1 Introduction and Historical Survey

1.1 Overview

Thermoplastic elastomers are a relatively new development in the rubber industry. If we could step back in time to about 1960, we would find almost all the conventional (i.e., vulcanizable) rubbers that we are familiar with today being sold and used. The only significant exception would be hydrogenated nitrile rubber (HNBR). However, while thermoplastic polyurethanes had just been introduced, in 1960 all the other types of thermoplastic elastomers were yet to be discovered. Since then, the rapid growth of thermoplastic elastomers that indicates that there was clearly an unmet need for these products. Their worldwide annual consumption was estimated at 1,000,000 metric tons/year in 1995 [1]. This is expected to rise to about 1,400,000 metric tons/year in 2000, which amounts to a 7% annual growth rate.

Three books cover thermoplastic elastomers in detail. The first two concentrate mostly on the scientific aspects of these polymers [2,3] while the other concentrates on their end uses [4]. Thermoplastic elastomers have also been the subject of recent articles in encyclopedias and reference books [5–10]. The object of this book is to provide a short introduction and overview of the whole field, with the caveat that it is rapidly changing, so all that can be done in this text is to give a “snapshot” of the situation at the time of writing.

The outstanding advantage of thermoplastic elastomers can be summarized in a single phrase: they allow rubberlike articles to be produced by the rapid processing techniques developed by the thermoplastics industry. Their relationship to other polymers is shown in Table 1.1.

This table classifies all polymers by two characteristics: how they are processed (as thermosets or as thermoplastics) and the physical properties (rigid, flexible, or rubbery) of the final product. All the commercial polymers used for molding, extrusion, etc., fit into one of the six resulting classifications; the thermoplastic elastomers are the newest. They have many of the physical properties of rubbers, e.g., softness, flexibility, and

Table 1.1 Comparison of Thermoplastic Elastomers with Conventional Plastics and Rubbers

	Thermosetting	Thermoplastic
Rigid	Epoxies Phenol-Formaldehyde Urea-Formaldehyde	Polystyrene Polypropylene Poly(Vinyl Chloride) High Density Polyethylene
Flexible	Highly filled and/or highly vulcanized rubbers	Low Density Polyethylene Poly (Ethylene-Vinyl Acetate) Plasticized Poly(Vinyl Chloride)
Rubbery	Vulcanized Rubbers (Natural Rubber, Styrene-Butadiene Rubber, etc.)	Thermoplastic Elastomers

resilience. However, they achieve their properties by a physical process (solidification) compared with a chemical process (crosslinking) in vulcanized rubbers.

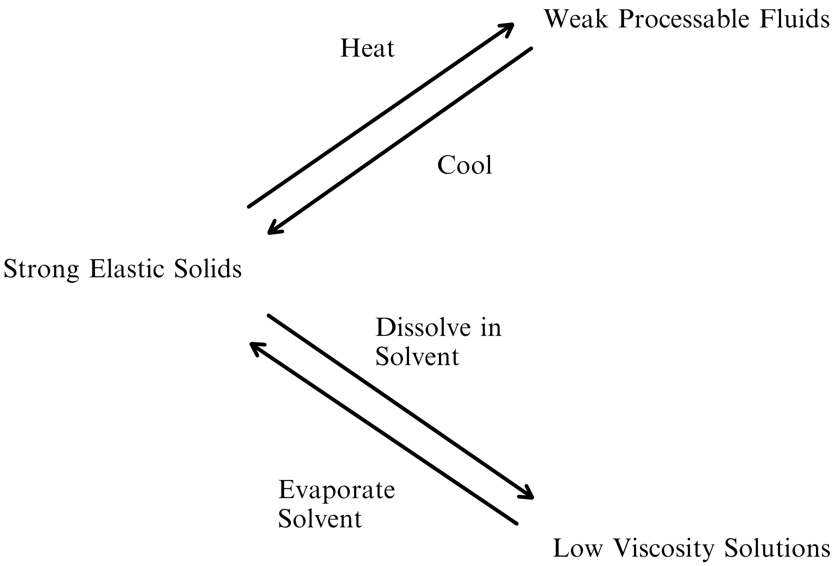
This solidification is accomplished in one of two ways: cooling or solvent evaporation, if the particular thermoplastic elastomer is soluble (most are not). In Table 1.2, the processes are compared with the vulcanization process needed to prepare usable articles from conventional rubbers.

In the terminology of the plastics industry, vulcanization is a thermosetting process. In other words, it is slow, irreversible, and usually requires heating. With thermoplastic elastomers, on the other hand, the transition from a processable melt to a solid, rubberlike, object is rapid, reversible, and takes place upon cooling. Thus, thermoplastic elastomers can be processed using conventional thermoplastic processing techniques, such as injection molding and extrusion. As with other thermoplastics, scrap can be recycled. Also, some thermoplastic elastomers are soluble in common solvents and can be processed as solutions.

Because they become soft and flow when heated, the high temperature properties of thermoplastic elastomers are usually inferior to those of conventional vulcanized rubbers. Thus, thermoplastic elastomers are usually not used in applications such as automobile tires. Instead, most of their applications are in areas where high temperature properties are less important, e.g., footwear, molded parts (including those used on automobiles), wire insulation, adhesives, and polymer blending.

Table 1.2 Transitions

Thermoplastic
Elastomers



Conventional
Vulcanizates

$$\text{Weak Processable Fluids} \xrightarrow{\text{Heat, Time}} \text{Strong Elastic Solids}$$

1.2 Historical Survey

The history of thermoplastic elastomers is inevitably part of the development of the whole history of polymer chemistry [11]. Although natural high polymers (e.g., cotton, wool, rubber) have been known for centuries, there was no understanding of the nature of these materials; essentially people used what was available. Probably the first significant attempt to improve on nature was the crosslinking (or vulcanization) of rubber, developed by Charles Goodyear in 1839. A few years before this, John Hancock reduced the molecular weight of rubber by milling. These two discoveries became the foundation of the rubber industry.

Note that both these discoveries were made pragmatically. There was no understanding of the principles involved. Williams and later, Harries, showed that natural rubber was derived from isoprene (C_5H_8). However, it was believed that rubber was some kind of aggregation or colloidal association, possibly of low molecular weight cyclic structures based on isoprene, what today would be called cyclic oligamers. Similar structures were proposed for proteins and cellulose. These and similar materials were considered low molecular weight compounds, held together by secondary valance forces. Very large molecules were thought to be impossible. Indeed, Emil Fischer, the famous organic chemist and Nobel Laureate, maintained that 5,000 was the upper molecular weight limit for organic compounds.

Despite this lack of fundamental understanding, important discoveries continued to be made. About 1870, Celluloid (a mixture of cellulose nitrate and camphor) was introduced. In 1910, Baekeland developed the first synthetic resin, Bakelite, derived from phenol and formaldehyde. In Germany during World War I, dimethyl butadiene was polymerized to produce a substitute for natural rubber.

The years before World War II saw two parallel developments. One was the introduction of more synthetic polymers; polystyrene (PS), polyvinyl chloride (PVC), and styrene butadiene rubber (SBR) are outstanding examples. The second was the development of the fundamental theory of high polymers by Staudinger and later, Carothers [11]. For the first time, workers in this field understood what was happening during polymer manufacture and processing. Carothers used this understanding to develop nylon and neoprene, the first a thermoplastic, and the second an elastomer.

The first developments in thermoplastic elastomers also occurred about this time [12]. The first work was based on PVC, a rigid thermoplastic. It contains a significant amount of syndiotactic structure that can crystallize and also amorphous atactic structure. (Tacticity is described in more detail in Section 4.2). At room temperature, the syndiotactic structure is crystalline, and the amorphous atactic structure is above its glass transition temperature. Thus, both structures are hard and rigid at room temperature. However, as Semon discovered about 1930, plasticizers can be added (e.g., dioctyl phthalate (DOP)) that swell the atactic polymer and reduce its glass transition temperature to well below room temperature. This converts it to a flexible product. The result is what we now know as the structure of most thermoplastic elastomers: a combination of a rigid phase (syndiotactic PVC) that becomes fluid at processing temperatures with a softer, flexible phase (plasticized atactic PVC).

However, plasticized PVC is not usually considered an elastomer. It lacks many elastomeric properties such as snapback, resilience, and high surface friction. But it was the first material that even came close to being a thermoplastic elastomer. In 1940, its elastic properties were improved by blending with another elastomer, nitrile rubber (NBR). PVC / NBR / DOP blends are now an important part of the thermoplastic rubber industry.

About 1937, workers in Germany at I. G. Farben developed the urethane reaction between an isocyanate and an alcohol. By using diisocyanates and glycols, the result was a long chain structure, similar in principle to nylon. By using two glycols (one short chain, the other long), blocks of two polyurethanes are produced. The first is crystalline; the second amorphous. Again, they form the basic two-phase system characteristic of most thermoplastic elastomers. Starting about 1955, this principle was used by workers at DuPont and at B. F Goodrich to produce elastic fibers and moldable rubbers. It was later extended to yield thermoplastic elastomers with both polyester and polyamide hard segments.

In the 1950s, anionic polymerization was developed. In this system, solution polymerization is initiated by a metallic anion, (e.g., sodium). Pure metals were used at first, but alkyl-metallics (e.g., butyl lithium) were found to give better results. The system is “living”; that is, in the absence of terminating agents, the polymeric product can initiate further polymerization. Thus, if a second monomer is added, the result is a block copolymer. Styrene, butadiene, and isoprene are the only common monomers that can easily be polymerized in this way. The first commercial products were polybutadiene and polyisoprene (anionic production of polystyrene is not economic). In 1961, attempts at Shell Chemical to improve the cold flow properties of these two elastomers led to the development of styrenic block copolymers. These were important for two reasons:

1. They offered a low-cost route to the production of thermoplastic elastomers with many properties of conventional vulcanized rubbers.
2. Their simple and unequivocal structure gave a clear picture of how other thermoplastic elastomers (or at least, those based on block copolymers) gained their properties. In other words, they served as model polymers.

Later, about 1975, similar polymers with improved stability were produced by selective hydrogenation of the elastomer segments in these block copolymers.

In the 1960s, other block copolymers, such as polycarbonate/polyether and poly (silphenylene siloxane)/polydimethylsiloxane, were found to have elastomeric properties without vulcanization, but the reasons were not clearly understood. Many other hard polymer/elastomer block copolymers have been investigated since then and have been shown to produce thermoplastic elastomers. For example, carbo cationic polymerization has been used to produce thermoplastic elastomers from block copolymers of styrene and isobutylene (see section 3.3), and metallone catalysts have been used to produce thermoplastic elastomers from block copolymers of olefins.

The basic requirements for a thermoplastic elastomer, a hard phase and an elastomeric phase, were now established. As well as hard polymer/elastomer block copolymers, there are several other ways of achieving this requirement. An obvious one is simple mixing. About 1960, two new polymers (both produced by Ziegler-Natta catalysts) were introduced. The first was a rubber, a copolymer of ethylene and propylene (EPR). The second was a thermoplastic, isotactic polypropylene. They are produced from low-cost monomers and should obviously be technically compatible with each other. At first only a small amount of EPR was mixed with the polypropylene to produce a high impact thermoplastic. When more EPR was added, often extended with oil, the result was a hard thermoplastic elastomer. Attempts to produce softer grades in this way were less successful; the large proportion of the weak EPR phase resulted in poor properties.

However, this problem was solved around 1975, when the elastomer phase (in this case, EPDM) was crosslinked during the mixing process in a system called "dynamic vulcanization". The resulting thermoplastic elastomers can be quite soft and their properties are often better than those of simple mixtures.

Other systems investigated include graft copolymers (an elastomer chain on which is grafted several hard segments) and elastomeric ionomers (an elastomer chain containing acidic groups with associated metal cations). While they have many interesting properties, they have not developed into commercial products.

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