for blending flexibility? Or, what is the minimum amount of blending equipment needed in the operation? And what about adjusting to future product changes or entirely new products, situations in which an operation might require the addition of extra additives at the press?

Mixing and dispersion issues: Because of difficulties in properly dispersing certain additives in the resin, this job may be better left to compounders that specialize in those additives. Conventional screw-processing equipment simply may not be suitable for effectively mixing certain additives with resin. An obvious example is nanoclay, which requires a compounding operation with the right specialized equipment, techniques, and expertise for proper dispersion (although adding nanofillers via masterbatch form is becoming one possible solution for nonspecialists). Other cases would include hard-to-disperse impact modifiers and long glass fibers, which require special pellet forms or direct compounding [18-6].

Consistency and credibility of an operation: Finally, much of the choice of additive forms relates simply to the knowledge and expertise of the people in an operation, and their familiarity with handling a given additive consistently. This is not an argument for only using compounding specialists to deal with additives; in fact, conversion or molding operations may have options for incorporating additives themselves that they are not yet aware of. Either way, much comes down to simply maintaining credibility with each customer, making the case that indeed the processor knows how to integrate additives to provide a consistent, acceptable (or superior) PO product.

References

(In each bracket, the number before the hyphen indicates the chapter in which the citation is first referenced.)

[1-1] Maier C, Calafut T. Polypropylene: the definitive user's guide and databook. Reference book (ISBN 1-88-420758-8)—Plastics Design Library. William Andrew Inc.; 1998.

[1-2] Vallaris N. Dow market overview. ABC 2005, conference proceedings. Society of Plastics Engineers; 2005.

[1-3] Modern plastics encyclopedia, reference book (ISBN 0-070-42805-0). McGraw-Hill; 2004.

[1-4] Markarian J. Design trends in colour and effects push plastics forward. Plastics Addit Compound [trade journal—Elsevier Ltd.] May/June 2006.

[1-5] Markarian J. North American compounders seek growth in innovation. Plastics Addit Compound [trade journal—Elsevier Ltd.] May/June 2006.

[1-6] Beene R. IAC chief touts in-house work to save money. Plastics News [trade journal—Crain Communications] 25 August 2008.

[1-7] O'Connor C. Right material, reliable results. Plastics News [trade journal—Crain Communications] 11 August 2008.

[1-8] Yang C. TPO formulations for bumper applications. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[1-9] Verespej M. More legislative challenges for plastics. Plastics News [trade journal—Crain Communications] 4 August 2008.

[1-10] Biron M. Fashionable and inevitable: free in every way halogen free, lead and other heavy metal free, VOC free… industry web report (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 14 August 2008).

[1-11] Verespej M. Even going green requires cutting costs. Plastics News [trade journal—Crain Communications] 22 December 2008.

[1-12] Bregar B. Collaboration takes advantage of scrap leather. Plastics News [trade journal—Crain Communications] 2 April 2007.

[1-13] Esposito F. Resin buyer sees volatile market. Plastics News [trade journal—Crain Communications] 9 April 2007.

[1-14] Esposito F. Resin makers positive despite challenges. Plastics News [trade journal—Crain Communications] 19 March 2007.

[1-15] Polypropylene market set to soar. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[2-1] Domestic production. Plastics News [trade journal—Crain Communications] 15 December 2006.

[2-2] Esposito F. Paying more for less. Plastics News [trade journal—Crain Communications] 13 October 2008.

[2-3] Global engineering resins market report, industry newsletter. CMAI; 29 October 2008.

[2-4] Esposito F. Asia, Middle East capacity to impact PP market. Plastics News [trade journal—Crain Communications] 9 April 2007.

[2-5] Blum HR. Functional fillers—a solution towards polymer sustainability and renewability. Functional fillers for plastics, conference proceedings. Intertech; 2008.

[2-6] Esposito F. Oil pushing PP price surge. Plastics News [trade journal—Crain Communications] 7 July 2008.

[2-7] Resin pricing histories. Plastics News [trade journal—Crain Communications] 29 December 2008.

[2-8] Esposito F. Global PP production growth to lower cost. Plastics News [trade journal—Crain Communications] 14 April 2008.

[2-9] Projected annual growth in PE demand, 2006–11. Plastics News [trade journal—Crain Communications] 9 April 2008.

[2-10] Strauss LC. What $300—a-barrel oil will mean for you. Barron's [business journal—Dow Jones & Company, Inc.] 8 September, 2008.

[2-11] Baumgarten S. Additives in flux. Industry report (www.icis.org). ICIS (Reed Business Information Ltd.); 28 March 2008 (downloaded 11 July 2008).

[2-12] Hess R. Plastics additives and additive concentrates markets and products. Leistritz Masterbatch Day, presentation (www.pa.clariant.com). Clariant GmbH; November 2003.

[2-13] Babinsky R, Gastrock F. Polyolefin additives amidst rapid change, suppliers seek to sell value. SPE Polyolefins 2006, conference proceedings. Society of Plastics Engineers; 2006.

[2-14] North American compounders. Plastics News [trade journal—Crain Communications] 4 August 2008.

[2-15] Major thermoplastic resin sales to US/Canadian compounders. Plastics News [trade journal—Crain Communications] 25 December 2006.

[2-16] N. American Compounders Survey, 2007. Plastics News [trade journal—Crain Communications] 2 July 2007.

[2-17] Kluth C. Compounding in Europe: market report. Plastics Eng [trade journal—Wiley Subscription Services] May 2008.

[2-18] Markarian J. US compounding industry faces challenging times. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2008.

[2-19] US Stretch & Shrink film demand. Plastics News [trade journal—Crain Communications] 28 January 2008.

[2-20] North American Film & Sheet manufacturers. Plastics News [trade journal—Crain Communications] 15 September 2008.

[2-21] Top injection molding materials. Plastics News [trade journal—Crain Communications] 4 April 2008.

[2-22] North American blow molders. Plastics News [trade journal—Crain Communications] 10 November 2008.

[2-23] Musgrave M. Developing ISBM-specific polypropylene resins. Annual Blow Molding Conference, conference proceedings. Society of Plastics Engineers; 2007.

[2-24] US caps and closures demand. Plastics News [trade journal—Crain Communications] 24/31 December 2007.

[2-25] US sterile packaging demand. Plastics News [trade journal—Crain Communications] 25 December 2006.

[2-26] Singhal RK. The US flexible packaging industry. International Polyolefins/Flexpack, conference proceedings. Society of Plastics Engineers; 2008.

[2-27] Markarian J. Compounders smell success in packaging. Plastics Addit Compound [trade journal—Elsevier Ltd.] January/February 2006.

[2-28] Tatarka PD. Polyolefin film enhancement using cyclic olefin copolymers for retort applications. International Polyolefins/Flexpack, conference proceedings. Society of Plastics Engineers; 2008.

[2-29] Bayer MaterialScience. Medical device and healthcare applications solutions with polycarbonates and polycarbonate blends. Online web seminar. Omnexus; 9 December 2008.

[2-30] Markarian J. Consumer demands push growth in additives for active packaging. Plastics Addit Compound [trade journal—Elsevier Ltd.] September/October 2006.

[2-31] Zerfas P. Fundamentals of processed meat packaging. International Polyolefins/Flexpack, conference proceedings. Society of Plastics Engineers; 2008.

[2-32] Cel-Span EG-600, supplier product fact sheet. Phoenix Plastics Co., Inc.

[2-33] Developmental bread mold inhibitor (trade name: ReNovus), supplier product fact sheet. Phoenix Plastics Co., Inc.

[2-34] Small European-made cars. Plastics News [trade journal—Crain Communications] 13 October 2008.

[2-35] Panel discussion (unpublished). Automotive Composites Conference and Exhibition. Society of Plastics Engineers; 16 September 2008.

[2-36] Panel discussion (unpublished). TPO Global Conference. Society of Plastics Engineers; 7 October 2008.

[2-37] Pomaville RM. Production scale-up of new thermoplastic composite resin formulations. Automotive Composites Conference and Exhibition, conference proceedings. Society of Plastics Engineers; 2008.

[2-38] Eller R. Economics, supply chain shifts, and the role of automotive TPOs. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[2-39] North American pipe, profile & tubing. Plastics News [trade journal—Crain Communications] 23 June 2008.

[2-40] Sachtleben reveals new anti-aging concept for polymers. Addit Polym [trade journal – Elsevier] October 2007.

[2-41] Markarian J. Wood–plastic composites: current trends in materials and processing. Plastics Addit Compound [trade journal—Elsevier Ltd.] September/October 2005.

[2-42] Florez L. Demand for agri-films rises as farmers seek greater productivity. Plastics Eng [trade journal—Society of Plastics Engineers] May 2007.

[2-43] How to boost growth and quality of roses, online product data sheet (www.specialchem4polymers.com). SpecialChem S.A. (downloaded 9 August 2008).

[2-44] Techmer PM. Film Additive Makes It Cooler Inside, supplier press release (www.techmerpm.com). Techmer PM, LLC; September 2007 (downloaded 23 October 2007).

[2-45] New masterbatches for greenhouse films. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[2-46] Mor E. Heat management IR-reflector technology for greenhouse. Agricultural Film, conference proceedings. Applied Market Information Ltd.; 2008.

[2-47] US decking demand. Plastics News [trade journal—Crain Communications] 29 December 2008.

[3-1] Stassen P. Stabilisation of polymer matrix polypropylene in LFT & new developments. SPE Automotive Composites Conference, conference proceedings. Society of Plastics Engineers; 2006.

[3-2] King RE. Introduction to polymer stabilization. American Chemical Society Meeting, conference proceedings. American Chemical Society/Ciba Specialty Chemicals; 2001.

[3-3] Peacock AJ. Handbook of polyethylene: structures, properties, and applications, reference book (ISBN 0-824-79546-6). Marcel Dekker; 2000.

[3-4] Pasquini N, editor. Polypropylene handbook, reference book (ISBN 1-569-90385-9). Hanser Gardner; 2005.

[3-5] Al-Malaika S, et al. editors. Specialty polymer additives, reference book (ISBN 0-632-05897-8). Blackwell; 2001.

[3-6] Fensterheim RJ. TNPP—Update on global risk assessments. International Polyolefins Conference, conference proceedings. Society of Plastics Engineers; 2008.

[3-7] Gelbin ME, et al. Liquid antioxidants for polyethylene. International Polyolefins Conference, conference proceedings. Society of Plastics Engineers; 2008.

[3-8] Ghosh J, et al. New additives approaches to BOPP film. Additives 2001, conference proceedings. Executive Conference Management; 2001.

[3-9] Lee RE, et al. The chemistry and service of stabilization. Additives 2001, conference proceedings; 2001.

[3-10] Polymer stabilizers for the plastics, rubber and polymer industries, supplier product guide. R.T. Vanderbilt Company, Inc.; 2007.

[3-11] Plastics additives guidebook for polyolefins, supplier product guide. Chemtura Corp.; 2007.

[3-12] Doverphos S-9228 high performance phosphite, supplier design guide. Dover Chemical Corp.

[3-13] We add performance with Doverphos HiPure 4 TNPP, supplier marketing literature. Dover Chemical Corp.; 2001.

[3-14] Chemtura's New Weston NPF 705 Phosphite Stabilizer: "Greener" Cost-Effective Alternative to TNPP, press release. Chemtura Corp.; 2007.

[3-15] We add performance with additive blends for polymer stabilization, supplier marketing literature. Dover Chemical Corp.

[3-16] Ciba TINUVIN 622, supplier data sheet. Ciba Specialty Chemicals, Inc.; 1999.

[3-17] Ciba IRGANOX E 201, supplier data sheet. Ciba Specialty Chemicals, Inc.; 1999.

[3-18] Irganox HP Products, supplier design guide (16142/e). Ciba Specialty Chemicals, Inc.

[3-19] Ciba IRGANOX HP 2215, supplier data sheet. Ciba Specialty Chemicals, Inc.; 1999.

[3-20] Ciba FIBERSTAB L 112, supplier data sheet. Ciba Specialty Chemicals, Inc.; 1999.

[3-21] Ciba CHIMASSORB 2020, supplier data sheet. Ciba Specialty Chemicals, Inc.; 2001.

[3-22] Ciba IRGASTAB FS 301, supplier data sheet. Ciba Specialty Chemicals, Inc.; 2002.

[3-23] Additives for polyolefins, supplier product guide (016269.00.094). Ciba Specialty Chemicals, Inc.

[3-24] Effects for polyolefins, supplier product guide (07-07-09.01). Ciba Specialty Chemicals, Inc.; 2007.

[3-25] Neri C, et al. Stabilization of polyolefin compounds for wire & cable applications. Wire & Cable, conference proceedings (paper no. 41). American Chemical Society; 2001.

[3-26] Stricker F, Horton M. New stabilizer solutions for polyolefin film grades. European PLACE Conference, conference proceedings. TAPPI; 2003.

[3-27] Plastic compositions including vitamin E for medical containers and methods for providing such compositions and containers, intellectual property description (WO/1999/003921). World Intellectual Property Organization; 1999.

[3-28] GUR (UWMWPE) with vitamin E for orthopedic implants, press release. Ticona Engineering Polymers; October 2007.

[3-29] Yu J, et al. A new phenol-free stabilizer solution for polypropylene fiber. International Polyolefins Conference, conference proceedings. Society of Plastics Engineers; 2008.

[3-30] Tolinski M. Plastics age gracefully. Plastics Eng [trade journal—Wiley Subscription Services] June 2008.

[3-31] Johnson B, et al. Benefits of no dust blends (NDB's). AddCon World 2001, conference proceedings. RAPRA; 2001.

[3-32] Maynard RB, Niedenzu PM. The interactions between TiO_2 surface and polymer additives. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[4-1] Maltby A. A clear improvement in UV absorption for polymers, online web presentation (www.croda.com). Croda Polymer Additives; 11 November 2008 (downloaded 8 December 2008).

[4-2] Solera P. Weathering and light stabilization of select plastic materials. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[4-3] Mara J. et al. Benzoates as UV stabilization strategies for polyolefins. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[4-4] New P-type black for premium performance in pressure pipe applications, supplier press release. Cabot Corp.; June 2006.

[4-5] A new angle on UV protection, supplier product guide (FP006 10/2008). Croda Europe Ltd.; 2008.

[4-6] Maier RD, et al. The significance of NOR technology for the UV stabilization of polyolefins. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[4-7] Botkin JH. Light stabilization of polypropylene: an independent perspective. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2007.

[4-8] Sherman LM. Additives for polyolefins: newest advances add ruggedness, good looks & easier processing. Plastics Technol [trade journal (www.ptonline.com)—Gardner Publications, Inc.] 2005 (downloaded 4 June 2007).

[4-9] Sale N. Pigment/additive interactions: the investigation of an urban legend. SPE CAD RETEC, conference proceedings. Society of Plastics Engineers; 2006.

[4-10] Uvinul 4050 H from BASF is the first light stabilizer in its class to obtain FDA approval for use in plastics, supplier press release. BASF; 10 October 2006.

[4-11] Goldstein S. Interaction of HALS and colorants. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[4-12] Glaser A, et al. Update of latest developments in light stabilization of polyolefins. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2006.

[4-13] Light stabilizers for polyolefins, supplier product guide. Ciba.

[4-14] Baleki R, et al. Fielding the challenges of artificial turf stabilization. FlexPack-Con and International Polyolefins 2008, conference proceedings. Society of Plastics Engineers; 2008.

[4-15] Lelli N. Stabilization and beyond: supporting the innovation effort of the thermoplastic concentrate industry. Thermoplastic Concentrates 2007, conference proceedings. Applied Market Information LLC; 2007.

[4-16] Nanoparticle boost Alok UV stabilizer. Plastics News [trade journal—Crain Communications] 24 September 2007.

[4-17] Wilson J, et al. Value of UV stabilizers for automotive applications. FlexPack-Con and International Polyolefins 2008, conference proceedings. Society of Plastics Engineers; 2008.

[4-18] Goldstein S, Coughlin G. Recent advances in UV stabilization systems for automotive TPO's. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2007.

[4-19] Stahmer M. Weathering of PE pipes, technical article (www.pipa.com.au). Plastics Industry Pipe Association of Australia Ltd.; November 2003 (downloaded 5 November 2008).

[4-20] New P-type black for premium performance in pressure pipe applications, supplier press release. Cabot Corp; June 2006.

[4-21] Fay JJ. Stabilization of polyolefin based wood plastic composites. WPCs 2006, conference proceedings. Executive Conference Management; 2006.

[4-22] de la Cruz M, Johnson BW. Aspects of UV stabilisation of agricultural films—benefits of a new additive physical form. Plasticulture Meeting, conference proceedings. Great Lakes Chemical Corp.; 2001.

[4-23] Cooper T. Some new developments in additive blends. New SA Plastics [trade journal—Summit Publishing] November 2004.

[4-24] Cytec keeps its commitment to help the agricultural film industry grow, supplier fact sheet (PAT-253-A). Cytec Industries Inc.; 2007.

[4-25] Solutions for the rotational molding industry, supplier fact sheet (PAT-252-A). Cytec Industries Inc.; 2007.

[4-26] Get a grip on light with Uvinul, supplier product guide (EVP 3306 e). BASF.

[4-27] Polymer additives product portfolio, supplier product guide (PAT-215-D). Cytec Industries Inc.; 2007.

[5-1] Non halogenated flame retardants, market survey (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 11 July 2008).

[5-2] US flame retardant market expected to exceed US$1 billion by 2011. Addit Polym [trade journal—Elsevier] October 2007.

[5-3] Flame retardant demand to rise. Plastics Addit Compound [trade journal—Elsevier] January/February 2008.

[5-4] Tolinski M. Pinpointing additive interactions. Plastics Eng [trade journal—Society of Plastics Engineers] February 2007.

[5-5] We add performance with superior, cost-effective flame retardants, supplier marketing literature. Dover Chemical Corp., ND.

[5-6] Dawson RB, Landry SD. Current issues & regulatory status concerning flame retardants, Environmental Division Newsletter, trade society newsletter. Society of Plastics Engineers; November 2006.

[5-7] Isarov A, et al. Non-halogen flame retardant polyolefin compounds via synergistic blends of metal hydroxides and mineral fillers. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2007.

[5-8] Luzenac talcs and Firebrake ZB, supplier marketing literature. Rio Tinto Minerals, ND.

[5-9] Pure Strategies, Inc., Decabromodiphenylether: an investigation of non-halogen substitutes in electronic enclosure and textile applications, report. University of Massachusetts Lowell; 2005.

[5-10] Ciba FLAMESTAB NOR 116, supplier marketing literature (FL.FL.0804.e.01). Ciba Inc.; 2008.

[5-11] Schmitt E. Phosphorous-based flame retardants for plastics. Plastics Addit Compound [trade journal—Elsevier] May/June 2007.

[5-12] Flame retardants: some recent developments. Plastics Addit Compound [trade journal—Elsevier] May/June 2008.

[5-13] Munro S, Farmer R. High performance nitrogen–phosphorous flame retardants for polypropylene. Polypropylene 2001, conference proceedings (11665). Maack Business Services; 2001.

[5-14] UL 94 Overview, web page (www.boedeker.com). Boedeker Plastics, Inc.; 2008 (downloaded 7 August 2008).

[5-15] Lassen C, et al. Deca-BDE and alternatives in electrical and electronic equipment—technical report (1141 2006). Danish Environmental Protection Agency; 2007.

[5-16] Information Sheet FMVSS 302, web page (www.sp.se). SP Technical Research Institute of Sweden (downloaded 8 August 2008).

[5-17] Datasheet DIN 4102, part 1, B2, web page (www.sp.se). SP Technical Research Institute of Sweden (downloaded 8 August 2008).

[5-18] Myszak EA, Sobus MT. New generation of inorganic colloids for flame retardancy and UV stabilization of polymers. Technical paper (www.nyacol.com). Nyacol Nano Technologies, Inc.; 2008 (downloaded 8 August).

[5-19] Buch R, et al. Silicone-based additives for thermoplastic resins providing improved mechanical processing and fire properties. Technical paper (www.specialchem4polymers.com) Dow Corning Corp.; 2001(downloaded 31 July 2008).

[5-20] Glow Wire Flammability Index—IEC 60695-5-12, web page (www.ides.com)—IDES; 2008 (downloaded 9 August 2008).

[5-21] Glow Wire Ignition Temperature—IEC 60695-5-13 web page (www.ides.com)—IDES; 2008 (downloaded 9 August 2008).

[5-22] Shields P. How to stabilize flame retardant polymer compounds. Technical paper. Ciba Specialty Chemicals; 2001.

[5-23] Lelli N. Stabilization and beyond: supporting the innovation effort of the thermoplastics concentrate industry. Thermoplastic Concentrates 2007, conference presentation. Ciba Specialty Chemicals; 2007.

[5-24] Mineral flame retardants for polyolefins. Technical presentation (www.specialchem4polymers.com). Albemarle Corp.; 2008 (downloaded 9 August 2008).

[5-25] Myszak EA. Use of submicron inorganic flame retardants in polymeric systems, technical paper. Nyacol Nano Technologies, Inc. (downloaded 8 August 2008).

[5-26] Italmatch introduces low-halogen flame retardant for polyolefins. Addit Polym [trade journal—Elsevier] February 2007.

[5-27] High flame retardancy and mechanical performance for HDPE tubes and cables, web page (www.specialchem4polymers.com). SpecialChem S.A. (downloaded 20 December 2007).

[5-28] Biron M. Halogen free retardant polypropylene HFFR PP synergistic effects between mineral additives and metal hydroxides, web article (www.specialchem4polymers.com). SpecialChem S.A.; 24 November 2008 (downloaded 4 December 2008).

[6-1] PCC Chemax polymer additives, supplier product guide. PCC Chemax, Inc.

[6-2] Antistatic additive packages, supplier product guide. Wells Plastics Ltd.

[6-3] Wheeler I. Metallic pigments in polymers, reference book (ISBN 1-859-57166-2). Rapra Technology Ltd; 1999.

[6-4] Fagan JJ, Peek CWL. EMI shielding solutions using stainless steel filled thermoplastic composites. Automotive Composites Conference and Exhibition, conference proceedings. Society of Plastics Engineers; 2005.

[6-5] Markarian J. New developments in antistatic and conductive additives. Plastics Addit Compound [trade journal—Elsevier Ltd.] September/October 2008.

[6-6] Tolinski M. Pinpointing additive interactions. Plastics Eng [trade journal—Society of Plastics Engineers] February 2007.

[6-7] Superb antistat for PE food packaging with GRINSTED PGE 308, supplier data sheet. Danisco USA.

[6-8] Efficient antistat performance in PP injection molding applications with DIMODAN HS K-A, supplier data sheet. Danisco A/S.

[6-9] A new efficient antistat for impact copolymer PP with DIMODAN HPL 70, supplier data sheet. Danisco USA.

[6-10] New conductive carbon blacks from Cabot, press release. Cabot Corp.; June 2006.

[6-11] Carbon black for pressure pipe, electrostatic discharge and polyolefin film. Mater World [trade journal (www.azom.com)—The Institute of Materials, Minerals and Mining] May 2003 (downloaded 5 November 2008).

[6-12] Biron M. Carbon blacks: what's new? Technical article (www.specialchem4-polymers.com); Elsevier Advanced Technology; 26 August 2008 (downloaded 29 August 2008).

[6-13] About xGnP, supplier web page (www.xgsciences.com). XG Sciences, Inc.; 2007 (downloaded 30 October 2008).

[6-14] Permanent antistatic additive, supplier web page (www.pebax.com). Arkema Pebax (downloaded 30 October 2008).

[6-15] MV 1074 SP 01, supplier data sheet (DPT/TDS/57006/August 2008). Arkema Pebax; 2008.

[6-16] Hausmann K. Permanent antistatic agent offers long term performance for films and containers. Plastics Addit Compound [trade journal—Elsevier Ltd.] May/June 2007.

[6-17] DuPont Entira antistat additives, supplier data sheet (K-17477 (10/07)). DuPont; 2007.

[6-18] Transparent, permanent, non-blooming and non-hydroscopic polymers with nano-zirconate antistatic agents, technical paper. Kenrich Petrochemicals, Inc.

[6-19] Ciba IRGASTAT P: permanent antistats for electronic and industrial applications, supplier marketing literature (R-0200.7). Ciba Specialty Chemicals; 2004.

[6-20] Diegritz W. Ciba IRGASTAT P permanent antistatic additives: solutions for industrial packaging, supplier technical presentation. Ciba Specialty Chemicals.

[6-21] How to make HDPE intermediate bulk containers (IBC) safe for the transportation of flammable liquids, technical article (www.omnexus.com). SpecialChem/Omnexus; 2007 (downloaded 10 September 2007).

[6-22] Transparent and colored ESD bags for content control, technical article (www.omnexus.com). SpecialChem-Omnexus; 2008 (downloaded 23 July 2008).

[6-23] Save money by eliminating cross-contamination and resulting off-spec materials stored in ESD, technical article (www.omnexus.com). SpecialChem/Omnexus; 2008 (downloaded 21 July 2008).

[6-24] Amine-free antistat for electronic packaging, supplier data sheet. Danisco USA.

[6-25] Nielsen B. New innovative antistat and antifog additives for PE and PP film. Addcon World 2006, conference proceedings. Rapra Technology Ltd.; 2006.

[6-26] Carbon nanotubes, supplier website (www.stratek-plastics.com). Stratek Plastic Ltd.; 2009 (downloaded 19 January 2009).

[6-27] Antistats, supplier technical service report (www.ampacet.com). Ampacet Corp. (downloaded 14 November 2008).

[6-28] Antistatic masterbatches, supplier technical service report (www.ampacet.com). Ampacet Corp. (downloaded 14 November 2008).

[7-1] Tolinski M. Polypropylene gets technical. Molding Syst [trade journal—Society of Manufacturing Engineers] May 1999.

[7-2] Tolinski M. Polyolefins' staying power. Plastics Eng [trade journal—Society of Plastics Engineers] April 2006.

[7-3] Tolinski M. Building new opportunities for plastics. Plastics Eng [trade journal—Wiley Subscription Services] October 2008.

[7-4] Schofield J, Sunderland P. Surface treatments for calcium carbonate fillers in high performance systems. Rubber Fibres Plastics Int [trade journal—Rapra Technology] March 2008.

[7-5] Product information: ExCAL CW calcium carbonate, supplier data sheets. Excalibar Minerals Inc.; 2005.

[7-6] Markarian J. Mineral modifiers fill the gap—keeping costs down without losing quality. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2007.

[7-7] Xia Z, Prendes D. A comparison study of inorganic fillers on the performance of polypropylene (Part 2). ANTEC, conference proceedings. Society of Plastics Engineers; 2007.

[7-8] Compounding compacted talc: some recent developments, technical article (www.specialchem4polymers.com). Elsevier Advanced Technology; 2002 (downloaded 12 December 2007).

[7-9] Talc in plastics, technical bulletin. Rio Tinto Minerals; 2007.

[7-10] Shearer G, Kochesfahani SH. An innovative masterbatch concept allows weight and cost reduction for automotive parts utilizing an extremely high aspect ratio talc. Automotive TPOs, conference proceedings. Society of Plastics Engineers; 2007.

[7-11] Kochesfahani SH, et al. Achieving extreme impact performance and tight dimensional stability with unique ultrafine talc technologies. Automotive TPOs, conference proceedings. Society of Plastics Engineers; 2007.

[7-12] Malacari PE. Ultrafine talc concentrates: the best way to enhance PP and TPO properties with a unique additive. Automotive TPOs, conference proceedings Society of Plastics Engineers; 2007.

[7-13] Wollastonite A to Z, supplier application guide (IN-403-05-1). Nyco Minerals Inc.; 2005.

[7-14] Chu J, et al. Scratch resistance of mineral-filled polypropylene materials. Polym Eng Sci 2000; April.

[7-15] Zilles JU. Wollastonite—a functional filler. Rubber Fibres Plastics Int [trade journal—Rapra Technology] March 2008.

[7-16] Tres PA. Hollow glass microspheres. Plastics Technol [trade journal] May 2007.

[7-17] Amos SE, et al. High strength, low density glass microspheres for extruded and injection molded plastics. Automotives TPOs, conference proceedings. Society of Plastics Engineers; 2007.

[7-18] Magnetite functional filler: a compounding study in polypropylene and polyamide, technical article (www.specialchem4polymers.com). Elsevier Advanced Technology; 2002 (downloaded 12 December 2007).

[7-19] New heavyweight compounds from Clariant give plastic parts a metal-like feel, technical article (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 8 August 2008).

[7-20] Hahn J, et al. Formulating high performance LLDPE blown films with optibloc high clarity antiblocks. Specialty Minerals Inc.; 2005. Technical paper (www.specialtyminerals.com).

[7-21] Kadir NA, et al. Physical and mechanical properties of mineral fillers filled polypropylene composites. International Conference and Exhibition on Composite Material & Nano-Structure, conference proceedings (www.itma.upm.edu.my). Universiti Putra Malaysia; 2008.

[7-22] About recycled glass, supplier web page (www.glassfillers.com). Vitro Minerals; 2008 (downloaded 29 August 2008).

[7-23] Karian HG, editor. Handbook of polypropylene and polypropylene composites, reference book (ISBN 0-824-74064-5, 9-780-8247-4064-1). CRC Press; 2003.

[7-24] Huber R, Auffermann J. Impact modifier boosts toughness of films. Plastics Addit Compound [trade journal—Elsevier Ltd.] January/February 2008.

[7-25] Williams MG, et al. New low-density EXACT plastomers and high performance impact modifiers. Automotive TPOs, conference proceedings (www.exxonmobilchemicals.com). Society of Plastics Engineers; 2003.

[7-26] Virosco J, Angove S. Polyolefin elastomers: adding new life to a maturing market. International Polyolefins 2008, conference proceedings. Society of Plastics Engineers; 2008.

[7-27] Lauzon M. Magnum plans Quebec compounding site. Plastics News [trade journal—Crain Communications] 29 August 2008.

[7-28] Process of discontinuous production of elastomeric alloys, presentation slides (www.spreelastglobal.com). Magnum D'Or Resources, Inc.; 2007 (downloaded 4 September 2008).

[7-29] US nanocomposites demand. Plastics News [trade journal—Crain Communications] 31 March 2008.

[7-30] World nanomaterial demand. Plastics News [trade journal—Crain Communications] 24/31 December 2007.

[7-31] Sherman LM. Nanocomposites: less hype, more hard work on commercial viability. Plastics Technol [trade journal—Gardner Publications] May 2007.

[7-32] Ramasubramanian H. Nanocomposites: fast track to commercialisation. Plastics Eng [trade journal—Society of Plastics Engineers] November 2007.

[7-33] NanoMax polyolefin masterbatch products, supplier technical bulletin (P-802). Nanocor; 2006.

[7-34] NaturalNano unveils mineral nanotube additives. Addit Polym [trade journal—Elsevier] January 2007.

[7-35] Successful pilot-scale demonstration of halloysite nanotubes in polypropylene, press release (2/22/07). NatualNano Inc.; 2007.

[7-36] Rich A. Carbon nanotubes: an additive with multi-functional properties and current commercial applications. Automotive Composites Conference and Exposition, conference proceedings. Society of Plastics Engineers; 2006.

[7-37] Schijve W. High performance at medium fibre length in long glass fibre polypropylene. Technical article (www.specialchem4polymers.com). Elsevier Advanced Technology; 2001(downloaded 14 May 2007).

[7-38] Markarian J. Long fibre reinforcement drives automotive market forward. Plastics Addit Compound [trade journal—Elsevier Ltd.] May/June 2005.

[7-39] Van Poucke J, James A. Long glass fiber polypropylene technology for automotive applications. Automotive Composites Conference, conference proceedings. Society of Plastics Engineers; 2006.

[7-40] Masterbatch technology utilized in new long fiber compounds from RTP Company, press release. RTP Company; 2007.

[7-41] Eller R. Future potential and inter-materials competition in lightweight automotive composites. Automotive Composites Conference, conference proceedings. Society of Plastics Engineers; 2004.

[7-42] Tolinski M. Tougher resins drive gears. Plastics Eng [trade journal—Society of Plastics Engineers] March 2008.

[7-43] Lindenfelser P. Thermoformable CFR composite sheet, a viable alternative to metal. Thermoforming Conference, verbal presentation. Society of Plastics Engineers; 2008.

[7-44] Tolinski M. Innovations in autos are plastics-specific. Plastics Eng [trade journal—Society of Plastics Engineers] January 2006.

[7-45] Florez L. Filling and reinforcing with natural fibers. Plastics Eng [trade journal—Wiley Subscription Services] April 2008.

[7-46] Pritchard G. Plants move up the reinforcement agenda. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2007.

[7-47] Denault J, et al. Wood and flax fiber polyolefin composites. Automotive Composites Conference, conference proceedings. Society of Plastics Engineers; 2006.

[7-48] Tolinski M. Real improvements for "fake wood". Plastics Eng [trade journal—Society of Plastics Engineers] June 2006.

[7-49] Tolinski M. Building new opportunities for plastics. Plastics Eng [trade journal—Wiley Subscription Services] October 2008.

[7-50] Aparecido dos Santos P, et al. Natural fibers plastic composites for automotive applications. Automotive Composites Conference and Exhibition, conference proceedings. Society of Plastics Engineers; 2008.

[7-51] Smith DR, Park DF. A novel organic fiber for fiber reinforced structural composites. Automotive Composites Conference and Exhibition, conference proceedings. Society of Plastics Engineers; 2008.

[7-52] Lee B-J, Jana SC. Strengthening of polyolefins by bottom-up self-assembly of POSS nanoparticles, ANTEC, conference proceedings. Society of Plastics Engineers; 2008.

[7-53] Mor E. Nanocomposite in polymeric materials. Die-Line, industry newsletter—California Film extruders and Converters Association; November 2006.

[7-54] Tolinski M. Small is big. Plastics Eng [trade journal—Society of Plastics Engineers] July 2007.

[7-55] Eberle APR, et al. Modeling the rheology and orientation distribution of short glass fibers suspended by polymeric fluids: simple shear flow. ANTEC, conference proceedings. Society of Plastics Engineers; 2007.

[7-56] Transmare 14CNF30.0.001, supplier data sheet. Transmare Compounding B.V.; 28 June 2006.

[7-57] Deans FS. Advances in high fiber composites. Automotive Composites Conference and Exhibition, conference proceedings. Society of Plastics Engineers; 2008.

[8-1] Barr G, Raisoni J. Heavy duty truck plastic composite door module and trim system. Automotive Innovation Awards, competition presentation. Society of Plastics Engineers; 2007.

[8-2] Dlugos C. Material selection for front-end carriers. Automotive Composites Conference and Exhibition, conference proceedings. Society of Plastics Engineers; 2006.

[8-3] 20% long glass filled polypropylene overhead console, Automotive Innovation Awards, competition presentation (unpublished). Society of Plastics Engineers; 2008.

[8-4] Injection molding compounding IMC LGF reinforced front-end carrier, Automotive Innovation Awards, competition presentation (unpublished). Society of Plastics Engineers; 2007.

[8-5] Viscomi P, et al. Composite assist step—2007 envoy/trailblazer, Automotive Innovation Awards, competition presentation (unpublished). Society of Plastics Engineers; 2007.

[8-6] Walton KL, Hemphill J. The case for higher impact efficiency elastomers for rigid TPOs, TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[8-7] Walia P, Ballot M. At-press TPO technology. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[8-8] Kochesfahani SH, et al. Talc-TPO automotive formulations for low temperature impact ductility at −30° and −40°C. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[8-9] Luzenac talcs to improve polyolefin pipe properties, supplier product literature (POL_T_GB_23_07). Rio Tinto Minerals; 2007.

[8-10] Luzenac talcs as reinforcing and barrier additives for polyethylene, supplier product literature (POL_T_GB_22_07). Rio Tinto Minerals; 2007.

[8-11] Jetfine and HAR talcs versus nanofillers in polypropylene, supplier product literature (POL_T_GB_25_07). Rio Tinto Minerals; 2007.

[8-12] Karian HG, et al. A study of the interaction between nanocomposites and titanium dioxide pigment in thin-film applications. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[8-13] Ciba IRGATEC NC 66—Highly effective stabilization system help expand the use of polyolefin nanocomposites, supplier product literature (PA-900A1C907, 07-093). Ciba; 2007.

[8-14] Miller SE. Dow Corning filler dispersion aid for the plastics/rubber industry, technical presentation (www.specialchem4polymers.com). Dow Corning Corporation (downloaded 12 August 2008).

[8-15] Bayer's nanotubes gain FDA approval. Plastics News [trade journal—Crain Communications] 12 January 2009.

[9-1] Harris RM. Coloring technology for plastics, reference books (ISBN 9781884207785) William Andrew Inc.; 1999

[9-2] Esposito F. Market improves, but faces hurdles. Plastics News [trade journal—Crain Communications] 10 March 2008.

[9-3] Kaverman J. The perception of color. Plastics Decorat [trade journal—Peterson Publications] July/August 2008.

[9-4] Fay JJ. Additives for the stabilization of plastics: building and construction applications. ANTEC 2008, conference presentation. Ciba Corp.; 2008.

[9-5] Bal JJ. Selection of colorants and other additives for durable products. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[9-6] Hocken J. The beneficial use of blanc fixe & zinc sulfide. Alternative White Pigments and TiO_2 Extenders, conference proceedings. Intertech; 2000.

[9-7] Smith C. Titanium oxide improved. Plastics News [trade journal—Crain Communications] 12 November 2007.

[9-8] Ampacet launches improved white masterbatch, celebrates 20 years in Europe. Addit Polym [trade journal—Elsevier] April 2007.

[9-9] The way forward for titanium dioxide? Plastics Addit Compound [trade journal—Elsevier Ltd.] May/June 2008.

[9-10] DuPont Titanium Technologies, technical presentation (www.specialchem4-polymers.com). SpecialChem S.A.; 2002 (downloaded 9 August 2008).

[9-11] New black colorants meet US food contact standards, supplier press release. Cabot Corporation; June 2006.

[9-12] Tolinski M. Both clarity & color push PP packaging. Plastics Eng [trade journal—Society of Plastics Engineers] January 2007.

[9-13] Grimm A, Weiser J. Transparent coloration of clarified polypropylene for packaging applications. Additives & Colors, conference proceedings. Society of Plastics Engineers; 2007.

[9-14] Waters JF. DiPietro TC. Enhancing the performance of polymeric dyes in polypropylene. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[9-15] Aluminum Pigment Center, website tutorial (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 31 July 2008).

[9-16] Schoppe R. Rotomolding with micro-pellets when using aluminum pigments. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[9-17] Kerr S. Creating special effects in plastics. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2006.

[9-18] Pearlescent effects offer enhanced stabilization. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[9-19] Color crystals, supplier product guide. Teknor Color Company.

[9-20] Ultracolor super concentrates, supplier product guide. Teknor Color Company.

[9-21] Clariant masterbatches showcases new visual and tactile effects at HBA 2007, press article. SpecialChem S.A.; 4 October 2007 (downloaded 14 November 2007).

[9-22] Special effect colors, supplier website (www.teknorapex.com). Teknor Apex Company; 2008 (downloaded 14 November 2008).

[9-23] Bregar B. Rotomolded fencing mimic stacked stone. Plastics News [trade journal—Crain Communications] 13 August 2007.

[9-24] Ciba UNITEX OB, supplier data sheet. Ciba Specialty Chemicals Inc.; 1999.

[9-25] Effect pigments for plastics, supplier product guide (BF-8811). BASF Corporation; 2007.

[9-26] New colors for construction application constitute A "color depot" for manufacturers of many building products, supplier press release. Teknor Color Company; 19 June 2006.

[9-27] CFP plans to expand color-delivery system. Plastics News [trade journal—Crain Communications] 24 March 2008.

[9-28] Ampacet presents warpage control products. Addit Polym [trade journal—Elsevier] December 2006.

[9-29] Newest "super-concentrates" provide highest level of melt distribution, greatest letdown ratio, supplier press release. Teknor Apex Company; 2008.

[9-30] Goldstein S. Interaction of HALS and colorants. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[9-31] Rosato D. Evaluating additive to additive interactions to maximize performance, website tutorial (www.specialchem4polymers.com). SpecialChem S.A.; 20 June 2008 (downloaded 14 August 2008).

[9-32] King RE. Discoloration resistant LLDPE: an overview of stabilization issues & opportunities. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2006.

[9-33] Tolinski M. Steady progress for paint-free TPOs. Plastics Eng [trade journal—Wiley Subscription Services] January 2008.

[9-34] Ampacet HDPE boasts high gloss. Plastics News [trade journal—Crain Communications] 5 February 2007.

[9-35] HDPE blow molded containers turn glossy with a new color masterbatch, news article (www.plastemart.com). Smartech Global Solutions Ltd. (downloaded 4 June 2007).

[9-36] Ampacet unveils new high-gloss and antistatic products. Addit Polym [trade journal—Elsevier] March 2007.

[9-37] Mulholland BM. Effect of additives on the color & appearance of plastics. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[9-38] Laser marking additive cleared for caps and closures. Plastics Addit Compound [trade journal—Elsevier Ltd.] January/February 2008.

[9-39] nGrain by Americhem offers the building products industry lasting, realistic woodgrain effects, supplier press release. Americhem; 24 September 2008.

[9-40] Color leveling additive allows package designers and molders to use the broadest palette of colors, supplier press release. Ampacet Corp.

[10-1] PP Nucleators Center, website tutorial (www.specialchem4polymers.com). SpecialChem S.A.; 2006 (downloaded 27 November 2006).

[10-2] Jacoby P. Beta nucleating masterbatch offers enhanced properties in polypropylene products. Plastics Addit Compound [trade journal—Elsevier Ltd.] May/June 2007.

[10-3] Ampacet designs masterbatch to minimize warpage when changing color in polyolefins, supplier press release. Ampacet Corp.; 29 October 2006

[10-4] Botkin JH, et al. Improving molding productivity and enhancing mechanical properties of polypropylene with nucleating agents. Technical paper. Ciba Specialty Chemicals Inc.; 2002.

[10-5] Horrocks M, Kerscher C. A novel agent for polyethylene. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2007.

[10-6] Rickle B. Fundamentals of extrusion & best practices: advancement in extruded sheet quality & capabilities. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[10-7] New PE nucleators enhance productivity and quality of HDPE blow molded bottles, case study (www.specialchem4polymers.com). SpecialChem S.A. (downloaded 31 July 2008).

[10-8] Malacari PE. Heterogeneous nucleation of PP: a new line of extremely efficient talc functional additives. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[10-9] Luzenac talcs for polypropylene nucleation, supplier product guide (POL_T_GB_31_07). Rio Tinto Minerals.

[10-10] Manolis Sherman L. New clarifiers & nucleators: they make polypropylene run clearer and faster. Plastics Technol [trade journal (www.ptonline.com)—Gardner Publications] 2005 (downloaded 27 November 2006).

[10-11] Milliken Chemical NPE 2006 Press Kit, bound press materials. Milliken & Company; 2006.

[10-12] Lauzon M. PP clarifiers prompting new applications. Plastics News [trade journal—Crain Communications] 21 June 2000.

[10-13] PP Clarifiers Center, website tutorial (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 24 November 2008).

[10-14] Kawamoto N, et al. Advantages of PP bottle application—ISBM-PP bottle with a novel clarifier. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[10-15] Maier RD, et al. Processability and end-use properties of polypropylene clarified by a high efficiency clarifier. ANTEC, conference proceedings. Society of Plastics Engineers; 2007.

[10-16] Lelli N. Stabilization and beyond: supporting the innovation effort of the thermoplastic concentrate industry. Thermoplastic Concentrates 2007, conference proceedings. Applied Market Information LLC; 2007.

[10-17] Ciba IRGACLEAR XT 386: next generation clarifier for polypropylene. Polypropylene 2006, conference proceedings. Maack Business Services; 2006.

[10-18] Burkhart B, et al. A novel PP clarifying agent creates a new aesthetics standard. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[10-19] Santamaria E, et al. Clarified polypropylene—old technology vs. new chemistry. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[10-20] Santamaria E, et al. Clarified polypropylene—a new benchmark. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2007.

[10-21] Antiblock masterbatch demonstrates clarity in polyethylene films. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2006.

[10-22] Miller TM. Yu TC. Extrusion blow molding of clarified rigid containers: influence of EXACT plastomers. SPE Polyolefins, conference proceedings. Society of Plastics Engineers; 2002.

[10-23] Graff G. Latest clarifiers open new markets for PP and PE, web article (www.omnexus.com). Omnexus/SpecialChem S.A.; 25 September 2008 (downloaded 3 October 2008).

[10-24] A clear choice for better plastics. R&D Daily [web journal (www.rdmag.com)—Advantage Business Media] 2008 (downloaded 26 November 2008).

[10-25] Manolis Sherman, L. New additives & colorants to debut at K 2007. Plastics Technol [trade journal (www.ptonline.com). Gardner Publications] 2007 (downloaded 26 November 2008).

[10-26] Jacoby P. Improving the thermoformability of polypropylene by modification of the crystal phase. Thermoforming, conference proceedings. Society of Plastics Engineers; 2006.

[10-27] Netzloff J. Increase your profitability in injection molded polypropylene parts with hyper nucleating agents, live web presentation. SpecialChem S.A.; 3 December 2008.

[11-1] Markarian J. Process modifiers improve output and cost competitiveness. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2006.

[11-2] Intelligent additive solutions for today's plastic industry, supplier product guide (TEB0031/062006). Struktol.

[11-3] Teufel N. Internal lubricants: process additives yield profits and productivity. Plastics Addit Compound [trade journal—Elsevier Ltd.] January 2001.

[11-4] Biron M. Additives for low energy process, web tutorial (www.specialchem4-polymers.com). SpecialChem S.A.; 2007 (downloaded 14 May 2007).

[11-5] Silicone gum: versatile and productive in a completely new form, supplier product guide. Wacker Chemie AG.

[11-6] EXCEREX Olefin Oligomer, supplier website (www.mitsuichemicals.com). Mitsui Chemicals America, Inc.; 2007 (downloaded 23 October 2007).

[11-7] High performance olefin oligomer for polymer processing, presentation (www.mitsuichemicals.com). Mitsui Chemicals, Inc.; 2007 (downloaded 28 November 2008).

[11-8] Axel introduces new additive that increases flow in HDPE at low loading levels, supplier press release. Axel Plastics Research Laboratories, Inc.; 2008.

[11-9] Gech M. Saxena PR. Boosting properties and performance of polyolefin compounds with silicone pellets. International Polyolefins 2007, conference proceedings. Society of Plastics Engineers; 2007.

[11-10] GENIOPLAST Pellet S, supplier product sheet (vers. 1.0/07.06.2008). Wacker Chemie AG; 2008.

[11-11] BYK-P 4101 processing additive for filled compounds, supplier fact sheet (TP-X51). BYK-Chemie GmbH.

[11-12] Plastaid multifunctional processing aids, supplier product guide. Fine Organics.

[11-13] Thermoplastics internal & external mold releases, supplier product guide. Axel Plastics Research Laboratories, Inc.

[11-14] MoldWiz additive improves flow and release in injection molded TPO instrument panels, supplier press release. Axel Plastics Research Laboratories, Inc.

[11-15] Sharma AH. New developments in flow and release additives for polyolefins. International Polyolefins 2008, conference proceedings. Society of Plastics Engineers; 2008.

[11-16] Better mold release in PP injection molding with DIMODAN HS K-A, supplier data sheet (HO 82006-IUS—02.08). Danisco A/S.

[11-17] LUPEROX organic peroxides, supplier product guide. Arkema Inc.; 2007.

[11-18] Polypropylene flow modifier concentrate for polypropylene injection molding applications, web tutorial (www.polyvel.com). Polyvel Inc.; 2006 (downloaded 22 July 2008).

[11-19] Yu J, Wallis E. Recent additive development for rotational molding. ANTEC, conference proceedings. Society of Plastics Engineers; 2008.

[11-20] Sheppard S. Advancements in clarified polypropylene blow molding. SPE Annual Blow Molding Conference, conference proceedings. Society of Plastics Engineers; 2007.

[11-21] Glass T. Fundamentals of polyolefin structure/property relationships in blow molding applications. SPE Annual Blow Molding Conference, conference proceedings. Society of Plastics Engineers; 2007.

[11-22] Tolinski M. Practical energy savings. Plastics Eng [trade journal—Society of Plastics Engineers] December 2007.

[11-23] Improving release in TPO, supplier fact sheet. Axel Plastics Research Laboratories, Inc.; 2007.

[11-24] Maltby A. Internal lubricants yield multiple benefits in injection molding. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2005.

[12-1] Patel P, Savargaonkar N. A review of additives for plastics: slips and antiblocks. Plastics Eng [trade journal—Society of Plastics Engineers] January 2007.

[12-2] Markarian J. Slip and antiblock additives: surface medication for film and sheet. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2007.

[12-3] Slip, website tutorial (www.croda.co.uk). Croda International Plc; 2008 (downloaded 30 October 2008).

[12-4] Finawax slip additives for polyolefins, supplier product guide. Fine Organics.

[12-5] Constant DR, Jester RD. Cyclic-olefinic copolymers as non-migrating polymeric slip additives in LDPE cast films. ANTEC 2002, conference proceedings. Society of Plastics Engineers; January 2002.

[12-6] Gardiner JL. Predicting LLDPE blown film properties with statistical design of experiments. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2006.

[12-7] Luzenac talcs for PE antiblocking, supplier product guide (POL_T_GB_32_07). Rio Tinto Minerals.

[12-8] Clear polyolefin film with specialty mineral talc antiblocks, web tutorial (www.specialtyminerals.com). Specialty Minerals Inc.; 2008 (downloaded 9 September 2008).

[12-9] Engineered minerals for high performance polymers and elastomers, supplier product guide (FF-608-07). World Minerals Inc.; 2007.

[12-10] IP1092 high clarity antiblock masterbatch, supplier press release. Ingenia Polymers Corp.; 24 October 2007.

[12-11] Patel PR. Process aid: a proactive approach. FlexPackCon 2008, conference proceedings. Society of Plastics Engineers; 2008.

[12-12] Bigio D, et al. Sharkskin elimination: fluoroelastomer coating evolution as a polymer processing aid. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[12-13] SOLEF and TECHNOFLON NM polymer processing aids (PPA), supplier product guide. Solvay Solexis SpA; 2007.

[12-14] Cel-Span 306P, supplier data sheet. Phoenix Plastics Co., Inc.

[12-15] COAD 12 calcium stearate series polyolefin applications, product data sheet (4/05). Norac, Inc.

[12-16] Baerlocher additives metallic stearates, supplier product guide (vers. 2). Baerlocher GmbH; December 2005.

[12-17] van Enckevort M. The effect of extrusion and casting process variables on stretch film performance. Stretch Film 2004, conference proceedings. AMI; 2004.

[12-18] Morris BA. Modifier for increasing output and reducing gauge variability in LLDPE blown film. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[12-19] Zhu S-H, et al. Effect of a polydimethylsiloxane-modified polyolefin additive on the extrusion of LLDPE. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[12-20] DuPont Entira Strong Polymer Modifier, supplier data sheet (K-11015 5/06). DuPont; 2006.

[12-21] Cel-Span 435, supplier data sheet. Phoenix Plastics Co., Inc.

[12-22] Ruiz FA. Modifying film conversion and end-use characteristics with mineral reinforcement, technical paper (www.heritage-plastics.com). Heritage Plastics, Inc. (downloaded 29 November 2008).

[12-23] Intelligent additive solutions for wood plastic composites, supplier product guide (TEB0040/062006). Struktol.

[12-24] Lubricant one-pack systems for wood plastic composites, supplier product guide (vers. 1). Baerlocher GmbH; September 2007.

[12-25] Peroxide concentrates, web tutorial (www.polyvel.com). Polyvel Inc.; 2006 (downloaded 29 November 2008).

[12-26] Finawax secondary amides, supplier product guide (1/2003). Fine Organics.

[12-27] Fulmer MS. Compounding and processing additives for woodfiber–plastic composites. 5th International Conference of Woodfiber–Plastic Composites, conference proceedings. Struktol Company of America; 1999.

[12-28] Tips for evaluating lubricant systems in wood–plastic composites, supplier fact sheet (TEB0036). Struktol Company of America.

[12-29] The use of calcium carbonate in molded containers, supplier technical service report. Ampacet.

[12-30] ANTIBLOCK—The basics, supplier technical service report. Ampacet.

[13-1] Eller R. Economics, supply chain shifts, and the role of automotive TPOs. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[13-2] Markarian J. Cost saving opportunities push foaming agents forward. Plastics Addit Compound [trade journal—Elsevier Ltd.] September/October 2006.

[13-3] Product guide, supplier product guide (www.bergeninternational.com). Bergen International (downloaded 18 December 2008).

[13-4] IF1890 CBA Compound (patent pending), supplier press release. Ingenia Polymers Corp.; 24 October 2007.

[13-5] Employing azodicarbonamide as a nucleating agent in thermoplastic foams, supplier technical report (www.ampacet.com). Ampacet (downloaded 14 November 2008).

[13-6] Optifoam: cost savings and high quality products in foaming extrusion, web page (www.omnexus.com)—SpecialChem—Omnexus; 2008 (downloaded 10 July 2008).

[13-7] The world of polyethylene foam, supplier web page (plastics.sabic.eu). Sabic Europe (downloaded 5 December 2007).

[13-8] Reedy international product selection, web product guide (www.myplasticsindustry.com). myPlasticsindustry (downloaded 30 October 2008).

[13-9] Gasbarro A. New TPO compounds enabling 30% weight reduction with injection molding. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[13-10] Introducing Adeka-Palmarole's blowing agents for synthetic wine corks, industry web site (www.packaging-int.com). Packaging International (downloaded 28 November 2007).

[13-11] Ticona Celstran LFRT and Trexel's MuCell Technology Deliver Flat, Light-Weight Large Parts in Less Time, supplier press release. Ticona Engineering Polymers; 3 March 2008.

[13-12] Cho SM, et al. Development of process and material for injection foaming molding for automotive. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[13-13] Ferretti D, Orzelski J. EPP Foam Insert for Compliance with FMVSS-202a, SPE Automotive Innovation Awards, unpublished presentation; 15 October, 2008.

[13-14] Gillette T. BMW X5 2nd Row EPP Rear Seat Cushion Riser, SPE Automotive Innovation Awards, unpublished presentation; 15 October, 2007.

[13-15] Monte SJ. Titanate and zirconate coupling agents in foamed polymers, technical report. Kenrich Petrochemicals Inc.

[13-16] Chaudhary AK, Jayaraman K. Foaming polypropylene with nanoclays. ANTEC 2008, conference proceedings. Society of Plastics Engineers; 2008.

[13-17] Sun NY. Technology attracts international group. Plastics News [trade journal—Crain Communications] 17 November 2008.

[14-1] Panchal J, et al. Effect of hyperdispersants in polyethylene masterbatch and rigid polyvinylchloride compound. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[14-2] Monte SJ, Neoalkoxy titanate and zirconate coupling agent additives in thermoplastics. Rapra Technology. Polym Polym Compos 2002; 10(1).

[14-3] Dean DM, et al. Novel coupling agents for high performance WPC. WPCs 2006, conference proceedings. Executive Conference Management; 2006.

[14-4] DuPont Fusabond coupling agents, supplier product guide (K-08789 (09/06)). DuPont; 2006.

[14-5] Clariant introduces licocene coupling agent for wood–plastic composites. Addit Polym [trade journal—Elsevier] March 2007.

[14-6] Yeh SK, et al. Synergistic effect of PP-g-MA and SEB-g-MA on polypropylene-based wood–plastic composites reinforced with nanoclay. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[14-7] Bowland C. A formulation study of long fiber thermoplastic polypropylene (part 1): the effects of coupling agent, glass content & resin properties on the mechanical properties. Automotive Composites Conference & Exhibition, conference proceedings. Society of Plastics Engineers; 2007.

[14-8] Monte SJ. Making nanotechnology work with titanates & zirconates, technical paper. Kenrich Petrochemical, Inc.

[14-9] US plastic bottle recycling, 2005. Plastics News [trade journal—Crain Communications] 24/31 December 2007.

[14-10] North American plastics recyclers. Plastics News [trade journal—Crain Communications] 26 May 2008.

[14-11] Ernst AC, van der Klooster FR. Using recycled polyethylene: avoiding the pitfalls, Environmental Division Newsletter, industry newsletter. Society of Plastics Engineers; November 2008.

[14-12] Tolinski M. Getting more from regrind. Plastics Eng [trade journal—Wiley Subscription Services] November 2008.

[14-13] Chen HY, et al. Olefin block copolymers as polyolefin blend compatibilizer. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[14-14] DuPont Fusabond E EC-603D, supplier product fact sheet (K-XXXXX 4/06). DuPont; 2006.

[14-15] Collins WJ. PolyMag process: separate & recover co-molded resins. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[14-16] Herron L, Fascias to air inlet panels: recycled TPO gets a new life in the GMT360 SPE Automotive Innovation Awards Competition, unpublished presentation. Society of Plastics Engineers; 2008.

[14-17] Nomination summaries, SPE Automotive Innovation Awards Competition, unpublished document. Society of Plastics Engineers; 2008.

[14-18] Hockensmith D. Industry debates: what's biodegradable? Plastics News [trade journal—Crain Communications] 6 October 2008.

[14-19] Hockensmith D. GP plastics challenged on "green" bag claims. Plastics News [trade journal—Crain Communications] 15 December 2008.

[14-20] A. Schulman provides "Green" Technologies for Real-World Solutions, supplier web site (www.aschulman.com). A. Schulman Inc.; 2008 (downloaded 26 December 2008).

[14-21] Product, supplier web site (www.biodegradableplastics.net). Willow Ridge Plastics, Inc. (downloaded 16 December 2008).

[14-22] Renstrom R. Officials: some mislabel bags as biodegradable. Plastics News [trade journal—Crain Communications] 11 June 2007.

[14-23] Cel-Span 480, supplier product data sheet. Phoenix Plastics Co. Inc.

[14-24] How does it work? supplier web site (www.degradable.net). Symphony Environmental Technologies Plc (downloaded 10 November 2008).

[14-25] Mojo S. Biodegradable and "activated" plastics, slide presentation (www.plastivida.org.br). Biodegradable Products Institute.

[14-26] Post-consumer plastic bottle recycled. Plastics News [trade journal—Crain Communications] 29 December 2008.

[14-27] Paisner M. The use of peroxide masterbatches in the processing of regrind and post consumer waste. GPEC 2008, conference proceedings. Society of Plastics Engineers; 2008.

[15-1] Polyvel concentrates for cross-linking PE. Plastics News [trade journal—Crain Communications] 21 July 2008.

[15-2] Wu T-S. Silane crosslinkable polyethylene compounds: applications and manufacturing methods. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2007.

[15-3] Silanes improve compounding of crosslinked polyethylene. Plastics Addit Compound [trade journal—Elsevier Ltd.] September/October 2006.

[15-4] Better yet silicones and silanes in the plastics industry, supplier product guide (5778e/09-04). Wacker-Chemie GmbH.

[15-5] Brown M. Application Note #117: PEX-AL-PEX Application, supplier application note (www.apcmedia.com). American Power Conversion; 2007 (downloaded 26 December 2008).

[15-6] Goto T. Material recycling of silane cross-linked polyethylene insulated cable using supercritical alcohol. Electrical Insulation News in Asia [trade journal—Institute of Electrical Engineers of Japan] October 2006.

[15-7] Tolinski M. Energetic surface treatments. Plastics Eng [trade journal—Society of Plastics Engineers] October 2007.

[16-1] Stewart R. Medical plastics & markets. Plastics Eng [trade journal—Society of Plastics Engineers] May 2007.

[16-2] Selection of materials for medical applications, supplier report. RTP Company; May 2007.

[16-3] The effect of sterilization methods on plastics and elastomers, reference book (ISBN 1-884207-10-3). Plastics Design Library, William Andrew Inc.; 1994.

[16-4] Material considerations: irradiation processing, technical report (www.sterigenics.com). Sterigenics (downloaded 29 December 2008).

[16-5] Portnoy RC, et al. A comparison of the effects on polypropylene using sterilizing doses from three different sources of ionizing radiation. ANTEC 2007, conference proceedings. Society of Plastics Engineers; 2007.

[16-6] Tolinski M. Packaging takes the heat. Plastics Eng [trade journal—Wiley Subscription Services] April 2008.

[16-7] Portnoy RC, et al. Superior stabilization of polypropylene for radiation sterilized medical devices and packages. ANTEC 2004, conference proceedings. Society of Plastics Engineers; 2004.

[16-8] Kozimor RA, Portnoy RC. Radiation tolerant polypropylene and its useful articles, patent (US patent 6231936); 15 May 2001.

[17-1] Biron M. Efficient marketing weapons: appealing plastics and rubbers thanks to their sensory properties, technical report (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 18 July 2008).

[17-2] Sharma AH, et al. Additive approaches to improving scratch and mar resistance in automotive polyolefins. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2004.

[17-3] Botkin JH. Technical approaches to improving the scratch resistance of TPO's part i: Surface lubrication. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2007.

[17-4] Lehmann K, Tomuschat P. New additive technology provides scratch resistance. Plastics Addit Compound [trade journal—Elsevier Ltd.] March/April 2008.

[17-5] Kaprinidis N, Wilson J. Improved impact properties of TPO/TPE systems containing scratch and mar additives: effect of the resin composition on the efficacy of the additives. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2007.

[17-6] Lehmann K, Malacari PE. Polyolefin based compounds scratch resistance guaranteed by functional alliance of talc and additive used. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[17-7] Glogovsky J. Softell—opening new dimensions and possibilities with soft touch polypropylene compounds. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[17-8] Weaver LB, et al. Low gloss flexible TPO sheeting for thermoforming. TPO Global Conference, conference proceedings. Society of Plastics Engineers; 2008.

[17-9] New antifog, special effect products unveiled by Ampacet. Addit Polym [trade journal—Elsevier] January 2007.

[17-10] Marketplace. Plastics News [trade journal—Crain Communications] 8 October 2007.

[17-11] Danisco introduces antifogging additives for PP film. Addit Polym [trade journal—Elsevier] April 2007.

[17-12] Nielsen B. New innovative antistat and antifog additives for PE and PP film. Addcon World 2006, conference proceedings. Rapra; 2006.

[17-13] Excellent antifog for polyethylene film with Grindsted PGE O 80, supplier data sheet. Danisco USA.

[17-14] Getman G. An advanced polymeric antimicrobial for plastic materials including polyolefin resins. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[17-15] Markarian J. Steady growth predicted for biocides. Plastics Addit Compound [trade journal—Elsevier Ltd.] January/February 2006.

[17-16] Shield 5P, supplier data sheet. Phoenix Plastics.

[17-17] Rosato D. Emerging antimicrobial additive technology, industry web report (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 10 September 2008).

[17-18] Biosafe silane-based antimicrobial products, supplier fact sheet. RTP Company; 2008.

[17-19] MCX 111281 Antimicrobial Masterbatch, supplier data sheet. RTP Company; 15 January 2007.

[17-20] Animal Aversives Center, industry web site (www.specialchem4polymers.com). SpecialChem S.A. (downloaded 30 December 2008).

[17-21] Renstrom R. Scent suppliers smell potential in plastics. Plastics News [trade journal—Crain Communications] 4 August 2008.

[17-22] Rosato D. Additive and colorant factors in food and beverage packaging, industry web report (www.specialchem4polymers.com). SpecialChem S.A.; 2008 (downloaded 19 November 2008).

[17-23] Just the ticket—new flame retardant compounds for the railways. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[17-24] BYK-P 4200 Stripping Agent to Reduce Odor and VOC Emissions in Polyolefin Compounds, supplier data sheet (09/2007). BYK-Chemie GmbH.

[17-25] Expanded polypropylene reduces in-car noise. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[18-1] Spook W. Lean compounding: the key to survival. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[18-2] Johnson BW, Keck-Antoine K. Benefits of polyethylene applications via the use of one-packs. Polyethylene 2001, conference proceedings. Maack Business Services; 2001.

[18-3] Markarian J. Worker health and safety in plastics compounding. Plastics Addit Compound [trade journal—Elsevier Ltd.] January/February 2008.

[18-4] Kapfer K. Twin screw extruders in compounding of polyolefins: an overview. International Polyolefins, conference proceedings. Society of Plastics Engineers; 2008.

[18-5] Rauwendaal C. New developments in mixing and screw design. Plastics Addit Compound [trade journal—Elsevier Ltd.] November/December 2008.

[18-6] Cho JW, et al. Nanocomposites: a single screw mixing study of nanoclay-filled polypropylene. ANTEC 2002, conference proceedings. Society of Plastics Engineers; 2008.

[18-7] Equipment news. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2008.

[18-8] Static mixers: consistency, high quality and cost savings for extruded parts, industry web fact sheet (www.omnexus.com). SpecialChem-Omnexus; 2008 (downloaded 10 July 2008).

[18-9] State of the art in gravimetric batch dosing and blending units, supplier press release. Motan Inc.

[18-10] Minicolor G—the new gravimetric dosing/mixing unit, supplier press release. Motan Inc.

[18-11] Flexibility key feature in Schenk's feeder. Plastics News [trade journal—Crain Communications] 7 July 2008.

[18-12] See-through vacuum loader has uniquely-shaped components for bridge-free discharge and "fastest material changes available", supplier press release. Novatec Inc.; 8 May 2007.

[18-13] Rothlin O. Processing wood–plastic composites place new demands on feeders. Plastics Addit Compound [trade journal—Elsevier Ltd.] July/August 2007.

[18-14] WPC masterbatch reduces additive costs. Plastics Addit Compound [trade journal—Elsevier Ltd.] September/October 2006.

Index