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Preface

The intent of this book is to compile and present a lifetime of experience involved in research and development in the rubber industry. This experience resulted from employment at several rubber companies, most notably 28 years in the research division at Gencorp in Akron. This was followed by teaching rubber-related seminars at several universities and at the Rubber Division of the American Chemical Society.

I would like to acknowledge the help, encouragement, and support of my wife, Nancy, and also the help with computer-related issues provided by our son, John. I also acknowledge the information obtained from my students, wherein the student became the teacher.

September 2013, John G. Sommer

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1 TSE and TPE Materials, Compounds, Processes, and Products

1.1 Introduction

This book is broadly organized according to the type of rubber or elastomer involved: thermosetting elastomer (TSE) or thermoplastic elastomer (TPE). The terms “elastomer” and “rubber” are used interchangeably.

1.2 Troubleshooting Difficulties

A major difficulty in troubleshooting a rubber problem is clearly defining the problem. As the old adage goes, a problem well stated is a problem half solved [1]. Persons closest to a problem, or those who will benefit most from its solution, often find it difficult to resist the urge to seek an immediate solution. Problem-solving includes the following steps:

1. Gather relevant data
2. Screen and analyze pertinent information
3. Construct a hypothesis from the best available information
4. Test the hypothesis
5. State the problem

Several additional troubleshooting suggestions or pitfalls to avoid include [2]:

- Avoid fixed opinions
- Don’t jump to conclusions
- Take nothing for granted
- Make firsthand observations
- Check critical items personally

Problems that occur can vary substantially from one factory to another [3, 4]. A partial list of these follows:

- Cold flow of polymers in the receiving area
- Mixing problems: mix quality, dispersion, stickiness
- Extrusion: die swell, extrudate appearance
- Calendering: blisters, release from rolls
- Molding: release, nonfills, porosity

Efforts needed to correct these problems vary; some can be remedied by technical personnel within a plant. Others may use technology developed by outside sources, for example reducing cold flow as described in a patent [5].

1.3 Aids to Troubleshooting

The author hopes that this book will provide a dual benefit to the reader. Namely, that it will provide troubleshooting information of immediate use as well as serve as a conduit to the technical literature via the numerous references provided. These references include current as well as older relevant references.

Among the many information sources for rubber literature is the science and technology library at the Rubber Division of the American Chemical Society at the University of Akron. Technical information is also provided by the myriad manufacturers of rubber chemicals and processing and manufacturing equipment.

Problems with rubber are to be expected considering the complexity of the many materials, processing, design, and testing steps (Table 1.1) involved in rubber product manufacture. Some of these are summarized below [6].

Table 1.1 Materials, Processing, Design, and Testing Steps Involved in Rubber Product Manufacture

Raw materials, including rubber chemicals, fillers, steel wire, etc.
↓
Mixers (internal mixers and rubber mills)
↓
Mixed rubber compound
↓
Shaping operations (calendering, extrusion, molding, etc.)
↓
Vulcanizing (also called crosslinking or curing)
↓
Post-vulcanization (deflashing, trimming, etc.)
↓
Testing and quality assurance

Problems can and do happen during these steps, either singularly or in combination. This book is intended to identify and examine these problems and then to consider potential actions directed toward correcting them.

1.4 Materials, Process, and Design Factors

It should be emphasized here that rubber products are basically systems that involve three main factors: material, process, and design, as shown in Figure 1.1.

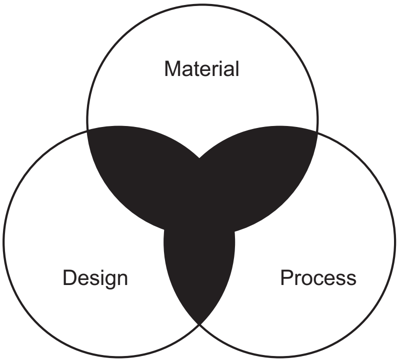

Figure 1.1 Schematic that shows interaction among material, process, and design

These three factors are often interactive. For example, it may be possible to manufacture a rubber extrusion to given dimensional tolerances from a harder rubber compound but not a softer one; the harder compound will be more dimensionally stable during the extrusion process.

Likewise, the successful molding of rubber articles that contain an undercut depends upon the compound used. Articles containing an undercut generally can be removed from their mold if they possess good hot-tear strength and the undercut is not too deep. Hence, it is important to consider both compound and design and view the manufacture of a rubber article as a system [7].

During processing, a cracked rotor in a Banbury mixer might introduce water into a compound and shorten the scorch life of the compound. The shortened life could easily have been interpreted as being caused by a change in the cure system.

The importance of design on final product cost cannot be overemphasized. It has been estimated that, while product design may represent only 5% of total product cost, its influence on product cost can be as high as 70% [8]. Hence, this 5% must be spent very wisely. There are many expectations for rubber products; some of these include a capability to [9]:

- Form a seal between two rigid, moving parts
- Accommodate misalignment between other components
- Absorb or isolate vibrations that cannot otherwise be eliminated.

Since these expectations are often expected to compensate for design shortcomings, increasing amounts of rubber are required.

The rubber industry has been increasingly competitive for many decades, especially so in recent times. This has often resulted in downsizing that minimizes the practice of pairing senior and junior technical personnel. This practice brought newer hires and current technology to an organization; senior people shared hard-gained experience with newer personnel [10]. Unfortunately, downsizing has set the stage for loss of technical knowledge over time and resulted in frequent reinvention of the wheel.

1.5 Book Organization

This book is broadly organized according to the type of rubber involved, be it TSE (thermosetting rubber) or TPE (thermoplastic rubber). These two types of rubber have been compared in terms of factors that include [11]:

- Recycling ability
- Bondability
- Cycle times
- Upper service temperature
- Molding equipment

While TSEs and TPEs share much in common, there are major differences between them that necessitate special consideration and equipment. A number of materials and processing options are suggested along with numerous references that will permit the reader to dig deeper. This book concludes with a relevant list of abbreviations and definitions.

1.6 Nature of Rubber

Rubber is composed of long flexible molecules that can be likened to cooked spaghetti. After crosslinking, these molecules can be stretched to several times their original length and then return to nearly their original shape upon release of the deforming force. Crosslinking connects the individual rubber molecules together such that the joined molecules act as a unit to provide the elastic behavior exhibited by an ordinary rubber band. This behavior is unique to rubber. A steel spring also exhibits elastic behavior similar to rubber, but only if the degree of stretching is limited to less than about 1 %. It is useful to compare the tensile properties of steel and rubber.

Steel possesses high modulus, high strength, and low breaking elongation. Strong forces between atoms account for its high modulus and strength. Weak forces between molecules account for the low modulus observed with rubber. The high strength of NR (natural rubber) is due to its ability to crystallize on stretching. Other types of rubber, for example SBR (styrene-butadiene rubber), attain high strength through incorporation of reinforcing fillers. The word “rubber” is generic and is associated with areas such as rubber types, rubber compounds, rubber processes, and rubber products [12].

These different areas vary in complexity but have in common the occurrence of many potential problems. Personnel must be adequately trained to effectively deal with these problems. Sometimes retraining of personnel is necessary as evidenced by the following example [13].

Prior to World War II, natural rubber (NR) was extensively used in tires because of its excellent processing and end-use properties. With the loss of the NR supply during WWII, GR-S (now called SBR) was substituted for NR, at which time significant processing problems occurred. NR possessed building tack that facilitated the building of tires; SBR lacked this property. With the return of the availability of NR after the war, workers had forgotten how to deal with the high tack in NR. Hence, retraining was necessary.

1.7 Training

In addition to training, a number of other factors are very important for running a successful polymer business. Bozzelli provides a number of these factors as a checklist [14]; three positive and three negative factors from his checklist follow:

Positive factors

- Solve root causes of problems
- Make effective use of consultants
- Provide employee training on request

Negative factors

- Manage business on a financial, not technical, basis
- Failure to maintain or advance experience in core competency
- Work around a problem rather than address its root cause

■ 1.8 Disclaimer

The information in this book has been compiled from many sources and is believed to be true and correct. No implied or expressed warranty can be made concerning its fitness, completeness, or accuracy. Patent references should not be taken as inducements to use or infringe on any particular patent. None of the information contained herein is intended to serve as a recommendation for any product.

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2 TSE Materials and Compounds

2.1 Introduction

Although TSEs and TPEs share many features in common, there are substantial differences [1]. Table 2.1 contrasts some of these differences.

Table 2.1 Contrasts Between TSEs and TPEs

Consideration	TPE	TSE
Recycling	Relatively easy to recycle	Crosslinked material very difficult to recycle
Energy	Easier recycling; uses less energy	More complex recycling steps; use more energy
Automation	Capitalizes on robotics used in plastics industry	Less amenable to automation
Bonding	Heat welding feasible	Generally requires adhesive and chemical bonding
Cycle times	Typically seconds	Typically minutes
Upper service temperature	Limited to T_g or T_m of TPE	Generally higher and limited by thermal stability of TSE backbone and crosslink stability

2.2 Cost Reduction

Cost reduction, the one constant in the rubber industry, might be considered the most important compounding variable. Over time, compounds continue to evolve that contain lower rubber content, directed toward continuing cost reduction. For example, a low-cost EPDM molding compound contains only 11.7% rubber [2]. Other compounds can contain even lower rubber content.

Multiple sources of elastomers are available to the compounder for preparation of compounds to perform a specific function. Costs vary substantially for these elastomers and their compounding ingredients. Caution must be exercised in selecting an elastomer (rubber) and its ingredients. For example a salesperson might suggest a lower cost accelerator as an exact replacement for a higher cost one currently used by a manufacturer [3].

Because of subtle behavioral differences among different rubber ingredients, switching to an alternative material without adequate testing can result in nonequivalent performance. Hence, ideally alternative candidates should be first tested, in the lab, then in a small-scale factory trial, followed by a full-scale factory evaluation to establish that the intended substitution is indeed satisfactory.

The value of recipes for compounds varies substantially within a company [4]. Some recipes fall under commodity status while others have some unique material or process innovation that causes a company to protect a recipe because of its value. Hence, it can be advantageous to mix commercially sensitive recipes in-house; recipes that require less secrecy can be mixed by an outside company.

2.2.1 Compounds and Compounders

Over time, the number of ingredients in a compound tends to increase because a new ingredient is incorporated in a compound to solve the "problem of the day." This practice leads to recipes with an excessive number of ingredients, the intended function of which may be lost over time [5]. Hence the number of ingredients in a compound keeps growing, and a compound could contain as many as 25 ingredients. Recipes that contain more than two types of carbon black or two types of mineral filler should be viewed with skepticism.

Production managers typically expect compounders to solve all production problems by changing recipes [6]. This often results in an excessive number of compounds and raw materials. Several cases showed that the number of compounds and raw materials can be reduced by 30 to 50% without losing customers or harming product performance.

Overemphasis on materials considerations to the exclusion of processing factors can be problematic [7]. One compound could cost more than another on a weight basis, but when considering processing factors such as shorter cycle times and easier demolding or extrusion, rubber articles might be produced at a lower cost.

Experiment design (DOE), judiciously used, can serve as a valuable aid in optimizing compounds and significantly reducing rubber scrap rates [8]. The range of experiment designs runs from simple to complex and comprehensive [9]. A comprehensive design established important factors that included compounding, processing, design, molding, and testing for injection-molded air ducts [10].

The terms "rubber" and "elastomer" are used interchangeably throughout this book. The latter term became necessary with the arrival of synthetic rubbers. Elastomers are available as high-viscosity materials that appear solid-like and as low-viscosity materials, some of which are pourable at room temperature. First discussed are high-viscosity materials.

2.2.2 High-Viscosity Elastomers and Compounds

It should be noted that elastomers and their ingredients form a compound that can ultimately be shaped into a rubber article. A compound should not only be designed for its specification properties at an acceptable cost, but it must process with minimum problems through factory operations. Compound processing and other factors significantly affect the final cost of an article. For example, an expensive process aid incorporated in an extrusion compound might appear initially to be economically unjustified. However, because the aid improved extrusion output by 10 %, its cost was justified [11].

A compounder may design a compound with wider safety margins than necessary to meet a given specification, resulting in unnecessarily high cost [12]. The selection of elastomer, filler, and other ingredient costs should be made on the basis that the resulting compound meets requirements at minimum cost. This requires the compounder to use good judgment in making selections. For example, contrast a compound for an aerospace application vs. one with substantially less demanding requirements, such as a floor mat.

The relative importance of ingredients in a quality compound follows [13]:

1. Polymer or blend of polymers
2. Curing system
3. Fillers

Selection of the remainder of the ingredients, while important, is not as important as the main ingredients listed above.

2.3 Elastomer Type

Different elastomers offer specific advantages such as oil resistance and tolerance for temperature extremes. Resistance to thermal degradation at high temperatures is an important factor in elastomer selection. Table 2.2 shows the highest service temperatures suggested for a range of elastomers. It should be noted that these are general suggestions, as other factors significantly affect the elastomer choice. It should be further noted that there are differences in elastomers of a given type [14]. For example, fluoroelastomers from different suppliers are said not to be interchangeable. To avoid this problem, BMW puts a specific elastomer with a specific process,

Table 2.2 Elastomer Type and Highest Suggested Service Temperature

Elastomer	Highest Service Temperature (°C)
Polyurethane	75
Styrene-butadiene rubber	75
Natural rubber	85
Polychloroprene rubber	100
Nitrile-butadiene rubber	125
Butyl rubber	125
EPDM	125
Chlorosulfonated polyethylene	150
HNBR	150
Polyacrylic rubber	150
Fluoroelastomer	200
Silicone rubber	250
Perfluoroelastomer	300

name, and supplier on part specifications to always ensure getting a specific material.

Carbon nanotube rubber is said to operate from –200 °C to 1000 °C [15]. Even at 1000 °C, when aluminum melts and steel softens, it is said to retain its shape. Viscoelastic properties are similar to those of silicone rubber. Carbon nanotubes in rubber are said to strengthen rubber and increase its conductivity [16].

Following are some characteristics of different elastomers, along with some of additives typically incorporated in them.

2.3.1 CR (Neoprene)

Nonstaining antioxidants must be judiciously selected for CR [17]. For example, nonstaining phenolic antioxidants actually impair the ozone resistance of CR. An encapsulated form of magnesium oxide works better with CR than conventional powdered MgO, which becomes inactive when exposed to a humid atmosphere [18]. Adding even minute amounts of ZnO to CR before the MgO can make CR compounds extremely easily scorched [19].

Vanex, a proprietary accelerator from R. T. Vanderbilt, is suggested to improve problems with marching modulus in CR [20].

2.3.2 CSM (Chloro-Sulfonyl-Polyethylene)

The saturated backbone in CSM provides outstanding ozone and weather resistance [21].

2.3.3 IIR (Isobutene-Isoprene)

IIR, known mainly for its very low resilience and low permeability to gases, is also available as derivatives [22]. These are BIIR (bromo-isobutene-isoprene) and CIIR (chloro-isobutene-isoprene), which make it more compatible with general-purpose elastomers. 10 to 20 phr of CR added to IIR eliminates the tendency of IIR vulcanizates to become softer with heat aging [23].

2.3.4 EPDM (Terpolymer of Ethylene, Propylene, and a Diene)

The residual unsaturated portion of the diene is in the side chain. EPDM with low crystallinity is best used in compounds intended to have low compression set [24]. Use of a 2% maleic-anhydride modified EPDM in a blend with NR is said to significantly improve the flex resistance of the blend.

Black scorch is a problem unrelated to curatives that occurs with EPDM [25]. It can sometimes be improved by adding a small amount of sulfur to the compound or by the use of a lower-structure carbon black. Bloom that occurs with EPDM compounds can sometimes be remedied by using the “triple 8” cure system shown below in Table 2.3 [26]:

Table 2.3 Triple 8 Cure System

Sulfur	2.0 phr
MBT	1.5 phr
TeDEC	0.8 phr
DPTT	0.8 phr
TMTD	0.8 phr

Bloom can occur on the surface of a rubber article when a partially soluble ingredient is used at a level in excess of its solubility at a given temperature [27]. It is affected by humidity and it reduces tack, with the most severe tack loss occurring in the first 24 hours [28].

Excessive amounts of an accelerator caused bloom in a rubber grip on a camera [29]. As a result of slightly higher than usual accelerator levels, grips could turn white in some production lots of materials. Zinc bis-(N,N'-dimethyldithiocarbamate) was identified in the bloom.

EPDM is well known for its good aging characteristics that are associated with its saturated backbone. EPDM seals are generally expected to be serviceable for several years [30]. When seals began to swell excessively and fail in only six months, the cause was found to be chloraminated water.

High-hardness EPDM compounds can be prepared using high-crystallinity EPDM [31]. High-styrene SBR resins can be used for the same purpose, but their higher polarity limits compatibility with the EPDM. Phenol-formaldehyde resins can also be used to increase hardness, although their higher polarity can cause bloom problems.

High molecular weight EPDMs with high levels of 5-vinyl-2-norbornene monomer (VNB) show considerable peroxide crosslinking efficiency [32]. Typically, thirty to fifty percent of the peroxide and co-agent combination can be reduced while maintaining desirable vulcanizate properties. This approach is said to result in considerable cost savings, reduced blooming, and improved aging characteristics.

To ensure that an EPDM compound meets demanding product requirements, a gel test methodology was developed that is based on an automated optical detection system [33]. The system uses clear polymer sampled directly from the polymer production process to minimize possible contamination and provides consistent and high-quality EPDM.

EPDM K8642, with an 80 Mooney viscosity, 70 weight percent ethylene, and 5 weight percent ENB, is said to offer excellent mixing behavior [34]. It also offers high green strength and a fast cure in sulfur-cured compounds. Green strength is a measure of resistance to deformation and fracture before vulcanization [35]. Other properties are good filler and plasticizer acceptance and outstanding aging resistance.

2.3.5 SBR (Styrene-Butadiene Rubber)

SBR has been available for many decades as E-SBR (emulsion SBR) and later as S-SBR (solution SBR). E-SBR, the original SBR, polymerized at 122 °F, is known as hot SBR; its counterpart, polymerized at 41 °F, is known as cold SBR [36]. Cold SBR has less branching and yields vulcanizates with higher resilience relative to hot SBR. The S/B ratio for all these rubber types can be varied to give a wide range of properties, especially low-temperature properties, with low S/B ratios possessing lower T_g values.

S-SBR in compounds generally results in higher viscosity than E-SBR [37]. The higher hydrocarbon content in S-SBR can be used advantageously by increasing the amount of carbon black and oil and thus lowering compound costs while providing equivalent properties. Other potential advantages are said to be improved product uniformity, lower rolling resistance, and increased abrasion resistance in tires. By itself, rolling resistance is said to be responsible for a startling 4% of worldwide carbon dioxide emissions from fossil fuels [38].

A study showed that rolling resistance depends on molecular weight distribution and microstructure, while wet tire performance depends on T_g [39]. As T_g increases, abrasion resistance decreases in an approximately linear manner. Wet grip improves approximately linearly with increasing T_g. Table 2.4 contains the contribution of different regions of tires to rolling resistance [40].

Table 2.4 Contribution of the Different Regions of Tires to Rolling Resistance

Tire Components	Rolling Resistance (%)
Belts	43
Tread	42
Sidewalls	13
Beads	2

Table 2.4 shows that the belt and tread regions are mainly responsible for rolling resistance.

SBRs with high S/B ratios (1:1 and higher) can be blended with SBR that has a conventional S/B ratio to produce high-hardness vulcanizates at a relatively low cost [41]. Fillers used to obtain high hardness increase viscosity and eventually cause a compound to become nonprocessable. High-styrene SBR can provide high hardness with acceptable processing [42]. An alternative to this is the use of a reinforcing phenyl-formaldehyde resin [43] to obtain high hardness, as exemplified by a high-hardness compound for a tire-bead apex.

SBR masterbatches, for example SBR 1606, are available wherein the manufacturer has incorporated carbon black in the raw rubber [44]. Their use shortens mixing time and can improve dispersion.

Calcium oxide and magnesium oxide are suggested as activators in sulfur vulcanization of S-SBR compounds, even though they result in lower cure rate and state of cure [45].

2.3.6 FKM (Fluoro Rubber of the Polymethylene Type)

FKM has substituent fluoro and perfluoroalkyl or perfluoroalkoxy groups on the polymer chain. FKMs have been polymerized from essentially the same monomers for more than several decades [46]. Changes in architecture have advanced their use substantially because of improvements in processing, reduced mold fouling, and hot-tear strength.

Fluoroelastomers containing PMVE can demonstrate improved low-temperature flexibility [47]. Carnauba wax incorporated in FKM reportedly improves mold release [48].

O-rings prepared from a typical fluoroelastomer formulation that contains iron oxide are thermally stable up to 380 °C provided that there is adequate air flow around them [49]. In stagnant air that might occur in the center of a large pile of O-rings being postcured, chemical reactions can build up sufficient heat over time to cause autocatalytic conflagration. Several practices can minimize this problem:

- Properly maintain and clean ovens, exhaust fans, discharge ducting, precipitators, scrubbers, and fire extinguishing systems.
- Avoid overloading postcure ovens.
- Provide sufficient air flow to cool articles to avoid autocatalytic oxidation and possible conflagration.

Finely divided aluminum powder underwent a violent exothermic reaction during remilling of a compound [50]. Charring occurred during extrusion and transfer molding of cold compound, a problem that was remedied by prewarming the Viton compound. The above reference provides other precautions to take when working with Viton.

2.3.7 Polyisoprene (NR and IR)

Natural rubber (NR) is important not only for its outstanding properties but also because it is consumed more than any single synthetic elastomer [51]. Being a natural product, there is inherent variability with NR that is not necessarily present in synthetic rubber because control can be exercised in the synthetic manufacturing process. Instruments are available today that further distinguish differences in NR.

Natural rubber and its synthetic counterpart isoprene rubber (IR) stand apart from other elastomers because of their strain-crystallizing capability, a property that is useful in many applications. Strain crystallization imparts outstanding tack and green strength and yields vulcanizates with good resistance to cut growth at severe deformations.

The strong tendency for NR to crystallize can be problematic in uncured rubber. Strain or distortion in an NR bale can accelerate crystallization, especially when temperatures are lower than about 20 °C. For this reason, bales prepared from crumb or comminuted NR crystallizes more slowly than those from sheet NR due to lower strain.

2.4 Crystallization

Crystallization increases the hardness of NR and attempts to mix crystallized NR have severely damaged internal mixers and mill rolls. Hence the crystallites must be melted before processing crystalline rubber; the rubber must be thawed much like an ice cube thaws and melts. Palletized frozen NR can take a considerable time to thaw; in a hot room at 50 °C, it takes about two weeks for the center of the pallet to reach 30 °C [52]. Crystallization also occurs in vulcanized NR articles [53]. Examples are elastomeric helicopter bearings that were in service in Alaska, laminated rubber bearings for offshore production platforms at subsea depths (+3 °C), and bridge bearings.

It is important to distinguish between the hardening due to T_g and that due to crystallization [54]. An elastomer below its T_g is hard and brittle and exhibits a modulus 1000 times higher than that in the rubbery state. Crystallization in NR will increase its modulus by about 100-fold. In this semicrystalline state the NR is tough but not brittle. In contrast, rubber below its T_g is brittle.

Crystalline NR is traditionally thawed by storage in a hot room at 40 to 50 °C just prior to use; the thaw time increases as the square of the block size. Figure 2.1 shows a block of NR that was only partially thawed as indicated by the dashed boundary line [55]. Crystallized rubber should be thoroughly melted before it is further processed to avoid damage to processing equipment such as an internal mixer.

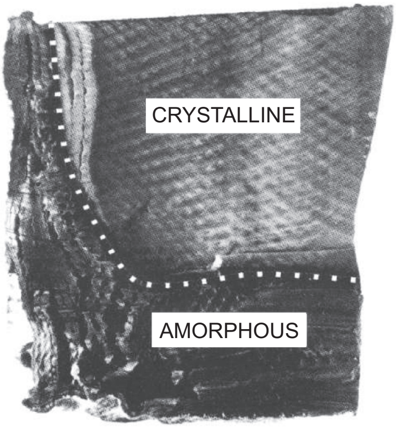

Figure 2.1 Coexisting amorphous and crystalline regions in NR

In Figure 2.1, above and to the right of the dashed line, the NR remained crystalline. To the left and below this line, the crystallites melted. Hence, further warming would have been necessary to totally melt the crystallites before additional processing of the rubber.