HANDBOOK FOR THE CHEMICAL ANALYSIS OF PLASTIC AND POLYMER ADDITIVES

Michael Bolgar
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PREFACE

Importance of Polymers

Polymers touch virtually all aspects of our lives, from everyday packaging to unseen applications such as gas pipelines under our streets. Polymers can include simple thermoplastics like polyethylene, a huge range of rubber compounds, adhesives, coatings, sealants, and many others. We wear polymers, we walk over them, we are fed with them, we coat our metals with protective polymers, and we even use polymers in the preparation of materials such as ceramics. Polymers, however, are seldom used in pure form. To make them more useful, easy to work with, or even more attractive, additives are added at many different times during the manufacturing process. The vast majority of commercial polymers are compounded with chemicals and/or other polymers to improve their usability or durability. These additives can be used to tune a polymer to a specific application, imparting high temperature oxidation resistance, improved flexibility, color retention, anti-static performance, or adding impact resistance to name a few examples. Compounding can also be done for technical reasons, where by a polymer is developed for a specific range of applications, using carefully selected additives. Other polymers are compounded for economic reasons, where a costly base polymer may be extended by addition of lower cost additives such as clays, reground polymer, other polymers, or a blowing agent that reduces density.

Formulation

Compounding is typically proprietary, with types and concentrations of ingredients carefully protected as intellectual property. Formulation information provided through Material Safety Data Sheet (MSDS) disclosure is typically incomplete or non-specific regarding the identity of all of the ingredients. Therefore, the end user may be left with little option but direct chemical analysis where composition information is imperative. Identifying the materials in the final plastic by analysis is extremely challenging. And although many reference handbooks currently exist that address the selection and application of performance-enhancing additives for polymers, there really is no good reference for the identification of these materials in finished goods. This handbook aims to fill this void by providing a comprehensive reference library for chemists, and to provide the information needed to extract, identify, and quantify additives used in polymers and plastic additives by common, readily available laboratory techniques such as gas chromatography/mass spectrometry (GC/MS).

Need for Analysis

The analysis of these materials is even more critical with recent increased interest in their environmental impact on ecological systems and human health. A number of frequently used additives, such as adipate plasticizers, have been identified as environmental pollutants, and the fate of these chemicals is the subject of on-going studies. Concern over the total composition of plastics has increased the focus on the total life cycle of polymeric materials. Government attention to toxic substances has increased over the years through the US Toxic Substances Control Act (TSCA) and the REACH initiative in the EU. These regulations may prohibit or otherwise impact the exportability of the plastic goods or other products that come in contact with the plastics. This, coupled with increased consumer attention and disclosures of 'chemicals' in consumer products, has increased the attention and need for a more complete analysis of polymeric materials. Combustion of rubber and plastic materials for energy production has also increased the awareness of organic and inorganic additives and the analysis of these products. Unintended combustion in fires, for example, has led to a significant increase in sensitivity to desorbed organic compounds and decomposition products in closed environments. This has significantly affected the formulation of polymeric materials used in aircraft furnishings and building wiring, for example.

Additives as Possible Hazards

Increased attention has also been directed to some of the higher volume organic additives in polymer compounds, such as plasticizers, flame-retardants, and antioxidants. Some of these are recognized endocrine disruptors, or suspected carcinogens. Ingredients that have been used for many years are now being increasingly detected during analysis when they may have been overlooked in the past for lack of reference information and/or suitable reference compounds. More and more consumer items are sold as 'phthalate free.' Some states such as California are taking additional steps to regulate these chemicals in consumer goods, for example, the recently proposed ban on bisphenol-A in children's items. Some of these compounds are regulated through government agencies such as the US Food and Drug Administration (FDA), and guidelines are available through the US Code of Federal Regulations (CFR) for use in consumer applications. Compared to regulations for other items, plastics and polymers are surprisingly unregulated for most uses. Consumers also need to know what is in the plastic that interacts with or holds their product. Everyone from toy manufacturers, to food packaging, pharmaceutical packaging and even wire and cable manufacturers, will be held accountable for the materials they use.

Analytical Protocols, Historical

Comprehensive protocols for the analysis of plastics/polymers need to be developed. In the past analytical protocols included extractions performed with a polar and a non-polar solvent which were used to extract organic compounds from a polymer for subsequent analysis by GC using a flame ionization detector (FID). But FID alone may not be a definitive test, since the identity is based on column retention time, which is not a unique characteristic for many of these complex organic compounds.

Purpose

This handbook's primary aim is to provide the tools to help a bench chemist to obtain a more complete listing of additives present in a particular matrix. The techniques that we have been using successfully are described in this book to help the analyst to correctly identify the complex nature of the materials that have been added to the plastic. We provide information on analyzing polymers through thermal desorption, and the use of GC with a mass selective detector (MSD). Many compounds break apart either during extraction or analysis, so identification by key fragments, and typical moieties for the final compound is critical. The use of the GC/MS system allows the analyst to characterize a compound based on the utilization of these fragments or moieties.

To add even more complexity to an already daunting challenge, many additives are disclosed by trade name, not chemical name or CAS number. This handbook aims to address all of these items by providing a listing that can be cross referenced by trade name, chemical name, CAS number, and even key mass unit ions from the GC/MS run. This handbook serves as a library of additives that can be used to identify individual compounds commonly found in plastics.

The primary function of this handbook is to serve as a reference for the chemist who is monitoring a plastic for regulatory or internal compliance. However, through many years of analysis of polymers for a wide range of applications, we have seen other applications where analysis could be used to troubleshoot or develop better compounding practices suited for specific applications, or for process improvement.

Polymers have undoubtedly changed the world and have provided countless products that directly improve our quality of life. As more regulations are promulgated, and with the continued oversight of possible health hazards presented by the multitude of additives incorporated into these plastics, it becomes imperative that the monitoring of these compounds can be supported by high-quality reference materials and dependable analytical techniques.

HOW TO USE THIS HANDBOOK

The information in this text was formatted in a consistent manner to make a usable bench handbook for a chemist performing real-world analyses. Compounds were chosen trying to obtain a representative sampling of all the primary classes of additives.

For each material or compound listed the following data is presented:

The data section:

- *Chemical Information.* Such information as the unique structure (if available), CAS and RTECs number (if available), common abbreviations, the formula and the molecular weight of the product can be found in this section.
- *Brand Names and Manufacturers.* Many of these products are produced under a variety of trade names. This section lists other companies that may produce this same compound as a different brand name. These other names are all cross-referenced in the subject index.
- *Physical Properties.* This section contains the general physical properties of the compound. For the solubilities the following abbreviations are used: U – Unknown, E – Emulsifiable.
- *Application, Regulatory and Environmental Information.* Information regarding the uses and regulations governing the compound are contained in this section. Laws and regulations, as well as our understanding of the toxicity and nature of chemicals change on an almost a daily basis. Please, use this text as a reference, but be sure to verify the current status of any regulations prior to proceeding with any project.

The Mass Spectral Information

This is the actual analytical run of the compound. It may contain from one to three pages, depending on the nature of the material. Tabulated for each spectrum is the mass-to-charge ratio of the five most abundant ions in the spectrum, as well as the molecular weight of the material.

Indexed in the back of the book are:

Appendix A

Chromatograms for all the compounds and their analytical conditions.

Appendix B

A list of definitions and abbreviations used in the text.

Subject Index

In addition to key words and terms, this index contains all the synonyms listed in text cross referenced to their corresponding pages.

Five Peak Index

This index can be used to identify an unknown compound from your own analytical data. It contains the following data, tabulated by the 100 percent abundance ion from each spectrum:

- The first five columns are the mass to charge ratios of the five most abundant ions in the spectrum - with the most abundant bolded.
- The MW column has the molecular weight of the parent compound as reported in the text.

- The relative intensities of the five most abundant ions (integral values, proportional to 100 for the most abundant ion).
- The compound name and page number of the compound of interest.

Molecular Weight Index

CAS Number Index

RTECs Number Index

The authors will be grateful to the readers of this handbook who make suggestions for future improvements, as well as calling our attention to any errors that may be discovered.

We look forward to adding additional materials in the future, and expanding the library of materials to cover an even greater sampling of the additives commonly found in consumer goods and the environment.

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CHAPTER 1

Overview of Polymers, Additives, and Processing

Introduction

Polymers are available in a wide range of formulations and properties achieved through selection of the base polymer and additives. Two types of chemical reactions produce polymers:

1) Condensation between polyfunctional molecules (monomers) that react with each other. This reaction is heat driven, sometimes with the aid of a catalyst. The longer the exposure to heat, the longer the polymer chain becomes. A common example of this is nylon, a reaction of a diamine with a dicarboxylic acid producing a polyamide.

2) Reaction of a molecule that is activated with an initiator to form a free radical. This free radical, when reacting with a "normal" molecule creates a new free radical, causing a full fledged chain reaction. This process creates, from a monomer, a long chain polymer instantaneously. No intermediate chain length polymers are present. This process is also called vinyl polymerization.

Both reactions are controlled by stoppers (telomers), which in the first process caps the ends, and in the second process captures the free radicals.

Most polymers are identified on the basis of their common name. Examples are polyethylene, polyvinyl chloride, butyl rubber, acrylonitrile-butadiene, styrene (co-polymer ABS). However, few polymers are used in pure form since they often require chemical modification to achieve optimum properties, and promote non-inherent performance. Some of these include improved resistance to oxidation, high temperatures, flammability, impact loads, surfactants, ultraviolet radiation, as well as modification of a wide range of other properties. The process of adding essential ingredients to polymers to achieve these results is termed *compounding*. However, it is generally not practical to precisely match the inherent properties of a base polymer to a specific application. While some polymers such as polyethylene are available with a wide range of properties based on a range of molecular weights, molecular weight distributions, and tacticity, other polymers have a finite range of properties for which compounding provides a practical method for adjustment of general or specific properties. For example, polyvinyl chloride is the most commonly used thermoplastic. In the raw form, this is a rigid, transparent polymer, however in the most familiar applications, this "vinyl" polymer is flexible and colored as in black electrical tape or a yellow rain coat.

As stated above, the modification to achieve these results is usually achieved by mixing a polymer with other polymers, both organic and inorganic materials including additives, metal powders, glass fibers, and other materials to match the end-use application.

This chapter addresses three basic classes of polymers and the approaches for processing them into compounds. These classes include thermoplastic polymers, and two types of elastomers - crosslinked elastomers, and thermoplastic elastomers. Compounds prepared from each class have a range of achievable properties, and each category of compounds may have overlapping properties. Each category is prepared by different technical approaches with varying controls, energy requirements, and limitations. A brief definition of each class follows. Also included, later in the chapter, is a detailed description of how additives influence the production process.

Overview of Polymeric Compounds

In the form of raw materials, polymers exhibit a wide range of compositions and properties. These properties can be enhanced or tuned to specific applications through the preparation of compounds. This section addresses three basic classes of polymers and the approaches for the preparation of compounds.

Thermoplastic Polymers

Thermoplastics are polymers that can be melted, made into a desired form, and then re-melted. Thermoplastics can be processed into a desired shape through many processes, the most common of which are injection molding and extrusion. Blow molding, transfer molding, calendaring, casting, and other forming operations are all possible with thermoplastics.

Elastomers

The properties that define polymers as an elastomer are that they must be amorphous when unstretched and must be above their glass transition temperature to be elastic. This can be compared to thermoplastics that must be crystalline or must be used below this temperature to preserve dimensional stability.

Crosslinked elastomers are polymers that are first prepared by compounding a base elastomeric polymer with property-modifying additives and a reactive crosslinking agent. Polymers of this type can be formed into a desired shape through many different operations, however the final operation requires that the shaped article be heated to a temperature at which the crosslinking agent decomposes to produce free radicals. These radicals react with the base polymer to form chemical crosslinks transforming the linear "two dimensional chain" into a "three dimensional object". Retaining elastomeric properties with the shape "frozen" by virtue of the chemical crosslinks. This class of material cannot be melted and reformed. Alternate crosslinking methods are used for special applications including the use of ionizing (gamma) radiation, ultraviolet radiation, and water-initiated (silanol) cure systems.

Thermoplastic elastomers are a more recently developed class of polymer in which the neat polymer has inherently elastomeric properties, yet it behaves thermoplastically. With some limitations, these materials can be formed by essentially the same operations as thermoplastics, but the final object has elastomeric behavior. Objects molded with thermoplastic elastomers can be melted and re-shaped. Since these are not crosslinked, their creep resistance and extended high temperature use are limited.

Compounding Objectives

Compounds must behave as a *system*, consisting of the base polymer and additives, selected to achieve a set of final properties. During compounding, mixing must occur at two fundamental levels; dispersive mixing and distributive mixing. *Dispersive mixing* relies on shear action to blend the additives into the polymer. Dispersive mixing must overcome differences in viscosity, surface energy, chemical compatibility, melting temperature, and others. Improperly dispersed polymer compounds will typically contain domains where ingredients have not been blended properly, as shown in Figure 1-1. Dispersive mixing focuses on short-range blending of the compound, while distributive mixing addresses the overall homogeneity of a batch. *Distributive mixing* places different requirements on the mixing process, depending on the type of equipment that is being used. This will be further addressed in the "Compounding Supplement" at the end of the chapter.

During the compounding process, it is essential that all ingredients added to a polymer remain in the compound in a manner that assures functionality. Thermal degradation and excessive shear action may selectively degrade different additives. It is imperative that processes are developed and validated by functional testing of the final compound. Mixing processes must be very carefully controlled to assure consistent quality. Variations in compound quality can have an adverse and varying impact on components prepared from the compound.

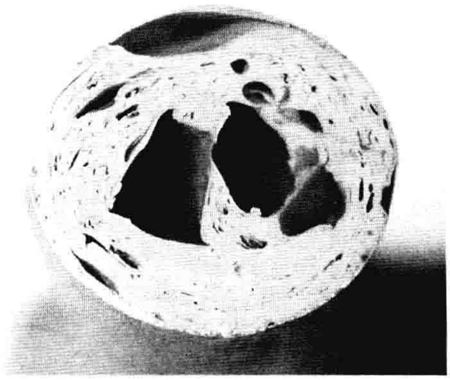

Figure 1-1 Example of Poorly Mixed Polymer Compound

Thermoplastic Compounding

Thermoplastic compounds are typically prepared by mixing organic and/or inorganic compounds with a single base polymer, copolymers, or blends. The base polymer may consist of a chemically bonded blend such as the block copolymer acrylonitrile-butadiene styrene (ABS) or a second base polymer may be used to enhance the overall end properties of the compound.

A base polymer, such as an ethylene-propylene (EP) copolymer, can be acquired in a range of compositions, molecular weights, various ethylene-to-propylene ratios, various molecular weight distributions, and a range of densities. Each of these variations results in a base polymer that has specific practical properties such as flexibility, elastic recovery, tensile strength and thermal limit to name a few. As a base polymer, ethylene-propylene polymers and most other non-crosslinked elastomers have no significant commercial application, since they are essentially a liquid with very high viscosity.

Organic Additives

Antioxidants

Thermoplastics may contain a wide range of organic additives that are incorporated into the additives to improve selected properties. In virtually all cases, an antioxidant must be added to allow the compound to be blended with other ingredients, to be pelletized or chopped into intermediate form, and to survive thermal stresses associated with the final forming process. In some cases, the base polymer is blended with an antioxidant at the time of preparation of the base resin. This type of antioxidant is intended to add thermal stability for processing considerations. External antioxidants can also be added to improve shelf life of the product and/or to improve its high temperature stability, while adding a stability margin during thermal processing.