HANDBOOK OF THERMOPLASTIC ELASTOMERS

Second Edition

Edited by
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CHARLES P. RADER

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PREFACE

Since publication of the first edition of this *Handbook*, the usage of thermoplastic elastomers (TPEs) has doubled, with a compounded annual growth rate of approximately 9 percent. This second edition summarizes and documents the technological and commercial progress that has given rise to this phenomenal rate of growth. Over the past decade, numerous suppliers and users of thermoplastic elastomers have entered the field, and some have retired from it, a process that almost certainly will continue.

This *Handbook* is intended to serve the broad spectrum of professionals actively engaged in the field of thermoplastic elastomers, which has seen a growth rate four to six times that of the rubber and plastics industries. As TPEs embrace both rubber and plastics technology, this book will be useful to rubber and plastics technologists with a broad variety of specific interests.

This edition emphasizes commercial practice and practical application rather than research activity. Technology and innovation are stressed, with polymer science functioning as a basis for understanding and communication. We have focused on those TPEs that we consider to be of significant commercial importance—the ones now used in the fabrication of useful articles, or which probably will be so used in the foreseeable future.

Prospects are excellent that TPEs will enjoy their unusually high growth rate well into the 1990s, with the annual rate of growth ranging between 6 and 10 percent. Thermoplastic elastomers are truly "where the action is," and likely will continue to be! The next few years, will certainly be exciting to watch.

We wish to thank the various contributors to this edition. These authors are acknowledged experts in their respective areas, and have worked tirelessly to produce superior manuscripts. We thank the many reviewers, who have carefully read these chapters and made valuable suggestions. Thanks are due also to our numerous colleagues and friends who have generously provided much competent advice and guidance in the preparation and publication of this book.

Benjamin M. Walker and Charles P. Rader

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PART I

MATERIALS

Chapter 1

INTRODUCTION

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1.1 THERMOPLASTIC ELASTOMERS AND THE RUBBER AND PLASTICS INDUSTRIES

A thermoplastic elastomer (TPE) is a rubbery material with the fabrication characteristics of a conventional thermoplastic and the performance properties of a conventional thermoset rubber. TPEs are processed by the same methods—extrusion, injection molding, blow molding, and so on—and with the same equipment as used for thermoplastics such as polyethylene, polypropylene, or polyvinyl chloride. The properties of a TPE, on the other hand, are extremely similar to those of a conventional rubber such as natural rubber, SBR, or EPDM. This rapidly growing field thus brings together the conventional commercial and technical disciplines of rubber and thermoplastics. Those persons most knowledgeable in processing TPEs are in the plastics industry; however, those most knowledgeable in marketing rubber articles fabricated from TPEs are in the rubber industry.

Since the days of Charles Goodyear in the 1840s and John Wesley Hyatt in the 1860s, the rubber and plastics industries and the disciplines associated with each have grown and prospered immensely, each making a unique contribution to twentieth-century society. Each of these giant industries is tens of billions of dollars in size. Thus, for more than a century, the rubber and plastics businesses and disciplines have coexisted with only modest interaction between them, each

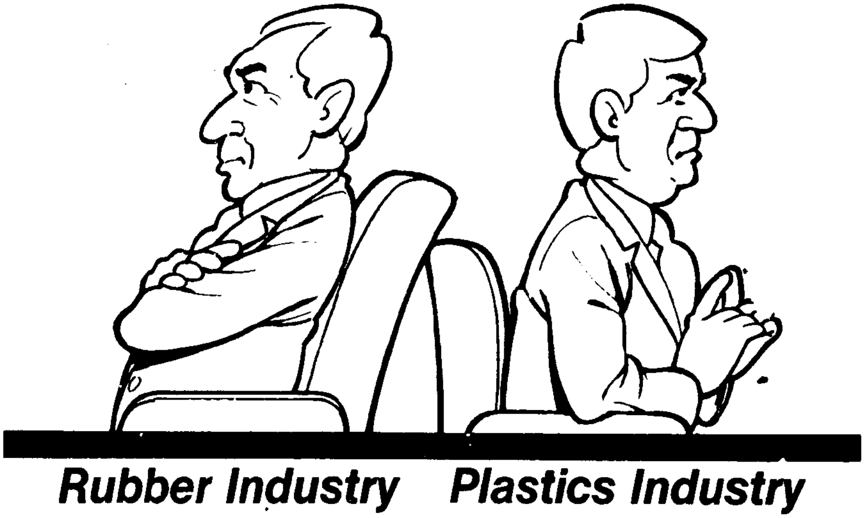

Figure 1-1. Two persons, sitting back to back and not talking to each other, personify a situation that has existed between the rubber and plastics industries for more than a century.

with its own materials, technology, fabrication methods, markets, jargon, and ways of doing things. Communication between the two (Figure 1-1) has been only modest at best, although their mutual proximity has been great.

The growing importance of thermoplastic elastomers has forced a progressive increase in the interaction between the rubber and plastics industries. This increase will most likely continue until the end of this century. The properties, applications, and marketing of TPE articles lie primarily in the province of the conventional rubber industry, whereas the processing and fabrication of these articles lie within the plastics industry. The thermoplastic elastomers industry, then, has one foot squarely in the thermoplastics industry and the other in the rubber industry. Each of these feet is constantly growing (Figure 1-2). There is excellent reason to believe that the barriers between these two giant industries will continue to shrink.

1.2 HISTORY AND GROWTH

TPEs first appeared as commercial entities during the late 1950s, with the introduction of thermoplastic polyurethane elastomers by both B. F. Goodrich and Mobay Chemical. This was followed by the production of styrene butadiene and styrene isoprene block copolymers by the Shell Chemical Company during the middle and late 1960s. A significant innovation in the TPE field was the commercial introduction of copolyester block copolymers by the Du Pont Company during the early 1970s, which was followed by the introduction of a group of rubber–plastic blends—primarily polypropylene and EPDM rubber—by the

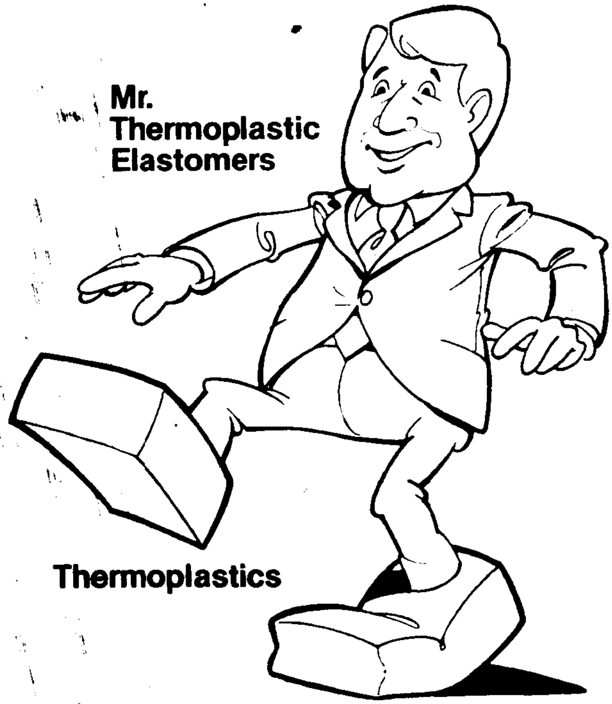

Figure 1-2. The relatively new field of thermoplastic elastomers rests with one foot in the plastics industry and the other in the rubber industry.

Uniroyal Chemical Company. By the late 1970s, when the first edition of this *Handbook* was published, TPEs were beginning to make an impact in the rubber products marketplace.

The 1980s saw the introduction of elastomeric alloy thermoplastic vulcanizates (TPVs), by the Monsanto Chemical Company in 1981, and elastomeric alloy melt processible rubbers (MPRs), by the Du Pont Company in 1985. The Monsanto TPV, based upon a unique process of dynamic vulcanization, consists of a two-phase system—a finely divided dispersion of a highly vulcanized rubber phase in a continuous phase of polyolefin. The Du Pont material is said to be single-phase. Thermoplastic polyamide elastomers are another high performance class of TPEs that have appeared during the 1980s (Rilsan, Upjohn).

The rapid increase in the use of thermoplastic elastomers is shown by Figure 1-3, which gives the consumption of these materials in the United States between 1960 and the present, with the projected consumption to the end of this century. It is most interesting that since the writing of the first edition of this *Handbook*, the U.S. consumption of TPEs has approximately doubled. Thus, at the beginning of 1987, the usage of thermoplastic elastomers in the United States was approximately 450 million pounds per year, with the worldwide usage

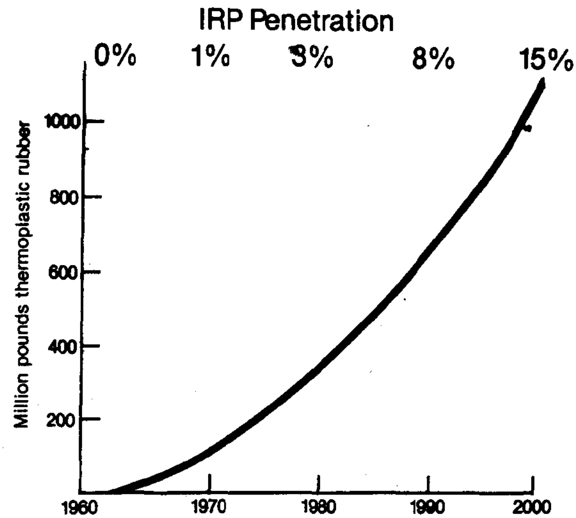

Figure 1-3. Actual and projected growth of TPEs in the United States for the period 1960–2000.

lying between 900 million and 1 billion pounds. By the early to mid-1990s, the U.S. consumption of TPEs should approach or exceed the magic 1 billion pounds per year, whereas the worldwide usage of these materials should approach approximately 2 billion pounds per year. Chapter 9 of this book details the past growth of the various markets for TPEs, and Chapter 15 covers their projected growth.

Various marketing projections for TPEs estimate a growth of 6 to 12 percent per year for the next decade, with the most probable figure being 7 to 8 percent. This growth rate is several times that of the mature rubber and plastics industries, each taken as a whole. The growth of each of these industries should parallel approximately that of the national and world economies, with the growth rate likely averaging between 1 and 2 percent per year. A salient conclusion is that the growth rate of the thermoplastic elastomers industry over the next decade will be several times that of either the rubber or the plastics industry. Thus, one can safely say that thermoplastic elastomers are where the action is, and where it will continue to be.

1.3 ADVANTAGES AND DISADVANTAGES

Thermoplastic elastomers offer a variety of practical advantages over conventional thermoset rubbers. Among these advantages are:

(1) Little or no compounding or blending. Most TPEs are fully formulated and ready for use as received. A commercial TPE is related to a thermosetting elastomer as a modern cake mix is related to flour. A TPE is fully mixed and ready for fabrication.

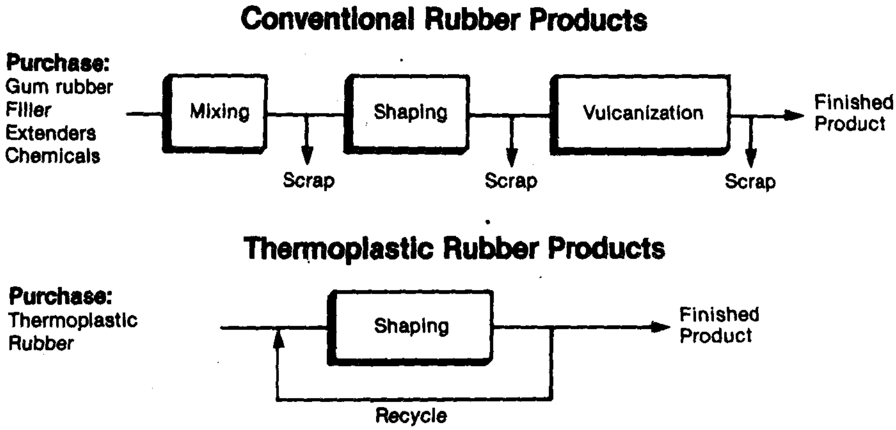

Figure 1-4. Comparison of thermoset and thermoplastic processing.

(2) Simpler processing with fewer steps. TPEs have the processing simplicity of a thermoplastic (Figure 1-4), giving more efficient processing and significantly lower cost for the finished rubber article.
(3) Shorter fabrication times (i.e., faster cycles), also leading to lower finished part costs. The TPE molding cycle is commonly measured in seconds, compared to minutes for the molding and vulcanization of a thermoset rubber. Thus, the productivity of a given piece of processing equipment is greatly improved.
(4) Recycling of scrap material (regrind). After each step, the scrap resulting from thermoset processing usually is discarded. Some fabrication methods will generate a weight of scrap comparable to that of the finished part. As with thermoplastics, the regrind from TPE processing can be recycled to give finished parts with the same properties as virgin material.
(5) Lower energy consumption. This is a result of the lower cycle times and the simpler processing of TPEs.
(6) Better quality control and closer tolerances on fabricated parts.
(7) Lower quality control costs, because of the greater reproducibility and consistency of the properties of TPE resins.
(8) In most cases, a density lower than that of a comparable thermoset rubber, giving additional cost savings. Both rubber and plastics are used on a volume basis; however, they are commonly purchased on a weight basis.

As all materials do, thermoplastic elastomers have some practical disadvantages. These include:

(1) New technology. Any significant innovation requires the communication of at least some new technology. In the case of TPEs, this technology is

unfamiliar to many rubber processors and fabricators, but familiar to most plastics fabricators. The barriers between these two industries have clearly been a deterrent to the commercial use of TPEs.

(2) Unfamiliar processing equipment. The equipment required for TPEs is familiar to the thermoplastics fabricator, but foreign to the conventional thermoset rubber fabricator.

(3) Drying prior to processing—a step that is almost never used in conventional rubber processing, but is quite common in the fabrication of thermoplastic articles.

(4) The limited number of low hardness TPEs. The great majority of commercially available TPEs have a hardness above 80 Shore A. The number commercially available progressively decreases with hardness. Below a hardness of 60 Shore A, the number of available TPEs is quite limited.

(5) Melting at elevated temperatures. This inherent property denies TPEs applications requiring brief exposures to temperatures above the melting point. A thermoset rubber, on the other hand, probably would be suitable for such a brief exposure.

1.4 CLASSES OF THERMOPLASTIC ELASTOMERS

The desirable performance properties of thermoplastic elastomers are derived from their chemistry and morphology. Thermoset rubber articles commonly contain a reinforcing agent such as carbon black. In TPEs, the polymer system itself provides this reinforcement, which is commonly due to two or more intermingled polymer systems, each with its own phase.

Chemical composition and morphology provide a rational, convenient means of categorizing the existing commercial thermoplastic elastomers. There are presently six generic categories of commercial TPEs:

(1) Styrenic block copolymers
(2) Rubber–polyolefin blends
(3) Elastomeric alloys
    a. Thermoplastic vulcanizates (TPVs)
    b. Melt processible rubbers (MPRs)
(4) Thermoplastic polyurethanes
(5) Thermoplastic copolyesters
(6) Thermoplastic polyamides (nylons)

To compare the different classes of TPEs, it is appropriate to locate them on a two-dimensional plot (see Figure 4-5) with the abscissa representing performance and the ordinate representing cost. Thus, the cost and performance of the generic categories of TPEs increase as one proceeds in the order styrenics, polyolefin blends, elastomeric alloys, polyurethanes, copolyesters, polyamides. For comparison with this plot of the different generic TPEs, Figure 4-5 also gives a plot of the different generic classes of thermoset rubbers. The thermoset rubbers also increase in both cost and performance as one proceeds from the lower left to the upper right portion of the plot. In comparing thermoplastic rubbers with the corresponding thermoset rubbers, it is important to remember that the processing costs of the TPEs are significantly lower than those of the thermosets.

1.5 CHAPTER COVERAGE

This second edition of the *Handbook of Thermoplastic Elastomers* is divided into two parts, with a total of 15 chapters. Part I, consisting of Chapters 1 through 8, embraces "Materials." It is broken down into the different generic classes of TPEs (see section 1.4). Part II is devoted to "Markets and Applications" of the different commercial thermoplastic elastomers, with emphasis on those specific market areas in which TPEs have been commercialized as materials for part fabrication.

Chapters 2, 3, 6, and 7 of Part I are updated discussions of four classes of thermoplastic elastomers described in the first edition of this *Handbook*. Chapter 2 deals with styrenic TPEs; Chapter 3, polyolefin TPEs; Chapter 6, copolyester TPEs; and Chapter 7, polyurethane TPEs. Each of these chapters has emanated from a leading laboratory in the science and technology of the class of TPE covered. Chapters 4, 5, and 8 cover new classes of TPEs that did not exist when the first edition of this *Handbook* was published. Chapter 4 discusses the rapidly growing thermoplastic vulcanizates, and Chapter 5 the new melt processible rubbers. Both of these groups of TPEs are classified as elastomeric alloys—synergistic mixtures of two or more polymer systems. Chapter 8 deals with polyamide TPEs, the highest performance and most expensive class of thermoplastic elastomers.

Part II, on "Markets and Applications," provides an in-depth focus on major market areas where thermoplastic elastomers have found commercial success. Chapter 9 gives an overall view of TPE growth to date and their projected market penetration, both in the United States and worldwide. For two decades, the automotive industry has provided a promising opportunity for a variety of thermoplastic elastomers. Coverage of this application area is given in Chapter 10. The uses of specific TPEs as materials for hose, tubing, and sheeting are covered by Chapter 11. The highly diverse mechanical rubber goods market—in which TPEs have found many successful commercializations—is surveyed in detail in Chapter 12.

The use of TPEs as a primary insulator for electrical conductors and also as a jacketing material for electrical equipment receives in-depth coverage in Chapter 13. The extremely promising applications of TPEs for food contact and biomedical applications are covered extensively in Chapter 14. The concluding chapter considers future usage of thermoplastic elastomers, through the end of the twentieth century. In all cases, these chapters are written by individuals with thorough knowledge of, and distinguished success in, their respective areas of the thermoplastic elastomer discipline.

We do not yet have a commercially viable pneumatic tire fabricated from thermoplastic elastomers, and it is highly unlikely that one will be made in the foreseeable future unless a major technological breakthrough occurs. Had the technology been available, pneumatic tires based on TPEs would have been produced commercially more than a decade ago.

A comparison of this edition of the *Handbook* with the first shows that the field of thermoplastic elastomers has moved forward extremely rapidly since publication of the first edition. Many new products and product lines have appeared and found increasing applications. Some product lines have matured, some have waned, and others have totally disappeared; but overall the field of thermoplastic elastomers has grown quite remarkably. There is every prospect that this growth will continue at least until the end of the twentieth century.

Chapter 2

STYRENIC THERMOPLASTIC ELASTOMERS

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2.1 INTRODUCTION

Styrenic thermoplastic elastomers represent a class of materials introduced about 1965. They have many of the physical properties of vulcanized rubbers (softness, flexibility, resilience) but are processed as thermoplastics. In the terminology of the plastics industry, vulcanization is a thermosetting process. Like other thermosetting processes, it is slow, is irreversible, and takes place on heating. In contrast, with styrenic thermoplastic elastomers, the transition from a processible melt to a solid rubberlike object is rapid, is reversible, and takes place on cooling. Styrenic thermoplastic elastomers can be processed on conventional plastics equipment such as injection molders, and scrap usually can be recycled. Advantages in machine outputs and material cost are obvious, and have given styrenic thermoplastic elastomers a significant and growing part of the total plastics market. However, because this transition to the final form is reversible, some end-use properties of styrenic thermoplastic elastomers (e.g., compression set, solvent resistance, and upper service temperature) are usually not so good as those of the corresponding vulcanizates. Applications of these styrenic thermoplastic elastomers are therefore in areas where these end-use properties are less important (e.g., footwear, wire insulation, adhesives, poly-