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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

Table of Contents

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.

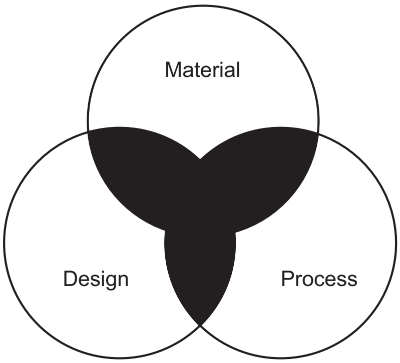

Figure 1.1 Schematic that shows interaction among material, process, and design

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.

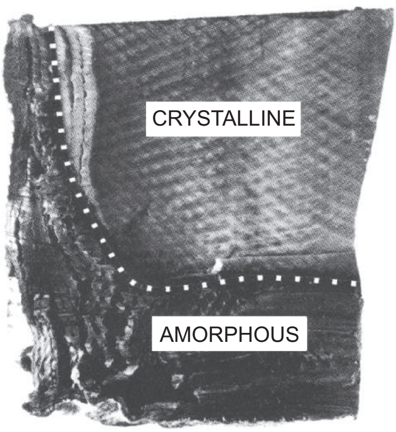

Figure 2.1 Coexisting amorphous and crystalline regions in NR

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.

NR latex can be stabilized by treating with 0.1 to 0.2% of a hydroxylamine salt [56]. Even after eight years of storage, the Mooney viscosity of stabilized rubbers rose less than 10 points above the original value of about 60.

Warming crystallized bales of NR is energy intensive [57]. Warming rooms should be as small as possible and kept as full as possible to minimize energy waste; they should be heated with waste energy from other processes. Microwave units require 30 minutes to initially heat a one-ton pallet.

Crystallization of uncured NR has been previously used to an advantage [58]. Crepe rubber soles die-cut from sheets tended to be concave on their edges rather than a desired square edge. This problem was corrected when the sheets were stored for six months at 10 °C to crystallize the rubber before die-cutting them. The finely crystallized rubber retained its hardness throughout the cutting process. Crystallization in NR crepe can adversely affect adhesion by reducing solvent penetration during application of primer [59].

Vehicles passing over an NR tube that counted traffic ceased to function after being in service for an extended cold period [60]. This behavior was attributed to the tube being cured with a low-sulfur, high-accelerator cure system that could crystallize easily. A high-sulfur cure system would be expected to inhibit crystallization and solve the problem.

■ 2.5 Crosslinking Factors

Different crosslinking systems substantially affect the resistance of NR compounds to fatigue and heat aging [61]. Low-sulfur compounds age much better than their high-sulfur counterparts, but their fatigue life is poorer. Additives can also affect these properties; for example, NBC is a strong degradant and pro-oxidant.

NR vulcanizates with predominantly long polysulphidic crosslinks show good flex life when cured to slightly less than optimum modulus [62]. The difference in flex life between the two extremes of long and short crosslink systems is a factor of about four. However, the shorter crosslinks provide greater resistance to reversion; addition of SBR or BR to an NR compound partly reduces this tendency [63].

A new crosslinking agent, Trial Product KA9188, is said to introduce into a network stable hybrid crosslinks that provide resistance to reversion [64]. It is claimed to be effective not only in NR-based compounds but also in SBR/BR-based compounds. Truck tire tests confirmed favorable laboratory test results with the KA9188.

Reversion is especially a problem with thick rubber articles; two additives, Perkalink 900 and Duralink HTS, are said to improve reversion resistance while maintaining performance properties [65]. Perkalink reduces heat generation and provides heat resistance, modulus retention, and good retention of tear and tensile properties. Duralink provides excellent heat resistance, modulus retention, and reduced heat generation.

Highest flex life in NR bushings was found at a sulfur/accelerator ratio of 1.7, a ratio that likely represents the best compromise between crystallizing capability and the ability to form polysulfide crosslinks [66]. Another factor affecting flex life is the presence of flaws and their size [67]. Flex life was found to generally decrease with increasing particle size of silica. A range of tests that incorporate modern automated test systems is now available to test for fatigue life [68].

A technique to obtain good flex life along with improved reversion resistance in NR vulcanizates involves a post-treatment that consists of introducing additional elemental sulfur in solution to a low-sulfur rubber article subsequent to curing [69]. Post-addition of sulfur substantially improved flex life of an NR automotive bushing [70].

The rheological differences between NR and PI are reflected in their injection-molding behavior [71]. Under some conditions PI compounds flow more readily after injection, but the inherent roughness of NR results in higher temperature during injection with an associated reduction in the difference between injection temperature and mold temperature.

2.6 Silicone Rubber

Silicone elastomers can be classified in three categories: pourable, pumpable, and millable [72]. The term “silicone elastomer” includes a range of types under this designation as described in ASTM D1418. Several examples follow:

- FVMQ: silicone rubber having fluorine, vinyl, and methyl substitute groups on the polymer chain
- PMQ: silicone rubber having both methyl and vinyl groups on the polymer chain
- PVMQ: silicone rubber having methyl, phenyl, and vinyl substituent groups on the polymer chain

Silicone rubber generally requires more freshening (remilling) than organic rubber [73]. Freshening reverses the “crepe-hardening” or “structuring” that occurs after the silicone compound is first prepared. The formation of hydrogen bonds between the hydroxyl groups of the filler and the hydroxyl bonds or oxygen atoms of the silicone cause structuring. Treatment of filler with silanes or siloxane process aids can reduce structuring.

Cold runner systems are strongly recommended for use with FVMQ compounds [74]. Freshening of these compounds is suggested to eliminate flow marks. If it is not possible to freshen a compound, the inventory of mixed FVMQ compounds should be minimized.

Modern cars need electrical connectors that are permanently protected against moisture [75]. Oil-bleeding silicone seals have met this requirement, and the thin film of oil on the seal surface facilitates seal installation. A newer oil-free seal is said to meet seal requirements. Xiameter ECE Sylgard HVIC is said to impart arc resistance, reduce electrical leakage, and minimize surface damage from electrical activity during extreme weather events such as salt storms [76].

Powersil UV is a silicone polymer used in the transmission and distribution industry that can be cured with brief ultraviolet light irradiation [77]. The curing then proceeds independently at room temperature. No by-products are produced, and the technology can be used for cable accessories, surge arresters, and bushings.

Another product is used as the key stamp material for microcontact printing [78]. This new PDMS stamp material reproduces and transfers the master mold formed by photolithography and minimizes impurities that could be problematic.

Aerosil SP fumed silica can improve the transparency of silicone rubber while retaining desirable mechanical properties [79]. Specialty silica with a low surface area can replace carbon black N990 in fluoropolymers with several advantages that include both improved processability and DeMattia flex resistance [80].

In contrast to general-purpose elastomers, traditional antioxidants are not used with silicone rubber [81]; however, low-cost heat stabilizers such as red iron oxide at 1 to 2 phr can sometimes be used. About 4 phr barium zirconate is useful for light-colored silicone compounds.

Silicone compounds can revert if they are not postcured to volatilize low molecular weight silicone species and peroxide decomposition products [82]. Most silicone rubber products require postcuring in an air-circulating oven to drive off volatiles, to reduce compression set, and improve chemical resistance [83]. Good air circulation is required to avoid reversion and to prevent the occurrence of explosions caused by volatiles. Wire mesh trays should support silicone articles in an oven to provide adequate air access to the rubber surfaces. The amount of fresh air recommended is 1.6 ft^3 fresh air/min per pound of LSR (liquid silicone rubber) moldings in the oven [84].

A new method of postcuring is said to be highly efficient and to offer numerous advantages [85]. Since all processes take place under vacuum, there is no risk of explosion risk at pressures below 150 millibar. Total emissions are at least 70 % lower compared to traditional processes.

Undesirably high levels of diatomaceous earth used to extend silicone compounds reduce tack [86]. Curing silicone rubber with a platinum catalyst instead of peroxide can reduce cure times by as much as 70% [87]. Other advantages are the lack of inhibition of the platinum cure by oxygen and the elimination of peroxide odors that can be quite strong. These advantages must be balanced against the higher cost of the platinum-cured silicone and its sensitivity to certain materials.

Platinum catalysts are sensitive to poisoning that leads to cure inhibition by materials that include sulfur, polysulfides, polysulfones, amines and amine-containing compounds, and organometallic compounds [88].

Additional materials that could lead to cure inhibition are vinyl plastics, chlorine-containing materials, certain epoxies, some leather, clays, and vulcanized rubbers [89].

Ovens heated by natural gas can introduce sulfur compounds that can inhibit a platinum cure [90]. Curing agents such as 2,4-dichlorobenzoic acid produce acid by-products. Silastic® AN-3 modifier is typically used in silicone rubber formulations to neutralize by-products and to prevent peroxide bloom [91]. It is also said to improve resistance of articles to prolonged contact with oils at high temperatures.

High-hardness silicone rubbers, for example, 80 Shore A, can present processing problems such as fracturing during calendering rather than flowing [92]. Unspecified additives resolved the problem without affecting postcure hardness.

Silicone rubber that exudes small amounts of silicone oil offers advantages that include higher cut strength for seals [93]. Mat seals and cable bushing mats made from Elastosil R are said to be sufficiently cut-resistant that they are not damaged even with the insertion of sharp-edged plugs.

Organic colors and many inorganic colors adversely affect heat aging of silicone rubber [94]. If used, it is desirable to masterbatch the colors to get good dispersion and closely matched colors.

Judicious selection of filler for silicone rubber can result in conductive silicone rubber compounds that have good processability [95]. Fumed silica improves rheological control, transparency, reinforcement, and other important properties [96].

Many of the materials used as blowing agents for silicone rubber sponge are flammable or worse and can vary in toxicological classification from known carcinogen to irritant [97]. It is recommended that anyone contemplating the manufacture of silicone should have a strong background in both toxicology and environmental compliance.

LSRs offer advantages such as biocompatibility, heat resistance, fast cycle times, and automated manufacturing of intricate shapes [98]. Further increases are expected in their popularity as more material data become available to manufacturers of LSR articles. Simulation software that optimizes mold features such as gate and runner location should further facilitate LSR growth.

Cleanliness, important with all elastomers, is especially important for LSRs used in medical applications [99]. Silicone purity is very important when molding implantable medical articles or parts that contact blood. Tolerance for off-ratio main components (A and B) is much greater than for small amounts of additives such as pigments.

Molding simulation programs require both materials and geometric information as inputs [100]. Rapra Technology can generate the required viscosity data using compounds without curatives; current cost for a complete characterization is about $850.

Material changes in LSRs can be problematic [101]. When pumping units are dedicated to a given formulation, contamination that occurs when changing barrels is a concern, as is cured material that forms downstream of the static mixer. However if a different formulation is used, the entire system must be purged and cleaned. Because this requires time and wastes material, a dedicated material should be used with a given system, if possible.

With transparency levels that are typically 98%, LSR 7000 is intended to replace materials such as transparent polycarbonate and PMMA [102]. LSR 7000 can meet the demands of 150 °C and blue-light radiation in high-power LED applications. It can be as soft as 5 Shore A and can be processed with very little waste.

LSRs, because of their very low viscosities, can flow into a 0.0002 inch opening and cause flash [103]. Hence, mold shutoffs have to be no larger than 0.0002 inch. Rigid mold construction and precise temperature are required to prevent flash. Flame-retardant LSR is said to contain no abrasive fillers and to reduce mold fouling [104]. A self-bondable grade is available for overmolding other materials such as aluminum and certain flame-retardant nylons.

2.6.1 NBR (Acrylonitrile-Butadiene Rubber)

NBR, formerly called nitrile rubber, is an emulsion copolymer of acrylonitrile and butadiene [105] wherein the acrylonitrile content generally varies from 18 to 50%. Higher acrylonitrile content results in better oil and fuel resistance but poorer low-temperature properties. The unsaturated backbone of NBR subjects it to attack by oxygen and ozone, problems that are largely corrected by hydrogenating NBR to convert it to HNBR.

2.6.2 HNBR (Hydrogenated Nitrile Rubber)

HNBR demonstrates significantly improved aging and ozone resistance as a result of its lowered unsaturation. Because of its good oil resistance at high temperatures, it is widely used in oil field applications. Some types of HNBR can be crosslinked with sulfur if there is sufficient unsaturation present [106]. However, peroxide cures usually result in better ozone resistance than sulfur cures.

HNBR is said to perform better in down-hole applications than relatively weak fluoroelastomers, partly because it retains good properties even when moderately swollen [107]. Strength is important in these applications because of the potential for explosive decompression.

Deeper wells and unpredictable mixtures of hydrocarbons that may contain hydrogen sulfide, carbon dioxide, and methane further interfere with the use of rubber in oil field applications [108]. The use of steam and brine injections to improve yields continue to place increased demands on elastomers.

Results from an experiment suggest that compounds with good scorch resistance, fast cure times, and low compound viscosity can be prepared from low-viscosity HNBR [109]. In addition to the oil well industry, applications for this technology include wire, cable, and automotive applications. Ultra-low-viscosity HNBR with the consistency of honey from Lanxess can be used to print gaskets [110]. A Shore A hardness of less than 40 can be achieved and the material can be processed using LIM. Low-viscosity HNBR is said to have aging properties similar to those of conventional HNBR [111]. Faster cure times are obtained with Z-2010EP [112].

HNBR also has the potential for overmolding rigid nylon using a two-shot process [113]. Unlike most silicone rubber, HNBR has good adhesion to nylon. Two plasticizers that performed well in HNBR are Rhenosin W759 (an ether-ester material) and Vulconol 85 (based on an ether-thioether material) [114]. However, volatility of the plasticizer did not correlate well with the behavior of a vulcanizate containing a given plasticizer. Weight loss of a vulcanizate at high temperature did correlate well with loss of low-temperature properties.

2.6.3 CM (Chloro-Polyethylene)

Peroxides, along with suitable acid acceptors and co-agents, were initially used to crosslink CM [115]. Later, sulfur-cure systems based on DETU (N,N'-diethylthiourea) and ECHO (a thiadiazole derivative) were used. Peroxide cure systems provide improved heat resistance relative to the DETU and ECHO systems. Zinc oxide and other zinc derivatives are to be avoided because they decompose CM. The favorable ozone and oil resistance of CM have resulted in its use in applications such as hose, tubing, and electrical cable covers.

2.6.4 CSM (Chlorosulfonated Polyethylene)

CSM is said to have become unavailable [116]; non-CSM compounds have been developed to replace it [117]. These include low- and high-hardness compounds for molded electrical connectors, oil-resistant connectors, hydraulic hoses, and industrial roll covers.

2.6.5 AEM (Ethylene Acrylic)

Some accelerators such as DPG and DOTG have a long history of use in AEM compounds [118]. They are going to be banned in the European Union. Replacements for these are: Vulcofac ACT 55 (a tertiary amine complex, 70% active on a silica carrier) and Lanxess XLA-60, a proprietary amine complex.

2.7 Elastomer Blends

The main reasons for blending two or more elastomers are to reduce compound costs, potentially improve compound processability, and improve specific properties [119].

Blending NR with SBR compounds represents an early use of blending to improve tack in the resulting blend [120]. Blending two elastomers with similar solubility parameters does not ensure that they will be miscible. During mixing, the large polymer molecules form continuous and discontinuous domains. Fillers such as carbon black can preferentially disperse in one of these domains and influence compound properties. Blending procedures must be carefully controlled to obtain reproducible results.

Another important blending factor is the distribution of crosslinking ingredients between or among phases. Curative solubility differences between phases can result in differences in crosslink density in different phases. These differences can result in undercure and overcure in the respective elastomers and cause poor physical properties. For example, the ideal accelerator for an EPDM-SBR blend needs to have higher solubility in the EPDM phase [121]. This is necessary to shorten the scorch time and increase the cure rate in the EPDM phase.

2.8 Crosslinking Systems

Sulfur is the most common agent used for curing unsaturated rubber [122]. Available in both the rhombic or amorphous forms, the rhombic form is most widely used for vulcanization. It exists as a ring structure composed of eight sulfur atoms (S_8). The amorphous form, with a molecular weight of 100,000 to 300,000, is metastable and polymeric in nature. Insoluble in rubber and most solvents, it is called insoluble sulfur. This insolubility is used to an advantage to prevent bloom on the surfaces of uncured compounds to maintain building tack. The temperature of insoluble sulfur must be kept below about 210 to 220 °F (about 98–104 °C) or it converts to the rhombic form.

Insoluble sulfur, because of its high molecular weight, is essentially a solid suspended in rubber and incapable of migration [123]. Because it is sensitive to handling and storage, the following precautions are recommended [124]:

- Store insoluble sulfur at temperatures below 40 °C.
- Store remote from materials that might liberate basic materials such as amines.
- Minimize inventories of preblended insoluble sulfur.
- Store preblended insoluble sulfur in a low-humidity, cool area.

Sulfur and peroxide, which comprise the two major crosslinkers for elastomers, have their respective advantages. Vulcanizates with higher sulfur levels generally produce higher ultimate elongations. For example, sulfur-cured vulcanizates generally produce higher elongation and flex life than their peroxide-cured counterparts, while compression set is generally lower for peroxide cures and aging resistance is better [125]. Higher C–C bond strength relative to the C–S bond strength is said to account for this difference.

Acidic clays should not be used with peroxides because they lower the state of cure relative to sulfur cures [126]. Nonacidic Burgess clay is an alternative. Paraffinic plasticizers will generally affect peroxide cures to a lesser extent than will other plasticizers. Co-agents, used with peroxides, can function to increase crosslink density [127].

Sticky flash that occurs with NR is a well-known shortcoming of peroxide cures that can be mitigated by using as low a concentration of peroxide as possible [128]. This is best accomplished by using a vulcanization co-agent, such as the methacrylate monomer-based systems developed by Sartomer. Scorch safety and mechanical properties for a peroxide cure system were both improved when using a combination of peroxide, a bismalimide-type co-agent, and a sulfur donor for curing saturated or low-unsaturation rubber [129].

By blending certain co-agents, it may be possible to optimize physical properties that would be considered mutually exclusive [130]. The effect of blending co-agents was demonstrated for EPDM, HNBR, CM, and FKM model compounds.

The scorch safety for accelerators used with sulfur cures can vary substantially as generalized below for the different classes of accelerators shown in Table 2.5 [131].

Table 2.5 Generalized Rating of Accelerator Scorch Safety

Accelerator Class	Relative Scorch Safety
Sulfenamides	Good
Sulfenimides	Good
Thiazoles	Some safety
Thiurams	Poor
Dithiocarbamates	Poor

Moisture in a compound can significantly affect compound properties, especially scorch time [132]. The sulfur/accelerator ratio affects scorch time as a function of moisture, with the least effect being shown in EV cure systems. Moisture also affected the mastication efficiency. A rule of thumb for curing rubber assumes that the cure rate is doubled or increases five minutes for every 0.25 inch thickness increase to the center of a molded article [133]. This rule of thumb, while oversimplified, is broadly useful.

Curing variables can significantly affect fatigue resistance of a vulcanizate [134]. For maximizing fatigue resistance at constant energy, consider curing for a longer time at a lower temperature (as contrasted to a shorter, higher temperature cure). The longer, lower temperature cure favors the formation of more polysulfidic crosslinks, which are associated with increased fatigue life.

Sulfur solubility at room temperature varies among rubbers, being relatively high in NR and SBR but low in NBR and in stereospecific BR [135]. Solubility increases with temperature in most types of rubber but much less so in NBR. Sulfur donors can be used to mitigate sulfur bloom; however, they are somewhat expensive [136]. Vulcanization begins only after a donor releases its sulfur; hence there is a delayed effect relative to sulfur alone. Past efforts to improve sulfur dispersion in a compound have involved mixing an aqueous dispersion of sulfur with SBR latex, followed by coagulating and drying the mixture [137].

2.9 Dispersion

Predispersions of chemicals are favored in Europe for reasons that include packaging in small units, improved finished compound quality, batch-to-batch consistency, compound homogeneity, and mixing time. Additional considerations include environmental and health-safety factors and the added cost to prepare predispersions.

Powder liquid dispersions (PLD) are prepared by absorbing a liquid onto a suitable powder or carrier [138]. They can give the appearance of a powder while containing a large proportion of a liquid; 72% solids content is typical for many PLDs, which offer the following advantages:

- Eliminate handling problems associated with high-viscosity liquids by converting them to powders.
- Eliminate heated inventory storage of high-viscosity liquids.
- Reduce batch preparation time and clean-up time.
- Shorten ingredient incorporation time.
- Reduce loss of materials that stick to containers.

Poor dispersion of curatives can adversely affect strength and dynamic properties [139]. It can result not only from inadequate mixing but also from exceeding the curative solubility limit in rubber. Many common curatives are used in amounts above their solubility limit at room temperature.

2.10 Crosslinking System Effects

Accelerators increase the rate of crosslinking of a rubber compound; however, they must not be so active that they cause premature crosslinking (scorch) during processing. When compounding temperatures exceed about 140 °C, sulfenamide accelerators must be mixed into the compound at lower temperatures [140]. For this reason, large batches mixed in internal mixers are commonly mixed in two stages. Noncurative materials are added in the first stage prior to the occurrence of high temperature; curatives are then added in a second stage, preferably below 100 °C. However, hot spots can occur in the second stage that cause localized regions in a mix to have reduced scorch time [141].

Advantages thate can accrue from blended curatives [142] are: a sharply reduced number of weighings, reduced dust in the weighing area, and improved cleanliness.

Some curatives in blends are quite reactive with one another and require stabilization. An example is a blend of sulfur, CBS, and DPG that proved to be unstable, especially in the presence of moisture. Phthalic anhydride was among the materials found to stabilize the blend.

Commercially available sulfenamides present potential stability problems during mixing [143]. Stabilization is improved by the addition of PVI.

Very active accelerators such as TMTD and TETD require lower temperatures during mixing compared to a sulfonamide accelerator, as they are more likely to cause scorch. Dust from thiurams can be problematic. Anyone who consumes alcohol and inhales dust from thiurams may become nauseated [144]. This response is the basis for using TETD in alcoholism aversion therapy. TMTD acts in a similar but less pronounced manner.

Nitrosamine products liberated during rubber vulcanization are a problem and are a continuing health concern in the rubber industry. Major automotive manufacturers have issued stringent requirements regarding their use. Improved accelerators are now available that are said to be nitrosamine-free [145]. One company has issued a restricted substances standard that prohibits nitrosamine levels in excess of 0.1 % of an article's total weight [146].

Secondary accelerators such as DPG, incorporated with primary sulfenamide accelerators such as Santocure®, can significantly increase cure rate compared to the use of only a primary accelerator. EV (efficient vulcanization) and semi-EV systems use higher than conventional accelerator/sulfur ratios. Their use results in more monosulfide and disulfide crosslinks that are more stable and reversion-resistant in NR compounds. Table 2.6 shows examples of conventional, semi-EV (efficient vulcanization), and EV cure systems for NR:

Table 2.6 Conventional, Semi-EV, and EV Cure Systems

Conventional	
Sulfur	2.5 phr
Sulfenamide accelerator	0.6
Semi-EV	
Sulfur	1.5 phr
Sulfenamide accelerator	1.5
EV	
Sulfur	0.5 phr
Sulfenamide accelerator	5.0

Changing from a conventional system to an EV system enabled NR to be used at up to a 20 °C higher temperature [147]. Semi-EV systems are expected to provide longer fatigue life than conventional curing systems [148].

Accelerator selection should be considered in conjunction with health and safety issues. Some accelerators, such as MBS, can liberate nitrosamines [149].

2.11 Retarders

These extend scorch time, and the ideal retarder would do so while maintaining a desirable rate of cure at low cost. Salicylic acid, a low-cost material, will lengthen scorch time, but it decreases the rate of cure. In contrast, CTP lengthens scorch time *and* maintains the rate of cure, but at higher cost.

2.12 Fillers

Fillers, which can be in particulate, resinous, or fibrous form, are an important part of a rubber compound [150]. Some fillers retard vulcanization; this tendency can be offset with the use of additives such as polyethylene glycols. The effect of some fillers, for example, clays, can be problematic especially when the clays are used at high levels. Amine-treated clays can be used to counter this problem.

Carbon black, because of its very wide use as filler in tires and other rubber products, deserves special attention. Carbon black aggregates are the smallest dispersible carbon black units [151]. Mixing breaks up groups of these aggregates into smaller aggregates. Carbon black, as produced, is a fluffy product that is difficult to handle and to incorporate in rubber [152]. To mitigate these problems, the fluffy product is converted into pellets that must be neither too soft nor too hard.

Too-hard pellets may not fracture while undergoing shear stress in a mixer; too-soft pellets produce dust that builds up at the mixer. Important factors concerning pellets are shipping container type, distance shipped, plant unloading and transport system, and mixing equipment.

With extensive use, mixing equipment requires rebuilding or upgrading [153]. When rebuilding or upgrading, it is important to consider equipment as a system. For example, increasing the torque on an internal mixer could have the adverse effect of damaging or destroying the gear train. Hence, consideration should be given to the possible interaction of changes made in equipment.

The design of dust and fume collectors on internal mixers is important because it can dramatically affect mixer life [154]. Also, dust and fume collectors must not be so aggressive in their function that they remove critical components from a compound such as accelerators that can be present in very small concentrations [155].

There is a specified ram weight-throat clearance that facilitates removal of air and generated gas.

Carbon black that is shipped in bags usually experiences less damage than black that is shipped in bulk [156]. Damage to bulk black can be minimized by

- having the black contact smooth and corrosion-free surfaces
- making incline angles for gravity feeding at least 60 ° off the horizontal (applicable also to silo bottoms used for storage)
- transporting black on belt conveyors whose angles are limited to a maximum of 15 ° off the horizontal
- using belt conveyors rather than screw conveyors.

The inventory associated with railcar-size bulk shipments of carbon black can be minimized by using intermediate-size containers [157]. Inventories were reduced from 500,000 to 1,000,000 pounds to 50,000 to 100,000 pounds by changing to bulk bags that hold 1000 and 2000 pounds of black. Trucks can deliver 10 to 12 of the latter at a time.

When difficulties occur, carbon black properties should be determined at the point of use (internal mixer, mill) because black properties can change in being transported.

Particle size and structure are two important carbon black parameters. For compounding tire treads, it is desirable to have a sufficiently fine particle size and a sufficiently high structure to obtain good wear resistance [158]. Table 2.7 shows the relative wear resistance associated with several carbon blacks.

Table 2.7 Relative Wear Resistance Associated with Carbon Blacks

Carbon Black	Relative Wear Resistance
N351	87
N339	95
N220	100
N234	108
N134	113

Table 2.8 lists typical relationships between carbon black properties and rubber properties that can serve as a useful aid in compounding [159].

Table 2.8 Increasing Carbon Black Surface Area, Structure, and Loading Effects on Rubber Properties

Rubber Property	Surface Area	Structure	Loading
Mixing temperature	Increases	Increases	Increases
Die swell	Decreases	Decreases	Decreases
Mooney viscosity	Increases	Increases	Increases
Loading capacity	Decreases	Decreases	–
Stress @ 300% elongation	Insignificant	Increases	Increases
Elongation	Insignificant	Decreases	Decreases
Hardness	Increases	Increases	Increases
Tear resistance	Increases	Decreases	[a]
Hysteresis	Increases	Insignificant	Increases
Abrasion resistance	Increases	Insignificant	[a]
Low-strain dynamic modulus	Increases	Insignificant	Increases
High-strain dynamic modulus	Insignificant	Increases	Increases

[a] Increases to an optimum before decreasing.

Whether used in tires or nontire applications, compound viscosity is an important consideration. Fillers of larger particle size with their accompanying lower surface area lower compound viscosity [160]; lower structure carbon blacks also lower compound viscosity.

Ground rubber can be used as extending filler in a rubber compound to reduce cost. The use of ground rubber of finer particle size results in better maintenance of tensile strength [161].

Titanium dioxide is typically used in white compounds to obtain maximum whiteness, for example, in white sidewall tires [162]. Lower cost fillers such as light-colored clay, calcium carbonate, and talc can replace some of the titanium dioxide in some applications directed toward reduced compound cost. Talc offers the potential additional advantage of shortened mixing times [163].

2.13 Process Aids

Process aids are used in the rubber industry to improve processing and to impart or improve specific rubber compound properties [164]. They can improve compatibility between rubbers, for example, between halobutyl rubber and highly unsaturated rubbers [165]. However, because some process aids can react with rubbers, care must be exercised in choosing them; some tackifying resins react with halobutyl rubber and decrease its scorch time [166]. Process aids can significantly improve the extrusion and molding behavior of a range of compounds.

Factice, which is vulcanized vegetable oil, is sometimes overlooked as a compounding ingredient. It can dimensionally stabilize extruded articles, reduce time to fill molds, reduce cycle times, improve ozone resistance, and promote flow [167].

Two phr factice can generally be substituted for one phr plasticizer or oil up to 15 phr with little effect on other compound properties [168]. As a partial replacement for oil or plasticizer, factice is nonblooming, nonvolatile, nonmigrating, and nonextractable.

2.14 Plasticizers and Oils

Petroleum-based oils, used in rubber for many decades, are classified mainly as paraffinic, naphthenic, and aromatic [169]. Oil is classified as paraffinic if one-half or more of its carbon atoms are present in paraffin side chains and the remaining atoms exist predominantly in naphthene rings. Aromatic oils contain 35% or more of their carbons in aromatic rings, with fewer carbons in naphthene rings and paraffin side chains. Naphthenic oils have a high content of cyclic hydrocarbons and limited n-alkanes. Plasticizers critically affect compound properties such as low-temperature behavior, weather resistance, ozone resistance, bloom, aging resistance, and tendency to crystallize.

Reactive plasticizers can bond to the backbone of their host elastomer. For this to happen, a reaction must occur between the reactive plasticizer and the double bonds in the host elastomer [170]. Results showed that approximately 60 to 70% of a reactive ester plasticizer bonded to HNBR. The choice and level of plasticizer plays a key role in the reactivity of the plasticizer to the elastomer.

High levels of plasticizer resulted in extremely low modulus compounds, for example, 0.12 MPa shear modulus; however, they reduced compound viscosity excessively and made processing difficult [171]. Significantly improved processing resulted from the use of a two-stage cure system, one a low-temperature system and the other a high-temperature system. The low-temperature system inserted limited but sufficient crosslinks to improve processing but not enough crosslinks to prevent rubber flow. Higher curing temperatures in the finished article subsequently achieved the desired level of crosslinking.

2.15 Antidegradants

Both antioxidants and antiozonants are classified as antidegradants, with some antidegradants functioning in both roles. Depending upon the application, selected waxes can be used to protect rubber from ozone under static conditions. The waxes usually consist of a blend of low- and high-molecular weight paraffin waxes and a microcrystalline wax [172]. Microcrystalline waxes are mixtures of alkanes, iso-alkanes, and cyclo-aliphatic hydrocarbons, and their rate and extent of blooming depends upon their compatibility with their host rubber.

Most antidegradants function best in only one role. An example is Wingstay 100, which imparts outstanding static and dynamic ozone resistance to CR [173]. A negative effect is that it slightly reduces scorch time. NBC, in contrast, does not affect scorch time, but it is a less effective antiozonant. Also, the green color of NBC restricts its use in light-colored compounds.

Rubber must be protected during processing, during storage, and during end use [174]. AO 1520 at very low levels is said to provide good processing stability even after long storage times.

Persistence of effectiveness is another antidegradant consideration, and higher antidegradant molecular weight favors greater persistence [175]. A higher molecular weight version of TMQ (Flectol H) is a very cost-effective general-purpose antioxidant that exhibits persistence over time. An alternative to improve persistence (and also resistance to extraction) is to chemically bond an antioxidant to the rubber backbone as was done with NBR.

Yet another factor in persistence is the potential for extraction of antidegradant [176]. Constant-velocity boots contain lubricants that can extract an antidegradant and thus reduce its effectiveness. The result can be a reduction in boot effectiveness when the boot is attacked by oxygen and ozone. Constitutive models have been developed to study network degradation and the formation of a secondary molecular network in a deformed state while at elevated temperatures in the deformed state [177].

Heavy metals such as copper, manganese, nickel, and cobalt are generally to be avoided in rubber compounds [178]. Coatings containing brass powder can severely degrade a rubber substrate as evidenced by a golf club grip covered with such a coating. Figure 2.2 shows a severely degraded grip caused by the coating.

However there are exceptions to damage caused by heavy metals. Copper in the form of copper stearate is a pro-oxidant in typical sulfur cures; it has an antioxidant effect in TMTD cure systems [179].

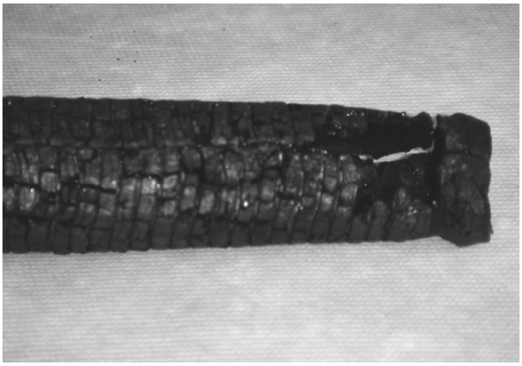

Figure 2.2 Golf grip severely degraded by its brass-colored coating

Compounding ingredients added to an elastomer can cause discoloration and staining [180]. Discoloration is an undesirable change in the color of a rubber product; staining is the development of color or discoloration in a material that an elastomer contacts or is located close to.

2.15.1 Discoloration and Staining

Discoloration and staining are major considerations in selecting antidegradants [181]. Generally, phenolic antioxidants are nondiscoloring; amine antidegradants are not. However, phenolic antioxidants reduce peroxide efficiency, with an exception being their use with CPE [182]. Lead-containing additives have been used in a number of different rubber compounds for some time, for example CPE, CSM, CR, and ECO [183]. The extractability of these additives can be reduced by

- replacement of litharge red lead with lower solubility stabilizers such as dibasic lead phthalate, dibasic lead phosphate, or tribasic lead sulfate
- use of blends of these materials that form extremely insoluble reaction products.

The major antidegradants used for protection of rubber are antioxidants and antiozonants: antioxidants to protect against oxygen and antiozonants to protect against ozone.

Absorption of only 1% oxygen typically halves the tensile strength of a rubber product [184]. When 1 to 2% oxygen combines with a product, the product is no longer useful [185]. Antioxidants of the proper type and level can delay or prevent this from happening. Although some antioxidants protect against heavy metal ions, for example, copper, general antioxidants often do not.

Agerite White can serve as a copper inhibitor for NR [186]. Without this additive, an NR vulcanizate melted after four days in an oxygen bomb at 80 °C; 2 phr of the inhibitor much improved aging behavior.

Microbes can also attack rubber, for example, seals on laundry machines [187]. Prolonged exposure to warm moist environments that contain detergent and clothing residues, body oils, skin cells, dirt, and microorganisms readily promote attack. A silver additive and a strong antifungal were incorporated in the seal for protection. A silver-based additive has also been used in LSR for catheters and wound drains to provide antimicrobial protection [188]. Manufacturers of gaskets for refrigerators and freezers, especially those located in Asia, also use nanoscale silver particles because antimicrobial properties of the silver reportedly help preserve food [189]. The antimicrobial effect is attributed to silver ions, not to nanoparticle-specific biological effects [190].

Antioxidant levels of 10 phr have been used in an NR impact absorber [191]. Antioxidants do not generally benefit sulfur-cured EPDM, but they can benefit their peroxide-cured counterparts. For example, a combination of primary and secondary antioxidants is said to enhance the heat resistance of peroxide-cured EPDM. EPDM is widely used in high-temperature applications such as appliance wires [192]. Even though its saturated backbone offers good resistance to oxidation, some applications require the use of an antioxidant for enhanced performance.

Antioxidants ideally should have low volatility, limited solubility, high chemical stability, process well, and be in a solid form. Their extraction in service such as hydraulic hose or in articles subject to laundering can be a serious problem [193]. Their optimum level depends upon a number of factors such as antioxidant type and rubber type. The solution to many aging problems involves selecting the proper curing system and then choosing the appropriate antioxidant [194].

Flexzone 3-C is said to offer a significantly higher level of protection against flex cracking and ozone attack than any other commercial chemical [195]. Additionally, it provides protection against copper.

Some antidegradants function as both as an antioxidant and an antiozonant, for example some para-polyphenylenediamines (PPDs). However, they tend to stain white components and thus cause problems with white sidewall tires and embossed white lettering on the sides of tires [196]. Among the more effective PPDs is N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. This class of chemicals is thought to function by scavenging free radicals before they can further harm a rubber network. A wax generally provides static protection against ozone attack. However, it can significantly decrease ozone protection under dynamic conditions.

Antiozonants like 6PPD, with a melting point of 40 °C, can present a handling problem [197]. When this product was first introduced in Europe in 100 or 200 kg drums, the drums were heated in a hot room for melting. When transferred through pipes heated by lagging, significant problems resulted if the lagging failed. Liquid forms of the material later allowed it to be shipped at room temperature in bulk form.

Alkyl-aryl PPDs offer superior dynamic ozone protection, and when combined with wax they offer superior static protection [198]. Additionally, they are normally free of problems with bloom. A pioneering study of antiozonants and waxes in a variety of elastomers and products established a basis for protection of rubber from ozone [199]. Elastomers included SBR, IIR, NBR, and CR; products included grommets, seals, hoses, and tires. Antioxidants were found to be effective in a number of elastomers and products. This work provided a guide for the production of ozone-resistant tires and mechanicals [200].

A small amount of a chlorinated polymer such as CR incorporated in peroxide-cured EPDM improved heat resistance [201]. The reason for this behavior is unknown.

2.16 Bloom

Bloom is the appearance of an undesirable material on the surface of a rubber article. Frosting is a bloom-like condition that occurs on many types of rubber in humid summer weather [202]. It is most noticeable at high humidity that occurs in the summer. Although Antioxidant 2246 alone did not prevent frosting, 1% 2246 combined with 0.5% of a microcrystalline wax appeared to protect against frosting during humid summer weather.

Tests based on color changes are available to identify blooms [203]. For example a light-induced change to a gray-brown color indicates an amine antioxidant bloom, while a pink color indicates a phenolic antioxidant bloom. A heat-induced color change accompanied by stickiness and/or embrittlement indicates oxidative degradation, while the absence of stickiness and/or embrittlement indicates an amine antioxidant.

An electron microscope was used to examine an apparent surface bloom on a medical product [204]. The surface showed a pattern indicative of stress-induced oxidation but no bloom. The result suggested that some crosslinking occurred before final molding. Altering the manufacturing process eliminated the problem.

An iridescent sheen occurs primarily in EPDM compounds that are exposed to sunlight and ozone [205]. Siliceous earth filler (Neuburg siliceous earth) is said to reduce iridescence in these compounds.

Iridescent blooms that occur on automotive weather strip are cosmetically very objectionable [206]. They have been found to be due to oxidation of chemical species present on the weather strip surface that turned the surface a yellowish or bluish color. Careful selection of accelerator based on melting point and solubility parameter improved miscibility and vulcanization efficiency. Other factors that affected behavior were EPDM characteristics, crosslink density, and processing conditions.

Light can induce gold iridescence in both solid and sponge EPDM weather seals [207]. A subtle discoloration of weather seal surfaces appears, first appearing as blue, red, or rainbow iridescence.

Pressurized suits protect astronauts from the vacuum of space [208]. These incorporated rubber adhesives (NR and CR) that were found to show signs of degradation after six months of shelf aging. Agerite White (N,N'-dinaphthyl-p-phenylenediamine) antioxidant incorporated in the rubber adhesives improved performance.

Rainwater can leach certain antiozonants from rubber compounds and diminish the protection they offer [209]. This occurred when acid rain leached antiozonants from window seals; the amount leached was found to be proportional to the acidic content of the rain.

Ozone cracking is quite complex and perplexing [210]. The crack density increases with increasing strain, while there is a concomitant decrease in the rate of growth. Maximum crack width occurred at 6% static strain. Most plasticizers reduce ozone resistance in CR with the exception of glycerides or esters of fatty acids such as butyl oleate [211].

Primary and radical trap antioxidants (optimally with a secondary or synergist antioxidant) were evaluated in different rubbers (HNBR, ACM, and EAM) that are frequently used in under-hood automotive applications [212]. Based on the test conditions used, antioxidant synergists resulted in no better aging behavior than an additional corresponding amount of primary antioxidant. For the three rubber types tested, antioxidant level predicted the best air-aging behavior at 177 °C. Naugard 445 was found best for high-temperature performance.

HT (high-temperature) ACM elastomer with a new curative and protection system is said to provide both long-term, high-temperature performance and excellent extrusion performance [213]. It is used in hoses and ducts. Another ACM offers good oil resistance over a temperature range from −40 to 200 °C for short intervals [214]. It has significantly lower cost than fluoroelastomers or silicones that offer similar temperature performance.

Some high-performance elastomers such as ACM that earlier incorporated additives have since been restricted [215]. DOTG is another additive that is under review because it can produce o-toluidine when used with other curatives. O-toluidine has been classified as a category 1 potential carcinogen by the German Research Foundation. Rhenogran XLA-60 has been designed to replace DOTG in selected cure systems.

Correlation between room-temperature and accelerated aging has been a subject of interest for some time [216]. NR compounds, one a control and the other with 2 phr phenyl-2-naphthylamine antioxidant, were compared. It was found that 21 days at 70 °C in an air oven is equivalent to 14 years at room temperature. After aging for 22 years, the antioxidant level decreased to one half its original concentration. When conducting accelerated aging tests, it is important to control factors such as air velocity in the aging oven and uniformity of temperature throughout the oven [217].

Higher temperature greatly increases the rate at which oxygen reacts with rubber, with about a 50-fold rate increase between room temperature and 70 °C [218]. Expressed in another manner, it would take approximately 8000 times as long to see a similar change at ambient temperature.

2.17 Flame Retarders

The flammability of rubber and rubber products continues to be a concern, especially for rubber used in applications such as cable insulation, conveyor belting, mining operations, and ventilation ducts [219]. Fluoroelastomers, because they contain significant fluorine, do not support combustion. However, they will burn in a supporting flame and self-extinguish upon removal of the flame [220]. Other elastomers often require compounding with special additives to render them sufficiently flame retardant for their intended application. Flame retarders like aluminum trihydrate are not only noncombustible; they liberate water to help extinguish a flame.

Halogen flame retarders tend to release corrosive compounds when the materials are burned, in addition to other issues [221]. For wire and cable applications, halogen-free retarders such as nanoclays, nanotubes, aluminum trihydrate, and magnesium hydroxide are potential alternatives.

2.18 Compound Properties

A typical rubber factory often has many more compounds and raw materials than required to meet product needs. More than 80% of a company's products can be made with 25% of the recipes, and there may be 150 to 300 ingredients in inventory [222]. Reducing the number of raw materials and compounds, rationalization of raw materials flow, and more effective utilization of factory space can result in significant savings and other advantages, including increased productivity, improved quality, decreased inventory and lead time, and a 10% decrease in energy consumption.

A major advantage of rubber is its extreme versatility and the range of compounds that can be prepared from rubber, for example damping applications. Damping is a property of deflected rubber or a rubber compound that converts mechanical energy into heat. Table 2.9 shows the effect of some compound variables on damping [223].

Table 2.9 Compound Variables that Affect Damping

Compound Variable	Low Damping	High Damping
Elastomer T_g	Low	High
Elastomer mol. wt.	High	Low
Carbon black level	Low	High
Plasticizer type	Certain esters	Aromatic oils
Degree of crosslinking	High	Low

Factors that controlled the dynamic properties of rubber were examined in detail [224]. Compounding variations included rubber type (mainly NR and SBR), fillers, oils, and level of crosslinking. Processing variations such as mixing, curing, and storage affected dynamic properties, as did design factors.

Several design considerations should be in the forefront for the designer of rubber articles. Two of the most important design objectives are making wall thickness as uniform as possible and radiusing the corners of articles [225]. For TPE, uniform wall thickness provides more uniform cooling in a mold; for a TSE, uniform wall thickness provides more uniform crosslinking. Radii make rubber articles stronger by distributing stress over a larger area of an article.

2.19 Testing

Test data often lists S-300 incorrectly as the modulus at 300% elongation [226]. S-300 is actually the stress at 300% elongation, not the modulus. For the two TPUs shown in Figure 2.3, this can lead to confusion because *E* (Young's modulus) for material B is higher than that for A. Yet the S-300 values are the opposite of that for *E*. S-300 could mislead a designer of rubber articles.

Physical properties such as tensile strength, elongation at break, hardness, and S-300 have long been the mainstay of rubber property measurement. These are rarely useful in indicating how a material might behave in actual rubber applications [227]. Instead, modulus measurements made at lower elongation values should be of more use in engineering applications.

Extensometers, usually used with rubber, are designed to measure large strains and cannot measure small strains sufficiently accurately [228]. Young's modulus can be estimated by hanging weights on a long rubber strip and measuring elongation with a cathetometer. Although tedious, this procedure yields satisfactory results.

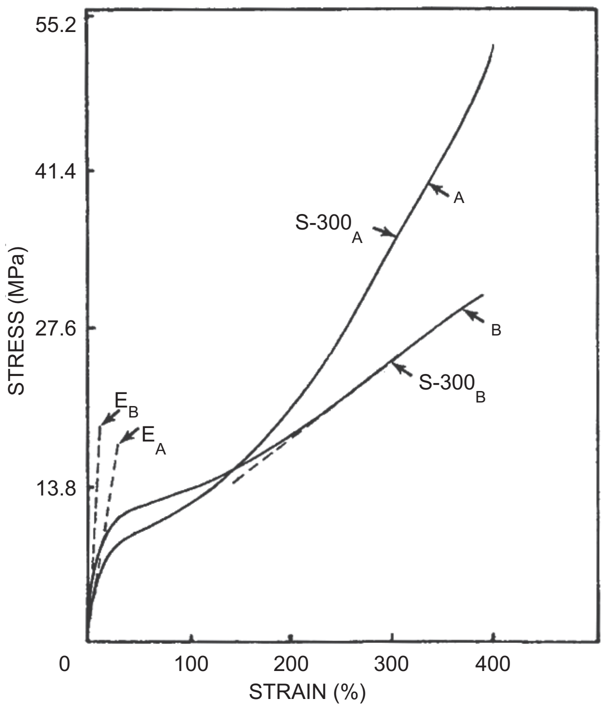

Figure 2.3 Stress-strain curves for two TPUs identified A and B, courtesy of Rubber World [226]

A concern when conducting tensile tests is the sharpness of the die used to prepare specimens. Dull dies can sharply reduce apparent tensile strength. A sharpened tensile die resulted in an apparent increase in tensile strength of 39% [229]. Hence, tensile dies should be properly sharpened before concluding that poor tensile test values are compound related.

Buffing has been used for decades to prepare specimens for testing [230]. When done carefully, buffed specimens provide results comparable to molded specimens. Grain and degree of cure appear to be more important than surface texture induced by buffing. If care is taken, splitting or buffing can be considered a satisfactory method for preparing specimens for test.

Keep in mind that prestretching a gum rubber results in substantially different stress-strain results than prestretching a black-filled rubber [231]. Figure 2.4 shows the effect on an unfilled vulcanizate not prestretched vs. one prestretched to 530% before testing.

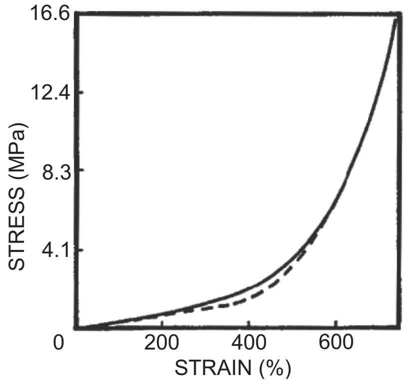

Figure 2.4 Stress-strain response for an unfilled vulcanizate not prestretched (solid line) and prestretched to 530% before testing (dashed line) [231]

The curves show that prestretching somewhat reduces the stress, especially at the lower strain values. Figure 2.5 shows that prestretching (to 420%) for a carbon-black-filled vulcanizate very significantly reduces stress values over a wide range of strain values, with the major reduction again occurring at the lower strain values.

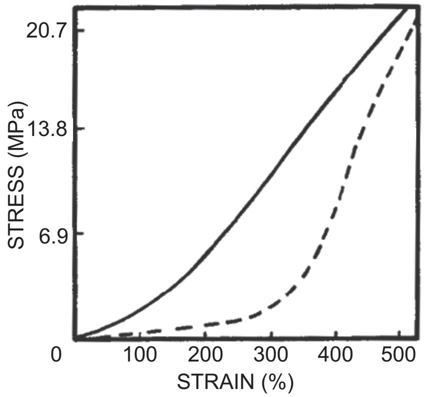

Figure 2.5 Comparison of the stress-strain response for black-filled vulcanizate not prestretched (solid line) with a carbon-black-filled vulcanizate prestretched to 420% before testing [231]

This means that a prestrained, carbon-black-filled vulcanizate will show a substantially reduced stiffness relative to its unfilled counterpart.

When compressing a rubber specimen between metal plates to determine compressive modulus, boundary conditions at the rubber-metal interface significantly affect the results, as shown in Figure 2.6 [232].

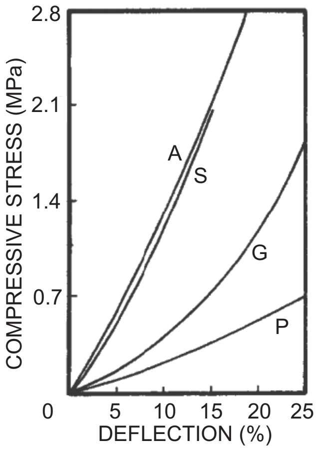

Figure 2.6 Boundary condition and deflection effect on compressive stress. A, adhered; S, sandpaper; G, graphite; P, petrolatum [232]

The use of sandpaper results in a compressive modulus essentially as high as the adhered specimen, with the petrolatum-lubricated specimen showing the lowest modulus.

It should also be recognized that different tear tests for rubber give substantially different results for the same compound [233]. Figure 2.7 shows three different tear specimens.

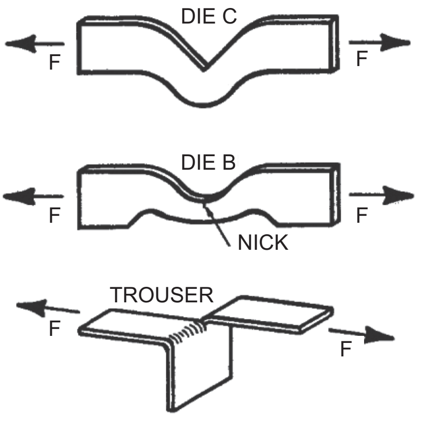

Figure 2.7 Die C, Die B, and trouser tear specimens showing direction of applied force (F) [233]

The Die B and Die C specimens described by ASTM possess a similar geometry and require a relatively high force to stretch them. The tear value obtained with these specimens includes a component of the stretching force. In contrast, in the trouser tear specimen nearly all of the stretching force is expended in generating new surfaces when tearing occurs, not in stretching the specimen legs as with the B and C specimens. Because of this, the B and C specimens exhibit significantly higher apparent tear values than the trouser tear specimen.

Some properties may change depending upon the pressure to which a compound is subjected [234]. For example, increased pressure can decrease the electrical conductivity of a high-viscosity, stiff EPDM. In contrast to this behavior, higher pressure can increase the electrical conductivity of a low-viscosity NBR.

Structural damping has been used for decades to reduce noise and vibration [235] and can be done by bonding a damping rubber layer between two steel plates as shown in Figure 2.8. Shearing of the rubber results in damping of a structure.

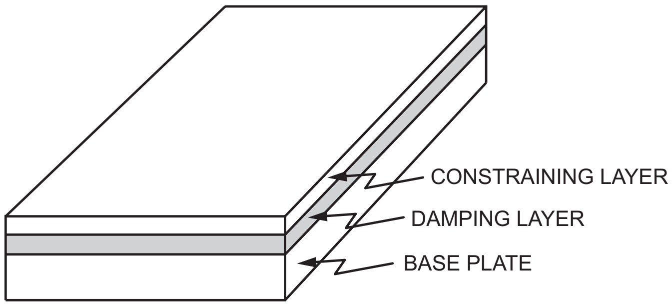

Figure 2.8 Constrained layer damping method

Constrained layer damping applied to a knocking diesel engine resulted in reduced vibration and noise levels [236]. In addition, it was possible to tune the combustion to reduce emissions, pollutants, and fuel consumption. The type of shear plate used was tuned to each engine.

2.20 Taste

Mercapto-type accelerators should not be used, or used only at very low levels, in rubber articles coming in contact with food because they can impart a bitter taste [237]. The compound o-tolyl biguanide is said to be the only nonvolatile basic accelerator to be approved for use in the manufacture of utensils that contact food [238].

2.21 Low-Viscosity Elastomers

Although most elastomers are supplied in a solid-like, high-viscosity form, low-viscosity, castable polymers are available. Polyurethane elastomers and silicone elastomers are among the low-viscosity elastomers discussed in this section.

Castable polyurethanes are the materials of choice for a number of applications that include in-line roller skate wheels, printing and coating rolls, industrial wheels, timing belts, and miscellaneous machine parts [239].

MDI ethers are used to prepare roller skate and skateboard wheels, mainly because their high resilience provides good speed performance and a smooth ride [239]. They are also the materials of choice for abrasion resistance for laundry equipment because of their excellent hydrolysis resistance. TDI esters are used for printing and coating rolls because of good solvent resistance and physical properties in low-hardness formulations.

In contrast to high-viscosity elastomers that require robust, capital-intensive equipment for processing, equipment for casting often costs significantly less. Where short pot life is a problem, heat-activated curatives can be “blocked” below a certain reaction temperature [240]. Viscosity depressants can extend pot life and minimize void formation; however they can contribute to higher shrinkage [241].

RIM (reaction injection molding) is an alternative method for mixing and molding low-viscosity polyurethanes. By this process, two reactant streams impinge at a high rate, react, and crosslink rapidly and thus provide short cure times.

Fillers incorporated in low-viscosity polyurethanes increase the viscosity of a polyurethane-filler mixture and therefore reduce the ability to easily pour the mixture. Hence, maintenance of good flow characteristics can limit the content of very fine particles to about 20% by weight of the liquid materials. Larger particle fillers such as spherical glass beads and microspheres are tolerated up to 200 parts because of their decreased effect on viscosity per unit of filler.

Moisture associated with fillers can cause problems [242]. Materials used in compounds that are cast into a vacuum chamber should possess very low vapor pressure in order to minimize void formation. Vapor pressures less than 4 mm (Hg assumed) at 120 °C are said to meet this goal. Vapor pressures of compounding ingredients vary widely at 120 °C: from 4.9×10^{-5} torr for dioctyl phthalate (plasticizer) to 9.5 torr for toluene diisocyanate. Pot lives as short as 15 to 20 seconds have been used with centrifugal casting, which rapidly distributes materials.

While centrifugal casting allows air bubbles to rapidly escape, it can cause separation of different-density materials in a formulation [243]. This problem worsens as pot life increases.

Table 2.10 summarizes some of the problems associated with low-viscosity polyurethanes and suggests possible remedies [244].

A number of techniques are available to mold polyurethanes, including open casting, compression and transfer molding, and vacuum centrifugal casting [245].

Polyurethane has been used to manufacture solid tires [246]. These tires are not usually used in environments above 100 to 120 °C because the hard segment in the polyurethane softens considerably.

Table 2.10 Problems with Low-Viscosity Polyurethanes and Some Possible Remedies

Symptom	Likely Cause	Possible Correction
High-viscosity prepolymer	–	
Processable prepolymer	Slight thermal degradation	Determine % NCO in prepolymer and adjust NCO/OH ratio
Nonprocessable prepolymer	Extreme thermal degradation	Discard material
Solids in prepolymer	Moisture contamination	Discard material
	Thermal degradation	Discard material
	Unmelted prepolymer	Increase melt time or temperature
Skin on prepolymer surface	Moisture contamination	Discard material

2.22 Silicone Rubber Viscosity

Silicone rubber is available over a very wide range of viscosities. Millable or high-viscosity silicone rubber is called high-consistency rubber (HCR); its counterpart, liquid silicone rubber, is called LSR. LSR provides better economics for high-precision articles, especially for articles with intricate shapes.

The components for LSR are typically supplied in equal-volume containers to molders. They are pumped at a 1:1 ratio through a static mixer before being fed into the barrel of an injection-molding machine. Meter-mix machines are designed to deliver components in equal amounts to within ±1%, an accuracy that favors the manufacture of both on-specification products and economical production.

Viscosities (at 25 °C) for two-component LSRs range from one Pa·s, which pours easily, to 10,000 Pa·s, which is paste-like [247]. Pumpable LSR formulations provide high strength and low compression set with no post-bake. They also mold rapidly and provide oil resistance for gasket applications.

Mixing machines must maintain metering accuracy while handling a range of viscosities; materials of construction that contact silicone components in machines must resist corrosion. Hoses that convey silicone components must be sulfur-free since sulfur inhibits cure in the mixed components and typical elastomer hoses contain sulfur. One-part LSR is now available that has a very long pot life [248].

Maintaining the mixed components at about room temperature or lower minimizes precure problems. In operation, a mixture is injected through a chilled nozzle into a heated mold that is usually at a temperature of 149 to 204 °C. Typical injection pressures are about 6.9 to 34.5 MPa, cure times 25 to 55 s, and cycle times 30 to 60 s. Attention should be given to the possible interaction between LSR molds and the material in which they are molded [249]. For example, the amine produced in an epoxy-matrix cure for a graphite-epoxy composite can attack the silicone rubber and reduce the life of a silicone mold. The attack can also distort a silicone rubber mold. The use of a barrier coating and a release coating on the mold can significantly increase mold life.

LSRs are moderate-viscosity siloxane polymers compounded with reinforcing filler, crosslinker, and a curing catalyst. Curing these compounds with a platinum-based catalyst offers several advantages that include short cycle times, tolerance for thin and thick cross sections, and the lack of by-products from the crosslinking reaction. Peroxides, more commonly used to cure silicone elastomers, produce by-products.

Fillers are incorporated into LSRs for several reasons: ground quartz reduces cost and lowers the coefficient of expansion of the resulting compounds; aluminum trihydrate improves flame retardance and high-voltage resistance; titanium dioxide modifies opacity and heat stability. The maximum allowable particle size for fillers requires attention because of the shallow gates in molds used with LSRs. When LSRs are pigmented to produce colored compounds, crosslinkable pigment masterbatches offer more uniform pigment dispersion.

A fiber-reinforced, platinum-catalyzed LSR offers much shorter cure times than that from a peroxide cure [250]. The fibers are potentially bondable to the matrix. Applications include a fiber-reinforced LSR pressure hose and textile-reinforced membranes.

After completion of crosslinking in an injection mold, a molded article should be ejected from its mold with a mushroom-shaped ejection pin rather than a tapered pin [251]. The larger face area of the mushroom pin distributes the stress at the silicone rubber-ejector interface and thus minimizes stretching of the silicone. To further ease ejection, air can be blown between the ejector pin and its surrounding wall. Because of the low viscosity of LSRs, the clearance between pin and wall should be minimized; a total clearance of 0.0003 to 0.0005 inch reportedly provides adequate venting while preventing flash.

2.22.1 LSR Molding Factors

Table 2.11 describes problems that occur with LSRs and suggests solutions [252].

Venting during molding is important with both higher viscosity polymers and with LSRs [253]. Machining of the parting line surface of molds to 16 to 20 rms for some very small LSR articles can adequately vent a mold.

The hot tear strength of some LSRs permits demolding of articles with large undercuts without damage [254]. Demolding factors for consideration include stripper plates, ejector pins, air eject, robotic handling, and roller sweep.

Table 2.11 Potential Problems, Causes, and Solutions for Molding LSRs

Problem	Cause	Solution
Underfill	Nonoptimal pressure or injection speed	Raise injection speed and possibly injection pressure
Flash	Shot size too large	Reduce shot size
	Clamp force too low	Increase clamp force
Undercure	Incorrect mix ratio	Clean supply lines and mixer
	Curing inhibited	Eliminate sulfur or tin contamination in LSR unit
Scorch	Too low injection speed	Raise injection speed and possibly injection pressure
	Mold temperature too high	Lower mold temperature
Demolding difficulty	Mold temperature too high	Lower mold temperature
	Mold construction	Optimize undercuts and adjust surface roughness

The ultimate in robot use is the handling of a raw egg without shell damage [255]. Soft silicone fingers grasp the egg; the bending of the fingers is actuated by air pressure.

It may be necessary to retune an LSR injection-molding process when changing from one supplier to another [256]. Special attention must be given to the viscosities of the components when injection molding an LSR.

Injection-molding machines for clean-room use can be built of stainless steel and anodized aluminum that requires no lubricant or hydraulic oil [257]. An LSR press for micro-sized articles has a 0.4 ton clamp and a shot capacity of about 0.75 gram. Injection pressure is 21,000 psi.

2.23 Coatings

Features of rubber coatings include resistance to hostile environments, resistance to sticking of in-process rubber sheets, and marking of the edges and center of roads.

Stable one-part elastomeric coatings that crosslink at room temperature bond well to elastomeric substrates and show excellent fatigue resistance and strength [258]. Other merits are improved ozone resistance when applied to NR and BR surfaces and the cosmetic appearance of molded elastomeric articles. Oil resistance of non-oil-resistant elastomers was improved through application of a fluorocarbon coating [259]. As little as 13 µm combined thickness coating effectively protected NR from hot oil even during dynamic cycling.

Other coatings are used to prevent adhesion during the manufacture of rubber articles such as tires [260]. Carboxylated latex containing a minor amount by weight of a heat sensitizer was sufficient to gel the polymer. Fillers, wetting agents, and stabilizers can be used to provide a water-resistant film on the surface of a rubber compound. The coated rubber can be stacked or assembled without sticking. A variant of this is described in reference 261.

Coatings for marking the edges and center of roads must dry quickly after application and must be durable [262]. The yellow coatings that originally contained lead chromate as the colorant have been phased out for toxicity reasons; they were replaced by organic materials.

2.24 Plastisols

A plastisol is a low-viscosity composition of PVC particles in a plasticizer that might consist of 100 parts by weight of dioctyl phthalate (DOP) plasticizer per 100 parts of PVC by weight, plus other materials such as pigments and stabilizers. Plasticized polyvinyl chloride (PVC) compositions are considered elastomers here because they are soft and flexible, have a high rupture elongation, and they compete with some products fabricated from conventional elastomers [263].

PVC-based homopolymer compositions are the most widely used plastisols, although some copolymer-based plastisols are used for specialty applications. For example, a formulation for a soft toy with 85 parts DOP might have a viscosity of 1 to 2 cP at 25 °C. A formulation with the same viscosity for a harder molded article contains 65 parts DOP and two parts of a viscosity depressant. A thermal stabilizer was included in a similar formulation that incorporated recycled PVC. Properties of the stabilized compound that contained the recycled PVC are said to be similar to those of a fresh plastisol.

PVC particles (initially suspended in plasticizer) contain crystallites as physical crosslinks that dissolve extremely slowly at room temperature, even though they are thermodynamically soluble. With initial heating, the plasticizer first swells and then gels the PVC particles. Additional heating fuses the crystallites and converts the mixture into a rubber-like solid.

Repeated dipping of an appropriate form into a plastisol formulation produces molded articles [264]. Either cold or preheated forms may be used, after which heating fuses the plastisol. Repeated dipping increases the thickness of the PVC deposited. After fusion and cooling, molded articles are stripped from the form. This technology is used for coating wire and screening. Dip-molded plastisol articles lend themselves to the production of complex-shaped articles with undercuts such as bellows. Rounded convolutes on bellows ease removal from forms and provide increased service life. Table 2.12 lists some dip-molding problems, probable causes, and suggests remedies.

Table 2.12 Selected Problems, Likely Causes, and Solutions for Dip Molding

Problem	Likely Cause	Solution
Nonuniform thickness	Incomplete drainage	Increase time for drainage
Variable coating weight	Poor gelation	Use faster solvating plasticizer
Cold dip	Change in rheology of plastisol	Use higher MW resin or slower solvating plasticizers
Hot dip	Inadequate control of preheated parts	Heat parts to a uniform temperature
Sagging	Viscosity too low	Incorporate thixotrope
Bubbles	Inadequate deaeration	Improve deaeration process
Pinholes in thin coats	Poor wetting of mold surface	Lower viscosity of plastisol

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3 TSE Processes and Equipment

3.1 Adhesion

Adhesion is affected by materials, process, and equipment. It plays a vital role in the success or failure of many rubber composites that involve a broad range of rubber types, adhesives, and substrates. Ease of adhering different types of rubber varies substantially. For example, polar rubbers like NBR are more easily adhered than nonpolar rubbers like EPDM. Some adhesive applications require two coats of adhesive, while single coat adhesives are satisfactory for others. Resins have been used for years to promote adhesion between rubber and wire reinforcement in tires [1], with two-component resins typically being used. Single-component resins have been developed to replace the latter.

3.1.1 Substrates

Substrates vary widely and include metals, plastics, fibers, and fabrics. Managing this range of materials requires considerable attention to detail if satisfactory adhesion is to be achieved and maintained. Different adhesion tests are available to the rubber technologist. Some tests are designed to determine adhesion under low-pressure (Figure 3.1) molding conditions by applying pressure through a rubber bladder rather than by a metal platen [2].

Conventional rubber-to-metal adhesion involves an adhesive to bond rubber and metal and a separate curing system to impart the desired physical properties [3]. Ingredients in a compound intended for bonding significantly affect adhesion. Among plasticizers (aromatic, naphthenic, paraffinic, and ester), bond strength decreases in the order aromatic, naphthenic, paraffinic, with the ester plasticizer the lowest [4]. Both the cure system and the antiozonant choice affect adhesion [5]. Of the antiozonants tested, PPD-type antiozonants most adversely affected adhesion. These same antiozonants showed less sensitivity to low-sulfur cure systems than to high-sulfur cure systems.

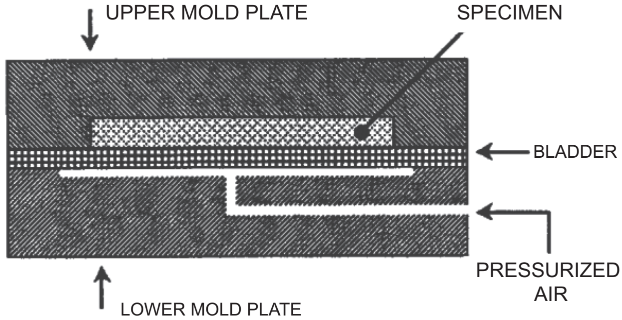

Figure 3.1 Rubber bladder applies pressure to an adhesion specimen. (Figure courtesy of R. J. Del Vecchio, Technical Consulting Services)

In another study, higher sulfur levels generally improved adhesion relative to the lower sulfur levels used in efficient vulcanization (EV) systems [6]. High-sulfur systems can be a problem if the sulfur blooms to the surface of a compound and interferes with adhesion.

Sulfur from EPDM compounds can be problematic in some electronic applications [7]. It can react with silver, which often is the material used for electrical contacts in switches and relays. The reaction product, a film of silver sulfide, is not conductive and can cause failure.

Self-vulcanizing solutions of rubber that contain sulfur and an accelerator can gel prematurely [8]. To avoid this problem, two solutions can be prepared, one containing the sulfur, the other the accelerator, and these are mixed just before use.

3.1.2 Substrate Surface Treatments

Chlorination increases the polarity of the surface of natural rubber and favors increased adhesion. A solution for treating a rubber surface follows [9]:

Distilled water	100 parts
15 % sodium hypochlorite solution	2
Concentrated hydrochloric acid	1

Chlorination can also be done with trichloroisocyanuric acid, an organic chlorine donor [10]. This material has been found effective in improving the bondability with an epoxy adhesive. Chlorinated surfaces produced bonds that retained much of their bond strength during immersion in seawater at elevated temperature.

Migrating ingredients such as stabilizers can cause adhesion problems as shown by poor adhesion that occurred between shoe and sole. An excess of stabilizer on the sole surface was found to interfere with chlorination of the sole and caused poor adhesion [11]. Chlorination of Kraton soles should be done without roughening the sole [12]. Bonding can be accomplished using solvent-based polyurethane adhesives.

Teflon film, bonded to rubber, can impart a very low-friction surface to rubber. The Teflon surface must be etched prior to bonding it to the rubber surface, for example by an oxidizing acid, a flame, or by a hydrocarbon dispersion of sodium [13]. Caution should be exercised when working with these hazardous materials. Sodium-etched rubber reportedly has doubled adhesion [14]. An alternative etching method, Tetra-etch™, can etch the surfaces of fluoropolymer materials [15]. It functions by stripping the fluorine atoms from a flouropolymer chain.

Rubber surfaces can be flocked to lower the coefficient of friction in glass sealing applications on automobiles [16]. Good adhesion between flock and rubber is important. Although low-friction coatings are available for the same purpose, flocking offers the advantage of filtering out debris that could scratch a glass surface.

A relatively new adhesive technique involves a fast-cure silicone bonder for silicone articles [17]. The bonder (Silicone Solutions SS-67B) is said to benefit assembly operations and increase production rate. A primerless solution is available to permit overmolding of an injection-molded plastic article with liquid injection-molded silicone [18]. The hard plastic in an overmolded rubber-plastic overmolded article makes ejection easier; however, the plastic must be cooled sufficiently so that only acceptable witness marks are evident on the molded article [19].

Newer grades of LSR permit overmolding of thermoplastics that favor damage-free demolding [20]. A new class of TPEs bonds to dissimilar thermoplastics such as COP, ABS, and PMMA [21]. Elastocon STK40BX, a 40 Shore A SEBS-based TPE, reportedly bonds to other polymers that include PC, ABS, PC/ABS, acrylic, COP, and various nylons [22].

Overmolding is widely used with TPVs to combine two different hardness materials and/or two different colored materials, a common practice with consumer materials [23]. PP is the ideal choice for the substrate material, but if the overmolded material is too thin, a poor bond may result; thickness less than 1 mm should be approached with caution. A thickness of 1 mm to 3 mm is common, and a constant wall thickness is desirable.

There are many polymer applications in which an engineered thermoplastic material provides the main functional strength in overmolded composites [24]. SEBS overmolded on a substrate provides the soft touch and high grip desired in many applications, such as toothbrushes. It can also enhance visual effects.

Plasma, an ionized gas, can alter the surface of silicone rubber to improve adhesion [25]. After using a plasma pretreatment, silicone rubber switches were coated with a polyurethane top coating. The treatment creates NH- and CN-groups on the surface, which give a higher surface energy, resulting in good bonding to the polyurethane coating.

Other plasma uses include treatment of EPDM to greatly improve bonding and encapsulation of side window glass with TPE [26]. This application previously required the use of harsh chemical treatments. Treatment of a cured silicone surface with phenol and sodium dichromate/sulfuric acid etch has also been used [27]. Earlier use of plasma required special conditions; it is now possible to maintain plasma in the atmosphere [28].

3.2 Effect of Ingredients

Silicone adhesion promoters are increasingly used in the rubber industry [29]. A promoter results in greater static strength and dynamic stiffness without changing vulcanizate characteristics.

Different compounding ingredients often have a different effect on compound properties such as ease and degree of adhesion [30]. For example, accelerator type had the most pronounced effect on tested properties, suggesting that type and distribution of crosslinks may be more important than crosslink density. Decreasing the level of accelerator in an NR compound increased the pullout force for vinyl pyridine latex adhesive; it decreased the pullout force for an SBR latex adhesive [31].

Other ingredients such as zinc stearate can reduce adhesion problems by blooming to the surface [32]. Zinc stearate, formed by a reaction between zinc oxide and stearic acid in a rubber compound, serves as an activator for vulcanization. Lauric acid, which has a lower molecular weight and improved solubility relative to stearic acid, can lessen bloom problems [33].

Some materials such as acetone can destroy the bond in adhered rubber articles [34, 35]. In some instances bond destruction is intentional. For example, immersion of a bonded rubber-metal article in liquid nitrogen, wherein the large differences in coefficient of expansion between rubber and metal result in large shear forces at the bondline, can induce bondline failure. Ultrasonic devices have been used to detect flaws in bonded rubber products such as engine mounts [36].

Rubber is typically bonded to metal cylindrical cores to produce rolls intended for a wide range of applications. After the rolls reach the end of their service life, the cores can be reclaimed using a Lepel low-frequency heater wherein the rubber-covered roller is passed axially inside a coil that preferentially heats the surface of the metal core. The heating softens the rubber at the bondline and enables the rubber to be slid off as a tube [37].

3.2.1 Substrate Considerations

Preparation of metal substrates for bonding often involves the use of solvents for degreasing metal surfaces [38], either by immersion or vapor degreasing. Using the vapor method, care must be taken that the degreasing solvent does not become so contaminated that it causes reduced bond strength. Vapor degreasing is considered more efficient than dipping or spray cleaning.

Effective degreasing ensures that the adhesive will thoroughly wet a substrate, which is often steel [39]. Substrates can become more contaminated after degreasing if the degreasing medium becomes excessively contaminated. After degreasing, the second stage of steel surface preparation involves removal of an oxide layer so as to expose the adhesive to an oxide-free surface. Chlorinated solvents are considered the most effective degreasing agents. However, they are now being replaced by aqueous chemical degreasing materials because of toxicity and ecological problems.

Grit blasting of metallic surfaces is simple and provides a good surface for bonding [40]. Ferrous surfaces are often phosphated to improve corrosion resistance and increase service life of bonded rubber-metal components [41]. Phosphatizing produces a relatively thin phosphate layer on a metal surface; typically 0.003 to 0.005 mm. Phosphated components should be protected from moisture and other contaminants by sealing them in containers before use. MetalJacket™ is a new corrosion-control system that eliminates phosphating and the need for a primer [42].

Among factors affecting bonding, contamination problems sometimes occur with phosphating [43]. For example, a phosphate bath deposited fatty acids in addition to phosphate on surfaces to be bonded. Analytical techniques such as secondary ion mass spectrometry characterized failures in molded articles, dried films from the phosphate bath, and lubricants used in the manufacturing plant.

Compressed air used for spraying adhesives is another potential area for contamination [44]. A filter should be incorporated in compressed air lines to eliminate oil and moisture; additionally, when spraying adhesives containing isocyanates, a refrigerated air-drying system should be used because isocyanates readily react with moisture [45].

Leakage and wasted energy are also concerns with compressed air [46]. Leakage surveys have shown that reducing leakage significantly reduces costs. In one plant survey, it was found that a plant's substantial compressor system was doing nothing other than feeding leaks. For factories with multiple compressors, electronic sequencing (rather than simple pressure switches) is suggested to control compressor operation [47].

Metal-forming lubricants should not contain silicone oil, which can interfere with adhesion; hence the use of silicone mold release agents must be carefully controlled. Airflow from fans used to cool a rubber molding area can entrain spray and potentially deposit it downstream on adhesive-coated substrates in a molding area. Hence, adhesive-coated substrates should be covered with clean plastic film to protect them.

Adhesive-coated metal inserts molded in a rubber article can be problematic, especially if the metal insert is heavy and requires a long time to reach mold temperature [48]. Preheating an adhesive-coated metal insert using hot air can cause the adhesive to cure prematurely because of the poor heat transfer that occurs between air and metal relative to induction heating, which selectively heats the metal. Induction heating reduced the heating time of a metal insert by 10% [49].

3.2.2 Adhesive Type

Adhesives are mainly solvent-based or water-based, with the water-based adhesives becoming increasingly used. The latter are dispersed in water as micelles (small particles) that coalesce into a film after the adhesive dries [50]. Water-based adhesives should be prepared by stirring, not shaking, to avoid foam formation [51]. Their use requires special attention to the slower evaporation rate of water relative to the solvent-based adhesives. Use of too high a temperature and airflow rate to increase the evaporation rate of water can be problematic [52]. The surface of the adhesive could form a skin that will slow the evaporation of water below the skin.

There is reluctance to change from solvent-based adhesives to water-based adhesives because the latter are considered more demanding to process and handle [53]. It is estimated that water-based adhesives are used in only about 10% of the global adhesive business. Even when a change is successfully made to water-based adhesives, a new contract may stipulate the use of solvent-based adhesives.

Skin can also form on the surface of solvent-based adhesives. However, organic solvent will permeate the film faster than will water. Use of solvent can be hazardous as evidenced by OSHA reporting that about five workers are killed annually in accidents involving solvents [54]. One worker was killed when lining a steel tank with rubber sheeting using a solvent-based adhesive. The latter adhesive was replaced with a patented solvent-free system that eliminated the risk of flammability. Changing from a solvent-based adhesive to a water-based adhesive reduced the amount of volatile organic compounds entering the atmosphere by 15,000 pounds [55].

Most bonding agents contain solids that must be homogenized and suspended if the adhesive is to function effectively. Weimar states that “more bond failures have occurred due to inadequate mixing than almost any other cause” [56]. Bonding typically requires a thickness of 7 to 13 μm of primer and 20 μm of cover coat, with the thickness required depending upon the substrate roughness. Rough substrate surfaces require more bonding material to cover peaks.

Freeze-thaw stability of water-based adhesives is a concern in winter [57]. Another concern is the ability of a water-based adhesive to wet a substrate surface compared to a solvent-based one. Also, water-based adhesives are considered more corrosive. Corrosion of steel cord is a critical consideration in determining the life of tires, especially truck tires [58]. A careful balance must be made between excessive corrosion and good adhesion.

Some technical problems do not show up until a product has been in service or stored for some time, as was the case with the radial 500 tire [59]. Adhesion problems with the tire were said to be associated with moisture that exited the bond between the steel cord and the surrounding rubber. The chemical reaction between these components could take place whether the tire was in service or in storage. The problem showed up only after the tire was put into service.

Where cements are used to bond sheets of rubber for roofing, the volatility of the solvent can play an important role. Low temperature can slow solvent evaporation time, which results in decreased productivity [60]. The use of more volatile solvents would increase productivity.

Tie gums are an alternative to solvent- and water-based adhesives in several applications. The first is a seaming tape for joining overlapping EPDM sheets (Figure 3.2) for roofing [61]. The strip, a lightly crosslinked blend of butyl rubber and polyisobutylene, imparts adhesive strength adequate for this static application. It is an alternative to solvent-based cement for the adhesive system.

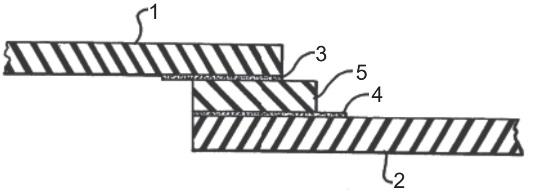

Figure 3.2 EPDM roofing membrane bonded with seaming tape. 1, 2: membrane; 3, 4: primer; 5: seaming tape, U.S. Patent 4,6001,935

In another application, a two mm thick tie gum provided good adhesion when used in the manufacture of solid rubber tires [62]. In other work, a one-part heat-curable urethane adhesive proved superior to other one-part adhesives [63].

Requirements for adhesives for some applications are especially demanding, as in timing belts [64]. Reactive processing is said to provide good fatigue resistance, high retention of strength, and resistance to creep of cord and belt. Excellent aramid-to-rubber adhesion resulted by first activating the aramid with epoxies prior to RFL treatment [65].

Bondline corrosion can be problematic. Aluminum oxide/hydroxide was observed as the predominant corrosion material in stored solid rocket motors [66]. Analysis of ruptured bondlines showed that the locus of failure for uncorroded samples was predominantly near the aluminum-primer interface. The primer was identified by its high concentration of chlorinated hydrocarbon.

Adhesives for bonding cathodically protected rubber-to-metal devices have been developed [67]. There is general agreement that chemical reactions that occur in adhesives cause a loss in adhesion. Eventually, rubber and adhesive delaminated from the metal; this was associated with an osmotic pressure increase as water accumulated at the bondline. Zinc phosphated steel generally improved performance, and a salt spray test can be used for measuring cathodic resistance.

Zinc phosphate processing equipment that is used for pretreatment must be temperature controlled within ± 5 °C (10 °F) with an immersion time of ± 0.5 min [68]. It should be noted that zinc phosphating did not remove heavy rust and weld scale. Different treatments are necessary for other metals: acid etching for stainless steel and chromate alodizing or anodizing for aluminum.

A very corrosion-resistant new alloy (Zn/Ni/Co) exhibits both passivation and cathodic properties [69]. Films of plasma-polymerized acetylene deposited on a steel wire can provide outstanding adhesion to NR compounds, with adhesion results comparable to that in pure brass. Reduced concentrations of zinc oxide are said to significantly improve bond fatigue life of brass-coated wire [70].

Advances in technology can place additional demands on rubber products. For example, hydraulic engine mounts with extended dynamic properties incorporate ethylene glycol, necessitating development of glycol-resistant adhesives [71]. The adhesive system demonstrates resistance to high temperature, boiling water, salt spray, and a wide variety of aggressive automotive fluids.

Environmental concerns and new technological factors affect adhesives technology. A major adhesives manufacturer used lead compounds and selenium to improve high-temperature and corrosion resistance [72]. A proprietary replacement for these materials was discovered that did not result in associated environmental concerns. A number of adhesion factors are involved with the molding of rubber articles, including allowing adequate time between adhesive coats for complete evaporation of solvents from the adhesives [73]. Ideal bonding conditions occurred when the rubber compound was under maximum pressure at minimum viscosity. Remember that water-based adhesives dry more slowly than solvent-based adhesives [74]. Hence, longer drying times must be provided for the water-based adhesives.

Another factor is the size and mass of metal used in molding a bonded rubber-metal composite [75]. A heavy metallic mass can act as a heat sink and lower the temperature at the bondline below the temperature necessary to activate the adhesive for formation of a good bond. Preheating metals prior to placing them in a mold can remedy this problem; care must be exercised to prevent precuring the adhesive on the substrate. Once an effective bonding process has been established, it is important to set up appropriate controls and training to ensure continuing good bonding practices [76].

Defects in molding should be tracked and recorded by mold cavity position so that trends or patterns can be observed and subsequently addressed [77]. This helps troubleshooting activities and deciding whether to replace just a portion of a mold or the complete mold.

The American Society for Testing and Materials (ASTM) provides a number of rubber test methods, with adhesion tests for rubber being listed under method ASTM D429. Adhesion tests should approximate as closely as possible the actual materials, stresses, and environmental conditions that a bonded rubber article is expected to see in service [78].

Merely specifying a peel test for adhesion is inadequate since peel forces for peeling rubber at an angle of 90° are often much higher than those for a T-peel arrangement [79]. Some established test methods are being improved. For example, Lord Corporation has developed a revised test method called a buffer [80]. It consists of a rubber section vulcanized between two metal parts with a convex surface (ASTM D429 Method F).

The design of molded rubber articles is important because it affects the stress at the interface of a rubber-metal article [81]. Use of a bonded rubber block with rounded corners significantly reduces the stress at the bondline because the peak stress moves from the bondline into the rubber.

Plastics are increasingly replacing metal in rubber composites [82]. Some of these can be bonded without the use of conventional adhesive. An example is the bonding of polyphenylene ether plastic to elastomer. The plastic, molded first, is overmolded with an elastomer. Chemicals in the elastomer form a bond with the plastic during overmolding. The plastic must resist the deformation that it encounters during the molding step to form the composite.

Suggestions for overmolding LSR onto thermoplastics include:

- keeping the thermoplastic clean and dry
- having the LSR contact a hot substrate surface
- avoiding thermoplastics with internal lubricants
- gently demolding an overmolded article
- providing a sample of substrate to an LSR supplier for preliminary testing.

It is now possible to mold a liquid silicone onto a plastic using a window in the mold that is transparent to UV radiation [83]. UV causes the silicone to crosslink at low temperature in about twenty seconds to form composites.

■ 3.3 Testing

It is pertinent to distinguish between tests that yield data for engineering design and quality control tests that merely verify that one batch of material has the same properties as another batch [84]. In an ideal world, such a distinction would be unnecessary; the tests used to generate design data could also be used for quality control purposes. In our nonideal world, tests useful for generating design data, such as shear modulus data, are often regarded as too tedious, costly, or difficult and consequently are rarely used on a routine basis.

Shear modulus is a very important property used to characterize many engineered rubber products; tests for it have improved over time [85]. Figure 3.3 shows the single-lap shear specimen originally used to determine shear modulus [86].

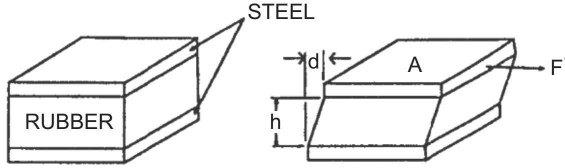

Figure 3.3 Bonded steel-rubber shear specimen without (left) and with an applied force [86]

This specimen caused testing difficulty because it tended to rotate during testing; changing to the double-lap specimen described in ASTM 945 solved the rotation problem. However, there was then a problem with unwanted stresses associated with the plates bonded to the rubber remaining parallel. The quadruple-lap specimen in Figure 3.4 solved this problem because the plates could move parallel to one another during testing.

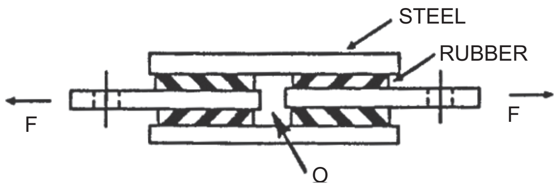

Figure 3.4 Quadruple-lap shear specimen, courtesy of Rubber World [86]

A range of physical tests is important to generate appropriate data for specifying properties for rubber products. The designer needs to communicate to the manufacturer of rubber articles the nature of the rubber material to be used and the properties required. This takes the form of a technical specification that normally defines acceptance criteria based on a number of standard physical tests. In establishing the specification, the designer should recognize the precision, or lack of precision, of the physical tests being used. ASTM generally includes statements that provide guidance for the normal within-laboratory and between-laboratory tests.

Test results obtained in the laboratory for rubber depend significantly more on test conditions than is the case for metals; for example, the force required to reach a specific elongation for rubber could vary by a factor of three over a range of test speeds [87]. Another feature of rubber is that its modulus, at for example 300%, will *increase* with increasing temperature for a range of temperatures well above T_g of the rubber.

Test results obtained with specimens using special test slabs prepared in the laboratory should be distinguished from specimens cut from a finished rubber article [88]. In preparing specimens from finished rubber articles, buffing is generally preferred for preparing soft rubber compounds, splitting for harder ones. An additional consideration is that factory processing conditions seldom exactly duplicate those of small-scale processing in the laboratory. Good dispersion of fillers is typically more difficult to achieve with large factory mixers than with small laboratory mixers.

Further, production-mixed batches reach higher mixing temperatures than laboratory-mixed batches. It therefore is prudent to experimentally verify that results from the two different types of test specimens are comparable when quantitative comparisons are needed. Tensile strength and elongation at break values obtained from test pieces cut from a finished component are often about 10% lower than results obtained from specially prepared test slabs. For this reason, some specifications provide for lower test requirements when test pieces are cut from finished components.

Dull or nicked dies are a frequent cause of low breaking elongation (short breaks) when testing rubber dumbbell specimens [89]. Hence, light daily honing of the cutting surfaces of dies is recommended. If short breaks occur, failed specimens should be stacked upon one another to determine if breaks occur at or near the same location in each specimen. If they do, a dull or nicked region in the die is indicated, and this region is the probable cause of the short breaks. Injection-molded dumbbells produced higher ultimate tensile strength than did die-cut specimens [90].

A highly volatile ingredient or low curing pressure can cause voids (porosity) in a compound that can serve as flaws and cause premature failure. Foreign matter, also a source of flaws, can come from unexpected sources. Foreign matter, for example, pieces of glass, cardboard, and even football tickets, were found in factory-mixed compound [91]. The foreign matter was ultimately traced to an overly zealous floor sweeper who dumped the contents of his dustpan into the throat of an internal mixer. When questioned, he innocently replied that he thought the mixer throat was a large dustbin, demonstrating that a little training can have a large payback.

Global Standards for Plastics Certification (GSPC) have been developed in England [92]. A comparable standard for rubber would appear to be quite useful, because implementing the GSPC training resulted in the following improvements:

- scrap rates reduced by at least one-third
- downtime reduced by 30 %
- 20 % to 30 % improvements in successful startups
- significant reduction in turnover of lower-skilled labor.

Most of the standard test methods adopted by the rubber industry are quality control tests that yield data that cannot be directly related to performance. While quality control tests are very important, they are inadequate alternatives for tests that yield design data. Because of the critical nature of some rubber articles, tests may be required on every article to establish its suitability [93]. Less critical articles can be tested on a statistical basis to save testing costs.

Compression set occurs in rubber placed under prolonged compression, and its extent depends upon a number of variables [94]. ASTM D395-98 describes methods for testing under either a constant force (method A) or a constant deflection (method B) for specified temperatures and times. The residual deformation of the test specimen is measured 30 minutes after its removal from the test device. The more common method B measures set under constant deflection, partly because it requires simpler equipment than that used for method A.

Compression set is of interest not only at higher temperatures but also at lower temperatures. NR vulcanized with a semi-EV curing system can be used when moderate exposure to cold conditions is expected, provided that certain conditions are met:

- Avoid reducing curative levels below the recommended levels.
- Specify the cure level well beyond the 95 % level on a cure meter.
- Warm a crystallizable rubber like NR to remove incipient crystallization.

A common misconception is that the lower the compression set, the better the rubber compound; hence, there is a tendency to write specifications that permit very little set. It is possible to achieve quite low values of compression set by overcuring the rubber. But overcure adversely affects other physical properties such as strength, flex, and aging resistance; thus, a low-compression set compound is not necessarily a better material. The rubber technologist has the difficult task of balancing these different properties to obtain the best combination of properties.

For many applications, stress relaxation is a more relevant test than compression set [95]. A thirty-minute recovery time is considered insufficient when measuring long-term compression set characteristics. The presence of filler is known to affect the stress relaxation rate considerably more than compression set values.

Testing of TSE broadly involves raw materials, compounds, and products. The frequency of testing of raw materials varies significantly among manufacturers. Smaller manufacturers of rubber products may accept raw materials from producers without in-house testing. This saves money in the short run but can be problematic if trouble occurs and there are no data available that could help resolve problems.

Specialized testing machines continue to evolve to meet specific testing needs, such as for dynamic testing of rubber [96]. These machines can test a rubber specimen with simultaneous triaxial dynamic linear deformations; they can simulate dynamic linear and torsional deformations to simulate the dynamic use environment of rubber articles such as a rubber mount or a rubber bushing.

Testing low-resistivity rubber compounds for resistivity can be challenging because of the very low electrical currents involved [97]. Using classical methods of measurement on samples with values of 10^{14} to 10^{15} ohm-cm, some negative readings were obtained. Using an improved testing method, more precise measurements could be made.

3.4 Processing

Processing procedures should ideally be prepared during compound development because of the interaction that can occur between the material(s) and process(s), as shown in Figure 1.1 [98]. Both processing factors and compounding ingredients significantly affect the quality of a rubber compound. An allowance of 10% decrease in most physical properties should be made when scaling up from lab to plant [99]. Much of this decrease is associated with the poorer dispersion that occurs in factory mixers relative to lab mixers. Other factors include

- scrap occurring in production (workaway) but not in the lab
- use of full rubber bales in production to simplify weighing
- blend problems that occur in production, but not in the laboratory
- inadvertent conversion of insoluble sulfur to soluble sulfur in production.

Yet another problem is the uniformity of products produced by different working shifts in a manufacturing plant. Evans has concluded that the vast majority of quality problems occur with the night shift [100]. For example, a compound that previously calendered trouble-free for a long time suddenly displayed high nerve (elasticity). The problem was traced to a worker on the night shift who had arbitrarily decided to reduce the number of mastication cycles, thus increasing nerve in the compound.

One anecdote concerns a Banbury operator who was overweight and wanted to avoid using the stairs to get to the restroom [101]. He urinated in the Banbury throat for convenience. This action might have been good for accelerator-deficient batches since the urea in the urine would be expected to act as an accelerator.

It should be noted that conditions can vary widely from plant to plant even within the same parent organization [102]. Individual machines such as internal mixers, mills, and extruders that perform comparable operations in the same plant can produce different results. Also, extrusion characteristics of a compound can vary as a function of the size of the mixer in which the compound was prepared [103].

3.5 Mixing

Mixing problems that occur with high-viscosity TSEs are influenced by a myriad of factors that include procedures, materials, equipment, and improperly compounded stocks [104]. Identifying causes of problems is sometimes more difficult than solving them, whether mixing on a mill or in an internal mixer.

One difficulty is the addition to, and uniform distribution of, very small amounts of an ingredient in a batch [105]. To alleviate this difficulty, minor ingredients can be weighed into plastic bags for subsequent addition to the mixer. When developing preweighed blends of powdered ingredients, attention should be given to potential reactions between ingredients.

It is important that bags have a melting point sufficiently low that they thoroughly disperse during the mixing cycle. EVA bags that have a melting range of 160 to 165 °F are said to dissolve in the mix without contaminating it [106]. Further, they are printable so that bar codes and other identifying information can be imprinted on them. Cri-Tech has developed a bar code system that permits identifying all details associated with a compound within 20 minutes [107]. The system provides batch mixing information, materials information, and applicable specifications.

Both in-process rubber and finished rubber articles can be marked for identification purposes [108]. Methods include printing with co-curable inks and indent marking.

Internal mixers fall into two main categories: Banbury (tangential rotors) and Intermix (intermeshing rotors) [109]. A major difference between the two categories is that mixing in the Banbury occurs mainly between the rotor tips and the cylindrical chamber in the mixer; mixing in the Intermix occurs mainly between rotors, with most mechanical wear occurring around the rotor surface. The Intermix is said to permit conversion of two-pass mixes to one-pass mixes because it maintains good temperature control while delivering a high-energy input to the mix [110].

While both the Banbury and the Intermix are used for medium-viscosity rubber compounds and general rubber goods, Intermix mixers are used for specialty compounding, extreme quality applications, and single-step mixing applications; the Banbury is used for high-volume applications and for plastic compounding applications [111].

Improvements in Banbury mixers include increased capacity, new rotor designs, hydraulically powered hopper assemblies, improved heat transfer, and materials with improved wear and corrosion resistance [112].

Internal mixers must resist not only the corrosive effects of the original ingredients but also of their reaction products [113]. Corrosion can be a problem not only with internal mixers but also with the screws in injection-molding machines and extruders. Fluoropolymers can damage screws as can some flame retardants [114]. Copper gauze and brass-wire brushes can facilitate removal of corrosive deposits.

Problems can occur with extruder gearboxes, motors, and screws [115]. Inspection and analysis services directed toward correction of these problems are available, with some services offering combined inspection and vibration analysis.

New-technology rotors have increased mixing capacity by 4.8%. The latest rotor designs have improved product uniformity, and the mixes can be discharged at lower temperatures. Because of this, two-step mixes can often be converted to one-step mixes. Hydraulically operated hoppers can replace pneumatically operated hoppers and eliminate the variability in ram force associated with compressed air fluctuations that occur within a factory. Additional benefits are reduced energy costs, improved quality, and midstroke ram travel for ram cleaning.

Modified end plates improve temperature control and eliminate or reduce sticking of compound to the plates. Additionally, temperature-controlled mixer ram/weights can be used. During mixing, overloading is characterized by one or more sharp decreases in temperature during an otherwise steady increase of temperature with time [116].

An efficient dust collection system removes most gases and vapors from a mixer. Gases and vapors that remain can cause corrosion when they penetrate the tight clearances and gaps of mating mixer components. They can also enter microcracks in hard surface coatings. Specialty composite coatings can be used to resist corrosion.

Mixers that are intended to be identical in their performance are not necessarily so. Each mixer is said to have a unique fingerprint and other characteristics; examples are the actual volume of the mixing chamber and the actual profile and mass of the rotors [117]. In addition to these factors, ingredient properties vary, and the following actions are suggested to minimize variability:

- Have a purchasing specification on file for each raw material that should include material data, packaging requirements, and documentation.
- Place limits on Mooney viscosity, fines levels, moisture, ash content, and so on for each material.
- Request quarterly SPC charts and other process-related data to ensure that the supplier maintains process control.

MixCont is a radical and new self-adapting approach to mixer control that examines what is happening in a mixer and then compares the observations with the desired results [118]. It then makes decisions about variables such as rotor speed, ram position, and so on. Further, it suggests an ideal fill volume for the mixer and triggers alerts for mixer malfunctions.

Scorch-sensitive compounds can require a two-step mix to avoid premature crosslinking [119]. A modified final mixing process that is said to be superior for mixing uses a Transfermix single-screw extruder in conjunction with a gear pump.

The hardness of fillers, which varies substantially, affects surface wear in mixing equipment. A hard-surface alloy can be applied to wear surfaces to accommodate fillers with different hardness. Table 3.1 shows the hardness for several fillers [120].

Table 3.1 Hardness of Selected Fillers for Rubber Compounds

Filler	Hardness, Mohr No.
Carbon black	1
Silica	3.5–7.5
Calcium carbonate	3
Aluminum oxide	9
Titanium dioxide	6–7

Variable wear occurs with the use of these fillers. Excessive wear can occur in several areas [121]:

- low ram pressure due to wear of piston and cylinder
- excessive dust stop wear
- wear between the rotor ends and the mixer body
- discharge door wear
- excessive clearance between rotor and mixer body.

3.5.1 Mixer Type

Choice of a mixer type depends upon a number of factors, with batch volume being a major consideration [122]. Tires represent more than half of rubber mixed, and their batch weights range from 400 to 1100 pounds.

After mixing in an internal mixer, the batch can be dropped onto a rubber mill that flattens the rubber into sheets or slabs, after which the sheets are cooled and stacked prior to further processing.

Stacking methods include [123]

- wigwagging of strips into a basket after removing the strips from the batch-off machine
- production of strips off-line wherein a full-width strip is slit into narrow-width strips by a slitter and then wigwagged into a basket.

New stacking procedures can significantly reduce the labor associated with manual stacking [124]. A rubber strip is fed to a RotoStrip cooler from an extruder, where it is then coated, cooled, and dried. Cooling is often done in a slab-dip tank [125].

Two-step mixing is often necessary with large batches to avoid scorch, wherein curatives are added in the second mixing step to avoid scorch [126]. Where possible, one-step mixing is desirable to save processing costs. Optimum batch size for a specific mixer should be used to obtain the shortest mixing time [127]. Optimum batch size occurs when a decrease or increase from optimum results in longer mixing time.

It is estimated that intensive mixers need to be rebuilt, replaced, or upgraded every eight to ten years for tire mixers and every ten years for mechanical-goods mixers [128]. Waiting too long to rebuild results in an increased wear rate and requires more replacement parts.

Before replacement or upgrading, it is recommended that a manufacturer determine the condition of the mixer and its components, including dust stops, gears, bearings, door mechanism, rotor condition, and cooling ability.

Table 3.2 shows some typical problems and suggests solutions for internal mixers [129].

Table 3.2 Troubleshooting Internal Mixer Problems

Problem	Probable Cause	Possible Solution
Ram does not rise	Materials sticking in hopper throat	Clean hopper throat
		Reduce batch size
Material sticks in hopper	Accumulated material	Clean hopper throat
	Oversize batch	Reduce batch size
Batch temperature rises	Cooling system inefficient	Clean cooling system
	Improper batch size	Resize batch
Batch temperature rises too slowly	Ram force too low	Increase ram force
	Improper loading sequence	Modify loading sequence
Excessive leakage through dust stops	Improper lubrication	Correct flow rates and lubricant supply
	Worn parts	Replace worn parts

3.6 Mills

Nip opening, mill roll temperature, and roll ratio are among factors that determine whether a rubber goes to the front or back roll during mixing on a two-roll mill [130]. Adjusting the nip can cause the rubber to travel to the front or back roll. A film of milk deposited on a roll surface can increase tack and reduce the tendency of rubber on the roll to bag [131]. Rubber with a narrower molecular weight distribution tends to bag more than one with a broader molecular weight distribution, as do compounds containing high levels of BR.

Available upgrades for rubber mills include improved roll adjustment mechanisms, lubrication improvements, improved heat transfer, and improved drivetrains [132].

Most mill rolls are generally ground to remove defects during rebuilding. Different types of rubber behave differently on rubber mills. Specific recommendations for milling silicone rubber follow [133]:

- Position mill such that the fast roll is accessible to the mill operator.
- Make fast roll adjustable, rather than slow roll, because silicone rubber favors the fast roll as the milling cycle nears completion.
- Use a nylon scraper rather than a metal scraper.

3.7 Dispersion

Small particle fillers are typically difficult to disperse; dispersion of curatives can also be a problem [134]. Good dispersion of curatives is a must to obtain uniformly crosslinked networks. Simple tests such as solvent swelling or stretching a vulcanizate can qualitatively indicate the degree of dispersion. Ideally an accelerator would melt and disperse in a rubber compound.

Dispersion of peroxides in lower viscosity elastomers such as silicone can be problematic [135]. Peroxide DBPH-50-EZD is said to improve both dispersion and clarity in softer silicone rubber compounds. Lower standard deviations obtained from RPA rheometer data and improved clarity confirmed the improved dispersion. Better dispersion typically results when oil is added to a batch after carbon black [136].

If compounds contain substantial oil levels, oil can wet the rotors and chamber walls and cause slippage between compound and metal surfaces that prevents effective mixing [137]. Adding oil and filler together, prior to adding the rubber (upside-down mixing), often overcomes this problem; time should be allowed for the oil to be absorbed onto the filler surface and into the interstices between the particles in agglomerates.

Another potential advantage to upside-down mixing is that it reduces excessive dust from entering the dust collector system [138]. However, a disadvantage to this procedure is that it can rapidly wear dust stops in internal mixers. Modern dust collection systems are said to be so efficient that mixing areas can be as clean as office areas [139].

Too-soft carbon black pellets generate more fines and take a longer time to wet out during mixing [140]. Cooling a batch from a first-pass mix overnight and then remilling it generally improves dispersion. Polarity of a rubber affects dispersion; silica will usually disperse better in a polar rubber such as NBR rather than a non-polar rubber such as NR [141].

Predispersion of materials offers the following potential advantages [142]:

- prevents direct worker contact with hazardous materials
- simplifies material handling
- improves distribution of active ingredients
- increases shelf life.

Different recipes describe predispersions that have been used to improve compound consistency and mixing cycles [143]. Examples are given for different elastomers that include NBR, chlorobutyl, and millable polyurethanes.

3.8 Contamination

Dust, dirt, and grit can come from multiple sources and contaminate rubber [144]:

- oil seepage from leaky oil seals in internal mixers
- residues of materials from previously used tote pans
- residual compound that sticks to the dump chute, mill pan, and mill guides
- poor housekeeping.

3.9 Extrusion

Extrusion and molding have both similar and different features. During extrusion of rubber through a die, the die shapes the rubber in the *x* and *y* directions (in the plane of the die). After exiting the die, the unrestricted dimensions (*x*, *y*, and *z*) of the extrudate are free to change. This means that dimensional control is more difficult with extrusion than with molding.

During molding, a mold cavity shapes and confines the rubber in all three dimensions. Crosslinking a TSE and lowering the temperature of a TPE fix dimensions, and shrinkage is the main concern.

With either process, it is desirable to have a record of process conditions that can be recalled for future reference when problems occur [160]. This procedure is known as constructing a time line, which is developed on the basis that a process was running satisfactorily for a period of time. There must be identifiable changes that cause a process to change, so former data can be used to identify likely causes for changes.

The extrusion process is intended to produce an extrudate with a uniform cross section that remains consistent throughout the process [161]. Extruder die design is an integral part of this process. It involves [162]

- controlling flow inside a die to give the intended velocity profile at the die exit
- determining the dimensional profile at the die exit that gives the desired product while accounting for swell, drawdown of the extrudate, and distortion downstream from the die face.

Face-relieved dies help fill thin edges of rubber extrudates, eliminate tearing, and avoid local velocity minimums in thin regions adjacent to thick sections.

Some slippage of a rubber compound on screw and barrel surfaces is necessary to obtain a smooth and satisfactory extrudate [163]. Compressed air has been blown into porous metal dies in order to increase slippage [164].

Spider die designs have an inherent flaw; they generate weld or knit lines that can produce longitudinal weakness caused by separation and rejoining of a compound during extrusion [165]. Split-flow technology is said to minimize these problems.

Many advances have been made in the rubber extrusion process, such as systems that include feedback microprocessor control [166]. Even with these technical advances, the extruder operator continues to play a disproportionate role in successful extrusion operations relative to other rubber processing operations such as molding.

Downstream handling of extrudates affects product quality. Treads for tires have been historically placed by hand on hinged shelves (called books). They are stored there prior to being applied to a carcass. A new system allows for automatic booking of treads and increases efficiency [167].

The ideal extrusion die distributes the rubber in the flow channel of the die such that the rubber exits the die with a uniform velocity [168]. Important factors in extrusion are flow properties of the rubber, flow channel geometry, flow rate through a die, and the temperature field in a die. These factors are highly interdependent. For example, if the flow channel geometry is optimized for a specific rubber compound for one set of conditions, changes in flow rate or temperature can move the geometry from the nonoptimum condition. With the exception of circular dies, flow channel geometry must generally be tailored to a specific compound and operating conditions for the compound.

Inability to effectively troubleshoot extrusion problems can result in poor extrudate quality, excessive downtime, and low productivity [169].

Table 3.3 lists some general problems with extrusion of rubber and suggests causes and corrections [170].

Table 3.3 Troubleshooting General Rubber Extrusion Problems

Problem	Possible Cause	Correction
Particles in extrudate	Poor ingredient dispersion	Modify mixing procedure
	Scorched compound	Modify mixing procedure or compound
Roughness on extrudate surface	Improper compound rheology	Improve compound rheology
	Die design	Incorporate die relief on input or exit side of die
Irregular feed	Irregular feed strip dimensions	Better control feed strip dimensions
Gradual decrease in output	Screw wear	Replace screw
Compound extrudes differently over time	Change in compound ingredient or source	Use proven ingredients

Table 3.4 describes some problems with extruding silicone rubber [171].

Table 3.4 Troubleshooting Silicone Rubber Extrusion Problems

Problem	Possible Cause	Correction
Soft, sticky compound	Too low molecular weight	Avoid overmilling
		Extrude without freshening compound
Compound overheating	Too large batch size	Reduce batch size
Feeding difficulty	Poor feed throat design	Redesign feed throat
	Improperly sized preform strip	Modify feed strip dimensions
Blisters in extrudate	Excessive humidity	Reduce humidity
Inadequate delivery of compound	Blocked screen pack	Replace screen pack

Suggestions follow for continuous vulcanization of extruded rubber profiles [172]:

- Design compounds with high viscosity for better shape retention.
- Use a cure system that develops a quick set in the extrudate.
- Consider factice as a process aid.

Methods of crosslinking extruded insulation for wire and cable include continuous steam vulcanization (CV) and hot air vulcanization (HAV) [173].

The HAV method requires less floor space than the CV method, which can be 250 ft long. The CV method produces more scrap during startup, an important consideration for short runs. Circulation of forced air in an HAV unit could double production because it induces turbulence that increases heat transfer.

It is recommended that an extruder for Santoprene insulation and jacketing be operated at medium to high speeds that are 40% of maximum or greater [174]. These conditions ensure generating the necessary shear to produce a homogenous melt temperature. The preferred feed screw incorporates a short feed zone that is 15 to 20% of total screw length, a gradual transition zone that is 30 to 40% of total screw length, and a metering zone that is 40 to 55% of total screw length.

3.9.1 Extrusion of Specific Types of Rubber

A statistical model examined the performance of a typical extrusion-grade polyacrylic rubber compound [175]. The model predicted the following key output responses of the extrusion process: extrudate output, temperature, surface appearance, and head pressure. It also identified complex interactions among factors that included screw speed, screw temperature, barrel temperature profile, die temperature, and land length.

Specific extrusion factors are associated with other rubber types such as elastomeric alloy, EPDM, and silicone rubber.

3.9.1.1 Elastomeric Alloy (EA)

Cellular elastomeric alloys, made by both chemical and mechanical processes, can have specific gravity from dense starting materials to as low as 0.25 [176]. The mechanical properties of cellular EA materials make them suitable as replacements for thermoset foams. Cellular EA materials have a very good heat aging resistance that serves them well in automotive sealing applications.

3.9.1.2 EPDM

Composition and structural factors that significantly affect the extrusion behavior of EPDM include molecular weight and MW distribution, long chain branching, monomer sequence distribution, ethylene/propylene ratio, and diene type and concentration [177].

3.9.1.3 Silicone Rubber

Although silicone and other types of rubber are processed on the same types of equipment as organic rubbers, silicone rubber ideally should be processed on separate equipment [178]. A number of problems can occur with silicone processing; several of these are shown in Table 3.5 [179].

Screen packs of 20 to 40 mesh are generally used with silicone rubber, with some being finer, in the 60 to 100 mesh range. They capture contaminants and larger filler particles; in doing so they slow extruder output rate.

Table 3.5 Troubleshooting Guide for Silicone Rubber

Condition	Probable Reason	Correction
Lumps in compound	Poor filler dispersion	Freshen compound
	Compound partially cured	Review compounding and processing steps
Poor feeding	Poor throat design	Redesign
		Adjust width of feed strip
Porosity in extrusion	Entrapped air	Add additional screen or use finer mesh screen

A wide range of elastomers is shaped by extrusion, and many of these contain carbon black [180]. Table 3.6 shows the general effect of changes in carbon black surface area and structure on extrusion properties.

Table 3.6 General Effect of Carbon Black on Extrusion Properties

Extrusion Property	Increasing Surface Area	Increasing Structure
Viscosity	Decreases	Decreases
Wall gauge	Little effect	Increases
Extrusion shrinkage	Decreases	Decreases
Extrusion smoothness	Decreases	Increases
Extrusion temperature	Increases	Increases
Extrusion rate	Decreases	Varies

A number of factors are important in extrusion, including screw design, output rate, die swell, die entrance, and appearance.

3.9.2 Extrusion Factors

3.9.2.1 Output Rate

Screw design is important because it can change output rate by a factor of two. In contrast, a properly designed compound can improve output by only 10 % or more [181]. A simple screw design is preferable unless there is a specific requirement such as significant additional mastication for a compound [182].

3.9.2.2 Die Swell

Rubber swells after leaving an extrusion die because it releases elastic stored energy [183]. A better term for “die swell” is “extrudate swell” since the die does not swell, the rubber does. However, the term “die swell” remains well established in the rubber industry. Figure 3.5 illustrates this behavior [184].

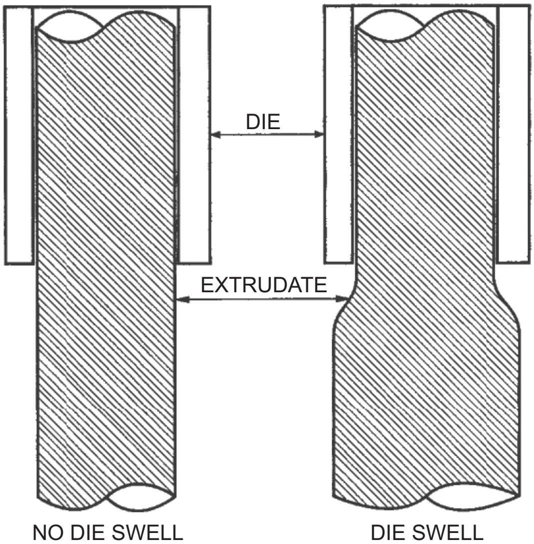

Figure 3.5 Die swell in an extrudate [184]

Rubber molecules normally are in a highly coiled or disordered conformation [185]. When constrained to flow through narrow dies, they tend to molecularly align in the flow direction. Upon emerging from the die, the tendency of the rubber to recoil produces an elastic memory effect and causes the extrudate to swell.

3.9.2.3 Die Entrance

The change in cross section at the entrance to a die should be gradual (tapered) as shown in Figure 3.6. An abrupt die entry favors the formation of eddies in the flowing rubber and increases residence time in the die, thus favoring scorch.

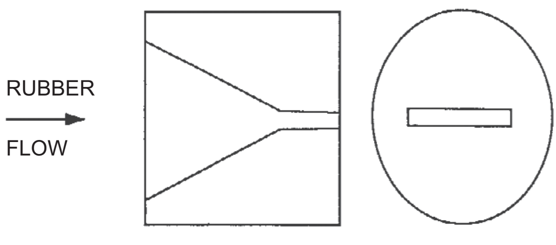

Figure 3.6 Tapered entry into an extruder die to smooth flow into die [186]

Die cross section is also important. A die with a round cross section will produce a round extrudate; however, a die with a square or rectangular cross section produces an extrudate with rounded corners [186] instead of square corners.

The modified die shape shown in Figure 3.7 is expected to produce the desired rectangular cross section extrudate. Often, this requires several iterations.

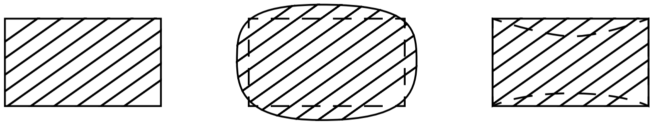

Figure 3.7 Effect of die shape on cross section of extrudate. Figure modified from [187]

Different grades of NR are reported to impart different degrees of die swell (extrudate swell) in a blend of NR and BR. Based on the 60-second relaxed extrudate swell, grade 5L imparts low swell, lower than 5CV [187]. SMR 10 and 20 imparted higher die swell to the compound.

Vulcanized vegetable oil is said to reduce die swell and improve dimensional stability in NR and SBR extrusion compounds [188]. Lowering the screw speed and increasing die length favor reduced die swell [189]. Die swell for TPE is said to be significantly less than that for TSE.

3.9.2.4 Extrudate Appearance

High-molecular-weight SBR is sometimes required to obtain the required physical properties [190]. Because its use can adversely affect extrudate appearance, oil-extended SBR is suggested as an alternative. Avoid using very high levels of *cis*-BR as it can cause rough extrusions. A heated die can reduce the torn-edge appearance of some extrudates by reducing compound viscosity and increasing velocity through thin sections of the die [191].

Strain-induced crystallization can occur above the critical shear stress of extruded NR compounds and cause roughness in the extrudate [192]. Additional mastication or increasing the compound temperature can move the critical shear stress for NR compounds to a higher output rate.

Incomplete filling of the extruder (starving the extruder) adversely affects extrudate appearance [193]. To avoid this problem, ensure that the metered feed rate is adequate for the extruder pumping capacity, the cross section of the feed strip is properly sized, and the feed section of the extruder can keep up with metering requirements.

A compound should be extruded below its critical shear stress (melt fracture point) to favor good extrudate appearance. Increasing extruder temperature reduces compound viscosity and increases the critical shear strain, assuming the increased temperature does not cause scorch. A longer barrel length extruder can result in improved appearance because it provides increased residence time for heat transfer to the extrudate [194].

Measurement systems for complex extrudates have typically involved noncontact optical width gauges [195]. Systems can now provide automatic process feedback control that is especially advantageous on multiple extrusion line processes. Results include faster startups with reduced scorch, continuous quality data records, and improvements in overall dimensional control.

3.10 Equipment

Original rubber extruders were of the hot-feed type wherein preheated strips from a rubber mill directly fed the screw feed section. Cold-feed extruders, developed later, were fed with ambient temperature rubber strips.

3.10.1 Hot-Feed

Hot-feed extruders are characterized by a relatively large screw depth and a short L/D ratio (length/diameter) that ranges from 3:1 to 8:1 [196].

Preheated compound entering a hot-feed extruder reduces the need to heat the compound in the barrel. The screw mainly functions to compact and pump the compound. Limited temperature control in a hot-feed extruder results in less-than-desirable control of extrusion rate, die swell, and extrudate dimensions. Hot-feed extruders still find use in some applications, such as in the extrusion of inner tubes for truck tires, where it is important to pass the compound through a screen pack just before the die.

3.10.2 Cold-Feed

Cold-feed extruders are manufactured in various forms with L/D ratios between about 10:1 to 20:1 [197]. Lower-viscosity rubbers like silicone tend to be used at the lower ratio, high-viscosity rubbers at the higher ratio. Longer screws provide more pump pressure that overcomes high back pressure. The 20:1 extruder uses about 175% more energy than its 10:1 counterpart; however it pumps more rubber per rpm. A 20:1 screw is often used in production extruders that require high back pressure, such as those used for hose and tubing.

Both hot- and cold-feed extruders compact and pump compound for extrusion [198]. In addition, cold-feed extruders plasticize compound and minimize the time between feeding the compound and its exit at the die. Cold-feed pin extruders are said to represent state of the art in producing profiles for passenger car tires [199]. Pins in the extruder barrel distribute the flow of compound without a considerable increase in temperature. Surging occurs in extruders when the extrudate exits its die at various viscosities and temperatures, and it worsens as screw rpm increases [200].

Wear on both screw and barrel can cause inconsistent extrusion [201]. Operation of an extruder with no material in the barrel is the primary cause of wear. Storage time of the compound can affect extrudate porosity, and storage times longer than a week can cause severe porosity.

3.11 Ram Extruder

Ram extruders are positive displacement pumps that push compressed rubber through a shaping die [202]. Some are designed to prepare preforms where, upon exiting the die, a rotating knife cuts preforms to a controlled weight. These preforms are typically solid pellets for molding electrical connectors or annular sections for O-rings.

Rubber to feed a ram extruder is formed into a roll (called a pig) on a rubber mill, after which the pig is placed in an extruder barrel and forced through a die. It is important to minimize trapped air in the pig so as to produce dense preforms. Since a vacuum in the barrel cannot remove air trapped in the pig, it is important to minimize the rolling bank on a mill, use a proper nip setting on the mill, and use a proper size mill.

3.12 Multicut Transfermix

The multicut Transfermix incorporates a highly interactive screw and barrel design that intensively mixes and blends a rubber compound [203]. It is expected to favorably process difficult-to-process tire compounds.

3.13 Crosshead Extruder

A crosshead extruder is used to produce extruder profiles that contain metallic inserts [204]. The main compound flows over a hollow-bored unit through which a steel profile is fed.

3.14 Continuous Extrusion

Continuous production of rubber profiles is desirable because it produces product at minimum cost [205]. The vulcanization system chosen for the profile compound plays a critical role for the several available methods of vulcanization. Heating methods such as a salt bath and hot air provide the necessary heat, and the effectiveness of these methods is essentially independent of the polarity of the rubber compound.

Different rubber types vary substantially in their polarity, with NBR being polar and NR being nonpolar. Microwaves heat polar NBR compounds much more rapidly than nonpolar NR compounds. However, carbon black in an NR compound improves its receptivity to microwave, depending upon the level and type of carbon black.

Calcium oxide added to a compound effectively removes moisture that causes porosity [206]. Attention should be given to the potential effect of calcium oxide on the scorch and curing characteristics of compounds containing it.

3.15 Extruder Design

An extruder is basically a machine in which a rotating screw forces rubber through a die that imparts the desired cross section to the extruded profile. The design of rubber extruders varies substantially to accommodate different products and materials.

3.15.1 Vacuum Extruder

Similar to molded rubber articles, trapped air and volatiles in extruded articles can be problematic. Decreasing viscosity by increasing temperature can increase the volatiles release rate; however, care must be taken to avoid scorch [207]. Additionally, vacuum applied in an extruder can remove air and volatiles and densify the extrudate.

3.15.2 Cavity-Transfer Mixer (CTM)

The CTM consists of a stator and a rotor, both of which have rows of hemispherical cavities. It is not a mixing unit in the sense that it does not break down agglomerates [208]. It is said to homogenize both temperature and ingredients. Disadvantages of a CTM are that it is not self-cleaning and it generates some heat and back pressure when processing high-viscosity compounds.

When cleaning an extruder with a purging rubber compound, a higher viscosity compound will displace a lower viscosity one [209]. Also, dark colored compounds tend to efficiently displace light colored ones. Hence, when mixed in sequence, light colored compounds should be run before darker ones.

3.15.3 Pin-Barrel Extruder

The popular pin-barrel extruder is applicable to nearly all extruder sizes and screw flight depths [210]. In operation, it splits and reverses the flow of rubber compound, followed by merging of the compound streams.

Pin-barrel extruders of the same size as conventional extruders produce higher quality extrudates, albeit at lower outputs [211]. Some of the pins can be removed from the pin-barrel extruder to alter the output and temperature. They are arranged such that they are moveable in a radial direction while keeping a minimum clearance of 1 mm to the core of the screw [212].

Pin-barrel extruders, used successfully in many extrusion operations, are especially useful in the tire industry because of the requirement for a high extruder output and a low extrudate temperature [213].

Black and white compounds established flow behavior in a pin-barrel extruder [214]. Slices in screw flights reduced pumping capability but improved mixing, with the introduction of pins greatly improving mixing.

3.15.4 Roller-Head Extruder

The main application for roller-head extruders in the tire industry is the production of low permeability inner liners [215].

3.16 Die Design

General rules for die design follow [216]:

- Avoid dead spots in the flow channel.
- Provide for a steady increase in velocity through the flow channel.
- Provide for easy assembly and disassembly of components.
- Avoid abrupt changes in flow channel geometry.
- Use small angles in the approach path.

Figure 3.8 shows a die with an abrupt change in direction where a compound enters a die that was used to extrude erasers for pencils.

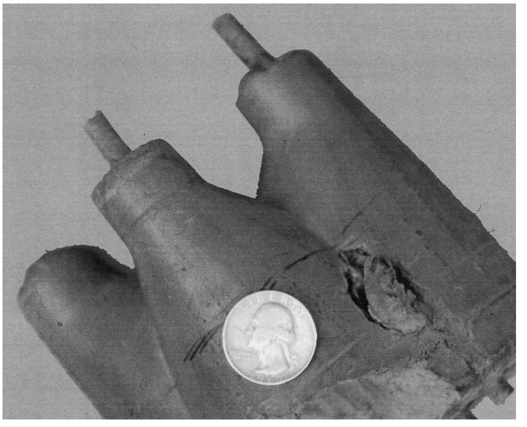

Figure 3.8 Scorched pencil erasers and extrusion die with too abrupt an entry geometry

Two problems occurred with this die. First, the compound experiences an abrupt change in geometry as it enters the die. Second, the extruder size is too large for the product size, resulting in too long a residence time in the barrel, thus causing scorch.

Problems often occur with dies because the die designer is given inadequate information or does not understand the implications of a particular design on the extrusion process [217]. Small design changes can drastically affect product extrudability. Following are some design guidelines for extruded products:

- Incorporate generous external and internal radii on all corners.
- Maintain wall thickness as uniform as possible, avoiding very thick walls.
- Design interior walls thinner than exterior walls to facilitate cooling.
- Minimize hollow sections in the extrudate.

Figure 3.9 shows how weather strip for automobile doors was earlier fabricated by joining rubber extrudates at their corners in a separate injection-molding operation [218]. Later fabrication techniques produce the corner exclusively by extrusion.

Metal carriers are often used to secure weather strip to an automotive body [219]. These are usually endless and have stamped slots or holes in them. Plastic carriers that replace metal in the carrier offer the following advantages:

- reduced material costs
- reduced weight
- lower capital equipment cost
- reduced corrosion problems.

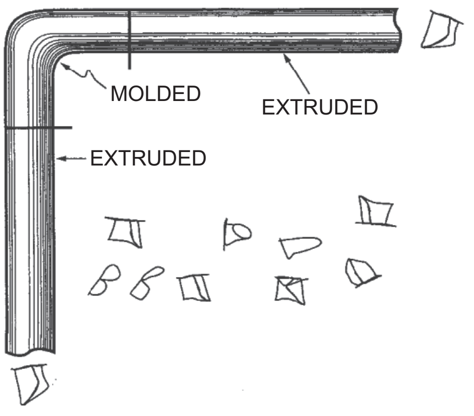

Figure 3.9 Extruded weather strip for automobiles joined by an injection-molded corner

A patented co-extrusion technique incorporates a nonmetallic carrier that is said to provide lower weight in the finished weather strip [220]. It combines a highly filled polypropylene with an EPDM soft profile to yield cost savings of over 20% compared to conventional EPDM profiles with a metal carrier.

An alternative and newer fabrication method involves extruding the corner rather than molding it [221]. The extruded corners are less labor intensive and more aesthetic. The curved extrudate forms result from a flow imbalance behind the die plate. The velocity of rubber exiting one side of the die opening is increased relative to the other side, causing the extrudate to curve. This directed flow die technology is part of a trend toward net shape processing technology, which essentially involves producing a product as close to its final shape as possible without secondary operations [222].

Changing from EPDM to TPV for corner moldings generally reduces cycle times [223]. Also, it is much easier to make a flash-free mold for TPV than for EPDM.

A patent describes a die assembly that curves an extrudate [224]. A new technique permits extruding a Santoprene seal directly onto a car door [225]. The technique is said to reduce material costs by 53% and capital expenses by 15%.

Modular die head designs are a relatively recent development that consist of a body fitted with different inserts that have their various internal surfaces shaped and sized to a required extrudate shape and size [226]. The different inserts are:

- flow channel inserts that transform the circular cross section into the required shape
- preformer inserts wherein the flow paths are aligned and combined into the required extrudate configuration
- die plates that form the flows from the preformers into the required sizes and shapes.

Efforts are being directed toward making the removable components as light and small as possible and shortening flowpaths to minimize viscous drag in the die head.

3.17 Feed Compound

Special attention should be given to scorch values for compounds intended for recycling. Scrap CR from extrusion operations should be formed into a thin sheet and promptly cooled to avoid scorch [227]. The CR should be inspected for contamination before blending it into fresh CR.

3.18 Gear Pumps

Gear pumps are positive-displacement devices that are typically installed between an extruder and its die [228]. They consist of two shafts with meshing gears wherein a rubber compound flows through the pump and lubricates it. By damping pressure fluctuations, more consistent die pressures and closer extruder tolerances can be obtained that result in higher yields and compound savings.

Because gear pumps can provide a pulsation-free extruder output and significantly lengthen screw life, they are finding increasing use in extrusion operations. Advantages claimed for gear-pump-equipped extruders relative to conventional extruders are compactness, lower capital cost, lower running cost, less variable output, and higher output pressure [229].

Gear pump use to increase pressure places less demand on the extruder that in turn leads to increased throughput for a comparable extruder size [232]. Purging a gear pump after a compound change appears compulsory, whether the pump bearings use the compound for lubrication or not [230]. Gear pumps are also recommended for straining operations in the mill room [232].

A quick cleaning capability for gear pumps is desirable when changing compounds or when longer interruptions occur in production [233]. A newer pump permits removal of individual components from the pump for cleaning by the operator, and the gear pump package can be hydraulically pushed from its housing.

A gear pump provides the pressure necessary to force compound through the head and die [234]. The screw must be only partially filled with compound in the region following the vacuum section to ensure a large surface area for removal of volatiles.

Extrusion essentially determines the *x* and *y* dimensions of an extrudate perpendicular to the extrusion direction (*z*). The extrudate dimension in the *z* direction depends considerably more on compound characteristics than those in the *x* and *y* direction. In contrast, most molding operations essentially determine dimensions in all three directions.

3.19 Molding

A wide range of equipment and compounds are available for molding rubber compounds. The main molding methods include compression, transfer, injection, and combinations of these, with compression molding being the earliest used method [235]. Molding problems can be corrected with varying degrees of difficulty [236]. Table 3.7 summarizes some common molding problems and their solutions.

Additional troubleshooting recommendations are described for silicone rubber [237]. Carbon black destroys the active portion of most peroxides that are commonly used to cure silicones. Dicumyl peroxide is said to cure silicone containing low levels of carbon black and to impart good compression set characteristics.

Occluded air (air bubbles) in an LSR is often associated with premature crosslinking, and possible reasons for its occurrence include too-high mold temperature, too-low injection rate, and too-high cold runner temperatures [238].

Here are supplemental comments for Table 3.7. When removing flash by cryogenic means, remember that flash needs to be removed from articles that are molded from rubbers with a wide T_g range. This means that silicone rubber with its very low T_g requires liquid nitrogen (–196 °C) as a refrigerant during deflashing; solid carbon dioxide (–78.5 °C) is an effective refrigerant for deflashing SBR that has a substantially higher T_g than silicone rubber [239].

When deflashing cryogenically, sufficient space should be provided within the blasting chamber for the rubber articles to tumble properly [240]. The tumbling action exposes the articles to both liquid nitrogen and blasting media. It is recommended that the size of the chamber be at least twice the size of the load of molded articles being deflashed.

Raising mold temperature reduces compound viscosity (in the absence of scorch), thus allowing more rapid escape of compound through mold vents. Ironically, higher temperature *increases* air viscosity and slows the escape of air through vents [241]; however, the effect of temperature on air is substantially less than the effect of temperature on compound viscosity.

Porosity or blow point refers to the allowable cure time during the cure cycle before voids appear in the center of a molded article [242]. This time can be as low as 25%

Table 3.7 Common Molding Problems and Their Solutions

Problem	Possible Cause and Solution
Dimensions and appearance	Remove flash by several methods that include: Hand trimming (high labor costs) Tumbling molded articles together below their T_g Revise tooling Provide uniform pressure across mold face Minimize gate size, especially on precision O-rings
Buildup of mold release agent	Clean mold Clean in-place with special cleaning compounds Minimize use of mold spray
Poor knitting and cavity filling	Improve compound flowability by increasing temperature (avoid scorch) or by recompounding Reduce compound nerve
Air marking	Increase state of cure Bump press (intermittent release and reapplication of press-closing force) Increase compound viscosity Increase air release rate by change in mold design Increase compound viscosity
Porosity	Increase state of cure Increase compound viscosity to increase molding pressure Minimize moisture in raw materials
Distortion	Try longer cures at lower temperature Increase state of cure Reduce thermoplastic resin content, e. g., high-styrene SBR Increase scorch time of compound
Poor knitting	Ensure sufficient compound to fill cavity Increase compound flowability Avoid excess mold lubricant
Backrinding	Reduce cure temperature Relocate backrind area to noncritical region of molded article Make sure press closes evenly (parallel platens)
Tearing upon removal of vulcanizate from mold	Avoid overcure Use effective mold release Increase tear resistance of compound
Pebbling	Improve dispersion of fillers and curatives
Sticking in cavity	Use effective mold release agent Avoid certain mineral fillers such as clay Use chrome-plated cavities

of optimum. It depends upon the compound modulus and is most problematic for low-modulus compounds.

Sensors can use ultrasound to detect cure in both tire and nontire products [243]. Ideally they would eliminate undercure while still allowing reductions in cure time of up to 25%. Additionally, they could minimize property degradation by avoiding overcure.

Overcure, a cure time longer than optimum, occurs when curing a range of rubber products [244]. It is important to know the effect of overcure on a product, which sometimes increases modulus while in other cases decreases modulus. The modulus of most NR and IIR compounds tends to decrease (become softer) with overcure; the modulus of most synthetic compounds tends to increase, for example in SBR and NBR. The modulus of compounds based on NR and SBR, cured with TMTD without elemental sulfur, tends to remain flat with overcure.

Several problems are associated with mold release agents, with some problems being immediately evident, while others can cause downstream problems [245]. A curing press operator using excessive amounts of mold release to minimize sticking of a molded article in a mold cavity can cause excess mold release to flow ahead of the compound during cavity filling, resulting in knit lines in an article. If a compound is to be bonded to an adhesive-coated insert in a mold, the release agent could enter the interface between rubber and adhesive and cause adhesive failure.

A mold release agent can also interfere with downstream operations such as painting the vulcanizate. Semipermanent mold release agents (SPMRA), which bond permanently to a mold, are designed to prevent some of these problems. Another advantage with SPMRAs is the labor savings associated with their use.

3.19.1 Molding Methods

Several different methods are used to mold the wide range of molded articles produced by the rubber industry. The major ones discussed here are compression, transfer, and injection. Some of these methods are used in combination, as in injection-compression and injection-transfer; with others, a different material requires the use of a modified method. Silicone rubber serves as an example. The first silicone rubber was called HCR (high-consistency rubber); its counterpart, liquid silicone rubber (LSR), became available later. Molding of LSR necessitated the development of special techniques and methods.

3.19.1.1 Compression Molding

Initially all thermosetting elastomers (TSEs) were molded by compression, a method that involves placing a preform—a piece of uncrosslinked compound—in the cavity of an open mold and then covering the preform and cavity plate with a mold cover plate. After the assembled mold is placed between the platens of a curing press, the press closes and causes the preform to take the shape of the cavity. A slight excess of compound ensures adequate pressure generation in the rubber, and the excess exits the mold cavity between mold plates.

After appropriate exposure to high temperature and high pressure, the closed mold is removed from the press, opened, followed by removal of the crosslinked (vulcanized) molded article(s), and the cycle is repeated. While compression is the oldest molding method, it is still widely practiced today because of its simplicity and economy. Compound viscosity plays an important role in compression molding as illustrated by the following example.

The modulus of a highly plasticized NR compound was too low for satisfactory processing [246]. A supplemental curing system that incorporated only a few crosslinks in the compound improved processing by slightly increasing viscosity. Then this partially cured rubber was placed in a compression mold at a higher temperature that activated its sulfur curing system. The compound attained final properties after the second crosslinking.

The inclusion of fabric in compression and other molding processes can present special problems [247]. The ability to deform fabric interstices, typically referred to as the depth of draw, can be a major factor. Rubber sheet goods are generally limited to about a 1:3 draw ratio. Spun yarns and multifilament yarns best conform to a molded shape without wrinkling; hence, they are the ones most frequently used in spread-coating operations.

3.19.2 Curing Presses

Different types of curing presses have evolved over time to accommodate diverse size and complex molded rubber products.

3.19.2.1 Four-Post Presses

Figure 3.10 illustrates a typical hydraulic four-post press [248]. The mold shown in the press is purposely shown undersize to emphasize the likelihood of damage when the press closes.

The importance of curing press maintenance is sometimes overlooked. Continual bumping of a typical four-post press tends to loosen the nuts on the press head that secure the press head on the post shoulders. Loosened nuts result in uneven stress in the posts, which can lead to post breakage. It is recommended that the post shoulder area be at least 60% of the cross-sectional area at the root of the threads on a post. Also recommended is the incorporation of a radius in the shoulder area in addition to incorporating relatively fine threads on the post. Force between mold

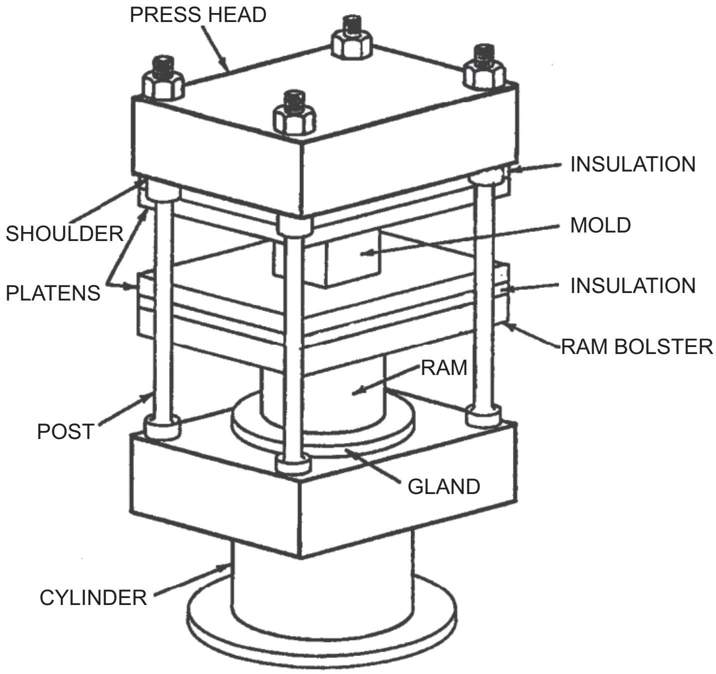

Figure 3.10 Hydraulic four-post press [247]

and platen should be distributed over at least about 80% of the platen area to minimize damage to mold and platen.

The posts on four-post presses limit accessibility to the daylight of a press. C-frame presses offer unobstructed daylight access to the front and both sides of a press. They must be extremely rigid to resist the high stresses encountered during press operation.

Ideally, the periphery of the mold in its press should remain within the confines of the press ram to minimize platen deflection. Often, mold boundaries extend beyond the ram diameter and thus cause uneven pressure between mold and platen. This uneven pressure results in the mold flashing, especially at the mold corners.

Even worse, oversize molds have been used in a press wherein the mold edges extended beyond the edges of the platens, a practice that is unacceptable mechanically and thermally. The mold area outside the platen will be at a lower temperature than the mold area located within the confines of the press platen. This arrangement caused the out-of-press portion of the molds to bend, producing unsatisfactory moldings and excessive flash.

3.19.3 Mold Size

There have been occurrences where a completed mold was sent to a rubber manufacturer only to find that it was too large to fit an available curing press [249]. There may be guide members, hinges, or other attachments on a mold that can cause this problem.

When loading and unloading compression molds on a service table located in front of a press, a mold transfers heat to the steel top of the table [250]. The amount of heat lost can be significantly reduced by welding half-round stainless rods onto the table with their axes aligned in the direction of mold removal. Doing this provides an air gap between mold and table and helps to maintain the desired mold temperature as shown in Fig. 3.11.

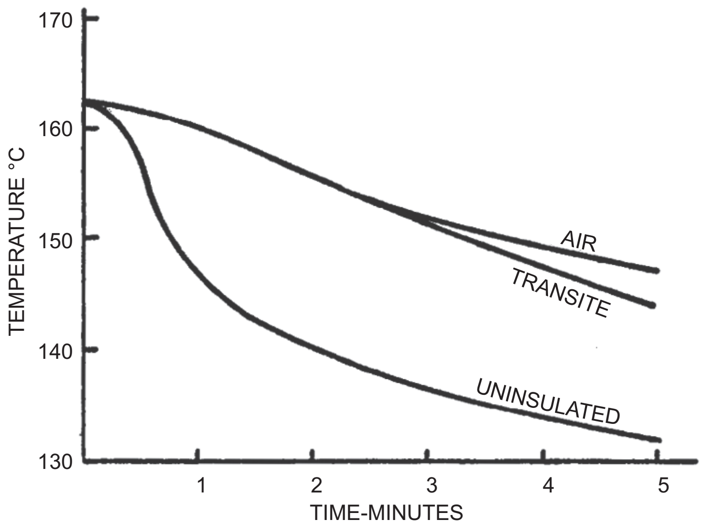

Figure 3.11 Effect of service table modifications on the cooling rate of molds [250]

3.19.4 Air Trapping

Trapping of air is a potential problem with all molds. Judicious shaping of a preform and properly locating vents in a mold minimize its occurrence [251]. For example, a rod-shaped preform, when compression molded, tends to trap air at the 6 and 12 o'clock positions of a closing mold. An elliptical-shaped preform, with its major axis contacting the mold first, pushes air toward the mold parting line as the mold closes and allows the air to escape (Figure 3.12).

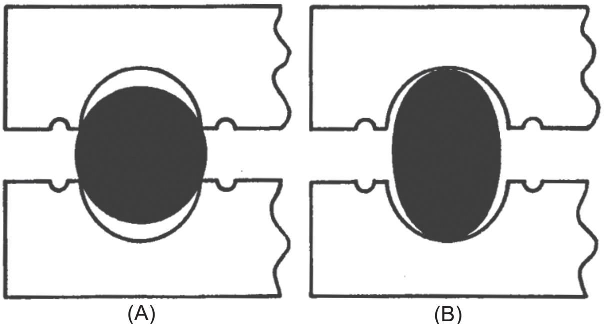

Figure 3.12 Round-shaped preform (a) vs. elliptical-shaped preform (b) positioned in a cavity with a round cross section [251]

3.19.5 Flash

Thick flash, while generally undesirable, is desirable for some applications. It can connect many small articles that normally would be demolded individually and necessitate longer-than-desired open mold times [252]. Figure 3.13 illustrates removal of molded articles as a sheet.

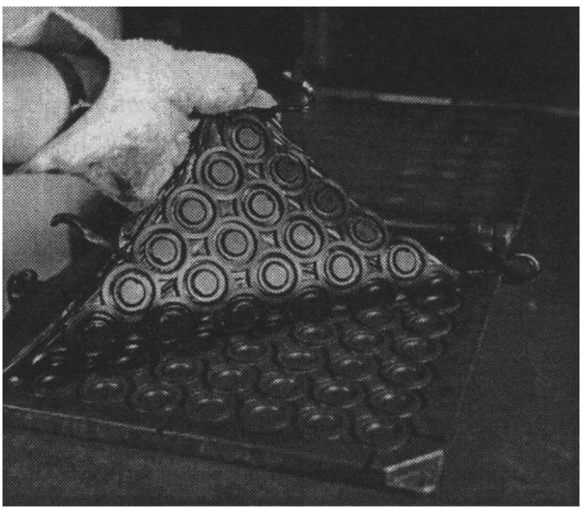

Figure 3.13 Removal of molded articles connected as a sheet from a multicavity mold

Following their removal, a matching die can punch the individual articles from the sheet. Connecting articles as a sheet can be an advantage for another reason. Molded rubber brake pedal pads for automobiles contain a deep undercut, and the pads are stretched over a metal brake pedal during installation. Upon release, the pad engages the brake pedal for retention. Although this undercut is useful for retention purposes, it makes demolding of individual pads difficult. This difficulty is significantly reduced when thick flash connects the pads so they can be removed as a sheet and subsequently separated by cutting with a die.

Use of too-small molds in a press can indent press platens [253]. When this happens, the air pocket between mold and press platen reduces heat transfer between platen and mold. Zone heating of platens improves platen temperature control [254]. Mold insulation can also improve temperature uniformity, and criteria for selecting insulation include [255]

- compression strength
- service temperature
- thermal conductivity
- water absorption
- maintenance of parallelism
- resistance to lubricants and hydraulic fluid.

Figure 3.14 shows the channels in a platen used for conveying heat transfer fluids [256].

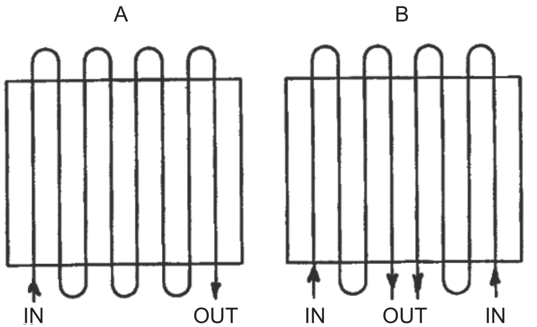

Figure 3.14 (A) shows entry and exit of heat transfer medium in one channel. (B) shows two channels [256]

With only one serpentine channel (A), steam or heat-transfer fluid enters a continuous serpentine channel on one side of a platen and then exits the other side. Temperature in this single channel decreases progressively from the inlet side to the outlet side of the platen as the platen cools the hot fluid. This temperature drop causes a cooler platen area on the exit side, a situation that can be corrected by the use of two channels.

Two channels, placed on either side of the centerline of the platen (B), improve temperature uniformity. Hot fluid enters the outside mold channels closest to the platen edge, after which it exits the channels near the platen center. Fluid flow in the channels should be turbulent rather than laminar to increase the heat transfer coefficient and thus raise the heat transfer rate.

3.19.6 Scorch Effects

Compression molding, the simplest molding method, requires attention to detail if good results are to be obtained [257]. Table 3.8 shows the effect of compression molding on shrinkage and distortion.

Table 3.8 Effect of the Molding Process on Shrinkage and Distortion

Time, min.	Shrinkage, %			Appearance
	With Flow	Across Flow	Average	
Minimal	1.7	1.8	1.75	Undistorted
1	3.1	1.4	2.2	Distorted
2.5	4.1	2.0	2.6	Very distorted

The movement of scorched rubber caused the uneven shrinkage and distortion because the preform contacted the hot mold surface for too long and partially crosslinked before the mold closed. Hence, time must be carefully controlled, especially for scorchy compounds, if shrinkage and distortion are to be avoided.

For multicavity molds, a loading fixture significantly shortens the mold loading time and mitigates this problem [258]. Another advantage for a loading fixture is that it minimizes precure of adhesive-coated metals that are loaded in a multicavity mold [259].

3.19.7 Shrinkage

Fibers and shaped fillers also cause uneven shrinkage [260]. Figure 3.15 shows that only a small amount of shrinkage occurs for a compound containing adhered fibers parallel to the fiber axis because the bonded fiber limits axial shrinkage. Perpendicular to the axis, shrinkage is invariant over the fiber level shown.

For bridge bearings (Figure 3.16) that consist of bonded alternating rubber and steel layers, most shrinkage occurs perpendicular to the plane of the layers because the steel plates prevent the adhered rubber from shrinking in the plane of the steel plates [261]. Mold designers must take this factor take into account to produce a bearing of the proper dimensions.

Lamiflex®, another high shape factor laminate, contains alternating layers of thin rubber and thin metal [262]. Layers of brass and intervening layers of rubber, each about 0.002 in. (0.05 mm) thick, are bonded together. The resulting laminate, which has a very high compressive modulus, can be easily bent with only finger force.

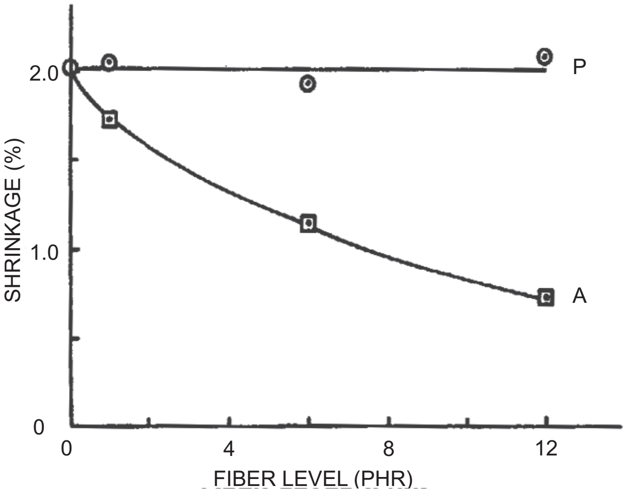

Figure 3.15 Effect of oriented fibers on the shrinkage of an NR compound along (A) the fiber axis and perpendicular (P) to the fiber axis [256]

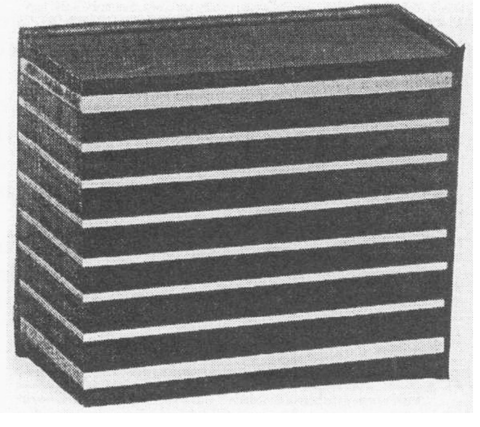

Figure 3.16 Section cut from a bridge bearing showing steel plates adhered to black rubber [256]

3.20 Potential Mold Damage

Another consideration is potential damage to a mold or molded articles. Tools used to assist removal of a molded article from its cavity must not damage the mold surface. Press operators should use hardwood, brass, or other soft implements to assist removal of molded articles from their cavities to minimize mold damage.

Molded articles or flash unintentionally left in a mold between cures can severely damage a mold [263]. A mold monitoring system can inspect a mold before closing the mold and prevent damage.

Another concern is potential damage to a bonded rubber-metal article during demolding [264]. Higher temperatures reduce bond strength and render a molded article more subject to damage. Bond strength at mold temperature can be an order of magnitude lower than at room temperature. Forcing a bonded composite from its hot mold cavity can damage the composite at the bondline.

3.21 Thermal Considerations

Very large molded articles present unique problems [265]. An example is the nozzle bearing for the space shuttle wherein the mold assembly weighed over 40,000 pounds and required over 100 thermocouples to monitor temperature during a 12-hour curing cycle. Proper adhesion between annular steel shims and very low modulus NR was obtained only after carefully placed thermocouples identified low-temperature locations in the mold.

Preheating rubber preforms for compression molding shortens subsequent cure times; however, care must be taken to avoid scorching the preform [266]. Preheating methods include hot air and microwave ovens. When heating preforms in a hot-air oven, the external surfaces of a preform can scorch before the interior is heated because rubber compounds have low thermal diffusivity. Microwave energy heats preforms more uniformly, and the rate of heating depends upon factors such as polarity of the rubber in the compound and on carbon black type and level.

3.22 Microwave Heating

Polar rubbers, for example NBR, heat more rapidly in a microwave oven than non-polar rubbers such as NR. Additives (diethylene glycol and triethanol amine) incorporated in lower polarity rubbers increase the heating rate. Microwave energy, used to preheat an NR preform for three minutes, reduced the transfer time in a six-cavity mold from 150 s to 40 s; cure time was shortened from 30 min. to 20 min. [267]. A newer microwave heating system directs more energy to the thicker cross section and less at the thinner edges [268].

3.23 Backrinding

Backrinding, which describes the torn or gouged appearance of some vulcanizates at their parting line, is caused by continued thermal expansion of compound in a mold after crosslinking commences [269]. This expansion forces partially crosslinked compound into the parting line where compound tears as a solid since it can no longer flow as a liquid. Backrinding can be reduced by

- lowering the mold temperature
- increasing the scorch time
- incorporating an effective retarder in a compound
- optimizing preform weight
- preheating a preform.

Addition of a rib in a spark plug boot moved the location of backrinding to a more acceptable area and maintained the desirable minimum wall thickness throughout the boot [270]. A molded rubber sphere is the shape that causes the greatest problem with backrinding because it has the minimum proportion of surface area to mass of any geometric configuration.

3.24 Mold Construction

Molds must be sufficiently robust to perform satisfactorily for their intended service life. Burton recommends that [271]

- mold plate thickness be a minimum of 3/8 in. at the thinnest part of the mold
- top plates be at least 11/16 in. thick to firmly secure dowels and locating pins
- there is sufficient metal thickness between cavities to avoid distorting metal between cavities.

Terminology sometimes causes confusion between press builders and molders. Press builders typically define daylight as the distance (Figure 3.10) between the upper surface of the ram bolster and the lower surface of the press head; the maximum available height. This definition does not consider insulation thickness and platen thickness that reduce available height for mold accommodation. A molder, in contrast, considers daylight as the height available between platens. Anecdotal information suggests that confusion about daylight opening has led all too often to the purchase of a press that was too small for its intended mold.

3.25 Insulation

Effective thermal insulation between press head and platen, and between bolster and platen, helps to save energy and to maintain the desired mold temperature [272]. In addition to insulation's resistance to hydraulic fluid, it should ideally provide other characteristics that include

- very low thermal conductivity
- resistance to creep under high compressive stress at high temperatures for long times
- good machining characteristics
- acceptable cost
- uniform thickness and parallel surfaces.

Several insulation materials, asbestos-concrete, mica, and calcium silicate, were compared with a fiberglass-reinforced, mineral-filled, resin composite—Glastherm®. The thermal conductivity of the Glastherm was lower than that of the asbestos-concrete but higher than the other two materials; flexural strength of the Glastherm was substantially higher than asbestos-concrete and calcium silicate [273]. Another insulation material is said to compensate for uneven surfaces between a hot platen and a press member; it consists of a thermal insulating board, composition inlay, and separating grease.

The use of high platen temperatures to reduce cure times can shorten the usable life of hydraulic fluid in the press cylinder (Figure 3.10). High temperatures also accelerate the aging of the gland material that seals fluid between ram and cylinder. Oxidized fluids, caused by high temperatures, deposit gums and varnishes on highly polished ram and cylinder surfaces. An upper temperature of 135 °F is recommended for fluids to extend their life [274]. Relative to petroleum-based fluids, water-containing hydraulic fluids are said to offer advantages of lower cost, easier cleanup, and low dermal and oral toxicity.

3.26 Mold Platens

Platen deflection affects the flash-forming tendency of molds. Press heads and ram bolsters must provide sufficient rigidity to minimize platen deflection, because press platens contribute only very minimally to rigidity. It is estimated that 500 to 1000 platens would be required to provide the bending resistance equivalent to that of the press head or bolster [275]. Hence, the primary function of platens is to uniformly heat a mold, not to provide rigidity.

Obtaining a uniform temperature over the surface of heating platens depends upon factors that include minimizing heat loss between insulation and press components and type and spacing of heat sources. Sources include electrical strip heaters and cartridges, or channels in platens that convey hot fluid.

Special platens have been developed to minimize or eliminate flash [278]. These contain a hydraulic compensation pad that can accommodate irregularities to 0.1 mm in cavity height without leading to flash.

3.27 Mold Heating

Platen surface temperature is often less uniform than desired, with the lowest temperatures typically occurring at platen corners. The four corners of a platen may be 10 to 25 °F cooler than the temperature setpoint, with the center zone of a platen being 5 to 10 °F hotter than the setpoint. The method for heating platens also affects temperature uniformity. Special multizone platens are available to provide significantly improved temperature uniformity [276].

O-ring mold temperatures varied as much as 5 to 10 °C from one side to another and as much as 4.7 °C from cavity to cavity [277]. Too-high temperatures caused flash or distortion, while low temperatures created surface defects. The problem was corrected by incorporating a closed-loop, multizone mold surface control system. Temperature variation was reduced to less than 2 to 3 °C across the mold, accompanied by significantly reduced scrap rates.

Fit of cartridge heaters in a mold is important [278]. Reduced clearance between the heater cartridge and its mounting hole in the mold increases heater life. Formerly, hole diameter was nominally about 0.005 in. (0.12 mm) oversize to facilitate ease of heater replacement; however, this resulted in poor heater life. A compromise in clearance provided a better balance between life and heat transfer. It is recommended that the heater manufacturer help determine this balance. Ideally, each heater should be linked with a device that would show that heaters are operating satisfactorily [279].

A meter can indicate when heaters burn out [280]. Heater bands should be checked for tightness after initial installation and periodically thereafter. For maximum service life of cartridge heaters, their power density should not exceed 4 W/cm^2 and they should fit into an accurately reamed hole. Control systems can be incorporated into equipment to indicate when a component is about to fail; for example, the signal from a thermocouple becomes noisy just before it fails, and this behavior can be used to actuate an alarm.

Application of Isobar® heat transfer technology substantially increased temperature uniformity in a platen that was heated by parallel cartridges located in platen channels [281]. Isobars, arranged in a bilevel grid pattern that was orthogonal to these channels, provided a uniform temperature distribution over 90% of the platen surface, and corner platen temperature uniformity also improved.

Steam-heated platens were the earlier standard in the elastomer industry. Although hot oil can provide higher temperatures than steam, it is considered less environmentally desirable and it involves higher maintenance costs. Electrically heated platens with either cartridge or strip heaters wired in series are popular today.

Where steam is used for heating molds and other factory equipment, good water treatment for boilers is an important consideration [282]. Scale and corrosion reduce heat transfer; a polymer-based additive for boiler water is claimed to be less corrosive than other additives, and it is said not to precipitate or form precipitates.

Electrical resistance in cartridge and strip heaters produces heat. Induction heaters operate differently; they consist of a top plate and a coil plate that includes a series of copper-wound induction coils. An alternating current applied to a coil provides energy that ultimately heats a platen. Advantages claimed for induction-heated platens include temperature uniformity across the platen face, higher heat transfer rates, and energy savings.

Anecdotal evidence suggests that strip and cartridge heaters exhibit shorter lives when used in the vacuum environment of a shrouded mold because of arcing and localized hot areas. Induction heaters are said to offer an advantage.

Long narrow cores form the interior of some products such as grips for golf clubs. When these cores are heated from only one end, core temperature decreases in a direction opposite to the heat source. The result is reduced crosslinking remote from the heat source. Isobars, installed in cores, heat cores faster and more uniformly along core length.

Heat loss increases with both higher mold temperatures and increasing air flow around the molds. Fans are often used for press operator comfort in the molding area of factories in the summer. Rapidly moving air from these fans can cool molds rapidly if it blows directly across molds, especially if a mold has a large surface area-to-mass ratio.

Digital thermography can effectively establish the temperature of molds and associated equipment [283]. Small, relatively inexpensive IR cameras are available that can identify problems and improve productivity.

Insulation with surfaces coated with aluminum foil attaches to molds to reduce heat loss. The surface of the insulation contacting the mold is corrugated and the outer surface flat. Energy saving is estimated at 2.5 kW/m^2 for an insulated mold relative to a noninsulated one.

3.28 Injection-Compression

During injection-compression molding, a controlled volume of preheated compound from an injection-molding machine enters a partially open compression mold [284]. Then the mold closes to squeeze the compound outward to fill the cavities of high-value articles such as O-rings, where flash must be minimized. This method requires the use of an appropriately designed and maintained mold. Injection-transfer and transfer molding are discussed in the next section.

Injection-molded O-rings that appear fault free can have hidden faults that become evident only after they are swollen by an appropriate solvent, for example NBR rings swollen by toluene [285]. Instead of being round, a swollen ring had the shape of an irregular ellipse, with its long axis coinciding with the flow direction through the gate. Greatest distortion of the ring occurred at the gate. Swelling sometimes serves as an inexpensive technique to troubleshoot anisotropy problems.

3.29 Transfer Molding

During transfer molding, a rubber preform is squeezed in a transfer pot between the ram and pot bottom until it fills the confined space in the pot. Then compound warms as it flows through sprues that connect the pot and cavity(s). During conventional hot transfer molding, compound remaining in the pot and in the sprues crosslink and this cured compound is discarded after completion of the molding cycle.

With cold transfer molding, compound in the pot does not crosslink and is therefore available for use during the subsequent molding cycle. Some technical, cost, and other factors include control of age of the compound, control of mold temperature and cycle time, proper mold design, and proper type and frequency of mold lubrication [286].

Transfer molds must be designed to have the projected area of a pad in the transfer pot sufficiently larger than the projected area of the cavity(s) [287]. Otherwise the mold will open at the parting line and allow the rubber to escape. A ratio of 1:4 or more (pad projected area to cavity projected area) prevents this occurrence.

3.29.1 Cavity Filling

Transfer molding places greater demands upon the processability of compounds than compression molding because the compound must pass through sprues and fill cavities before crosslinking occurs. The use of an effective scorch retarder such as CTP permitted the use of higher preheat temperatures for a sulfur-cured NR compound without evidence of flow marks after molding [288].

Different layers of equal viscosity colored compound in a transfer pot established flow patterns in a mold cavity [289]. Another useful technique involved transfer of an inadequate amount of compound (short shot) to fill mold cavities. Doing this identifies the gate or sprue that needs to provide more rubber to fill the mold cavity in a balanced manner. Uneven filling of mold cavities is a general problem for both transfer and injection molding.

Physical properties can differ for the same compound molded by compression vs. injection molding. For this reason, small injection-molding machines were developed to mold by the method anticipated in production [290]. The small machine was equipped with pressure sensors that enabled the determination of viscosity. Viscosity results determined on this machine and on a capillary rheometer compared well and related directly to the injection-molding process.

3.29.2 Adhesion

Factors involved with both a compound and the molding process can affect the adhesion obtained between an elastomer and its substrate. Compressed air used to spray adhesives should be free of moisture and compressor oil. An effective filtering system for compressed air minimizes the occurrence of contaminants in spraying operations.

An adhesive film should have a sufficiently high viscosity to resist wiping the adhesive during molding. Viscosity of the film can be increased by preheating adhesive-coated inserts to partially crosslink the film and thus improve wiping resistance. This procedure must be done under very carefully controlled conditions to avoid crosslinking the adhesive to the extent that it doesn't have sufficient residual reactivity to react with the rubber to which it is to be bonded.

Alternatively, an adhesive might be used that deposits a film with a higher viscosity. During molding, if compound leaking at the cavity parting line is found to wipe away adhesive, reducing preform weight to the minimum amount to fill cavities should be beneficial. This approach is less satisfactory if there are large variations in the volumes of inserts in the mold.

Adhesives for molding should be considered in terms of anticipated molding temperatures [291]. An adhesive with a high volatility that is satisfactory for bonding during compression molding (low temperature) can be problematic during injection molding (high temperature). In one instance, volatiles from an adhesive designed for compression molding migrated through the sprue and runner system in an injection mold and bonded the mold plates together. Consideration was given to reworking the mold until the cause of the problem was resolved.

3.29.3 Dimensional Factors

Dimensions measured at three locations along transfer-molded spark plug boots from three different compounds A, B, and C yielded the shrinkage values shown in Table 3.9 [292].

Table 3.9 Shrinkage as a Function of Location and Compound

	Shrinkage (%) for Indicated Compound		
Dimension	A	B	C
1	2.1	2.1	2.5
2	3.9	4.0	3.5
3	4.7	4.5	4.9

Both compound and cavity location in the mold affected shrinkage, with location being most important. The location effect is about five times greater than the compound effect for these compounds and the mold used to cure them. This result emphasizes the need to establish final dimensions on the finished product using the same molding method that will be used in production, as opposed to a simpler geometry using a different molding method such as compression. This large location dependence is likely related to complex flow patterns in the mold for a spark plug boot.

Because shrinkage calculations often produce uncertain results, it is best to be conservative when establishing mold dimensions. For example, when designing a mold for a tubular shaped article, the core that forms the bore of a tube should be designed large enough to permit metal removal from the core diameter to obtain the specification bore diameter in the molded tube, should that be necessary. Likewise, the mold cavity dimension that forms the outer tube diameter should be small enough to permit metal removal to obtain the specification outer tube diameter. Doing this minimizes the need to build up metal surfaces by welding and subsequent machining.

3.29.4 Shrinkage

Shrinkage measurement and control in molded elastomer articles is one of the more difficult problems encountered by elastomer technologists. It is problematic even for compression molding, where the flow in the mold is generally minimal relative to transfer and injection molding. Shrinkage values determined in the laboratory on a compression-molded sheet often do not agree with shrinkage values obtained on molded articles made by other molding methods and for articles with a complex shape; generally, the more complex the shape, the greater is the problem of nonuniform shrinkage.

Unsaturated carbon-based rubbers typically are crosslinked with sulfur, and the sulfur remains in the crosslinked compound. Silicone rubbers are often cured with peroxides that decompose and release volatiles that increase shrinkage [293]. Hence the shrinkage of elastomers like NR and SBR is due mainly to thermal effects; the shrinkage in peroxide-cured silicones (and other peroxide-cured polymers) is due to both thermal effects and loss of volatiles. Because silicone rubber is often postcured in an oven, much of the shrinkage occurs during postcuring. Total linear shrinkage of vulcanized silicone rubber varies from 1.5 to 7% [294].

Atmospheric oxygen reacts with many types of peroxides and can destroy the free radicals they produce, thus interfering with crosslinking. Bis-(2,4-dichlorobenzoyl peroxide), since it is not inhibited by oxygen, is considered a good alternative to peroxide as long as its acidic by-products are removed by postheating [295].

3.29.5 Compound Flow

Flow of compound during transfer molding is much more complex than during compression molding. An analysis provided insight into the flow behavior during the transfer molding process [296]. A key finding showed that flow essentially occurred in two stages. In the early molding stage when the transfer pad was still relatively thick, sprue size and number dominate flow behavior. In the later molding stage, resistance to transverse flow between plunger face and the top of the sprue plate significantly affected flow behavior. This work yielded a predictive model.

3.29.6 Cold Transfer Molding

Cold transfer for molding automotive brake cups is said to be flashless [297]. Circulating oil at 80 °C in the top platen contacts the transfer pot and controls pot temperature. Four stepped dowels align the plates in a hinged, three-plate mold. Flats on one side of the dowels provide the clearance required during mold opening and closing. Transfer molding displaced the compression-molding method and increased both productivity and material savings.

3.29.7 Sprues

Sprues that cure during hot transfer molding can break or remote to the surface of a molded article during demolding [298]. The major portions of sprues are therefore removed along with the cured transfer pad. With cold transfer molding the rupture site moves to the junction of the uncured-cured compound and leaves uncured compound at the junction, which can be problematic (sticky). This can be avoided by the use of special heat-stable polyester and nylon fabrics moved into position to capture and remove the sprues as shown in Fig. 3.17. The fabric, with its captured sprues, is then discarded.

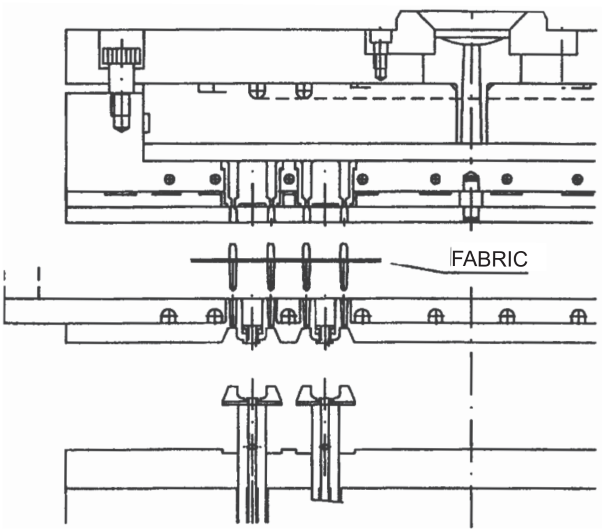

Figure 3.17 Open cold transfer mold showing fabric that captures sprues

3.29.8 Injection-Transfer

Relative to conventional transfer molding, reduced flash and scrap are advantages to combining injection and transfer molding methods [299]. By injection-transfer, an injection molding machine forces preheated compound through a sprue located in a transfer plunger into a transfer pot. The plunger then forces compound into mold cavities. Additional advantages of injection-transfer molding are as follows:

- Preheated compound shortens transfer times and cure times.
- Space that is ordinarily occupied by runners, gates, and so on in a conventional injection mold can be used for cavities.
- Sprues can be machined into plungers of existing transfer molds for low-cost trial runs.

With another arrangement, an extruder supplies preheated compound to the transfer pot.

When possible, use standard-size tools for machining runners and gates to preclude the time delay and cost of acquiring special tools. Hard metal components for molds are often machined using a conventional half-inch, four-flute solid carbide ball mill [300]. More rapid machining is said to be accomplished with a two-flute Ingersoll Chip-Surfer™ high-feed mill with a bull-nose tip.

3.29.9 Transfer Mold Design

Pressures in the pot and cavity must be appropriately balanced for a transfer mold to function effectively [301]. In a single-cavity mold, the area of the transfer plunger in contact with the compound should exceed the area of the molded article by about 40%. This keeps the mold closed at the parting line located between the bottom of the transfer pot and the cavity plate.

Pot-plunger clearance must be balanced against leakage of compound from the pot and the ease of removing the plunger from the pot after completion of the molding cycle [302]. A clearance of about 0.002 to 0.003 in. on a side (about 0.005 in. on the diameter) between the plunger and pot is typical. Larger clearances cause excessive leakage of compound from the pot into the region between the plunger and cavity plate. Compound in this region distributes the press closing force over a larger area and results in lower cavity pressure and wasted compound. Compound entering the interface between a dowel and its bushing makes mold opening more difficult, especially when reverting compounds like NR enter this region.

The maintenance of intended pot-plunger clearance depends upon several factors. If a plunger is affixed to the top platen and remains in the press while the pot is outside the press during mold servicing, the pot cools. The associated thermal contraction of the pot decreases pot-plunger clearance upon subsequent entry of the plunger into the pot. Several approaches are used to minimize compound loss from the pot.

A sealing board attached to the face of the plunger can reduce elastomer loss. Further loss reductions are made possible by placing fabric such as muslin or cheesecloth over the preform in the pot. After curing, the fabric facilitates removal of the pad and sprues from the pot. In another approach, a crosslinked elastomeric pad attached permanently to the bottom face of the plunger is said to reduce the amount of cured scrap from the transfer pot. The pad, about 80 to 90 Shore A hardness, is approximately 0.1 to 0.2 in. thick. Yet another approach is the use of a piston ring (glass-filled polytetrafluoroethylene) that fits in a groove on the plunger. Options available to the designer of transfer molds include parting line location, the design of individual components in the transfer mold, vents and their location, and the injection-transfer mold.

3.29.10 Parting Line

Parting line location is an early and important consideration in designing transfer molds, as it is for all molds. The location of the parting line must provide favorable access to the open mold for easy removal of cured articles. Once removed, flash on the cured article must be accessible for easy removal. These factors should be jointly considered along with their effect on cost and ease of mold manufacture.

While most transfer molds incorporate a single transfer pot, some incorporate multiple pots. One or more dovetail slots milled into the plunger face can temporarily retain cured pads on the plunger face such that pads can be more easily removed.

The term "hot transfer molding" is used when compound cures in the pot. The resulting cured pad is undesirable because it increases costs, especially when expensive compounds are molded. Cold transfer molding can be used to save compound. Here, the term "cold" refers to maintenance of temperature in the transfer pot sufficiently low that compound in the pot does not cure during the molding cycle. The residual compound from a previous molding cycle is used in a subsequent cycle. Equipment modifications that improve temperature control include the use of an insulation plate.

The compression resistance of the insulation plate at temperatures of approximately 180 to 200 °C should not be less than about 200 to 2000 kg/cm^2. The thermal conductivity of the plate should preferably be less than about 0.5 kcal/m/hr/°K. The plate is intended to maintain the compound in the transfer pot at a temperature sufficiently low that compound is still uncured after completion of a molding cycle [303].

A transfer mold can incorporate a pot with a closed bottom such that sprues machined in the pot connect directly to the cavity(s). With this design, sprues must align with specific cavities that determine sprue location. In contrast, a bottomless pot design accommodates different mold configurations because sprues are located in the top cavity plate, not in the bottom of the transfer pot.

A small lip machined into the bottom inside diameter of a pot prevents leakage of compound between the pot and the top surface of the sprue plate [304]. Relief in the bottom of the plunger face provides the needed clearance between the lip and plunger in the closed mold. Pressure developed in the transfer pot during molding forces the lip downward to contact the top of the sprue plate. This arrangement prevents leakage between transfer pot and sprue plate.

Several factors influence pot shape. Plungers and pots are typically machined round on a lathe, while square or rectangular pots are machined on a milling machine. Round pots might be preferred because of better control of their dimensions during machining on a lathe. Regardless of pot shape, a small taper on the open face of a plunger facilitates plunger entry into the pot.

Preform shape is another consideration in transfer molding. Square or rectangular preforms cut from a sheet produce less material that would subsequently be blended with fresh compound. Round preforms result in proportionately higher amounts of compound for recycle after the preforms are cut. Depending upon compound characteristics, increased heat history associated with several recycling steps could cause a scorch problem.

3.29.11 Plunger

A concentric bronze hoop is generally located on a round plunger at the entry point of the plunger into the pot [305]. If similar metals are used for pot and plunger, a hardness difference of 4 to 8 R_c (Rockwell C scale) is suggested, using the higher hardness in the most critical area. The use of dissimilar metals, or metals with dissimilar surfaces, is generally recommended to minimize problems with galling. To minimize problems with cocking of the plunger in the pot, the plunger should sufficiently engage the pot before the plunger face contacts the preform in the pot.

3.29.12 Sprues

Sprues are important for both technical and cost reasons. The cost of machining sprues is typically a very significant part of the total cost of fabricating a transfer mold. Sprues convey compound from the pot to the mold cavities, and their type and number significantly affect the rate of transfer and even the appearance of the molded article at the junction of the sprue and molded article.

While runners in transfer molds can convey compound to sprues, more often sprues convey compound directly from pot to cavities. Sprues are generally round and tapered, with their narrowest diameter located at the entrance to the cavity. Decreased diameter reduces the size of the blemish on a molded article at the sprue-molded article junction. A tapered sprue releases easily and is removed along with the cured transfer pad during the demolding process.

Number, size, and geometry affect sprue selection. Many sprues with large diameters are sometimes used to shorten transfer time of compounds that have a very high viscosity and a short scorch life. Lower viscosity compounds with good flow and scorch characteristics permit the use of smaller sprues, which result in higher temperature compound entering mold cavities. Flow through smaller diameter sprues shortens cure time and reduces waste.

Several factors influence the choice of sprue diameter and number. The number of sprues affects not only mold-filling behavior but also functionality and surface appearance of a molded article. A single gate on a molded article results in a more pronounced depression on the surface of a molded article. The use of multiple sprues can smooth the surface at their junctions and improve appearance. However, multiple sprues result in more junctions of flowing compound, which can be problematic.

Sprue diameters that are found to be too small in an existing mold can be enlarged relatively easily by drilling them larger. If the number of sprues is found to be insufficient, more sprues can be added with associated higher machining cost. Since the flow rate is exponentially related to the sprue diameter, small changes in sprue diameter disproportionately affect the flow rate, which must be sufficiently rapid to avoid scorch during filling.

3.30 Injection Molding

Material, process, and design requirements for injection molding of thermosetting elastomer are typically much more demanding than those for compression and transfer molding [306]. Because flow paths to the cavity during injection are generally much longer and temperatures much higher than for compression and transfer, injection-molded TSE compounds usually require longer scorch times.

Adequate scorch resistance is especially important at the junction of flowing fronts of rubber that meet in injection molds [307]. Weld-line strength decreased with increasing rubber viscosity and shorter scorch time.

Injection molds require high-quality steel to withstand the high temperatures and pressures they encounter during the molding cycle. Among major differences between transfer molding and injection molding are:

- degree of sophistication and automation of the injection method
- reserve of plasticized warm or hot rubber available for injection
- ability to inject a compound at a temperature approaching mold temperature
- the need for relatively high-volume production to offset increased machine and mold costs
- time schedules for designing and building molds.

Factors that influence cost follow [308]:

- ease of handling smaller machines and molds
- loss of production as a function of machine and mold
- increase in scrap associated with a larger number of cavities
- higher injection and mold temperatures permissible with smaller machines and molds
- communication difficulties between mold builders and molders that use sophisticated machining capabilities.

In contrast to the typical practice of maximizing the number of cavities in a mold, reduction in the number of cavities is said to lower production costs [309]. Additional advantages include greater planning flexibility, lower tooling costs associated with smaller tools, and shorter cycle times.

Molders prefer mold makers who can receive drawings created by computer-aided design (CAD). However, differences among computer programs can be problematic.

The American Mold Builders Association suggests guidelines and considers a number of factors directed toward improving prints for molded articles, databases, and communication. In these guidelines, moldability is assumed. Other issues addressed are dimensioning, print revisions, use of 2-D and 3-D databases, and production schedules.

Some molded rubber articles require a very smooth surface. This requirement might be only partially achievable because of vibration that occurs in a machine tool, for example, a conventional milling machine that experiences high forces at positions other than its center of gravity [310]. Newer machine tools that incorporate center-of-gravity technology can significantly reduce machine vibrations, significantly improve machined surfaces, and reduce the need for mold polishing.

Improved software has advanced mold simulation substantially, allowing simulation in the cloud, that is, using a remote computer on the Internet [311]. It provides access to remote supercomputers to analyze huge simulation models with many millions of mesh models and essentially allows renting a supercomputer for one second, thus shortening computing time substantially.

3.30.1 Injection-Molding Problems

Some injection-molding problems and suggested remedies follow in Table 3.10.

Table 3.10 Injection-Molding Problems and Suggested Remedies

Problem	Suggested Remedy
Nonfills (caused by scorch)	Increase scorch time of compound
	Lower barrel and mold temperature
Undercure	Increase mold temperature
	Increase barrel temperature
Trapped air	Review vent size and location
	Open plugged vents
	Incorporate vacuum in mold
Particles in molded article	Improve cleanliness
	Remove all debris from the previous cycle

To improve injection-molding operations, it is suggested that a company appoint one or two individuals with total operations responsibility directed toward harmonization [312]. Otherwise friction among departments will trump economics.

Establishment of the optimum molding cycle time to improve productivity is a general goal of any molding operation. It is especially important for injection molding because of higher equipment cost. Among the factors that play a role in the attainment of this goal include selection of the basic elastomer characteristics of a compound, such as molecular weight (MW) and molecular weight distribution (MWD).

Polymers today tend to have a bimodal distribution that includes a low MW fraction that favors good flowing characteristics, a broad MWD for good hot tear strength, and good cured properties. Favorable effects, such as higher tear strength that reduces tearing during demolding, can improve molding behavior of fluoroelastomers. Good hot tear strength is needed to avoid tearing articles during demolding, especially molded articles that tend to stick in mold cavities.

Plasticizers also affect injection-molding behavior. Petroleum-based plasticizers, such as paraffinic oils, do not react during vulcanization and therefore do not become part of the elastomer network. Liquid EPDM polymeric plasticizers, such as Trilene, are said to reduce viscosity of EPDM compounds, shorten injection-molding cycles, and become part of the network. Trilene can be cut with a knife and does not stick to surfaces it contacts [313]. An ultra-low viscosity EPM was used to replace conventional elastomers or as a plasticizer to replace oil [314].

Depolymerized NR can act in much the same way in high molecular weight NR as was described for liquid EPDM [315]. It offers advantages that include higher permissible filler loadings, reduced scorch, improved mold flow, and nonvolatility (resists extraction).

Although FKM elastomers have been based on the same monomers over the last several decades, their architecture has changed. Changes resulted in improved properties and processing characteristics such as mold fouling (discussed later). Compounding changes that can improve the hot tear strength of a fluoroelastomer include substitution of N330 black for N990 black, adjustments in calcium and magnesium hydroxide levels, and adjustments in peroxide and coagent levels.

FKM with improved processing demonstrated a longer scorch life that allowed compounders to lower the plasticizer level from 2 phr to 1 or 0.5 phr [316]. The improvement comes with a cost penalty, since the improved polymer can be more expensive than gold on a weight basis (based on value in 2006). Apparently the extreme cost is justified and is tolerated in applications such as the use of perfluoroelastomer in watch straps for high-end watches [317].

A bisphenol system improved curing efficiency in FK, and it eliminated the demolding and mold fouling problems associated with peroxide curing [318].

Special grades of FKM have been developed that can withstand extreme operating conditions [319]. Although most TSEs operate at a maximum temperature of 180 °C, the special grades are said to operate continuously at temperatures of up to 205 °C, with temperature excursions up to 315 °C. This capability coupled with good low-temperature behavior makes these grades good candidates for use in extreme temperature applications.

Excess of magnesium oxide caused a fatal explosion in an FKM compound [320]. Hot spots within the compound degraded the rubber and led to gas emissions.

3.30.2 Injection-Molding Machines

An objective of any industrial process is to produce saleable articles at minimum cost. For injection-molded TSE articles this means that materials, processes, and molding equipment must be judiciously chosen and controlled. An operating region (OR) is the combination of parameters that results in the production of good-quality articles [321]. For example, the OR represented the variables TSE temperature in the injection barrel, mold fill time, and mold temperature.

As mold temperature increased in this study, scorch became more problematic for a TSE and the OR decreased; for a TPE, in contrast, *increased* mold temperature lowers TPE viscosity and expands the OR. The reason for these opposing TSE and TPE behaviors is that a TSE typically stops flowing because of scorch; a TPE stops flowing when lower temperature increases viscosity.

The rubber exiting the nozzle of an injection-molding machine has a higher temperature on its external surface than in its central region [322]. Using thermal camera measurements on an NBR compound, the temperature difference was 10 °C for compound exiting a 5 mm diameter nozzle, and 51 °C after adding 250 mm long runners of 8 mm diameter. The use of a fill balancer reduced cure time significantly.

A coaxially arranged screw and barrel in an injection-molding machine resulted in a FIFO (first in, first out) compound delivery system with less complexity, a shorter flow path, and easier cleaning.

Retraction of the screw-barrel unit allows for easier compound changes along with improved accessibility for maintenance. The coaxial machine is favored today because of these and other advantages. Screw diameter influences the dimensions required for the feed strip that is used to feed an injection-molding machine. For a screw about 45 mm in diameter, a strip about 50 mm wide by 7 mm thick is recommended [323]; strip dimensions as large as 120 by 12 mm might be used with a 90 mm screw. Additional factors are important in strip feeding.

The strip must not break when transported from its container to the throat of an injection-molding machine. Since strip at the bottom of its container is under the considerable weight of the strip above it, the strip may flow excessively and lump together just as powdered compounds do. Compounds with low green strength are problematic. Release coatings applied to strips minimize this problem, and some of these have minimal effect on compound physical properties.

Injection molding of silicone rubber presents special feeding problems, and devices have been developed to assist feeding. One of these is called a Silicone Stuffer®. Another feeder, which monitors strip breakage, measures metering performance using volumetric change per screw revolution [323].

During the injection-molding cycle, compound from the barrel flows through the nozzle and is injected through a sprue bushing attached to its mold. The nozzle can be considered an extension of the mold, and its diameter should provide a temperature rise during injection of about 20 to 30 °C. It should be large enough to provide short injection times (five seconds or less) but not so large that the temperature rise in the nozzle is inadequate [324]. Large-volume injection-molded articles require longer times; for example, a 56 kg trawler bobbin required a 32 s injection time.

Injection time should be short enough to avoid scorch during mold filling. Collecting sufficient compound (called an air shot) and then measuring the temperature of the collected compound with a pyrometer can determine the temperature of compound that exits the nozzle. Doing the same with the nozzle removed indicates the temperature of compound entering the injection chamber and provides useful data.

Compounds containing abrasive fillers can wear nozzles rapidly, especially so for small-diameter nozzles [325]. A nozzle with a 0.060 in. initial diameter increased in diameter to 0.100 in. after only 400 shots. Nozzle wear was substantially lower for larger diameter nozzles.

The radius of the nozzle tip is usually made smaller than the radius of its mating sprue bushing to minimize leakage of compound at the nozzle-bushing interface. Nozzles with a fine polish and with a reverse taper angle of 4° to 5° are suggested. Excessive nozzle temperature can cause scorched material that could enter a subsequent shot.

To minimize sprue-to-nozzle heat transfer, nozzles can be separated from the sprue bushing after mold filling. Another approach involves placing a thermal insulator such as a polyamide material between a sprue plate and its mold. Polyamide exhibited the best combination of low thermal conductivity, high compression strength, and reduced heat transfer from mold to nozzle [326].

A number of factors influence the selection of either a horizontal or a vertical injection-molding machine [327]:

- Vertical mold suspension increases difficulty of changing molds.
- Larger capacity horizontal machines require more floor space than vertical machines.

- Changes to cylinder capacity are more easily made on vertical machines than on horizontal machines.
- Maintenance on horizontal machines appears to be more critical than on vertical machines.

3.31 Molds

Injection molds, because of their complexity and the need to be more robust, are generally more expensive than other molds. The design of an elastomer product mainly determines the key parameters for mold design [328]. While product design represents only 5% of the total product cost, its influence on product cost is estimated to be 70% [329]. Hence, design is an extremely important consideration for both an elastomer product and its mold. Since design affects cost as well as product quality, it is of major importance.

Ease of removal of a molded diaphragm from an injection mold influences overall cost [330]. A vacuum applied to the cavity for an injection-molded diaphragm eased entry of rubber into the mold (remember rubber can't fill a mold cavity until the air has exited). Following curing, pressurized air forces the diaphragm off the male part of the mold. A mechanical ejector assists ejection (Figure 3.18).

Lower-hardness compounds require the use of ejector pins with a larger surface area to minimize stretching of the rubber during ejection.

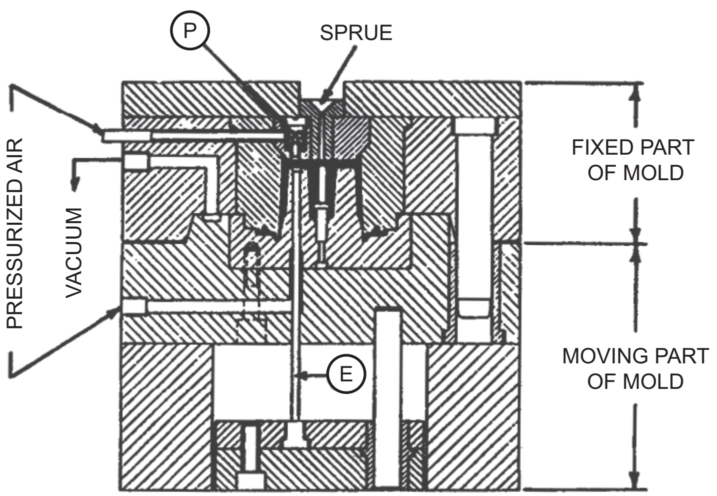

Figure 3.18 Injection-molded diaphragm: P, a pin actuated by compressed air; E, an ejector pin that is mechanically actuated

Vacuum applied to mold cavities significantly reduces porosity in molded articles. A cord can be fitted into the groove of either the lower or upper mold plate [331]. It should be located at as great a distance as possible from the mold cavities to minimize potential damage from the mold operator or from injected rubber that can be forced into the cord groove.

Microgrinding mold plates to a specified finish is an alternative to the use of vacuum [332]. This technique allows air to escape at the mold parting line while preventing flow of rubber.

3.31.1 Mold Materials

Steel used in molds for elastomer articles should be fine grained and free from dirt, porosity, holes, and other imperfections [333]. Ease of machining is another important consideration, but not one that should dominate the steel selection. Prehardened steel is more difficult to machine than softer steel, requiring up to 28% more time to machine than softer, free-machining steel.

Other desirable characteristics of steel for molds include stability and ease of welding. NAK 55 steel, said to possess very favorable characteristics for molds, is replacing alloys such as 4140 and P20 [334]. Prehardened steel is widely used for injection molds because it provides the required durability. Modern machining methods and improved steels eased some of the difficulties formerly associated with difficult-to-machine materials.

Heat treatment of some types of steels increases their hardness to only a limited depth below their surface [335]. Other types of steel provide improved hardness uniformity throughout their depth. High hardness is especially desirable in the land region of injection molds to resist imprinting, if flash remains in the mold from a previous molding cycle. Flash is more likely to imprint the critical land region of softer molds. This emphasizes the importance of completely removing flash between molding cycles to maximize mold life. The following types of steel are suggested for fabricating injection molds, using the American National Standards Institute (ANSI) nomenclature [336]:

- 4140 and 4130 alloy steel for toughness of a mold body
- 420 and P20 tool steel for mold cavities
- H13 hot-rolled steel for ejectors
- 6150 alloy steel for nozzles.

NAK 55 is a precipitation or age-hardened material that possesses a through hardness of 40 R_c in a six inch section thickness [337]. In contrast, the hardness of 4140 or P20 decrease significantly over this thickness.

Steel selection information is available from suppliers of metals and standard mold components and from mold builders. Steel types are arranged below in three groups in order of increasing cost.

- Low carbon (to 0.35%) steels are the least expensive and can be hardened only by surface treatment such as carburizing.
- Medium carbon (0.35 to 0.5%) steels can be hardened to about 54 R_c depending on carbon content.
- High carbon (0.5 to 1.0%) steels can exhibit high hardness.

3.31.2 Mold Handling

All but the smallest of molds should be provided with a means for slinging and hoisting to facilitate handling [335]. Molds should be provided with tapped holes for threaded, forged eyebolts that should be located in a solid portion of a mold and be sufficiently large to safely carry mold the weight. Further, provisions should be made to handle each part of a mold separately.

3.31.3 Cavity Finish

Cavity finish depends upon a number of factors. As a general rule it should have a roughness of 0.05 to 0.1 μm to facilitate demolding [336].

3.31.4 Mold Heating

Obtaining a uniform temperature over the surface of heating platens depends upon factors that include minimizing heat loss between insulation and press components and the type and spacing of heat sources [337]. These sources include channels in platens that convey hot fluids and electrical strip heaters or cartridges.

Isobar® heat transfer technology substantially increased temperature uniformity in a platen that was heated by parallel cartridges located in platen channels. Isobars, arranged in a bilevel grid pattern orthogonal to these channels, resulted in a temperature distribution of ± 3 °C over 90% of the platen surface, and temperature uniformity also improved at platen corners. It is also possible with integral systems to provide variable watt density along the heater length to compensate for local heater losses [338].

Both Isobars and thermosyphons contain a fluid that transfers heat as the fluid goes through cycles of evaporation and condensation. Thermosyphons require their evaporator region to be lower than their condenser region because gravity returns condensate to their evaporator region. In contrast, Isobars work in both vertical and horizontal planes because a wick returns the working fluid to the evaporator by capillary action. Application of heat to individual zones of a mold can also improve temperature uniformity.

Injection molds may be externally heated by platens or internally heated by electric cartridges. Regardless of the heating method, both temperature control and uniformity critically affect crosslinking of TSEs and therefore product quality. A study established the heating and crosslinking behavior of injection-molded elastomers. Jacketed thermocouples, one mm thick, were inserted into holes of varying depths in a mold wall [339]. Information from these sensors correlated well with measured physical properties on molded articles. A heat flow sensor even detected the use of a different release agent.

Thermocouples often have rounded ends, with thermocouple wires embedded at their far end [340]. When inserted into a thermocouple well that is formed by a typical drill bit, the rounded end of the thermocouple does not contact metal because the angled shape formed by the drill bit does not conform to the rounded end of the thermocouple. Using a tool with a rounded end to form the thermocouple well permits contact between the end of the thermocouple and the base of the thermocouple well and thus provides more accurate temperature readings.

3.31.4.1 Heating Methods

The use of steam and hot fluids is less favored today because of leakage problems. Resistance and induction heating methods could be preferable because they provide rapid temperature response, with temperatures up to 204 °C [341]. Electrically heated platens are increasingly used even though they may provide less-than-optimum temperature uniformity. Strip heaters are normally used for lower temperature applications, cartridges for higher temperature.

Heaters can be arranged to provide zone heating that is said to minimize the cooling effect of air moving across the platen edge. Higher wattage heaters used at the edges of platens can provide the same result. Ideally, each electrical heater should be provided with a fault detector to avoid cold spots that otherwise might go undetected with heater failure.

Magnesium oxide in a cartridge sheath, being slightly hygroscopic, should be dried to avoid conduction between adjacent coils [342]. Swaging compresses magnesium oxide and increases heat transfer by about ten-fold [343]. Lower watt density ratings and tighter fitting cartridges lower resistance-wire temperature. Swaging positions the resistance wire in a heater, and it produces good heat-transfer characteristics and dielectric strength. Lower temperature lengthens cartridge life; as a rule of thumb, each 100 °F decrease in temperature is said to increase resistance wire life by about three-fold.

Cartridge life depends upon factors such as the tightness of fit of a cartridge in its mounting hole, the position of the cartridge in its mounting hole, and the use of a vacuum on a mold.

Tightness represents a compromise among efficiency of heat transfer between cartridge and mold, ease of cartridge insertion, and ease of cartridge removal. Cartridges should not extend beyond the opening to the mounting hole because of potential overheating in the out-of-mold portion of the cartridge.

The lead end of a heater used in a vacuum application should be located outside the vacuum to minimize problems with arcing. When located in a vacuum, the leads can be encapsulated to extend their life. Anecdotal evidence suggests that inductively heated platens function better in a vacuum environment [344].

3.31.5 Gates

Locate gates in an injection mold so that compound entering the mold cavity does not impinge directly upon and displace adhesive [355]. By following this practice, scouring of adhesive was avoided even with injection pressures on the order of 30,000 psi. Scouring can also lead to edge failure if excessive adhesive builds up at the periphery of a bonded component. Adhesives used in injection molding, relative to compression and transfer, generally require greater resistance to wiping. An alternative to injecting compound midway between plates is to inject it through the opening in one plate, normal to the other plate.

A gate mark or blemish generally occurs on a molded article after demolding separates the gate from a molded article. Compound hardness affects the appearance of the gate mark on the surface of a molded article, wherein marks were evident as either a depression or a projection. Compounds softer than 50 Shore A hardness resulted in a typical depression or projection from the article surface of 0.015 in.; those harder than 50 showed a typical value of 0.007 in.

3.31.6 Leader Pins

Leader pins and bushings should be securely anchored in their respective mold plates. They should be appropriately dimensioned and hardened because they are subject to stress and wear during mold assembly and during mold closing and opening in service. Leader pins should terminate in a through hole rather than a blind hole to facilitate their repair and replacement. Leader pin diameter should be a minimum of 0.875 in. [346]. Of course, mold size and other factors affect this diameter. Assembly and disassembly of mold plates accelerates mold wear when mold plates are at different temperatures.

Tapered interlocks incorporated in a mold provide more accurate alignment than do leader pins and bushings. Round interlocks consist of tapered plugs that engage matching round sockets. Interlocks are commercially available from Detroit Mold Engineering. Line boring of clamped mold plates helps align the holes for plugs and sockets for their subsequent installation in mold plates. The male side of rectangular interlocks engages a matching opening with a trapezoidal cross section. Mating sets of rectangular interlocks are mounted in-line and/or perpendicular to one another—never parallel. Both round and rectangular interlocks rely on metal-to-metal contact to provide improved alignment.

When closing a mold with a core, leader pins should engage bushings before the core enters the cavity. This sequence avoids damage that would likely occur if contact occurs between core and cavity. Also, when the mold plates are separated, the longer pins prevent damage to the core if the top plate is placed core-side-down on a flat surface.

Offsetting of leader pins and bushings in mold plates allows only one-way assembly of the mold plates, thus preventing mold damage because of incorrect mold assembly. A 0.25 in. offset for pins and bushings, readily recognizable when assembling a small mold, will be less recognizable with an intermediate size mold, and probably unrecognizable with a large mold. Hence, the amount of offset should be proportional to the size of the mold plate to make obvious the proper orientation of mold plates during assembly [347].

3.31.6.1 Core Pins and Bushings

Securely anchor core pins and bushings in their respective mold plates to withstand the stress they encounter during opening and closing of a mold [348]. Anchoring methods include the use of screws and snap rings [349]. Pins and hinges for hinged molds should be capable of withstanding severe service conditions experienced during mold opening and closing. Pins should be tapered so that only a short shoulder length of the pins engages bushings. Doing this facilitates mold opening and closing while still effectively aligning mold plates.

Heavy production molds that are handled manually are problematic because of ergonomics. They should have securely mounted handles that are integral to mold plates for safe handling.

3.31.7 Lands

Mold land width is the distance between the outer cavity diameter and the inner diameter of the overflow groove [350]. Land widths generally range from as narrow as 0.005 in. to as wide as 0.1875 in. Narrow land widths pinch off flash closer to a product edge and generally produce thinner flash; however, they wear more rapidly than their wider counterparts. A more typical range of land widths ranges from about 0.0312 to 0.062 in. For silicone elastomer, land widths of 0.010 in. (0.25 mm) are popular; for cryogenic tumbling, land widths of 0.030 to 0.040 in. (0.75 to 1.0 mm) are suggested.

Land top surfaces are usually in plane with the rest of the cavity plate, making it more economical to machine a mold. However, a land can be raised or lowered slightly with respect to the plane of the plate surface. Raising the land by about 0.001 to 0.002 in. results in higher pressure in the compound above the land; this increases resistance to flow of compound as it exits the cavity. Care must be taken to avoid exceeding the yield strength of the steel in the raised land by raising the land too much.

The land can be lowered slightly below the plane of the plate surface to provide a controlled flash thickness to facilitate trimming. Raising or lowering a land results in higher mold cost because of added machining operations.

Excessive flash can be problematic, not only at the mold parting line but also at the nozzle [351]. The following steps can be taken to minimize flash problems at the nozzle:

- Decrease injection pressure.
- Check nozzle wear and nozzle bushing wear; machine if necessary.
- Increase compound viscosity.
- Decrease nozzle size.
- Decrease back pressure.

Flash is especially problematic in medical applications because of its potential to break away from an article and get into the bloodstream. Medical rubber is typically molded in clean rooms, and dedicated air conditioner systems are needed for clean-room molding operations wherein the air changes very frequently. Because of this, higher-than-necessary ceilings add to the cost of clean-room operation.

Rubber use in medical applications is growing at a faster rate than for other applications; it grew at a 7.2% compound annual growth rate between 2000 and 2009 [352]. Important properties for medical articles include transparency, ease of forming and joining, and resistance to bad things that compromise medical treatment.

Medical devices fall into three classes as outlined below [353].

- Class I: not intended for use in supporting or sustaining life
- Class II: performs in specified applications without causing injury or harm
- Class III: supports or sustains life with associated tests and equipment being of substantial importance.

Medical devices with silicone rubber components continue to cost lives and money even though efforts have been made to improve education and hygiene practices

[354]. Microbes that attach themselves to catheters and ventilator systems can cause infections. Silver-based antimicrobals, released upon exposure to moisture, reduce the population of viable bacteria at or near the treated surface within 24 hours.

HM 4100 is a commercially available stable antimicrobial polymer that is thermally stable and nontoxic [355]. It is said to be fast acting, have a broad kill range, and can be used in a range of materials. Another material (Statsil) uses the positive charge carried by ionic silver to alter negatively charged groups of biological molecules that inhibit bacterial and microbial growth [356].

Drug packaging is a related area wherein elastomer materials contain low levels of extractable materials that must be nontoxic [357]. The FDA requires that a wide range of tests be run on drug packaging applications. Since elastomer constitutes one-half of a typical pharmaceutical stopper, cleanliness is of vital importance in ensuring low levels of extractable and leachable materials [358].

3.32 Overflows

Overflows collect and confine excess compound that exits the cavity after a mold closes. Without overflows, compound flows in an uncontrolled manner beyond the cavity wall and increases the projected area of the compound at the parting line. This increased area increases variability of flash thickness and reduces mold cavity pressure.

To be effective, the overflow volume typically should be sufficiently large to accept excess compound from the mold cavity *without* filling the overflow. An exception is the interconnecting and filling of overflows to permit all cavities in a mold to be stripped from a mold as a sheet. Overflow volume is often 10 to 20% of cavity volume for typically sized elastomer articles. It depends upon factors such as preform complexity and the volume of a molded article. The percent overflow volume is typically smaller for large articles and larger for smaller articles.

Crosslinked material collected in overflows serves as a “handle” to grasp and remove a molded article from its mold. Properly sized and designed overflows prevent flow of compound past the outer diameter of the overflow. Compound flowing past the outer diameter of an overflow ultimately makes mold opening more difficult if compound flows between leader pins and their bushings.

3.32.1 Overflow Design

Different overflow designs (Figure 3.19) offer relative advantages and disadvantages [359].

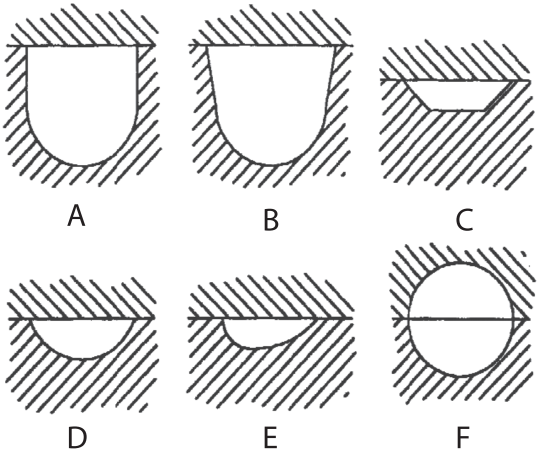

Figure 3.19 Overflow cross sections: (A) deep semicircular; (B) deep and tapered semicircular; (C) trapezoidal; (D) reduced depth; (E) teardrop; (F) full round [329]

Increasing the depth of semicircular overflow (A) increases overflow volume without changing the land width. This increased volume is obtained without changing the area of the overflow at the parting line, thus permitting a closer cavity arrangement. The deeper overflow has two disadvantages: one is increased difficulty in removing cured compound from deeper overflows, and the other is the reduction in cavity wall stiffness adjacent to the land. The lower stiffness reduces the resistance of a cavity wall to deformation caused by pressured compound in the mold cavity.

Removal of overflow from (B) is easier than for (A), but machining the tapered overflow increases costs and necessitates increased cavity spacing.

Trapezoidal overflow (C) is an advantage for thin mold plates. A disadvantage is the tendency for the corners in the grooves to become fouled with compound. Fouling is generally more severe in sharp corners than in curved areas of a mold.

If overflow depth (D) is less than the radius of the forming tool—commonly a ball end mill—then overflow depth critically affects the width of the land. Decreased overflow depth results in increased land width.

Teardrop overflow (E) increases cavity wall stiffness; however, it costs more to machine and it necessitates wider cavity spacing.

Full round overflow (F), an alternative to the semicircular one, provides greater overflow volume per unit area of mold plate surface and thus permits closer cavity spacing. The projected area of a round overflow is 0.71 times that of its semicircular counterpart with an equivalent cross section. This means that there is a decreased tendency for compound in the round overflow to separate mold plates if the overflow were to completely fill the overflow and pressurize it.

Crosslinked compound in a round overflow is easier to remove from a mold because it projects above the parting line, assuming sufficient compound flows into the overflow. This advantage could be outweighed by the higher cost of overflow grooves in both top and bottom mold plates, rather than only in the bottom plate as was done with the semicircular overflow.

3.33 Holes

Holes or other openings can be formed in a molded article by a core or a pin during molding, or they can be formed later in a post-molding operation by punching or by a laser beam. Recommendations for forming holes during molding include [360]:

- Form holes as wide and shallow as possible, consistent with product requirements.
- If a core pin with a small diameter at its unsupported end is used, taper the pin to increase its stiffness.
- Design mold to have the axis of the hole in the mold-closing direction to avoid the need for retractable core pins.
- Provide sufficient wall thickness around holes in a molded article to minimize tearing the article.

Where feasible, incorporate a minimum of one hole diameter between holes and between a hole and the edge of the molded article (this is generally not feasible for electrical connectors that contain many pins and sockets).

Incorporate through holes rather than blind holes if feasible, since this procedure permits anchoring core pins at both ends. Anchoring becomes increasingly important with smaller core pin diameters.

Although nonround holes can be formed in molded articles, round holes are preferred [361]. D-shaped holes in a rubber seat on a swing set split at the stress-concentrating corners of the D-shaped holes. The big advantage of a round hole is that it has one continuous radius, hence no stress concentrators.

3.34 Runners

Ideally, mold runners would contain a radius to facilitate flow in the region where a runner changes direction, but increased cost often precludes this option. Either hot- or cold-runner systems are used for molding TSEs. Compound in a hot-runner system crosslinks during the molding cycle, while that in a cold runner does not—at least not intentionally.

A runner system called “Turbo-Cure” incorporates a split runner that directs hotter rubber to the inside and cooler compound to the outside of the runner [362]. This arrangement is said to reduce cure time by up to 35% without damaging a compound by excessive shear.

3.34.1 Hot Runner

Cured compound in a hot runner is generally discarded as scrap; however, it can be ground into small particles for incorporation into fresh compound for subsequent use [363]. Scrap resulting from a hot-runner system is a major disadvantage because costs are incurred not only with compound loss but also with disposal costs for the runner scrap.

An objective in designing runner systems is to fill all mold cavities simultaneously so that all the resulting molded articles will possess the same state of cure. A balanced runner system is a necessary but insufficient condition to meet this objective. Gate design and other factors such as temperature significantly affect flow behavior.

Although runners can be designed scientifically, they are most often designed on the basis of a mold designer’s experience. Very long production runs can justify the added cost of designing molds scientifically. Mold designers frequently fabricate an injection mold with undersized runners, make a few trial moldings, and then increase the runner cross section as required. It is easier to remove metal from a runner channel than to add metal to a channel by welding and machining the runner again.

The molding of very small articles could require a mold design that produces an undesirably high ratio of runner volume to molded-article volume. In addition, a runner that feeds small articles molded from a high-viscosity compound might cure after the articles do. When this occurs, the runner determines the cure time rather than the molded articles. A semicircular runner will cure faster than a circular one when both are the same diameter. The faster cure for the semicircular runner is advantageous relative to the circular runner if one disregards the higher decrease in pressure associated with the semicircular runner.

3.34.2 Cold Runner

Cold-runner systems maintain the temperature of compound in the runner system below that necessary to cure the runner. Hence, compound required for the next injection cycle is not wasted as described above for a hot-runner system. Cold-runner systems are more expensive than their hot-runner counterparts. However, the increased cost can be justified for high-volume molding operations and especially for expensive compounds.

3.35 Mold Design

Options available to mold designers are virtually limitless, with each providing relative advantages and disadvantages. Figure 3.20 shows a two-plate mold that can be used to mold ring-shaped articles [364].

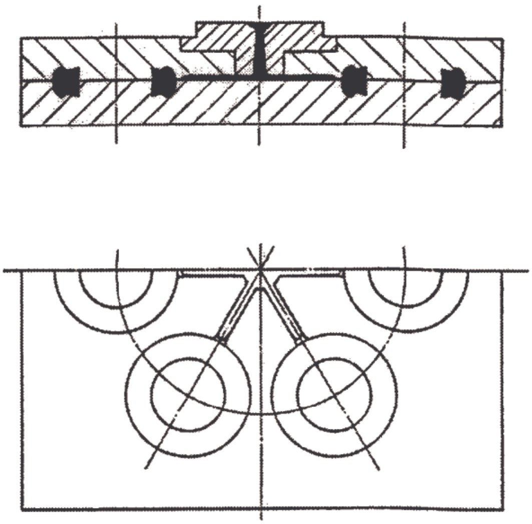

Figure 3.20 Two-plate mold for curing ring-shaped articles [363]

Edge gates, frequently used with two-plate molds, usually leave small gate marks [365]. A three-plate mold (Figure 3.21) is usually necessary for molding deep articles to facilitate removal of a molded article from its cavity. Pin gates, mostly used with three-plate molds, tend to be self-degating.

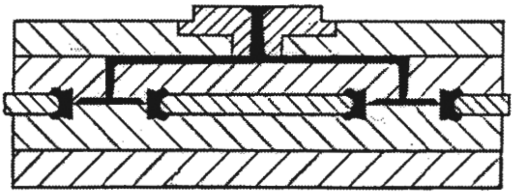

Figure 3.21 Three-plate mold for curing ring-shaped articles [363]

Because of memory in rubber compounds, the designer should be aware that the shape of a mold article can differ from the shape of its cavity, depending upon whether it was molded in a two-plate or a three-plate mold. For example, a hollow hemisphere, pin-gated at is pole, tends to be egg shaped; its edge-gated counterpart will tend to be oval shaped at its equator.

Although molds should be balanced thermally, geometrically, and rheologically, this is often not the case. For example, the H-pattern cavity layout shown in Figure 3.22, while balanced geometrically, is not balanced rheologically; the cavities marked with an "x" often fill first [366]. The cause for this behavior is asymmetrical shear distribution within the flowing rubber that is associated with temperature stratification.

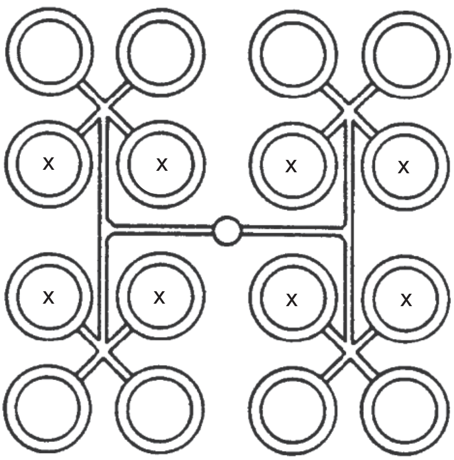

Figure 3.22 H-pattern mold with 16 cavities [366]

A device called a "melt flipper" addresses this problem by changing the orientation of the flowing rubber [367]. The device can be fitted to a new mold or retrofitted to an existing mold at a total cost that is said to be generally less than 2% of the mold cost [368].

A runner with a curvilinear design is said to eliminate dead spots in the flow stream and to optimize flow paths to facilitate balanced filling [369]. However the design is not achievable by gun drilling the channel.

3.36 Gates and Venting

Rubber can fill a mold cavity only after air has exited the cavities. Air expulsion occurs because a flowing rubber front pushes air to a vent in advance of the flowing rubber. It can also occur because a vacuum has removed air from a cavity before rubber enters. A higher vacuum is not necessarily better. Use of an absolute pressure of 300 mbar in a cavity provided the best results, and lowering the pressure increased the scrap rate [370].

The old adage that three things are important in real estate, *location*, *location*, *location*, is also true for gates. Locate gates to effectively expel air during mold filling so as to avoid air entrapment. The best position for vent location can be determined by progressively increasing the volume of compound shot into an injection mold (called short shots). This technique is also useful for establishing the fill pattern for mold cavities.

The gate design (Figure 3.23) for a bellows shows that compound first enters the mold midway along the axis of the bellows [371].

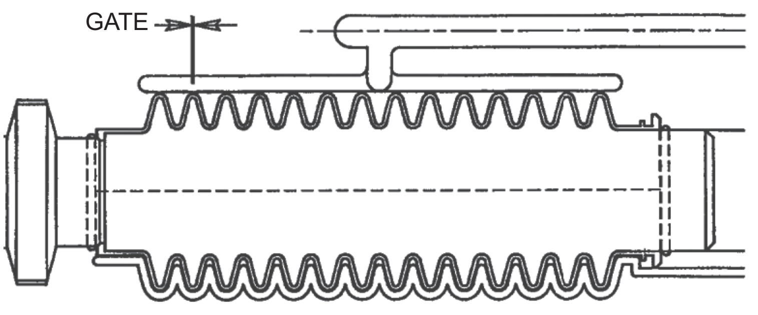

Figure 3.23 Gate locations for an injection-molded bellows

Filling then progresses axially, pushing air toward the ends of the mold where the air escapes. As this occurs, compound progressively flows around the circumference of the mandrel. The last locations to fill are at the ends of the bellows opposite the runner. Feeding the mold at an end is an alternative; this approach doubles the length of the axial flow path for the compound to fill the mold.

Pressurized air applied at the interface between the end of the bellows and its mandrel serves as a lubricant for demolding the bellows. The blemish on the bellows surface at the site of the rupture of the gate can sometimes serve as a flaw that propagates when the bellows is blown off the mandrel by compressed air. This occurrence could require redesign of the gate to reduce stresses in the gate region.

Placing a mold cavity under vacuum generally eliminates imperfections associated with trapped air [372]. One method of applying vacuum is the use a vacuum shroud that completely encloses a mold and forms a seal before complete mold closure. In one arrangement, the top platen moves through an arc where it engages the lower platen. When both platens become parallel, the moving shroud on the top platen slides on the static shroud on the lower platen and seals the mold from atmosphere. Vacuum is then applied and the molding cycle completed. Other advantages for vacuum use are the removal of potentially health-hazardous volatile materials during curing and reduced mold fouling.

Vacuum shrouds on molds are being used for a range of products as they become more common. They are said to virtually eliminate chances of bubbles forming during curing, and this scrap-reducing feature is especially important when molding expensive polymers such as fluoroelastomers.

3.37 Cost Factors

Forming techniques other than molding can significantly reduce the cost of some rubber articles. Articles that are lathe cut from extruded rubber tubes can be produced in a range of designs [373]. They do not require different molds for different designs.

Users of elastomer products may designate unnecessarily costly specifications for rubber products, thinking that the best possible quality is always desirable [374]. They should be aware that the added quality increases mold cost and may require costly in-process controls and inspection procedures. RMA (Rubber Manufacturer's Association) provides a guide for specifying dimensions of rubber products. For example, an "A2" designation requires the use of precision-machined molds kept in good repair, among other considerations. The "A3" designation is suggested for most products.

Ring gating is commonly used for rubber articles with center holes such as washers, spark plug boots, small belts, and so on [375]. In contrast, tab or submarine gates are generally used for articles with undercuts, long bellows, and specification O-rings where direct gating is not permitted.

3.38 Fouling and Cleaning

It is a rare mold that doesn't become fouled in service and require cleaning [376]. Mold fouling, the process by which undesirable material deposits on molds, is important because it affects both the appearance of molded articles and their costs [377]. Fouling also refers to the material deposited on a mold. It appears initially as a stain that thickens progressively as more articles are molded. In severe cases, the fouled material can adhere to a molded article and ultimately pull fragments from the molded article. The many factors that can contribute to fouling sometimes go unrecognized. Sometimes a single factor such as compound is cited as the cause when in fact fouling can result from other factors in addition to interaction among factors.

3.38.1 Mold Fouling Factors

Material, process, and mold design are all factors that influence mold fouling. The elastomer and its compounding ingredients, mold temperature, and mold design can all affect the nature of the fouled deposit as well as the difficulty of removing the fouling. It is not surprising that the composition of fouled deposits varies substantially, considering that an estimated 2500 elastomers and ingredients were available as early as 1961. The fact that molding conditions alter the original composition of materials placed in a mold complicates the issue. Deposition and accumulation of mold release agents further complicate issues because some of these agents oxidize and others may corrode a mold surface.

The severity of the problem is indicated by the fact that several elastomer producers have developed elastomers, such as NBR, that are designed to reduce fouling [378]. Fouling by NBR has been attributed to the formation of a complex interlayer formed between NBR and steel during molding [379]. Some elastomers such as CSM (chlorosulfonated polyethylene elastomer) form sulfurous acid during crosslinking that results in mold fouling. Stainless steel molds are recommended for production of articles that incorporate CSM.

Often, if only mold hardness is specified, tempering at a lower temperature will be used to heat treat a mold. While this procedure provides the maximum corrosion resistance, it provides the lowest toughness [380]. Hence, both parameters should be considered simultaneously.

Semipermanent mold release agents can last as long as a factory shift and minimize the need for frequent spraying of mold release agents [381]. Another approach is the use of an oil-bleeding silicone rubber composition that is said to minimize mold fouling and to provide smooth mold release [382].

The severity of the fouling problem is further indicated by the effort that has been directed toward mold cleaning.

3.38.2 Mold Cleaning Methods

Cleaning methods include

- blasting fouled molds with particulates
- wire brushing and scraping
- immersion of molds in chemical solutions, in the presence and absence of ultrasonic excitation
- heating molds to high temperatures in salt baths and fluidized beds
- use of lasers
- in-place cleaning with special elastomer compositions.

Mold damage is another consideration in addition to cleaning effectiveness. Of special interest is the potential damage to critical mold edges. Blasting with harsh media can round the critical mold edges and cause formation of a radius at the junction of the surfaces of the land and the mold cavity. The associated increased flash thickness caused by the radius increases the time required to cryogenically deflash molded articles. Other considerations include disposal of cleaning materials, potential hazards to personnel, relative costs for the different methods, and nonuniform mold fouling.

3.38.3 Fouling Sites

Fouling tends to preferentially occur at the junction of flow fronts, where there is a widening cross section, at trapped air sites, and at sharp corners and undercuts.

Ironically, the most difficult areas to access for cleaning are often the regions of a mold most likely to foul. Competitive pressures dictate that compound costs be minimized, such as by increasing filler levels. High filler contents reduce compound cost but can reduce hot tear strength, making demolding more difficult, and they favor formation of fouled residues in areas of molds difficult to access.

3.38.4 Causes of Fouling

Oxidized residues from fouling can degrade to form hard deposits that adhere tenaciously to a mold surface, making their removal quite difficult. Oxidation is a major factor likely to cause fouling – especially with unsaturated elastomers such as NR, SBR, and NBR. Another cause is the layered buildup of materials that migrate from a compound and deposit on a mold surface. Tetramethylthiuram disulfide (TMTD) tends to bloom because of its relative insolubility, especially in nonpolar rubbers. Changing to the more soluble tetrabutylthiuram disulfide (TBTD)—at increased cost—should reduce blooming.

Other work established zinc sulfide as a major source of mold fouling [383]. The inorganic zinc sulfide, a reaction product of zinc oxide and sulfur, reportedly forms condensation centers for deposition of low molecular weight organic materials that then oxidize and form resins. Mold release agents affected fouling, and higher-grade steels are said to reduce fouling.

Additional potential sources of fouling are the rubber-to-metal adhesives that are extensively used in bonding a range of composites. High mold temperatures soften these adhesives during molding, and internal mold pressure can then displace adhesives and foul molds.

3.38.5 Mold Cleaning

Blasting with solid carbon dioxide can effectively remove glass-like fouling from a mold. Most of the above methods require removal of a fouled mold from a press to a remote area for cleaning. In-place cleaning offers several advantages that include elimination of the need to remove and reset a mold, a factor especially important and costly for injection molding. Magnetic clamping of a mold is said to drastically shorten mold change times [384]. Clamping and unclamping times can be as short as five minutes at temperatures up to a maximum of 445 °F (230 °C).

In-place cleaning was accomplished by curing a special rubber compound in a fouled mold [385]. Additives in the cleaning compound permeate the fouling and release it from the mold; the released fouling bonds to the cleaning compound and is removed with the cleaning compound during demolding.

Laser cleaning is a relatively recent mold cleaning technique that permits in-place cleaning of hot tire molds. It works by aiming a brief but powerful laser pulse at the fouled mold surface [386]. The pulse vaporizes a portion of the fouled material and converts the rest to dust that is collected by a filtration system. Only organic material absorbs the laser beam, since the metal surface of the mold reflects rather than absorbs the laser energy.

The cleaning process is repeated until the desired degree of ablation is reached. A five-axis articulated device actuates the laser unit, which is capable of cleaning both two-piece and segmented tire molds over a range of sizes. The unit cleans uniformly because the laser beam scans from four different angles, and typical cleaning times are 45 to 60 minutes. The laser unit is said to completely clean 1.5 mm diameter vents in tire molds. Smaller 0.6 mm diameter vents, located mostly in the tread area of a tire mold, are cleaned to only a depth of a few mm.

Attention now shifts from molding to calendering.

3.39 Calendering

Calendering consists of passing rubber through counter-rotating steel rolls [387]. It is used for a number of operations that include sheeting, laminating, coating, and embossing. Table 3.11 lists selected calendering problems and their possible causes.

Table 3.11 Calendering Problems and Their Possible Causes

Off-Gauge Compound	Incorrect Roll Crown
Blisters in calendered sheet	Incorrect roll crossing or roll bending
	Too-large feed bank
	Excessive breakdown of compound
	Too-high calender roll temperature
Scorched compound	Too-high roll temperature
	Bank too large
	Too-thick sheet
	Too-fast running speed
	Too-high feedstock temperature
Holes in calendered sheet	Improperly sized rolling bank
	Insufficient breakdown of compound
	Too-low stock feed temperature
Excessive scrap and amount of rework of compound	Trim knives improperly set or maintained
	Defective stock guides

A number of additional calender problems and their solutions have been described [388]. Calendered product quality is affected not only by the calender but also by associated equipment, for example, horizontal misalignment in a festoon [389]. Festoons are said to be generally inefficient and require high volumes of air passing at right angles to rubber sheets as they pass through a cooler [390].

3.39.1 Calendering Equipment

Calendering equipment must be extremely robust because it processes high viscosity compounds that produce high stresses, often over long service periods. Proper maintenance is mandatory to obtain continuing good results. One large manufacturer estimated in 1970 that $ 125,000 in excess compound was lost annually on the face of each calender roll that had worn by 0.0005 in. [391].

It is suggested that used calenders can be repaired or upgraded to perform like new for approximately one-half to two-thirds the cost of a new calender [392]. Problems that occur with calenders include wrong friction ratio, rolls with hot spots, poor roll adjustment, and rolls with uneven thickness in the cooling area.

The number of rolls, their arrangement, and size differentiates calender types [393]. The rolls that squeeze the rubber must be concentric, hard, operate without distortion, have a smooth surface finish, and operate within narrow temperature limits.

Four operations are used in basic calendering: unsupported sheets, plying-up, frictioning, and skim coating [394].

3.39.2 Feed Material

Quality of feed material affects calendered sheet quality more than any other factor except for the temperature of calender rolls [395]. Running speed can be critical, with slower running speeds favoring improved quality. Different materials that feed a calender vary substantially in their properties; for example, accurate roll temperature control is necessary because of the considerable temperature sensitivity of CR [396].

Because all compounds process differently, optimum roll temperatures must be established for each CR compound. CR compounds should be cooled as soon as practical after calendering to reduce their tendency to scorch and to stick to liners. Plying-up (done when thick smooth sheets cannot be formed in one operation) of thin sheets improves quality of the final thicker sheet.

3.39.3 Calendering Factors

Skim coating is similar to plying-up of sheets [397]. However, in skim coating a friction ratio is used between the feed rolls to warm the compound and to prevent the compound from sticking to the top roll.

Soft compounds do not provide enough shear stress to rupture trapped air bubbles. Very viscous compounds can trap air because they tend to remain in the nip; preheating the compound to lower its viscosity reduces this tendency. Addition of 5 to 10 phr of a high *cis*-BR is said to improve roll release of CR compounds [398].

Soft, tacky, nerve-free CR compounds that adhere well to the center calender roll are best for frictioning. Milk, applied to the center roll, is said to facilitate adhesion of the CR to the roll. Neoprene W compounds effectively resist collapse and distortion and are therefore better for calendering than some other CR types. Incorporation of factice reduces nerve, a problem with some CR compounds. An increased plasticizer level is said to be ineffective in reducing nerve in CR [399].

Misalignment of calender rolls is a frequently occurring problem that causes difficulties with tracking and product quality [400]. It can be caused by the inescapable settling of a calender on its foundation and daily wear and tear on a machine. Services are available for aligning calender rolls.

3.39.4 Blisters

Blisters are especially a problem with calendered IIR compounds because of the impermeability of IIR [401].

3.39.5 Tack

Tack is the ability of a surface to form an instantaneous bond when brought into contact with another surface for a short time [402]. The measurement of tack requires selecting an appropriate test and the use of the proper testing conditions for bonding, dwell, and debonding.

Some types of rubber possess natural tack, such as NR; others such as NBR and EPDM are deficient in tack. Liquid NBR (Hycar 1312), added to a higher molecular weight NBR, improves tack, and phenolic resins effectively improve tack in general-purpose rubbers [403]. An important advantage of *p*-alkylated phenolic resin tackifiers is their ability to promote and to maintain tack at elevated temperatures.

Rubber cements applied to a rubber surface can improve tack [404]. Addition of a nonsolvent (ethanol) to an NR rubber cement reduces the viscosity of the cement. For example, 4 % ethanol reduced the viscosity of an NR cement (NR dissolved in hexane) from 3000 poise to 900 poise.

Nonmaterial factors such as factory temperature and humidity can affect tack, with humidity being especially important [405]. Higher humidity levels reduce tack.

3.40 Laser Engraving

Lasers have become important tools for processing and cutting a number of materials, including rubber [406]. Different types of rubber respond differently; for example, NR sheets containing TiO_2 remained tacky after engraving, as did NR containing up to 50 phr $CaCO_3$. With 100 phr $CaCO_3$ clean engravings were obtained.

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4 TSE Products

4.1 Product Considerations

Regardless of product type or application, durability is a major product consideration [1]. A flow diagram for life prediction includes a number of factors that includes materials, geometry, and other considerations:

- crack growth
- chemical deterioration
- thermal aging bond failure
- fluid ingress.

Geometrical considerations, analytical aids, and design aids include fracture mechanics, stress analysis, thermal analysis, and diffusion analysis.

A wide range of materials, methods, equipment, and designs are used to produce thermosetting elastomer (TSE) products. Materials vary widely in viscosity, and they affect in a major way the method selected to produce a rubber product. Other determinants are product shape and the quantity to be produced. Two major production methods are extrusion and molding, therefore, the importance of good communication between product designer and fabricator of a rubber product cannot be overemphasized. Austin recognized the importance of a systems approach by stating [2] that "each business entity, under commercial pressure, will try to optimize its own operation with no one optimizing the total system."

Del Vecchio points out that "within the rubber industry, the most dangerous area of technical communication lies between the rubber technologist and the mechanical engineer" [3]. Hence, it is not surprising that problems occur in this area. A broader materials background would significantly benefit engineers, but the already loaded undergraduate curriculum leaves little room for additional courses.

Many rubber products, for example O-rings, are fabricated without reinforcement; others such as tires and V-belts require reinforcement to function properly. Materials such as cotton, rayon, nylon, polyester, aramid, fiberglass, in addition to steel are common reinforcement materials. Table 4.1 compares important properties of some of these materials [4].

Table 4.1 General Properties of Some Reinforcing Materials

	Rayon	Polyester	Fiberglass	Steel
Tenacity, gpd	5.0	8.0	9.0	3.4
Elong. @ break., %	9.0	17.0	4.0	3.0
Modulus, gpd	120	80	260	280
Shrinkage, %	0.1	3.0	0.1	0.1
Moisture regain, %	11.0	0.3	0.1	0.1
Specific gravity	1.52	1.38	2.52	7.83
Heat resistance	Fair	Good	Excellent	Excellent

Tires, air conditioning, brake and hydraulic hoses, power transmission belts, air springs, and seals are examples of reinforced rubber products [5]. High strength-to-weight ratios are said to be achieved for fiber-reinforced polymers through the use of Corpo technology that offers the following advantages [6]:

- higher potential pressure levels
- increased durability
- up to 50% reduction of fiber in rubber composites
- increased flexibility
- cost reduction.

Table 4.1 shows a wide range of properties for the reinforcing materials with some properties like shrinkage and moisture regain varying by more than an order of magnitude. It is not surprising then that products made from these materials vary substantially in their load-carrying capability, dimensional stability, and strength and durability. These materials are available in different forms such as yarn (an assembly of fibers or filaments arranged in a continuous strand), fabric (planar structure produced by interlacing yarns), and cord (a long slender flexible assemblage of fiber or wire).

Yarn is used for air conditioning hoses, brake hoses, timing belts, and power transmission belts. In these applications it must impart physical properties to meet tenacity and defined elongation properties, exhibit resistance to temperature and chemicals, and bond to different types of rubber. Cotton earlier was used in a number of applications because it showed good mechanical bonding. However, modern textiles have largely replaced cotton because of its low mechanical strength. The myriad of textiles and range of rubbers available, especially low polarity rubbers like EPDM, place considerable demands upon adhesion systems.

Rayon and cotton are cellulose-based materials that generally provide poor performance at temperatures regularly at 135 °C and higher [7]. In addition, they discolor and show a rapid loss in tensile strength.

4.2 Effect of Aging

Aging, especially aging at elevated temperatures or exposure to light, can alter materials [8]. For example, CR and other chlorine-containing materials lose minute amounts of chlorine, generally in the form of hydrogen chloride (HCl). If antioxidants or acid accepters do not reduce the corrosive effects of the HCl, it reacts with acid-sensitive reinforcing materials such as rayon. Other reinforcing materials such as aramid resist degradation [9].

4.3 Composites

The working load of different composites varies substantially [10]. Conveyor belts are usually designed to function at 10 % of their ultimate strength, while the accepted safety factor for hose calls for a six-fold increase in strength over operating stress. When more than one ply or layer of textile is used, each ply will contribute approximately 75 to 80% of its strength as measured before its incorporation in the composite.

Adhesives, to be effective with different products, must be tailored to a specific material. The myriad variables involved require careful attention to detail for good service to be obtained.

4.4 Belts

Belts represent a wide range of applications and products in the rubber industry. Some are a component in rubber articles, such as steel belts in radial tires. Others are stand-alone products for power transmission. It is important that the reinforcement in these belts be uniformly spaced so that missing reinforcement will be evident [11]. An inspection system uses digital signal analysis to detect faults.

Other belts are stand-alone articles for multipurpose applications; for instance, O-rings can be used as belts in some light-duty applications. An interesting twist on belting is the Möbius strip, which has only one side, in contrast to an ordinary surface that has two sides [12]. Practical use of this scientific curiosity was made in designing a conveyor belt for hot material, wherein a face-reversing twist about its longitudinal axis alternately inverted the faces presented to the hot material [13].

Conveyor belts offer the most economical means of transportation for systems that are in service for long periods, especially when compared with truck transportation [14]. Some applications are very demanding; belts can be as long as 12.5 miles for conveying tar sands in northern Canada [15]. These belts must remain flexible to as low as –46 °C (–50 °F) and endure being impacted by large frozen chunks of sand. Serious cracking occurred when the belts were cleaned with diesel oil.

Finite element analysis (FEA) successfully predicted the behavior of the force-displacement relationship of steel cables in steel-rubber composites used for studying conveyor belts [16]. Actual and predicted results were strikingly close for such a complex structure.

Equal distribution of force across the area of large conveyor belts during cure is problematic [17]. Improved force distribution results from newer press designs that incorporate a larger number of hydraulic cylinders that more evenly distribute the force. Presses can be equipped with up to 156 hydraulic cylinders and provide 27,558 U.S. tons of closing force. Press lengths up to 77 ft are feasible.

NBR compounds are widely used in conveyor belts that encounter severe mining service such as that which occurs in northern Canada [18]. Low-temperature properties of belts decreased with time as a result of plasticizer loss by migration. The use of nonextractable plasticizers in a compound resolved this problem. Another problem was transfer of hydrocarbons from the bitumen into the belt surface, either by exchange with plasticizer or as replacement lost by volatilization.

Heavy-duty cable jackets required special compounding considerations. Even a small amount of an untreated zinc oxide caused an XNBR compound to scorch, but a zinc peroxide masterbatch provided the required cure activation along with adequate scorch safety.

Five phr zinc oxide typically has been used in rubber compounds in combination with 2 phr stearic acid [19]. This combination formed zinc stearate that served as the activator for accelerated cure systems. Electron microscope investigations showed that ZnO-stearic acid and zinc stearate differ in their behavior in NR and SBR [20]. Zinc stearate was molecularly distributed in the rubber, whereas ZnO particles did not react or had reacted only on their surface with the stearic acid. Zinc monomethacrylate compounded into accelerated sulfur systems can activate the curing system [21].

Environmental concerns now favor the reduction of zinc oxide in rubber compounds. ZnO levels above about 2 phr are said to offer insignificant benefits [22]. The amount of zinc leached from ground rubber particles depended upon factors such as particle size distribution and surface area [23]. The amount of zinc leaching increases in proportion to the zinc oxide concentration in tire compounds up to a certain level, after which it levels off.

4.5 Rubber Lining

Grinding mills incorporate both rubber and steel as linings [24]. Rubber linings cost no more than conventional steel linings and are much easier to install. With rubber linings, only the main impact elements need to be rotated at about 600,000 tons throughput. Rubber as a lining material becomes less competitive with steel as the hardness of the mineral being ground decreases [25].

Linings that have typically been made by calendering can now be made by newer technology such as roller head extrusion [26]. Quality control of lining can decrease for unusual reasons. When lining quality abruptly decreased, it was discovered that a key man involved in lining production had taken a week off to go fishing [27].

4.6 Balloons

Balloons, discussed above in Chapter 4, are often filled with water for recreational purposes. Although filling them with water and tying a knot can be problematic, a device is now available that fills a balloon with water and ties the knot [28].

4.7 O-Rings

Factors associated with O-ring failures follow [29]:

- materials with low tear strength
- damage done during ring installation
- excessive abrasion
- improper sizing
- chemical incompatibility.

O-rings are used in a multitude of sealing applications that can be very costly if O-ring failure occurs. Ring breakage occurred in an aircraft fuel pump and caused fuel leakage [30]. It was found that snaking of an oversize ring into a groove to make it fit likely caused the problem, as a hump of rubber formed in the O-ring.

O-rings used to seal a rotating shaft are sometimes made smaller than the shaft diameter, with the intent of providing a better seal [31]. Because of the Joule effect, an O-ring under tension tends to contract as it warms up, resulting in the generation of more heat and higher temperatures. This ultimately leads to failure through cracking or charring. To avoid this, it is suggested that the ID of the ring be about 5% greater than the shaft diameter.

Another source suggests that the inner diameter should be 1 to 3% larger than the shaft, and the outer diameter of the gland should ensure that the O-ring is compressed on the shaft surface. A seal stretched on a shaft failed after four minutes, while a seal with an oversize inner diameter ran 100 hours without failure [32].

Seals failed prematurely in two different oil field applications [33]. Ironically, it was found that corrosion inhibitors used to protect metal components led to premature seal degradation. Evidence suggested that vinylidene fluoride/hexafluoropropylene copolymers, widely used in oil field applications, can be attacked by amine-type corrosion inhibitors.

Sensors can be used to place O-rings in devices for automatic assembly [34].

4.8 Rubber Mirror

Conventional optics incorporate mechanical systems to vary the focal length of mirrors [35]. Reflective coatings such as gold on optically smooth rubber surfaces can be used to provide mirrors with a wide range of focal lengths. The focal length can be changed by air pressure behind the mirror, eliminating the need for complex mechanisms. Appropriate choice of the elastomer and suitable cleaning of the vulcanizate with solvents prior to gold coating minimize bloom. A rubber mirror was installed in a telescope by Berkeley scientists [36].

4.9 Cow-Related Applications

Rubber mats offer superior sleeping accommodations for cows compared to sawdust, cut straw, or peat dust [37]. The latter are initially soft but harden in service and can cause swollen knees and heels that become infected. Rubber mats are soft and hygienic, offer protection against humidity and cold, require little maintenance, and contribute to udder comfort.

Rubber galoshes complete with surgical socks are fitted on cows that have been medically treated for bovine foot rot, infections, and corns [38]. Milking inflations are molded from organic rubbers such as SBR and NBR as well as from silicone rubber [39]. Surface cracks that form in organic rubber can widen and harbor bacteria that cause mastitis. Silicone rubber is said to be an excellent polymer for milk-contact applications.

TPEs that comply with regulations aimed at preventing transmission of so-called "mad cow disease" have become available [40]. They are said to be free of animal-derived materials such as beef tallow that may be used in other polymers.

4.10 Regenerative Brake Systems

Most energy-using systems are grossly inefficient [41]. It seems ironic that the energy expended in getting a vehicle moving should then be wasted as heat when the vehicle is braked. Rubber has an energy storage capability two orders of magnitude higher than that of steel. Rubber regenerative brake systems store and then use this energy to set a vehicle in motion.

4.11 Rubber-Covered Horseshoes

Horses that travel on hard surfaces can become lame when their steel horseshoes are heated by the road surface [42]. Rubber-covered horseshoes provide cushioning, traction, and protection from heat. Two-color polyurethane horseshoes are available for more upscale horses [43].

4.12 Rubber Bullets

Conventional bullets used in an airplane cabin to subdue a terrorist could inadvertently penetrate a fuselage [44]. Special rubber bullets have been designed for use in aircraft without damaging the aircraft; larger size rubber bullets are used for crowd control.

4.13 Bungees

Bungees (rubber ropes) are used in myriad applications [45]. Among them are devices for testing child safety seats and for use on aircraft landing gears.

4.14 Rubber Band Ligation

This procedure, which gets to the bottom of a problem, involves placing a small rubber band around the base of a hemorrhoid [46]. After a few weeks, the dried remnant is sloughed off. At the other end of the rubber band sizes, Goodrich once produced a rubber band 120 feet in circumference and 6 feet wide [47].

4.15 Rubber Bands

Rubber bands are intended to be the power plant for a full-size airplane with a wingspan of 68 feet and a propeller 18 feet in diameter [48]. The power plant consists of 800 each 25 foot long strands of model airplane rubber in a loose bundle. Upon release, 18 hp will be initially delivered to the propeller, followed by a decrease to 4 hp after 20 s.

4.16 Floor Mats

Mats, which have served their function for many decades, are now expected to improve acoustics in a vehicle cabin [49]. Mats are tuned for individual vehicles to absorb cabin-generated noise or to pass the noise through the mat into sound-absorptive carpet.

4.17 Mounts

For a rubber mount to behave as a spring, it must be able to change shape. Successful mount designs should consider avoidance of excessive local stresses, inclusion of metal inserts, tolerances, mount instability, and clearance around a mount.

A designer must provide adequate clearance around mountings to prevent damage to supported equipment while a mount undergoes excursions about its static positions. This is especially so for engine mounts used in aerobatic airplanes that can undergo as much as 10 g under intensive maneuvering.

Simplified theories assume that a mount system operates with a single degree of freedom during oscillation, which is on either the vertical, longitudinal, or transverse axis. Figure 4.1 illustrates the simplest form of periodic motion with only one degree of freedom [50].

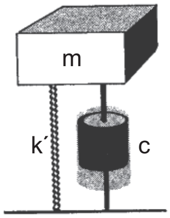

Figure 4.1 Rubber mount with one degree of freedom: m is the mass; k' is the elastic spring rate; c is the damping coefficient [50]

During operation, the mass moves vertically about a reference position such that the displacement can be represented by a sinusoidal curve. Maximum motion of the body occurs when the angular frequency approximately equals the quantity $(k'/m)^{0.5}$. Known as the resonant frequency, this frequency represents the condition wherein vibration becomes most objectionable.

While simplified theories can help analyze engine mounts, they ignore the possibilities of yaw, pitch, and roll that are encountered in service [51]. A further complication with simplified theories is that they have no real way of dealing with asymmetric distributions of loadings. Because most systems rely on the use of multiple bearings, simple theories become totally inadequate.

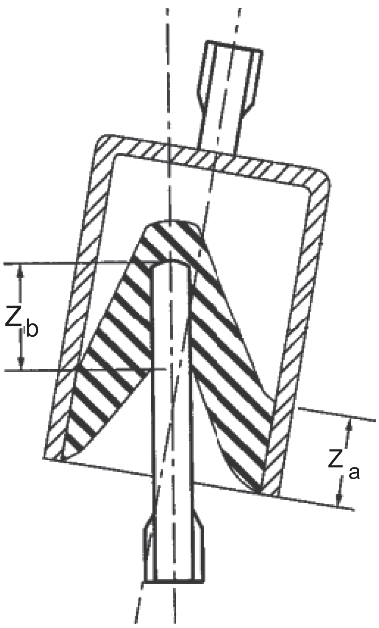

Figure 4.2 Elastomeric mount with six degrees of freedom [53]

Real vibrating bodies are concerned with six degrees of freedom: vertical, longitudinal, transverse, pitch, roll, and yaw. Mounts can be designed to provide combinations of stiffness and damping in various directions, for example, soft in all directions, soft in two directions and stiff in one, stiff in two directions and soft in one, stiff in two directions translationally and soft torsionally [52]. A patent describes an elastomeric mount (Figure 4.2) with six degrees of freedom [53].

Multiple-degree-of-freedom rubber bearings are critical components in offshore drilling rigs in the North Sea [54]. These rigs must accommodate the sway, surge, yaw, heave, pitch, and roll experienced by a free-floating vessel. A number of degrees of freedom of motion influence the clearances required during mount operation.

One of the assumptions in classical vibration isolation theory is that the structures on either side of an isolator are rigid. Actually, the mounting support structure can reduce the effectiveness of a mounting system by as much 50% [55]. Hence, the mounting structure is an integral part of the mounting system.

Although real-world structures are not absolutely rigid, the concept of transmissibility is generally useful. Transmissibility, described as the difference in vibration amplitude across an isolator, is the ratio of output to input [56]. Mounts should be designed to provide a resonant frequency considerably lower than the lowest frequency of the forcing frequency. Where this is not possible by changing mass or spring rate, one can increase damping in the rubber (dashpot effect). At resonance, only damping limits peak transmissibility [57].

Addition of carbon black to a rubber compound increases both damping and the dynamic modulus; these properties become amplitude dependent [58].

When engine, car, and drive components pass through resonances that cannot be altered, dynamic absorbers can be used [59]. For example, a crankshaft may be the main spring-mass system with the absorbing mass being a torsional vibration damper. The main mass-spring system might be the car body, with the engine serving as the absorber to control shake.

Designing to obtain the needed k and c values is the principal task of the design engineer and the materials specialist. Then the manufacturing process must be implemented and carefully controlled to keep these parameters within acceptable limits. These tasks must be accomplished while working within engineering constraints concerned with assembly, geometry, size, and cost.

Figure 4.3 illustrates the effect of damping on isolation and transmissibility (T) as a function of frequency ratio [60].

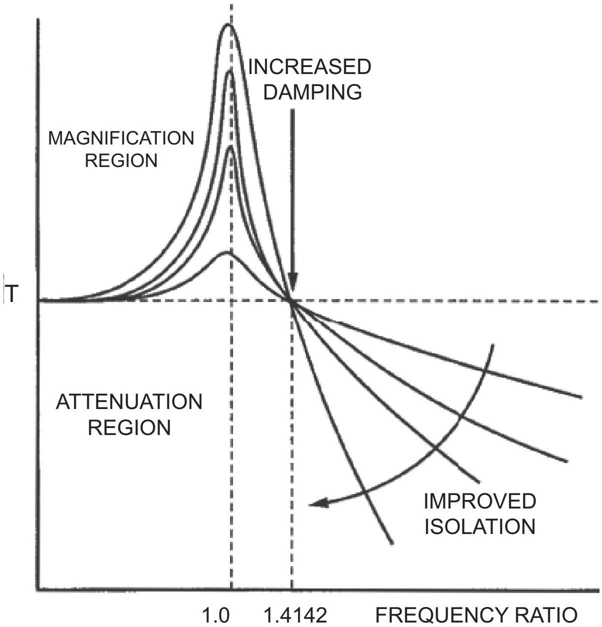

Figure 4.3 Effect of damping on isolation and transmissibility (*T*) as a function of frequency ratio [60]

The curves show pronounced transmissibility increases for values of f/f_0 (frequency ratio) of about one (the magnification region). Passing through resonance where $f/f_0 = 1$ can cause damage, especially in an undamped system. For example, after starting a car engine and then stopping it, f/f_0 goes through the resonant frequency.

In an undamped or lightly damped system, severe excursions of the engine occur if the engine frequency doesn't pass quickly through resonance. Increased damping minimizes this problem but creates another, namely reduced isolation at the higher frequencies that occur in a vehicle at highway speeds.

Low transmissibility values are desired at highway speeds so that vehicle occupants experience the effects of minimum engine vibration. Hence, the designer must compromise engine mount design in the low- and high-frequency range.

■ 4.18 Stress Concentration

As a general rule, excessive stress should be avoided because it can ultimately lead to product failure. Minimizing high stress is especially important for bonded rubber products, where very high stresses can occur at the rubber-metal interface. Incorporating radii and fillets (Figure 4.4) minimizes stress concentrations at the edges of composites [61].

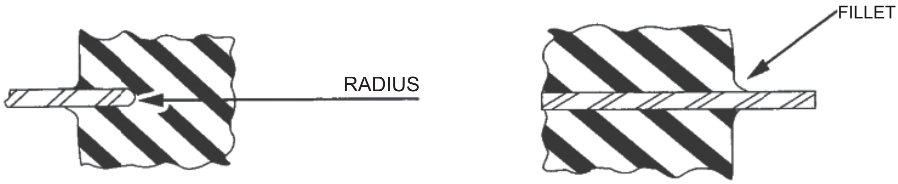

Figure 4.4 Radius or fillet in rubber and metal reduces stress concentration [61]

The compliant nature of rubber makes it the ideal material to combine with high modulus materials such as steel to produce mounts with a wide range of stiffness and damping that can be directionally controlled for different applications [62].

The spherical bearing design in Figure 4.5 provides high stiffness in the axial direction while allowing the bearing to deflect in three shear modes: yaw, pitch, and roll.

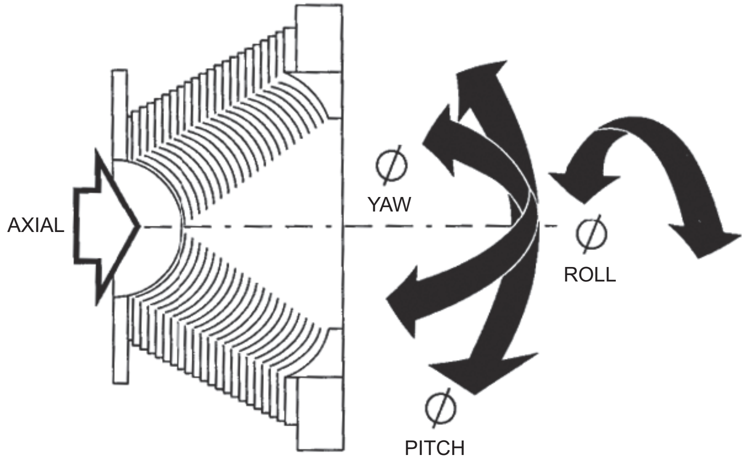

Figure 4.5 Axial compression with three shear modes: yaw, pitch, and roll [63]

This multiple-degree-of-freedom bearing is widely used in vectoring nozzles for solid rockets and on oil drilling platforms for service in the ocean [63].

An elastic CV joint fitted to a drive shaft decouples the drive train and rear axle of all-wheel and rear-wheel drive vehicles from rotational speed irregularities of the engine [64]. It is positioned at the interface between the engine and the prop shaft and is said to adjust to any driving situation.

A patented damped drawbar used for towing a trailer represents another use of rubber in shear [65].

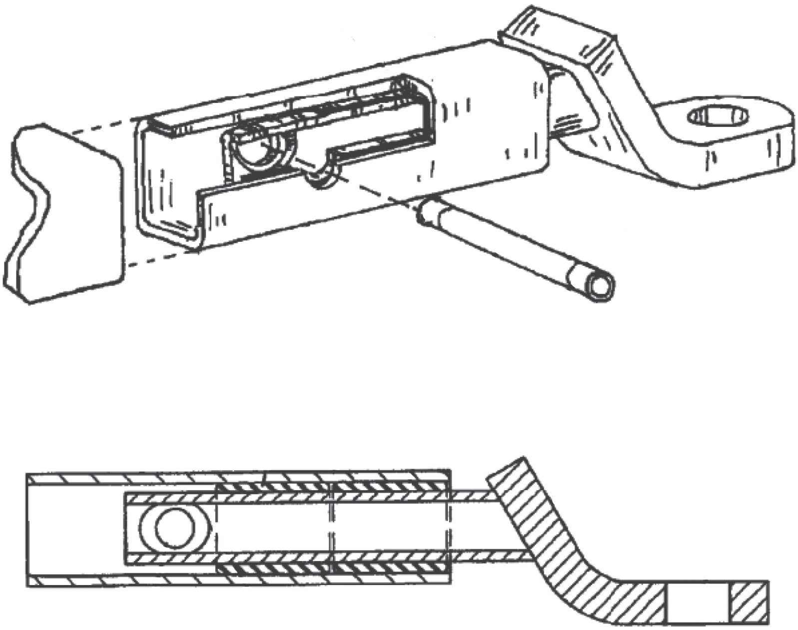

Figure 4.6 Damped drawbar for towing a trailer [65]

Rubber, sandwiched between outer and inner steel tubes, attenuates noise, shock, and vibration during towing. A hitch pin acting in conjunction with ovate holes in the inner tube provides a mechanical fail-safe feature.

4.19 Roofing

EPDM has been the material of choice for roofing low-slope commercial buildings for some time [66]. However, TPO is rapidly gaining in market share and can be produced in 10 feet wide sheets. Compared with EPDM, TPO offers the advantages of heat-welded seams and heat reflectivity [67]. Solar reflective roofs can reduce roof temperatures from 150 °F to less than 100 °F [68]. Single-ply roofing membrane is most frequently used in mechanically attached and fully adhered roofing systems. Few reinforced thermoplastic products such as TPO or PVC are fully adhered.

Several analytical techniques characterized a fully adhered EPDM roofing membrane [69]. The stain on a membrane resulted from some fraction of a rubberized asphaltic adhesive diffusing through the membrane and being oxidized by atmospheric oxygen and solar radiation.

4.20 Finite Element Analysis

Finite element analysis (FEA) has been used in the design of products such as high-capacity laminated elastomeric mounts [70]. It showed that the maximum compressive strains and compression-induced shear strains occurred in the rubber layers near the large end of the bearing. FEA successfully identified the locations and layers where failure occurred; a redesigned bearing showed much longer times to failure. It is considered necessary for the analysis and troubleshooting of O-rings [71]. Problems with leaky O-rings have been traced to rusted and pitted O-ring glands and to pinched or missing O-rings [72].

FEA has been used successfully in varied areas such as predicting thermal stresses associated with rubber-metal articles, examining heat generation resulting from the deformation of rubber, and establishing the optimum cure profiles [73].

FEA use was earlier limited to larger rubber companies with in-depth technical capabilities. It has now become a standard tool even in smaller rubber companies because costs for FEA use have decreased, so FEA has become very cost competitive with the cost of producing and testing prototype rubber articles [74].

Finney provides an in-depth treatment of finite element analysis for use in a number of products that include timing belts, dock fenders, rubber boots, bumpers, and down-hole packers [75].

FEA was applied to the products cited above and additionally to tires [76]. It can provide insight into internal stress and the tendency for heat generation for particular tire shapes and constructions in just a matter of days.

Its use in tire technology ranges from tire building to tire curing [77]. Modeling of the manufacturing process is useful because flaws can occur at different stages of tire fabrication. Results obtained using FEA correlated with observations for different types of tires.

4.21 Air Springs

Air is considered an ideal load-carrying medium because it is highly elastic, its spring rate can be easily varied, and it is not subject to permanent set [78].

Air springs in an air suspension system function when an external force compresses the gas in an air spring [79]. Conventional steel spring characteristics do not change when in use; adjusting gas pressure in an air spring can compensate for different loads. Thus, air spring characteristics can be maintained independent of the load and provide a more comfortable vehicle ride.

Single, separate polyamide fibers can replace the traditional cross-ply arrangement of fabric layers used in an air spring [80]. They are precision-laid in one direction along a length of the rubber cylinder that forms the body of the spring. This construction eases the expansion of the air spring relative to air springs with fabric reinforcement.

Air springs can last up to ten years; however, a four- or five-year life is more typical [81]. They are an important product because 90% of trucks are fitted with them. The main rubber materials used in them are CR or a natural-synthetic blend (NR and BR). CR is said to perform better at higher temperatures; the blend is said to perform better at freezing temperatures.

4.22 Keyboard Springs

This dome-shaped article, used as a computer keyboard spring, must snap through its skirt when a key is pressed [82]. Design of the springs is difficult because the springs buckle when pressed down; FEA successfully predicted behavior of the keyboard springs.

4.23 Gloves

Rubber gloves are used to protect workers in several applications that include protection from electrical shock. An innovative glove construction consists of a five-ply composite of alternating conductive and nonconducting layers such that if the wearer punctures a glove, the two conductive layers contact one another, close an electric circuit, and sound an alarm [83].

Surgical gloves have caused contact dermatitis. Accelerators such as dithiocarbamates, thiurams, or mercaptobenzothiazole could cause the problem. Allergic contact dermatitis can occur with gloves prepared from NR latex.

Low-protein NR latex is said to reduce but not eliminate allergic reactions [84]. Airborne powder from medical gloves can cause serious allergic reactions in sensitized workers, even if the workers are not wearing gloves. For this reason Germany banned powdered latex gloves in 1998, and the number of suspected cases of latex allergy decreased by 80%.

4.24 Inflatable Dam

These are often the most cost-effective method of temporarily or permanently blocking a water channel [85]. Engineers concluded that dynamic forces on a dam would be about four or five times the static forces, based on a scale model dam; they stated that the overall safety factor should be more than ten.

4.25 Inflatable Traffic Hump

This inflatable device was designed to give a smooth ride to drivers that obey speed limits, as it automatically deflates for automobiles moving below the speed limit. A valve fitted in the unit controls the rate of air escape when driving over the hump. It is designed to deflate for large emergency vehicles, such as fire engines [86].

4.26 Tennis Balls

As with tires, loss of air from tennis balls is problematic; however, it can be reduced by inflating balls with a gas different from air [87]. Sulfur hexafluoride (SF_6) significantly extended a tennis ball's playing time. The permeability coefficients for air and SF_6 are respectively 9.9 and 1.3 $(mol/m \cdot s \cdot Pa)10^{16}$. An interesting side effect was an audible ping produced when balls containing low-permeability gases impacted a racket. The ping, which proved objectionable to some players, could be attenuated by a small piece of urethane foam in the ball.

4.27 Tires

Tires serve multiple functions that include supporting the load of a vehicle, isolating road irregularities, and transfer of driving, braking, and steering forces [88].

A wide range of tires is available to meet specific technical requirements as well as to provide sensational effects [89]. An example of the latter is a spinning tire that produces colored smoke. Spinning of tires is a part of a racing subculture called drifting. Pneumatic tires are a complex product produced in greater volume than all other rubber products. As such, they deserve detailed consideration if troubleshooting activities are to be minimized [90].

Tires are an assemblage of components that include tread, sidewall, inner liner, breakers, carcass plies, and bead wires.

Each of these components requires attention, not only to the specific component and its processing but also to the assemblage of these materials that form a tire. Each rubber and nonrubber component in a tire serves a unique and specific function [91]. Tire reinforcement and adhesion between components is especially important, as tires are well known to incorporate a range of reinforcements, for example steel wire, organic cords, and textiles. Different adhesives are available to bond reinforcements in tires and other rubber products. Table 4.2 Advantages and Disadvantages of Some Types of Tire Cordslists some of the relative advantages and disadvantages of different types of tire reinforcement [92].

para-Aramid pulp efficiently increases modulus and imparts low hysteresis, thus making it a suitable candidate for reinforcing different parts of a tire [93]. Applications in the tire crown include the tread base of high-performance tires. Its use in the tread improved tire handling characteristics, provided more uniform tread wear, and improved tread chipping and chunking resistance. Tread wear of compounds is said to be improved by up to 10% by the incorporation of soybean oil [94]. Tires with the improved tread wear are expected to be available as early as 2015.

Table 4.2 Advantages and Disadvantages of Some Types of Tire Cords

Cord Type	Advantages	Disadvantages
Rayon	Dimensional stability and heat resistance	Moisture sensitivity and cost
Aramid	Very high strength and stiffness; heat resistance	Difficult to process (cut) and cost
Nylon	Heat resistance and strength	Heat set during cooling and long-term growth in service
Polyester	High strength and low growth in service	Poorer heat resistance than rayon or nylon

Processing and materials costs are increasingly important in today's competitive tire manufacturing market. Efforts to achieve these goals include increasing manufacturing flexibility [95], lowered energy costs, reduced number of manufacturing steps, more effective use of floor space, and robotics [96].

4.27.1 Tire Manufacturing Systems

Substantial efforts by major tire manufacturers have resulted in the following alternative manufacturing approaches:

- Continuous Cold Compounding (C3M) [97]
- Modular Integrated Robotized System (MIRS) [98]
- Bridgestone Innovative and Rational Development (BIRD) [99]
- Modular Tire Manufacturing (MTM) [100]
- Advanced Tire Operation Module (ATOM) [101]
- Automated Production Unit (APU) [102]
- Integrated Manufacturing Precision Assembled Cellular Technology (IMPACT) [103]

C3M and MIRS share some common features [104]. Both use a small amount of floor space and begin by building tire components on a drum that remains with the tire throughout the curing process [105]. Successive extruded layers partially overlap and form the desired profile. No cooling is done during production of C3M tires, in contrast to conventionally built tires. As a result, a warm tire enters its curing mold and significant energy savings result, along with shorter curing cycles. Rather than use bladder-applied pressure in the curing mold, an electrically heated mold closes on the tire in the C3M system.

The 26-step C3M process (depending upon the tire) is said to take 20 minutes, which includes a 10 minute cure cycle [106]. Using C3M, three or more strips of rubber with different properties can form a tire tread [107].

4.27.2 Modular Integrated Robotized System

MIRS is designed for flexibility rather than for large volumes or long tire runs [108]. It is said to reduce the number of steps in the traditional tire-making process from fourteen to three. Microcomponents, rather than a large tread and a large sidewall, produce a MIRS tire [109]. As a central clamp and spindle lock segments together, a barcode reader tracks the tire around the building cell. The MIRS process incorporates a series of extruders that surround a toroidal tire-building drum [110]. Extruded strips of rubber, rather than sheets, used during fabrication, significantly reduce the need for monitoring personnel.

MIRS is said to improve tire uniformity by 30% relative to tires produced on traditional equipment [111]. Another advantage claimed for MIRS is that, being modular, production can be added without the need for traditional mixing and semifinishing lines [112].

4.27.3 Bridgestone Innovative and Rational Development

All stages of tire manufacturing by the BIRD system are automated, from materials processing to final tire inspection [113]. The system is said to be capable of simultaneously producing several different tire types and sizes. A plant is expected to make 8000 units daily that will include high-performance, ultra-high performance, large-rim, light truck, and passenger tires.

4.27.4 Modular Tire Manufacturing

The MTM system uses rubber compounds that are delivered to manufacturing cells in strip form on pallets; finished brass-coated wire is delivered on reels [114]. Fabric reinforcement is supplied as reels or bobbins of single-dipped cord. Three people operate each cell in the system, namely, a supervisor, an operator, and one forklift driver [115]. The MTM system can produce different tires, with each having a different width, outside diameter, or cord angle, without requiring changeover time [116]. The system offers the possibility for a vehicle manufacturer to set up a tire plant adjacent to or within a vehicle manufacturing plant [117].

4.27.5 Advanced Tire Operation Module

The ATOM system is designed so that no one touches a tire until the tire is cured and has undergone final inspection [118]. It is said to reduce space needs and is designed for small-lot, multiproduct tires. Each tire assembly module contains twelve extruders. Belts, beads, inner plies, sidewalls, and treads are built in separate areas, and the system is said to eliminate splices.

4.27.6 Automated Production Unit System

The APU system combines up to nine tire-making steps and reduces the length of the tire production line by one-third [119]. It reduces upstream production of components to a minimum, and it provides a just-in-time supply of components to a building station.

4.27.7 Integrated Manufacturing Precision Assembled Cellular Technology

Everything from the inner liner to the apex is assembled serially while the rubber is hot using the IMPACT system, eliminating the need for tackifiers to improve adhesion [120]. Goodyear states that its system, which can be applied to almost any tire type, improves quality and reduces the number of processing steps. Each station in the system consists of a hot former, a unit similar to a two-roll mill. One roll has a smooth surface, while the other has a profiled surface. A cold-feed extruder provides compound to the unit at a volume flow rate that matches that of the component being made at a specific station.

Components, once laid down, are formed into a spool large enough to build 100 or more tires. They are then moved to a two-stage building machine, and each assembly is cut to length. A typical truck tire package made by this system is about 19% lighter than one made by more traditional assembly techniques. IMPACT is said to significantly improve positioning of components compared to conventional systems [121].

Bead wire temperature during conventional tire molding increases when heat flows through rubber around the bead bundle; a slow process. Induction heating can now directly heat bead wire [122].

The bias-belted tire was introduced in 1967 by Goodyear as its answer to the radial tire [123]. Its capability to be built on existing tire manufacturing equipment delayed the conversion to radial tires along with the need to purchase much new equipment. Firestone produced bias-belted tires that were an early success, but poor adhesion later proved problematic. Moisture between the steel cord and the surrounding rubber was found to be the cause.

A belt on an aircraft tire is advantageous because it limits the centrifugal growth of a tire during high-speed tire rotation [124]. A bias-ply airplane tire may expand radially by as much as 12% at a speed of only 100 km/h, even more at higher speed before takeoff. This stretching of rubber in the tread makes it easier to cut the rubber under tension. A radial tire under the same conditions stretches only about 8%, still too much for best tire longevity.

Different levels of NR are used in bias and radial tires as shown for components in Table 4.3 [125].

Table 4.3 NR Use in Bias and Radial Tires

Tire Component	% NR in Bias Tires	% NR in Radial Tires
Tread	47	82
Skim coat	70	100
Sidewall	43	58

Reasons for increased NR content are increased adhesion between components, improved green strength, and higher tear strength.

Tire wear that occurs on automobiles is of considerable interest [126]. Tires produced from reclaimed rubber during World War II provided hardly 10,000 miles at a speed of 35 mph. After the war, virgin rubber availability and technological improvements resulted in significantly improved tire mileage as shown below [127]:

- 23,000 miles for bias construction
- 30,000 miles for bias-belted construction
- 40,000 miles for radial construction.

Improper placement of two new tires and two partially worn tires has led to several tragic accidents on wet roads [128]. Where to place a pair of two new tires? Although it may seem counterintuitive, placing the two new tires on the rear axle is recommended when only two new tires are installed.

Aircraft tires operating on land wear differently from those operating on aircraft carriers [129]. Tires on aircraft carriers wear out two to three times faster than their land-based counterparts. The high wear rate of tires on carriers is due to the maneuvering on deck to position an airplane. Rollout and alignment prior to launch and straightening the airplane after arrestment impose severe cornering forces on aircraft tires.

Aging of tires and its effect on tire properties and behavior are a subject of continuing interest [130]. The effect of oven aging at 70 °C relative to on-road aging in Phoenix, Arizona, suggests that six to seven weeks of aging at 70 °C is equal to four years on the road in Phoenix. Studies show that different tire types and brands age at dramatically different rates.

Tire compounds continue to evolve. It is anticipated that legislation will prohibit the use of high-aromatic extender oils that impart favorable dynamic properties to tires [131]. A study indicates that some higher-viscosity naphthenic in tire compounds can mimic the dynamic behavior of high-aromatic extender oils while retaining mechanical and physical properties. Most well-known tire makers are switching all production from aromatic oils [132].

New carbon blacks have been developed for both tread and nontread applications [133]. One of these has high specific surface area and was developed for high-performance applications. They provide excellent abrasion resistance, improved high-frequency behavior, and a good balance of other properties. A nontread black has a very high structure, wide aggregate size distribution, and specific surface area intermediate between tread- and carcass-grade blacks. Various tire components can use this grade advantageously.

Reactions between modified para-aramid short fibers (Sulfron 3001) and carbon black are said to start at the beginning of the mixing cycle [134]. The Sulfron interacts with the hydroxyl groups on the carbon black to form a bond that depends upon the mixing temperature. Lower heat buildup during tire operation is claimed.

Changes in tire components can significantly reduce tire weight; the use of lightweight steel cord and other technical improvements have reduced the weight of some tires by 20% [135]. This is important because tires can account for two-thirds of the mass of rubber articles used in an automobile. Other significant advances, such as in tire fabrication, make extensive use of robots [136].

4.27.8 Components

A typical passenger radial tire has 12 to 16 components, and servers traverse behind tire building machines to supply all components to the tire builder [137]. This has simplified building since early radial tires often had more than 10 items just to build the carcass. Carcass quality now depends less upon the tire builder.

A radial tire incorporates numerous materials that must be appropriately selected, combined, and processed to form intermediate components that, when joined and crosslinked, comprise the finished tire [138]. Components must adhere to one another properly to realize satisfactory performance and to provide expected service life. Materials used in the complex engineered tire structure must be processable, cost competitive, and meet myriad performance demands.

Radial tires, when compared to bias and belted-bias tires, provide the best mileage, quickest steering response, best impact resistance and traction, best cornering control, and the smoothest ride at highway speeds [139].

Figure 4.7 shows the components in a radial tire and describes their relative placement [140].

Bead wire is drawn, plated with brass, and then twisted and wound into filament bundles. The beads, one on each side of the tire, anchor an inflated tire to its rim.

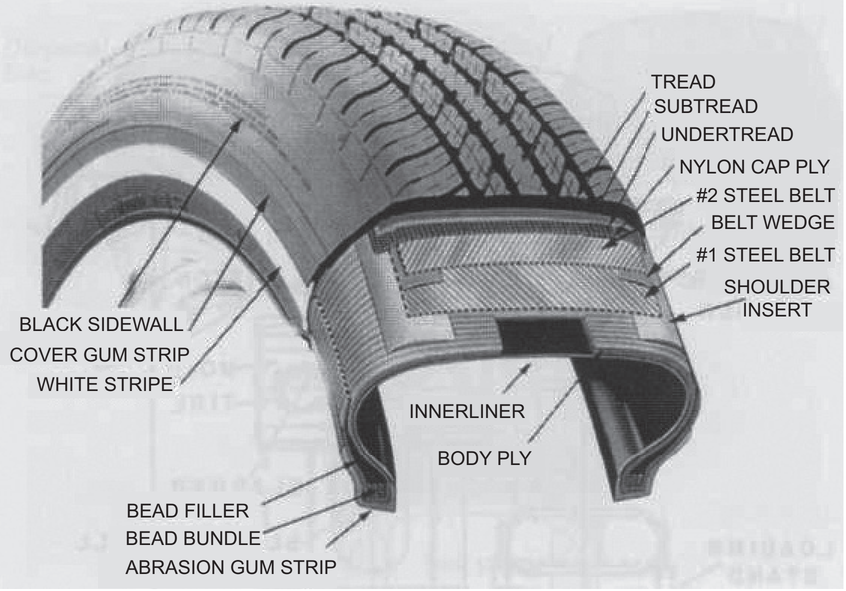

Figure 4.7 Components in a radial [140]

Inner liner, a thin specially formulated compound located on the inner surface of tubeless tires, improves air retention by decreasing permeation outwards through a tire [140]. The best inner liners for both cars and trucks are said to be based on a bromobutyl rubber compound reinforced with carbon black [141]. Bromobutyl rubber is used extensively for inner liners for reasons that include superior adhesion, requirements for lighter tires to reduce rolling resistance and improve fuel economy, improved flex-crack resistance after aging and lower cost with the use of thinner inner liners [142].

Tubeless tires provided the potential for considerable savings in labor relative to tires with tubes [143]. One of the early problems with them was the entry of dirt into the interface between tire and rim during severe vehicle maneuvering, with attendant loss of air pressure. Modification of the rim surface that contacted the tire corrected this problem.

Decreased carbon black and increased oil levels mitigate the hardening of halobutyl rubber compounds [144]. Exxpro inner liners can be as much as one-fifth the thickness of conventional halobutyl inner liners, and these are expected to significantly reduce rolling resistance [145]. Their use can save as much as 500 g in every tire while maintaining the same performance as halobutyl rubber [146].

Nonbutyl, puncture-resistant inner liners have been developed that can protect a tire in most pressure-loss situations [147]. They function by stretching and distorting around a penetrating object, thus preventing air loss.

Belt edge separation is the most common durability failure in tubeless radial tires [148]. It is associated with high shear concentrations at belt edges and can cause separations at the cord-rubber interface. The following are considered critical external factors affecting belt edge separation: field age of a tire, temperature, and partial pressure of oxygen in a tire [149].

Nylon cap strips reduced tire and belt edge separations by more than 50% [150]. The tread separation rate on sport-utility vehicles with a cap ply was three to five times lower with the cap ply than without [151].

Revealing marks often form when treads separate [152]. These can be used to determine the duration of the tread peel and whether the casing was inflated at the time of the separation. Yaw scratches result from road abrasions that occur after the tread peels completely.

Separation between reinforcing steel belts in radial tires can lead to uneven tread wear [153]. When the separation is pressurized by air infiltration, wear rate increases sharply.

Body ply skim is the rubber coating that encapsulates the radial ply reinforcing cords; it is calendered onto body ply cords in thin sheets, cut to width, and spliced end-to-end into a roll. Open cords allow rubber to penetrate into a cord bundle and avoid localized corrosion attack by moisture that could otherwise enter a cord bundle [154].

Higher strength compounds prevent spreading of body cords during second-stage expansion of radial tires [155]. Hence, body skim compounds that were used earlier on bias-belted tires proved unsatisfactory for use on radial tires. Higher levels of NR and the use of smaller particle size carbon black provided the required higher green strength.

Bead bundles consist of bronze-plated bead wires that are rubber coated and then wound into a specified-diameter bundle and configuration before incorporation in a tire. Their function is to retain a tire on its rim seat, and there is some controversy whether the test for bead retention should be static or dynamic [156]. It was concluded that the currently used static test method is useful because field problems are generally linked to severe under-inflation or to tripping of the tire-wheel assembly by an anomaly in the road surface.

Bead filler (also known as the apex), applied on top of the bead bundles, fills the void between the inner body plies and the turned-up ply ends. Cracks can sometimes form in the bead area and spread entirely around a tire and cause a tire to rotate unevenly [157].

Sidewalls that protect the body plies from impact, abrasion, and flex fatigue are compounded to resist cracking, ozone, and aging. Blends of NR and BR in the range of 40:60 to 60:40 are normally used in sidewalls for car and truck tires [158]. The sidewalls on the space shuttle tires needed to be much stronger than those on conventional aircraft tires because they could deflect as much as 65% [159]. Also, shuttle tire pressure loss is only about 0.1 psi per day as compared to loss of several psi per day for commercial airliners. The load on a very large aircraft tire can be enormous, for example 33 metric tons on an individual Airbus 380 tire [160].

An outboard sidewall of a high-performance tire, reinforced with a carbon fiber insert, helped provide stiffness for improved handling [161]. The insert is composed of threadlike strands of pure carbon. At high speeds a 20 mm increase in tire diameter can affect handling [162].

It is now possible to measure the indentation modulus of a rubber product, such as a tire, with improved resolution to about 10 to 30 microns [163]. This resolution enables one to make measurements on compound close to steel cords and fabric, from which modulus can calculated.

Belt skim is the rubber coating applied to brass-plated steel cords. It is calendered or extruded onto the steel cord in the form of sheets, then spliced into continuous rolls for tire assembly. Belts (stabilizer plies) are applied at opposite angles to one another under the tread area on top of the body plies. Belt wedges consist of small strips of belt skim or other fatigue-resistant compounds that are placed between belts.

Shoulder inserts are small, sometimes contoured rubber strips located on the body ply under the ends of the belts.

Treads provide traction for driving, braking, and cornering. They are specially compounded to provide a balance among wear, traction, handling, and rolling resistance. Polymers with a relatively low T_g such as NR and BR are known to impart good ice traction [164]. NXT® coupling agent for silica-filled tread compounds is said to reduce the number of nonproductive steps while improving processing and performance of silica-filled tread compounds. It is also said to improve hysteresis of a tire [165]. Effective silica systems are based on highly dispersible silica, an appropriate elastomer, an effective coupling agent, and a specific mixing process [166].

New technology associated with silica-filled treads is said to reduce rolling resistance by about 30% relative to the carbon-black-containing treads that preceded them [167]. Spherical silica particles with an average diameter of 150 nm can decrease compound viscosity while maintaining desirable mechanical performance [168]. Properties such as heat buildup are said to be improved.

Epoxidized NR compounds that contain silica are said to require no coupling agents to assist in filler-to-polymer bonding [169]. This feature results in major cost savings and is said to simplify the handling of production compounds.

Modified precipitated silica has a significant organic surface on its core [170]. It is said to improve filler-filler and polymer-polymer interaction for passenger tread applications. Further, it is claimed not to produce alcohol during mixing. Conventional silanes used in tires release ethanol equal to about two-thirds of their weight during the manufacturing process and during their subsequent use [171].

NXT Z silane is said to offer processing and performance advantages in silica-containing rubber compounds [172]. These advantages include improved vulcanization kinetics and the elimination of silane-derived ethanol emissions that occur during the mixing process and during tire life.

New types of more easily dispersed silica for tires are sufficiently stable for incorporation into a tire compound before any structure breakdown [173]. Silica compounds require low mixing temperatures, between 90 °C and 115 °C, to assure sufficient viscosity and to avoid ethanol formation that could lead to surface blisters.

Microcrystalline cellulose can replace silica and reduce the viscosity of compounds containing it [174]. This reduction is said to facilitate the formation of rubber articles with different shapes prior to vulcanization.

A worn ultra-high-performance tire with one-half of the tread remaining is said to provide an average of 8% better stopping distance at 50 mph when compared to a conventional tire [175].

Subtread, when used, is typically a low-hysteresis, under-the-tread compound intended to reduce rolling resistance and to improve noise and handling.

Two different approaches have been used to reduce noise in tires [176]. One incorporates a noise-optimized tread pattern and a belt overlay of polyethylene naphthanate. The other suppresses noise caused by resonance of air inside the tire.

Undertread is a thin layer of rubber under the tread-subtread composite to increase adhesion between tread and stabilizer plies and to cover the ends of cut belts.

Because of today's emphasis on energy conservation, rolling resistance is an especially important property. Lower rolling resistance is associated with radial tires because their carcass is more flexible [177]. Ratings follow in Table 4.4 for the rolling resistance associated with different elastomers [178].

Table 4.4 Ratings for Rolling Resistance of Different Elastomers

Elastomer	Rolling Resistance Index
NR	100
High *cis*-BR	94
Solution SBR	93
Emulsion SBR	90
IIR	73

Components for tires and complete tires are molded using different techniques. For example, flat precured treads used for retreading tires are molded in C-frame curing presses in a discontinuous operation. Some of these treads are up to 36 feet long. Bladder molding is the most common method used to mold tires [179].

Truck tires are expected to be retreaded for a minimum of three to four times [180]. Meeting this expectation places considerable demands on treads and undertreads that can be accomplished by reducing heat buildup and judicious use of antidegradants and appropriate adhesives. Maintaining adequate ozone resistance of retreaded truck sidewalls over their expected one-million-mile service life is a demanding requirement [181].

Carcass and belt durability are major factors in retreading tires [182]. Monolyx is said to protect the belt package in radial truck and bus tires. It consists of at least two single plies of monofilament fibers twisted together that contain either polyamide or other types of monofilament fibers.

Nondestructive test equipment for retread tires is said to be a major advance in tire retreading [183]. The new equipment allows inspection of the tire interior to determine the presence of defects. This capability has resulted in equal or lower adjustment rates for retreads compared to new tires in many plants.

While most new commercial aircraft are equipped with radial tires, there is a need for both bias and radial tires because aircraft are designed for a specific size and type of tire [184].

Because the supersonic Concorde aircraft had to meet an extremely severe combination of load and speed requirements, only new tires were used on it, in contrast to other aircraft tires that are retreaded many times [185].

In conventional nontire molding, a compound is typically squeezed and cured between rigid metal mold surfaces. This technique contrasts with the molding of pneumatic tires wherein a flexible bladder forms the inner tire surface, while a rigid mold shapes the tire sidewall and tread as shown in Figure 4.8.

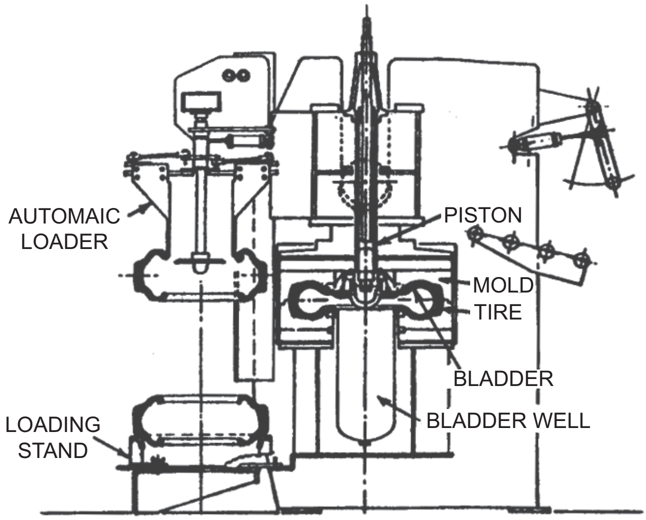

Figure 4.8 Tire curing press and ancillary equipment [186]

After placing the uncured tire in the lower half of an open mold, the mold is closed [186]. Then a rubber bladder is raised from a bladder well and inserted in the interior of the uncured tire, followed by inflation of the bladder with low-pressure steam. Steam or hot water, introduced in the bladder at high pressure, force the green tire against the mold surfaces. Hence, the hot bladder provides the heat to cure the inside of the tire, while the hot mold provides the heat to cure the outside.

A bladder must meet demanding technical requirements. It must have the physical properties required for its intended service, and it must possess good heat aging and flex resistance. A bladder stretches as much as 5 to 10% during service. Cycles of bladder inflation and deflation position the bladder in the uncured tire during the molding cycle. This is analogous to the bumping of a curing press to expel air as was described above for nontire molding.

Curing resins offer the best performance properties for tire bladders, but they impart inherent mixing and processing difficulties [187]. Polymer-bound resin products along with Aflux 1 are said to offer consistent and cost-effective curing systems for tire bladders.

After tire curing, the piston returns the bladder to the bladder well, the mold opens, and the partially cured tire is placed on a conveyor. Tires can then be placed on an automatic postcure inflator that prevents deformation in certain types of cords in cured tires. Curing continues as the tire cools.

One problem that occurs in tire molding is that a hot tire mold can heat an uncured tire that awaits cure on its loading stand. Radiated heat from the mold unevenly heats the green tire. Temperature differences of up to 15 °F have been observed between the hot and cool sides of an uncured tire awaiting transport to its mold. These temperature differences can cause uniformity problems in a finished tire.

Insulation reduces heat losses from a mold by radiation, conduction, and convection. With proper measures, heat flow reductions of up to 40% are possible. Insulation also results in improved product quality and significant energy savings. It is important that insulation used between platen and mold show very low compression set.

4.27.9 Tire Molds

Information stamped or engraved on tire molds transfers from the mold face to the surface of a tire during molding. A machine that provides five axes of simultaneous motion can position a cutting tool to cut normal to the mold surface to provide the identification. Heat transfer from mold to tire is an important consideration.

The heat conductivity of an aluminum alloy widely used in tire molds is about four times that of steel, and the alloy is said to reduce cycle times by up to 20% [188]. Additional advantages for the alloy are easier machining, lighter weight, and resistance to corrosion provided by an oxide film.

The type of tire being molded mainly determines the mold geometry. Two-piece tire molds were dominant prior to the advent of radial tires that are so widely used today. The inclusion of wire in the belts of tires made it difficult to form and then extract tires from two-piece molds because of the radial tire's decreased flexibility.

The preform for both bias and radial tires is called a green (uncured) tire. Fabrication of the green tire begins with the placing of a thin sheet of rubber (inner liner) onto a building drum of a tire-building machine. Then subsequent components are applied, ending with the application of a tread.

Pressure applied to the assembled components on the tire-building drum sticks components together. The drum then collapses to permit removal of the green tire. At this stage, green bias tires are shaped like a barrel with both ends open; green radial tires are shaped like a torus with more of a completed-tire shape. Hence, the molding process deforms bias tires significantly more than their radial counterparts.

Another difference is that the removal of radial tires from two-piece molds is generally more difficult than removal of bias tires. Forces as much as 2000 pounds may be required to remove a radial tire from its mold. Segmented molds (Figure 4.9) ease removal of radial tires from their molds, especially radial tires with stiff treads [189].

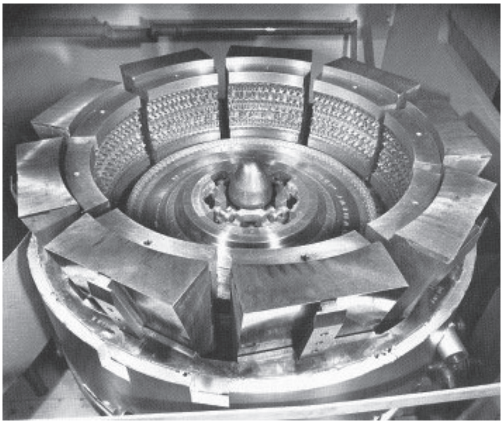

Figure 4.9 Segmented tire mold [189]

Each mold half of a two-piece mold shapes a sidewall and a portion of a tread; the mold parting line is not necessarily equidistant between sidewalls. In a segmented mold, separate mold components shape sidewalls and the tread. During a molding cycle the sidewall portions of the mold move toward one another to their final curing position. Then, pneumatic or hydraulic mechanical linkages move the tread segments radially inward and close the opening between the tread segments.

Open radial tire molds, with separation between the segments, provide increased diametrical clearance between tire and mold. This feature greatly eases removal of a radial tire from its mold. In contrast, the fixed-diameter bias tire mold causes its tire to deform more during demolding. In a sense, bias tires are removed from their mold, but with radial tires, the mold essentially is removed from the tire. Pressurizing the bladder forces a green tire against the mated components of a closed segmented mold. Air trapped between the bladder and the inner liner, and in the tread and sidewall, can cause defects in a finished tire.

To prevent these problems, special lubricants and special patterns molded on the surface of the bladder can vent air from the interface of the bladder and inner liner. Mica in the inside tire paint facilitates venting of air and eases slippage between the bladder and the inside surface of a tire.

Requirements for slippage at this interface vary, depending upon tire construction. The cross section of an uncured (green) radial tire resembles that of its curing mold, so a radial tire deforms less during shaping than that of a comparable-size green bias-ply tire. Hence, a bias-ply tire requires greater lubrication during shaping.

Exterior tire surfaces and nontire molded articles share some common venting problems. In nontire molds, optimal preform shape and judicious location of the mold parting line facilitate air removal. The objective is to have the preform push air toward the parting line during mold closure. Because the green tire constrains these options, it determines the preform geometry. The shape of the cured tire and other factors establish the parting line for a two-piece tire mold or the parting lines for a segmented tire mold.

4.27.10 Venting Tire Molds

Air trapping and associated defects in the tread and sidewall portions of tires has been a long-standing problem [190]. This is evident from the several techniques discussed below that are directed toward improved mold venting. First discussed is the traditional method for venting air from tire molds, a method that consists of drilling many holes of perhaps 0.060 in. diameter directly in the sidewall and tread portions of a tire mold.

An alternative is to place vent plugs into larger holes drilled in a tire mold. These plugs, fabricated from powdered metal, are essentially a tube with a shoulder on the tire side of a mold. With the use of either direct-drilled vents or vent plugs, compound flows into the vent orifice and leaves whisker-like appendages on tread and sidewall surfaces. These appendages are generally removed later by trimming in a postmolding operation that leaves small marks on tire surfaces.

Electron beam radiation on selected outer tire surfaces reduces vent projections by inhibiting flow of irradiated rubber into vent holes. Removable aluminum screens placed between a beam outlet and the tire surface can control the beam power. Substantial improvements are available in electron beam equipment for tire-related processing activities.

Other venting techniques include microvents with a maximum diameter of 0.020 in., porous metal vents, use of vacuum, and mechanical vents.

Microvents fill with rubber rather easily, and it is difficult to trim the small appendages that form in them. Porous metal, which leaves no appendages, is subject to plugging and when plugged needs replacing.

There can be up to 5000 vent holes per tire mold [191]. Cured compound can be removed from vent holes by drilling or by blasting with solid carbon dioxide. Applying a vacuum to a mold cavity eliminates these problems. Vacuum use requires a special press or molds and adds to maintenance costs for ancillary equipment such as vacuum pumps and controls. Another means of air removal involves the use of air vents that automatically close after the air exits the mold. This technique is said to provide a tire with a smooth, flawless surface.

Both retreaded and new tires are produced in segmented molds (Figure 4.9) [192]. Retreading of a top-treaded tire involves application of compound only in the tread area. In contrast, compound is applied to both the shoulder and tread of a full-treaded tire.

Because the mold segments in a segmented mold close around the tire, a precise circular fit is necessary before curing commences. Segmented molds used with new truck tires help maintain quality because they virtually eliminate shifting between carcass and belt components in tires.

Very large spliceless retreads have been made by injection molding [193]. Their large size requires platen sizes of 6 ft by 6 ft on the machine and large shot sizes of 40 pounds. The retreads are manufactured in a completely automated plant where the operation is microprocessor controlled.

The development of nondestructive test equipment for retread tires has been a major advance. This equipment has resulted in the adjustment rate of retreads being equal to or less than rates for new tires [194]. Additionally, computerized retread equipment results in accuracy unheard of earlier. Ultrasound is used to inspect the casings of tires for retreading, and shearography is being considered for this purpose [195].

4.27.11 Run-Flat Tires

These allow a vehicle to operate for a limited time after pressure loss. Techniques for run-flat behavior include self-supporting tires whereby the sidewall is reinforced to support the vehicle load and another wherein an internal support provides run-flat capability [196]. Yet another incorporates a pocket filled with lubricant attached to the inner sidewall of a tire, as shown in Figure 4.10 [197].

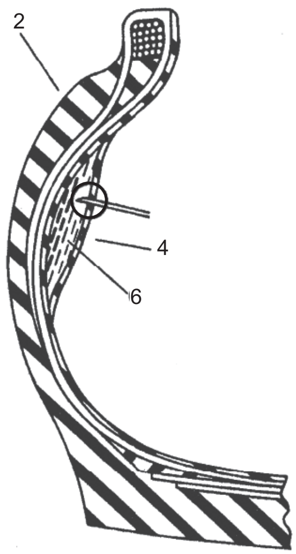

Figure 4.10 Cross section of a run-flat tire; (2) tire; (4) pocket; (6) lubricant [197]

Upon rupture, the lubricant prevents rubber-to-rubber contact when a tire is operated in an underinflated or deflated condition. The lubricant is based on a water and ethylene glycol mixture, containing polyethylene oxide, a polysaccharide, and other ingredients [198].

Another system enables tires to remain inflated at the desired pressure without electronics or external pumps [199]. It uses a small pump along with other components contained in the tire. The energy produced by the rolling tire powers the pump.

Dimples, 8 mm in diameter, molded into the sidewall regions of a run-flat tire reduced deflated tire temperatures by 50 °F and extended the run-flat distance by some 2.3 times [200]. Circular dimples provide greater surface area for radiating heat, and they disturb airflow, increasing heat transfer.

4.27.12 Semi-pneumatic Tires

In contrast to their pneumatic counterparts, semi-pneumatic tires operate at ambient pressure, and are in a category between pneumatic and solid tires. Internal and external pressures are balanced by the passage of air through a hole that is molded into a semi-pneumatic tire.

Vibration-related illnesses could be associated with long-term driving of trucks with solid tires [201] Advanced seating systems could be a solution to this problem, rather than eliminating vibrations associated with the solid tires. Solid tires can be made from either conventional rubber or from polyurethane [202]. Polyurethane tires that carry heavy loads can build up enough heat to melt their centers.

Textile or wire reinforcement in conventional pneumatic tires resists the expansion forces caused by pressured air in a pneumatic tire. Semi-pneumatic tires, in contrast, do not incorporate textile or wire reinforcement. Hence, stiff thick walls support the loads imposed on semi-pneumatic tires rather than pressurized air.

The basic steps in fabrication and molding of semi-pneumatic tires are as follows:

1. Extrude a tube.
2. Cut and splice the tube to form a doughnut-shaped preform.
3. Place the preform in a mold and close the mold.
4. Force a hollow needle through the thick sidewall of the preform to access the preform cavity.
5. Inflate the tube by pressurizing with air or an air-steam mixture.
6. Remove the needle and open the mold.
7. Remove the tire upon completion of the cure.

Internal pressure of up to 400 psi during molding of pneumatic tires requires very robust molding presses. These pressures generate extremely high forces tending to open a tire mold. Following are force estimates for molding several different tire types: 350,000 pounds for typical passenger tires, one million pounds for truck tires, and two million pounds for typical off-the-road (OTR) tires.

Each OTR tire can be given a unique serial number so that it can be tracked if a failure should occur [203]. Because of their size, a cure time of eight hours is required to produce a 63 in. rim diameter, 10,000 lb. OTR tire.

Molds used for some earthmover tires are massive in that they measure 15 feet in diameter and weigh more than 60 tons. One press is capable of curing earthmover tires up to seventeen feet in diameter. Under maximum pressure, a force as high as 28 million pounds can be developed, a force equivalent to more than *three times* the thrust of a Saturn 5 rocket [204].

A sensor placed in contact with a curing tire can detect the degree of cure [205]. It emits a pulse of ultrasound energy and then measures the time of flight before an echo returns to the sensor. The time of flight varies throughout the curing cycle of the tire.

4.27.13 Tire Aging and Safety

Aging of tires is an important consideration. Some tires age extremely well, as evidenced by a front tire on an 1889 bicycle that was still serviceable in 1982 [206]. Nitrogen, as an inflation gas for tires, significantly slowed the deterioration of rubber properties [207]. It has been used for years to inflate tires on race cars, large commercial trucks, and even the space shuttle.

Underinflated tires cause several problems that include significantly increased fuel consumption and release of carbon dioxide into the atmosphere [208]. Each extra pound of body weight in all of today's vehicles requires more than 39 million gallons of gasoline use each year—yet another reason to minimize weight [209]. A safety issue is that 0.8% of road fatalities are attributed to underinflated tires [210].

Fully automatic X-ray inspection of tires can be conducted wherein operators can save labor by supervising a number of production lines instead of one [211]. By this method, a tire rotates at constant speed, and detector signals are digitized and transmitted to a PC while the next integration occurs. Spacing between cords can be detected along with other measurements in the body cord area that include an open ply splice, a broken cord, narrow body ply cords, and misplaced chafers [212].

Appropriate sensors can detect different types of damage to tires, for example damage between belt layers [213]. For sidewall inspection, laser sensors can detect small bulges, dents, or depressions by profiling the tire geometry at frame rates of 4000 or more profiles per second [214]. As a tire rotates, a full 3-D profile is provided that allows detection of small defects wherever they are located. Lasers can detect and quantify defects and dimensional variations during both in-process and final inspection in high-volume tire manufacturing operations [215].

4.27.14 Tire Recycling

Tire fires associated with large stacks of worn-out tires have been problematic for some time. With considerable effort, gains have been made with recycling tires, as evidenced by some 75% of the 42 million scrap tires in California being recycled each year [216]. Even this percentage is below the national recycling rate of 87%. Recycled tires are used in applications such as a replacement for mined construction aggregate in landslide repair.

4.28 Nontire Products

4.28.1 General Design Considerations

A number of design factors apply to wide-ranging rubber products; first considered are general design factors for these products [217]. Because rubber can be formed into almost any shape, a designer can be tempted to form it into a shape that is unnecessarily complicated for its intended purpose. However, doing this increases development and other costs for producing rubber articles.

The flow behavior of compounds for extrusions is especially important because an extrusion die must be frequently modified to obtain an extruded profile that meets its required specification(s). Rates of extrusion are also important because they directly affect product cost. The designer should be aware that requiring a difficult-to-obtain compound property could adversely affect extrusion behavior. Hence, a designer and customer should jointly consider the rubber article as a system.

Compression molding is generally used for short product runs. Dimensional control of a compression-molded rubber article in the mold-closing direction is poorer than for injection molding that is used for longer product runs. These and other factors should be addressed to provide the best technical and economic outcome.

Some general design considerations follow [218]:

- Maintain uniform wall thickness where possible.
- Locate the parting line of a mold to minimize air entrapment.
- Locate the parting line to provide for easy removal of a molded article.
- Avoid feather edges on rubber articles.

Uniform wall thickness minimizes sink marks, shortens molding cycles, and favors more uniform crosslinking in a rubber article.

Holes in rubber articles are generally produced and formed easiest during molding. Holes formed by drilling are problematic because of rubber’s flexible nature. Make holes as wide and shallow as possible, keeping functional requirements in mind. Through holes are preferred to blind holes because pins that form them can be anchored at both ends, making the pins less susceptible to deflection during molding. Locate the axis of pins that form holes in the mold-closing direction to avoid the need for retractable pins. Provide sufficient rubber thickness around holes for mounting to avoid rubber tearing.

Undercuts can be incorporated easier in low- to medium-hardness rubber; however, they are best machined into hard rubber. An undercut with a radius facilitates demolding and helps expel air from a mold. A 50% cure in the middle of a molded article is usually sufficient to demold the article without porosity [219].

Inserts, both metal and plastic, are often used with molded rubber articles to increase their functionality. When used, insert positions in an article should be staggered to keep rubber thickness as uniform as possible, directed toward minimizing stress concentrations. Ideally, edges on an insert should be provided with a radius, again to minimize stress concentrations.

When magnets are used to hold metal inserts in place in a horizontal injection-molding machine, it is recommended that a low-pressure mold protection system be used to prevent damaging the mold should an insert dislodge from its intended location [220].

The need for draft in a molded rubber article depends upon the design of an article and its rubber properties. Most articles with hardness less than about 90 Shore A do not require draft. Alternative shaping methods include extruding a rubber sleeve and then lathe cutting the articles from the resulting tube. This approach can lower cost relative to molding, when feasible.

The wall thickness and outside diameter of hose determines the minimum allowable mandrel or core radius that can be used for forming hose. The minimum radius should be at least 1.5 times the outside diameter. Bend radii are getting smaller and life expectancies longer, placing greater demands on hose [221].

Provide generous radii in the walls of rubber bellows to facilitate molding and minimize stress concentrations.

When identifying letters and numbers are molded onto the surface of rubber articles, they generally need to be raised no more than 0.020 in. for legibility. Disposable aluminum tags stamped with information are a frequently used alternative to identify tires. These imprint tire sidewalls with the desired information.

Over specification of dimensional tolerances and other requirements of rubber articles increases costs without benefit. Doing so can require tighter process controls, higher scrap rates, and increased costs.

A sometimes overlooked design consideration is that space must be provided for rubber to expand in one direction if compressed in another [222]. Design recommendations are provided for TPV tubes, ducts, and bellows [223].

Table 4.5 lists some effects of selected convolute design factors for the bellows shown in Figure 3.23.

Table 4.5 Effect of Selected Convolute Design Variations on Bellows

Factors	Variable	Effect
Convolute height (H)	Taller	Increased flexibility
		Lower collapse and extension force
	Shorter	Reduced flexibility
		Higher collapse and extension force
Convolute width (W)	Wider	Easier extension
		Harder to collapse
	Narrower	Harder to collapse
		Increased crush resistance
Convolute angle	Larger	Harder to collapse
	Smaller	Easier to collapse
		Harder to extend
Convolute root radius	Larger	Easier extension
		Harder to collapse
	Smaller	Easier to collapse
		Harder to extend

Different organizations facilitate the writing of specifications for materials and associated requirements for elastomer-related applications. Standard specifications facilitate the materials development and design process and promote communication among those involved. Selected organizations follow:

- ASTM (American Society for Testing and Materials): Provides classification of rubber materials and test methods for numerous automotive and mechanical goods applications.
- SAE (Society of Automotive Engineers): Provides test methods and other information primarily relevant to automotive applications.
- Several countries have started to adopt ISO (International Standards Organization) standards as their preferred standards [224]. ISO standards are available from the American National Standards Institute (ANSI).

Yielding to pressure to prematurely bring a product to market often results in false economy that can lead to a less-than-desirable product design, increased manufacturing costs, and potential downstream liability costs. The Government Accountability Office (previously the General Accounting Office) has noted that more than half of jury awards in product liability cases go to attorneys [225]. Liability insurance costs in the U.S. are 15 times higher than in Japan and 20 times greater than in Europe.

As many as possible design issues should be covered in the quotation stage even before finalization of a design [226]. This practice helps avoid unforeseen costs for producer and later for the customer.

4.29 Bridge Bearings

Bridge bearings, placed between a bridge deck and its fixed supports, have three main functions [227]:

- support the dead weight of the bridge deck and live loads due to vehicle traffic
- accommodate changes in length of the bridge deck and live loads due to traffic
- accommodate the slope and changes in slope caused by bending.

These functions require a bearing that is extremely stiff in the vertical direction, soft in both the lateral directions and in rotation. A rubber metal laminate with a high shape factor provides these characteristics. NR and CR are the most-used elastomers in bridge bearings because of their excellent records in engineering applications that require high load-carrying capability and long fatigue life.

The incorporation of strongly bonded steel plates in a bridge bearing alters compression stiffness without affecting shear stiffness [228]. Codes for stress in a rubber bearing limit the allowable stress to about 1000 psi (7 MPa). This limit was chosen previously because of the allowable stress on concrete. Laminated rubber bearings with stress values several times this value are in use on helicopter rotor bearings.

Bearings accommodate flap, lead-lag, and pitch motions for helicopter blades. A low shear modulus vulcanizate for construction of flexible bearings, particularly for rocket motors, consists of a mixture of two natural or synthetic copolymers [229]. It is lightly filled and contains a low proportion of sulfur so that the vulcanizate has the required low shear modulus.

NR and CR have their respective strengths and weaknesses. Although NR is more susceptible to ozone attack than CR, it has a record of almost a century of successful application in bridge bearings. This behavior occurs because oxygen and ozone degradation are confined to the first few millimeters of NR's surface. This degradation has little effect on large, bulky bearings. However, it is suggested that all outer surfaces be covered with a 6 mm thick layer of rubber to protect the metal from corrosion [230].

The average of shear stiffness of the two bridge bearings was tested after 38 years of service [231]. Shear stiffness of the aged bearing was only 7% greater than the stiffness of the original prototype. Mechanical tests on rubber specimens prepared from a sectioned bearing showed acceptable properties in the bulk of the bearing. Significant rubber oxidation occurred within a surface zone limited to depths of 10 to 20 mm.

Lower temperature exposure increased crystallinity and stiffness of both NR and CR. Increased stiffness transfers higher loads to structures that support the bearing, such as a pier that supports a bridge. NR, being less prone to crystallize and stiffen, is preferred for low-temperature applications. Ester-based plasticizers should be avoided in CR for low-temperature applications because they speed its crystallization [232].

4.30 Earthquake Mounts

These offer seismic protection and can reduce the forces on a medium-rise building by ten-fold when used in conjunction with rock or stiff soil [233]. An effective mount prevents energy transfer from the soil to a structure by mismatching the frequencies of the earthquake and the structure, not by absorbing the energy of incoming vibrations [234].

Earthquake mounts on rock and stiff soil sites typically have an acceleration peak at about 3 Hz; unfortunately, this corresponds with the natural frequencies of a range of buildings [235]. Earthquake mounts must be sufficiently soft in shear to give a horizontal natural frequency that is substantially below the frequency of the earthquake input frequency.

The vertical frequency of the mounts must be sufficiently high to prevent rocking of a building during an earthquake. Most earthquakes in California typically have a

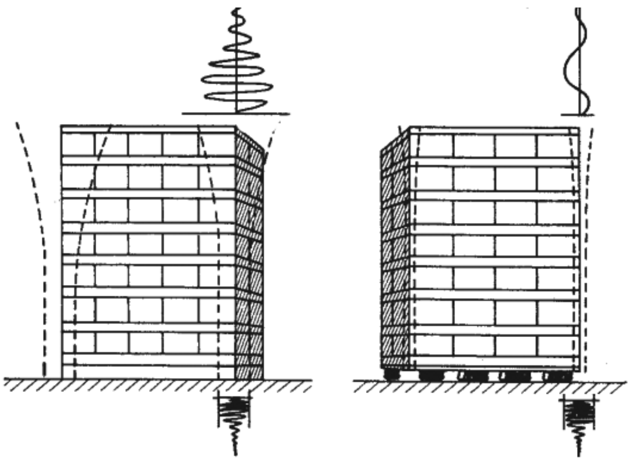

Figure 4.11 Response of a normal building (left) compared to one on earthquake mounts (right) [237]

vertical motion that is just one-third to one-half the horizontal movement [236]. An effective mount changes the nature of the motion of a building from flexure to that of a rigid body, as shown in Figure 4.11 [237].

Creep, which is another property of interest, is an increase in deformation with time at a constant load; for example, in springing applications such as an earthquake or building mount [238]. A building supported at its base on rubber mounts must be limited to minimal settling. Hence creep is of special interest for rubber mounts used to support large buildings [239].

Creep can be measured in the laboratory, but there is always concern about extrapolating the data from the laboratory to actual building behavior. Measured creep on actual mounts used to support buildings provided confidence that a building could be expected to last 100 years with acceptable settling. Curing systems are suggested for preparing low-creep mounts for buildings and other applications [240].

4.31 Expansion Joints

Fabric-reinforced rubber expansion joints offer a number of advantages that include free movement in straight piping runs, protection of piping from thermal expansion reactions, and damping of pump-induced vibration pulses [241].

Factors involved in proper joint selection include identification of material to be handled, percent solids or abrasive materials in the conducted fluid, operating pressure, and pipe movement (frequency and displacement). Rubber expansion joints are recommended for piping systems operating at less than 250 °F.

4.32 Seals

A seal’s function is to retain fluid within a mechanism and to exclude foreign matter that may form part of the exterior environment of the mechanism [242]. Although often low in cost, seals are frequently one of the most important components of a product. Elastomeric materials predominate as nonmetallic seals because they are flexible and can function at relatively high temperatures.

Earlier, compression set was used as a property to measure the effectiveness of compounds for sealing applications. Today, compressive stress relaxation (CSR) is the method of choice for measuring seal effectiveness [243]. It involves placing the seal compound under fixed compressive deformation and observing the initial force required to produce the deformation. The loss of force with time is then noted to obtain a CSR value.

Stress relaxation causes a decay of stress with time under constant deformation, for example in sealing applications. Unfortunately, the majority of standards for testing pipe sealing rings and pipe sealing ring compounds don't contain a stress relaxation requirement—the most dominant performance parameter in determining long-term behavior [244]. Compression stress relaxation is likely to replace single-point compression testing for seals [245]. A method for determining stress relaxation under dynamic conditions can be used in development of a range of elastomers and products that include timing belts, engine mounts, and seals [246].

During installation of pipe sealing rings, it could be necessary to stretch the ring over the pipe [247]. This degree of stretching is unlikely to be near the breaking elongation of most rubbers. Hence, tensile and elongation-at-break values are expected to have little relevance to service conditions.

4.32.1 Automobile Sunroof Seals

Gaps in sunroof seals, typically 4 to 6 mm, must be effectively sealed [248]. TPV in this application is said to provide good sealing and long-term color retention at a lower specific gravity and cost than TSE.

4.32.2 Radial Lip Seals

Radial lip seals like the one shown in Figure 4.12 are used widely in engine transmissions and transfer case components [249]. They must be retained in their housing when the seal assembly is thermally cycled. During molding, rubber must be gated at an appropriate location; if it is not, early failures can occur [250].

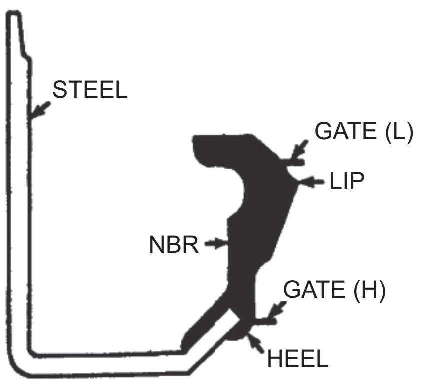

Figure 4.12 Lip seal showing gate locations at the heel and the lip of the seal [249]

Heel-gated seals leaked after a test period of 15 to 18 minutes, while their lip-gated counterparts lasted as long as 300 hours.

A compression spring typically is installed in the semicircular groove shown in Figure 4.12. A new-technology lip seal can eliminate the need for this spring and is said to offer the following advantages [251]:

- significantly reduced friction between seal lip and shaft
- lower seal lip temperature
- seal performance maintained when large seal misalignments occur.

PEEK (polyether-ether ketone) offers improved chemical resistance, thermal properties, and mechanical performance compared to other thermoplastics [252]. Combined with a range of elastomers, it forms composites for use in diverse applications.

4.32.3 O-Ring Seals

Temperature is an especially important consideration in O-ring design. Designers sometimes are tempted to make the inside diameter (I. D.) of an O-ring slightly smaller than the I. D. of a rotating shaft to improve seal performance [253]. This doesn't work because the friction between shaft and seal increases seal temperature. For an O-ring in tension, the Gough-Joule effect causes the ring to grip the shaft even tighter and increase in temperature. To avoid this, the I. D. of the O-ring should be about 5 % greater than that of the shaft.

4.32.4 Gaskets

EVM (ethylene-vinyl acetate copolymer) is used in heavy-duty gasket applications for diesel engines that encounter oil formulated to PC-10 guidelines [254]. A 70% EVM compound provided the best sealing force retention after six weeks aging in oil at 150 °C.

Perflouoroelastomer seals must resist chemical degradation in MIL-L-23699 lube oil as well as engine soakback temperatures up to 550 °F [255]. They increased seal life more than 250% over prior fluoroelastomer seals and eliminated 10,000 hours of unscheduled maintenance.

If EVM has a lower-than-desired viscosity for good molding and extrusion behavior [256], peroxides can be used to improve these properties.

Cork and rubber form a composite that has a Poisson's ratio of about zero [257]. This means that the cross section of the composite does not change when compressed. Rubber-cork composites find use as gaskets in diesel and gasoline engines. Cork that contains tiny airtight cells recovers 90% of its deformed shape after 50% compression. Hence it finds wide use for wine bottle corks.

4.32.5 Wine Bottle Corks

EVA and compounds based on SEBS (styrene ethylene-butadiene styrene) have successfully replaced corks in wine bottles [258]. These materials show advantages relative to cork because they permit a wine bottle to be stored in any orientation, whereas a cork seal needs to be kept moist. Hence, a cork must remain in contact with the wine.

4.32.6 Casket Seals

Sometimes sealing can be too good, as in casket seals [259]. It is possible for caskets, sealed tightly to protect a loved one's body from the elements, to exclude oxygen and cause flesh to liquefy and form gas that can burst a casket. Some burial services specify that a seal not be used because tightly sealed caskets in mausoleums can hasten casket deterioration.

4.32.7 Aircraft Runway Seals

Neoprene seals, used for many years on airport runways, are said to have twice the life of silicone [260]. Higher hardness neoprene runway seals, useful for military and space applications, avoid penetration by foreign objects such as rocks that embed themselves in softer seals.

4.32.8 TPU Seals

The sensitivity of TPUs to some fluids, such as water and acids, has precluded their use in seals and other applications where rubber is typically used [261]. Newer TPUs can now be used in some of these applications, and they are said to be superior to rubber. Some TPUs tend to swell less and are superior to low-temperature NBR materials.

4.33 Inner Tubes

Inner tubes are mainly used for heavy trucks, buses, and farm equipment [262]. However, the change from bias to radial tires is also cutting into these markets.

Lap splices for inner tubes are somewhat stronger than butt splices; however, butt splices can be nearly as good as lap splices with the use of a Weldstitch splicer [263]. Regardless of the splicing method used, the spliced tube should relax for 3 hours minimum before chilling, shaping, and curing. Storage time of the extruded tube is important [264]. Increasing storage time from 20 minutes to 24 hours increased butt-splice strength by about 20%; increasing the time to 36 hours decreased butt elongation. It was concluded that butt strength after 24 hours is a reasonable test of rubber compound quality.

EPDM is useful for blending with IIR for inner tubes directed toward improved ozone resistance [265]. Although air permeability increases with higher EPDM levels, the blends are considered satisfactory for inner tubes. EPDM levels of 20 phr and higher were necessary to obtain ozone resistance significantly better than 100% IIR compounds.

Glass flake reduced the permeation rate of air in tire inner liners; a 20 phr loading reduced permeation rate by 45% [266]. Removal of a small amount of carbon black compensated for the increase in hardness caused by the glass flake.

4.34 Windshield Wiper Blades

A sharp wiper edge is important for good windshield wiper performance [267]. The most critical properties of a wiper compound are hardness, permanent set, tear resistance, abrasion resistance, and resilience. A hardness of about 60 IRHD allows the wiper edge to compress and form a thin contact line that facilitates wiping.

Extruded blades, rather than molded blades, eliminated the need for costly molds [268]. A sharp wiper edge is formed on extruded pairs of blades by slitting the extrudate lengthwise to form two wiper blades.

Silicone-rubber-based wiper blades are claimed to last two to three times as long as traditional organic rubber blades [269]. This is due to their resistance to ozone, UV radiation, and extreme hot and cold. Teflon can be co-extruded with NR for an improved wiper edge. Other blades incorporate synthetic alloy-grafted polymer [270]. These are said to change the surface tension so that water does not sheet, permitting the wiper to more easily remove the water.

Chlorination reduces the coefficient of friction (COF) of wiper blades against windshields [271]. It was found that COF decreases rapidly during the early stages of surface chlorination, with little further reduction after about 10 minutes.

FEA, applied to blade design, helped analyze and predict a blade contact angle for a given load application and COF [272]. Monoprene wet-grip TPE is said to retain a nonslip surface and a secure grip even when wet [273].

■ 4.35 Friction Drive

A lack of discussion at the early stage of a product design can be problematic, as evidenced by a conventional rubber band that was used as a friction drive in a printer application [274]. Rubber bands are generally protected with an antioxidant that can bloom to the surface as flat crystals that reduce frictional properties of rubber. Used in this application, the bloom rendered the band inoperable; the problem, once identified, was easily solvable.

■ 4.36 Baby Bottle Nipples

Baby bottle nipples in service turned purple as a result of sterilizing them in a hypochlorite solution [275]. Analysis of the nipples showed the presence of two curatives that liberated substituted aromatic amines during cure; the hypochlorite oxidized the amines to give a purple-black color.

Laser beams have been used to form holes as small as 0.006 in. and as large as 0.020 in. in baby bottle nipples [276]. They can be focused to spot sizes as small as 0.1 mm diameter.

Natural rubber products such as baby bottle nipples and gloves contain protein that can cause allergic reactions in certain individuals [277]. *cis*-1,4 PI (synthetic NR) can be polymerized without these proteins.

4.37 Belts

These are broadly classified as V-belts and conveyor belts. V-belts transmit power or motion between V-shaped sheaves [278]. They provide dependable service life, are an economical means of varying speed ratios of motion devices, and require only low maintenance. Different designs for V-belts follow:

- ribbed belts that have fabric-faced Vs, Vs reinforced with short fiber that are subsequently ground, and Vs that are molded with short fiber flock on their face
- V-belts with a cut edge
- V-belts that are wrapped with one or more layers of fabric.

Variable-speed V-belts for snowmobiles place severe demands upon belt design that differ substantially from those used for most industrial belt applications [279]. Aggressive snowmobile riding twists the frame and causes significant component misalignment.

Several of the essential properties considered necessary to meet the original criteria for automotive timing belts follow [280]:

- flex crack resistance
- appropriate hardness at low and high temperature
- heat and ozone resistance.

Timing belts that contain HNBR must operate satisfactorily at temperatures up to 140 °C and resist the effects of motor oils and fuels [281]. Even higher operating temperatures are projected. A popular belt construction consists of a glass-fiber reinforcing layer and a nylon friction face. Glass fiber replaced the steel in CR belts used earlier because it favored longer flex life.

V-belts, cured under tension that approximates the tension experienced in service, provide improved dimensional control [282]. Factors occurring during V-belt processing can significantly affect adhesion of RFL (resorcinol formaldehyde latex)-treated cords [283]. For example, RFL-treated cords exposed for only two days to ultraviolet rays retained only about 20% of their original adhesion value.

Ozone levels of 5 pphm (parts per one hundred million) can significantly affect the adhesion between rubber and polyester cord when using an RFL adhesion system [284]. Higher humidity and temperatures decrease adhesion. Black polyethylene sheeting or kraft paper wraps provide protection from light after treatment of cord. RFL-treated cords should not be touched, and they must be protected from air, light, and temperature and humidity changes [285].

4.37.1 Serpentine Belts

Serpentine belts have essentially replaced V-belts in automotive applications; a single serpentine belt saves weight by replacing the several V-belts formerly used [286]. A serpentine belt, driven by a crankshaft pulley, drives accessories such as an alternator, air conditioner compressor, and a power steering pump [287]. Projections on the timing belt register with corresponding depressions in the crankshaft pulley and accessories, an important feature for timing belts. Failure of a timing belt can cause loss of synchronization between valve and piston motion and result in very costly repairs [288].

4.37.2 Aircraft Recorder Belts

Rubber belts used in aircraft recorders must function over a wide temperature range, as low as –55 °C and as high as 71 °C [289]. Silicone rubber belts meet these requirements along with requisite stress relaxation requirements [290]. Equations are available that provide information for sizing pulleys for belts and for O-rings that could serve as belts [291].

4.37.3 O-Ring Belts

These are ideal for many applications because they can be supplied in hundreds of standard sizes and can be used in both open and crossed-drive applications; lathe-cut belts function only on open-drive applications [292]. Lathe-cut belts used in these applications have the advantage of being substantially lower cost. Flat belts should be run on crowned drive pulleys to maintain their position on pulleys [293].

4.37.4 Conveyor Belts

Conveyor belts provide the most economical means of transportation over long time periods, especially when compared to other transportation means such as trucks [294]. They are used extensively in mining operations to convey materials and minerals. Changes in reinforcement—from rayon in the 1950s to nylon in the 1960s—improved belt durability and extended belt life. The fiber or fabric reinforcement in conveyor belts provides the strength necessary to transmit power to drive the conveyor belt and to support its load [295]. Polyester's high strength-to-weight ratio and nylon's good fatigue resistance favor these fibers for a wide range of belts.

Conveyor belt characteristics vary widely. A belt used in coal-mining operations in England is 6.5 miles long, four feet wide, and one inch thick [296]. Among safety concerns with conveyor belts used in mining operations are belt slippage and flammability. CR could be preferred in belts because of its inherent flame retardance. A burning test is conducted with an 18 m length and the width of the actual belt [297]. Wood is placed under and on the belt in a specified manner and then ignited. Flame cannot travel more than 10 m beyond the flame source.

Rubber used in conveyor belts for the tar-sand mining in Canada must meet special demands [298]. It must resist swelling by the tar sands and possess good low-temperature properties—two properties difficult to achieve in the same compound. However, low acrylonitrile NBR provides the desired combination of properties. Another conveyor belt transports hot clinkers wherein the temperature of the top cover of the belt can vary between 171 and 227 °C [299]. Techniques were developed to minimize high-temperature damage to the belt.

New Mine Safety and Health Administration standards affect mining belts [300]. Underground belts had to be flame resistant starting in 2010. Several manufacturers of halogenated flame-retardant (HFR) materials are replacing HFR with eco-friendly nonhalogenated systems [301].

Long belts, initially cured in short sections, are subsequently overlapped to obtain the final desired belt length [302], causing overcure in the overlapped sections; hence, it is necessary to establish that the rubber in these sections has the required belt properties.

An empty conveyor belt must conform to the shape of its idlers to operate properly [303]. A belt that has too many plies and is therefore too stiff will not conform to the shape of the idlers and will not run straight. A belt must not be so compliant that it won't retain stability when loaded. In coal mining operations where pillars support the roof, the conveyor belt must snake around the pillars, placing extra strain on a belt [304].

4.37.5 Timing Belts

Rubber used in timing belts must meet twelve essential properties that include [305]

- tensile and elongation at break
- hardness ratio at 120 °C vs. 25 °C
- permanent set at 120 °C
- ozone resistance
- flex crack resistance after aging for 70 h at 120 °C.

An HNBR compound exhibited the best overall properties for timing belt service.

4.38 Mountings, Bearings, and Bushings

Rubber mounts are widely used to prevent or minimize the transmission of dynamic oscillations to a supporting structure [306]. Vibration isolators are designed to give a natural frequency of the spring mass system that is considerably lower than the lowest frequency component in the forcing frequency [307].

NR is typically considered the elastomer of choice for use in vibration-isolation applications [308]. It is one of the few elastomers that is strain crystallizing, and as such possesses inherent strength without the addition of particulate reinforcement. This feature allows fabrication of NR mounts that exhibit very low modulus, high strength, and low damping. However, environmental factors, such as solvent resistance and high temperature, preclude NR use in some applications.

Rubber mounts often are combined with a higher modulus material, for example steel, to prevent excessive distortion and to provide for mount attachment [309]. Reasons for preventing vibration from traveling to or from a mechanism include noise reduction, higher operating speeds, more accurate operation, and reduced physical and physiological effects on humans.

Rigidity of a mount's supporting structure, along with mount system strength and geometry, are very important considerations [310]. This same principle applies to earthquake mounts. If a supporting structure is too flexible, it can defeat the purpose of using a mount; that is, the mount must be the most flexible element in a system.

Rubber mounts fail for a variety of reasons. Table 4.6 lists some problems, their causes, and suggested remedies [311].

DesiCal P is dispersion of CaO in paste form that serves as a desiccant for processing rubber [313]. It is individually wrapped in low-melt polyethylene for handling and convenience, extra moisture protection, and easier incorporation into rubber. It appears not only to reduce crosslink density but also to accelerate the cure rate at lower temperatures [314].

When joining rubber and plastic to form a composite, the plastic should generally have a heat deformation temperature near to or greater than 400 °F [316]. This requirement could exclude materials like PVC and polystyrene. A problem occurred with a rubber-polycarbonate article because the polycarbonate plastic leached plasticizer from the rubber and degraded the polycarbonate. Additional causes of rubber failure and suggested remedies follow in Table 4.7 [315].

Natural rubber is widely used in mountings because of its unique combination of properties: high strength, outstanding fatigue resistance, high resilience, low sensitivity to strain effects in dynamic applications, and good resistance to creep [317].

NR is among the few strain-crystallizing elastomers, a phenomenon that contributes to its high fatigue life and its high strength without the need for reinforcing fillers.

Table 4.6 Reasons, Causes, and Possible Remedies for Failure in Rubber Mountings

Problem	Cause	Possible Remedy
Excessive deformation	Work softening	Reduce dynamic and static stresses Improve compounding
Softening	Reversion in NR mount Rubber temperature too high	Optimize cure schedule Shield rubber from heat source Cool mount if possible
Blow-out	Internal heating	Use more resilient compound Use different-hardness compound and/or higher thermal conductivity Change mount design
Porosity	Undercure and/or moisture in compound	Optimize cure schedule Include CaO in compound
Swelling	Oil or solvent reaching compound	Shield rubber or coat it with oil-resistant coating
Surface crazing or cracking	Lack of ozone or weathering resistance	Incorporate effective protective system or change to alternate rubber
Delamination	Defective manufacture in compression molding of laminated sheets	Improve molding techniques

[a] Calcium oxide (CaO) is useful as a desiccant in rubber compounds to avoid porosity [312]. It generally causes a lower state of cure and significantly higher compression set properties. A chlorine-containing factice material is suggested to correct this problem.

Table 4.7 Additional Causes of Rubber Failure and Suggested Remedies

Symptom	Probable Cause	Possible Remedy
Excessive deformation	Work softening	Use more resilient rubber. Reduce dynamic and static stresses
Softening	Rubber splashed with solvent	Shield rubber from solvent
	Rubber at too high temperature	Shield rubber from heat
	Overcure	Reduce cure time
Hardening	Excessive heat	Shield rubber from heat Cool rubber
Large cracks	Local overstressing	Redesign

Hence, NR compounds can exhibit a combination of low modulus, high strength, and fatigue resistance, along with very low damping.

Silentbloc flexible bushings are widely used in a range of applications to reduce noise, vibration, and shock [318]. They provide high load-carrying capacity, accommodate component misalignment, and eliminate the need for lubrication.

A Silentbloc assembly consists of a rubber insert located between an inner and outer metal sleeve as shown in Figure 4.13 [319].

Figure 4.13 Silentbloc bushing that shows a rubber insert between inner and outer metal sleeves [319]

In-mold chemical bonding of the bushing is an option. High-frequency performance of a mount may be less than satisfactory if a metal component of a bonded mount has secondary frequencies in the frequency range of interest [320]. An elastomer ring in a bearing reduced axial and radial vibration and airborne noise.

4.38.1 Engine Mounts

Engine mounts, used in a wide range of applications, vary substantially in design. When designed for the shear-compression mode, they can develop substantially different stiffnesses in two perpendicular horizontal directions and a third stiffness in the vertical direction [321]. FEA can determine static and dynamic spring rates of engine mounts and then determine the effectiveness of a particular design in isolating vibrations at idle and other undesirable engine vibration modes.

Engine mounts operate in increasingly hostile environments; engine temperatures reach 130 °C near the catalytic converter of an automobile, and even higher temperatures are anticipated [322]. Higher temperatures necessitated the use of expensive silicone rubber in selected automotive engine mounts [323]. Decreased available space for ventilation can further increase engine mount temperature.

Service temperature varies both among and within mounts, as evidenced by a failed engine mount on the author's station wagon. Shore A hardness measurements on a failed mount ranged from 70 to 88, with the highest value occurring in the rubber nearest the exhaust manifold [324]. This result indicates that different locations within the failed mount experienced substantially different service temperatures.

Engine mounts on jet aircraft must withstand stress from sources not experienced by automobiles [325]. For instance, engine mounts for Cessna CJ3 aircraft had to withstand engine damage equivalent to two birds flying into an engine fan blade without failure.

Continuing changes in technology necessitate changes in product requirements. For instance, adhesion systems for automotive engine mounts formerly did not require resistance to ethylene glycol [326]. But with the introduction of mounts that contain ethylene glycol in chambers to control dynamic properties, new adhesives were developed that provided the needed glycol resistance.

Hydraulic engine mounts were developed to avoid the need to compromise engine bounce and engine isolation [327]. They permit the use of softer rubber, while an internal fluid controls engine bounce at resonance.

Engine mounts that incorporate a hydraulic fluid such as ethylene glycol have eliminated the need to compromise engine bounce and engine isolation [328]. Mounts provide high damping at low frequencies and low damping at high frequencies. They do this by transferring a fluid through an orifice between mount chambers that controls engine bounce [329]. Hence, the effects of fluid-flow damping and elastomeric damping are combined [330].

Figure 4.14 illustrates this principle wherein a fluid transfers between chambers 10 a and 10 b to provide damping in the radial direction [331]. The fluid provides high damping, and various types of orifices or tubes can be used to vary damping properties of bushings.

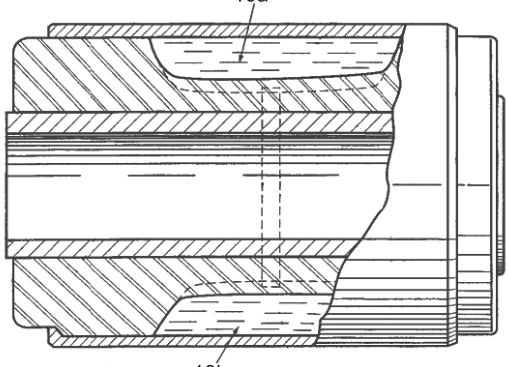

Figure 4.14 High-damping resilient bushing [331]

Magneto-rheological fluids encased in a shock absorber for vehicle seat damping represent another advance [332]. They consist of suspensions of minuscule magnetizable particles in oil, and magnetic fields soften or stiffen the mixture.

Another engine mount has a vacuum switchable bypass and decoupler that improves engine and idle isolation [333]. It provides sufficient damping to mitigate powertrain shake and provide comfort; however, it is still sufficiently soft to provide isolation during engine idling. This engine mount is expected to be especially useful with diesel engines.

Servohydraulic testing machines have typically been used for tests in axial testing, and newer machines can test in orthogonal axial torsion and even in triaxial modes [334]. Special requirements of the reaction frame and a control system for multiaxial test frequencies from static to 400 Hz have been considered [335]. ASTM provides a standard guide for dynamic testing of vulcanized rubber and rubber-like materials using vibratory methods [336].

Under-hood temperatures continue to increase, while available space for engine mounts decreases [337]. Silicone rubber mounts offer better temperature performance and can be tuned to the desired damping properties.

A troubleshooting guide for dynamic testing follows in Table 4.8 [338]. It shows several examples of symptoms, possible causes, and corrections.

Table 4.8 Symptoms, Possible Causes, and Corrections for Dynamic Testing Problems

Symptom	Possible Cause	Correction
Dynamic or static rate is higher than expected	Strain amplitude is too low; preload/strain is too high	Confirm machine is reaching desired strain inputs
Dynamic rate vs. frequency curve has a peak. Machine squeals	Resonance in tooling or specimen	Redesign tooling to move resonance from test range
Test machine cannot hold zero preload on soft articles	Test article is too compliant for load range	Use displacement control mode and hold zero displacement

An RPA 2000 testing machine can conduct troubleshooting and quality monitoring on both uncured and cured rubber compounds [339]. Careful modeling facilitates development of a specific test configuration to evaluate mixing, processing, and dynamic characteristics for a compound.

4.39 Hose and Tubing

Air conditioning, brake, and hydraulic hoses are examples of reinforced rubber hose [340]. High strength-to-weight ratios are said to be achieved for fiber-reinforced polymers through the use of Corpo technology, which provides optimized fiber paths on axially connected isotensoidal cells [341]. An isotensoid is a filamentary structure in which there is a constant stress in any given filament at all points in its path. Advantages for Corpo technology include higher potential pressure levels, increased durability, up to 50 % fiber reduction in rubber composites, increased flexibility, and cost reduction.

Yarn is used for air conditioning and brake hoses. In these hoses it must impart physical properties to meet defined elongation properties and tenacity, resistance to temperature and chemicals, and adhesion to a range of rubbers used in these products. Cotton was used earlier in a number of applications because it showed good mechanical bonding. However, modern textiles have largely replaced cotton because of cotton's low mechanical strength. The myriad of textiles and the range of rubbers available, especially low-polarity rubbers like EPDM, place considerable demands upon adhesion systems.

The RMA Hose Handbook describes many types of rubber and plastic materials, fibers, reinforcing cords, and manufacturing and vulcanization methods for hose [342]. It lists elastomers such as CR, NR, IIR, NBR, and FKM along with properties that include resistance to solvents, ozone, and aging. Plastics used in hoses include nylon, polyethylene, polyvinyl chloride, polyester, and fluorocarbon. Fibers include cotton, rayon, glass, nylon, and polyester.

Varied types of hose terminate with different connectors that must be leak proof [343]. A finite element model successfully simulated leakage of a hose with crimped connectors. Automotive hose that was reinforced with Santoweb cellulose fibers has been fabricated without a mandrel [344]. In a computerized extrusion operation, the die head shifted to create bends and angles in the hose and also to increase wall thickness in the area most likely to collapse under vacuum [345].

Another approach to manufacturing hose without a mandrel is said to apply to four-layer hose with textile reinforcement, hose with spiraled textile reinforcement, and hoses with knitted textile reinforcement [346].

Different types of rubber compounds respond differently to various fluids. Ideally, a hose would tolerate a range of fluids while maintaining acceptable swelling characteristics and other properties [347]. For example, one hose can handle biodiesel fuel and also ethanol and gasoline [348]. The cover on the latter hose resists degradation from fuel blends, and it also resists abrasion. The hose inner tube helps resist swelling, softening, and cracking that may be caused by alternative fuels. For hose that is used under vacuum, helix wire reinforcement reduces risk of hose collapse.

Heat from an exhaust system can shorten hose life [349]. Insulation on the hose exterior can delay hose degradation.

Laboratory tests concerned with the degree of swelling of a rubber compound generally establish whether a compound is sufficiently oil resistant [350]. They establish how much oil is absorbed by the compound and more importantly how much the oil affects a rubber compound. For many purposes it will not matter how much oil is present as long as it is confined near the surface of a product.

Analysis of a failed fuel hose established that an incompatible chemical agent contacted the hose and caused the hose to swell and distort while it was constrained by its wire jacket [351]. Volatilization of the agent left the hose in a severely stressed state. Because plasticizer had been leached from the hose prior to swelling, increased hardness made the hose prone to cracking under stress.

During the early stages of swelling, up to about one-half of the total equilibrium value, the amount of liquid absorbed per unit area of rubber is proportional to the square root of time. Figure 4.15 shows the relationship between liquid viscosity and penetration time.

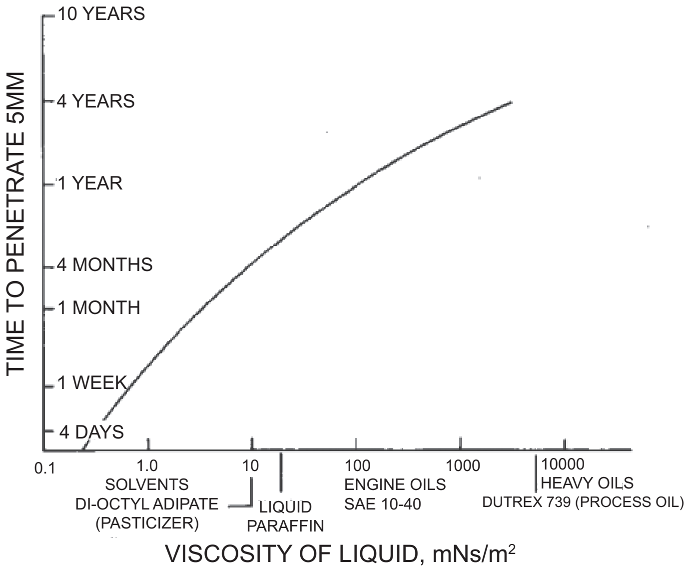

Figure 4.15 Relationship between liquid viscosity and penetration time [352]

Since the depth of penetration of the liquid depends on $(\text{time})^{1/2}$, it will take 100 times as long to penetrate 10 times a given distance [352]. The bulk of thick products such as bridge bearings and engine mounts essentially protect these products.

4.39.1 Self-Sealing Fuel Cells

Widely used in military aircraft, fuel cells must seal when pierced by a bullet and then retain sufficient fuel for an aircraft to return home [353]. Their construction includes an NBR inner lining that resists swelling so as to contain fuel. In service, a nonfuel-resistant rubber swells upon contacting the fuel and closes the opening caused by a penetrating bullet. The fuel cells can be fabricated over a core of papier-mâché, after which the core is crushed and the resulting crushed pieces are withdrawn through the largest available fuel cell opening.

4.39.2 Radiator Hose

Key properties of radiator hose include adequate tear strength for removal from a mandrel, low compression set to retain hose-clamping force, good burst strength, and good high-temperature heat resistance [354]. Coagents in EPDM compounds enhanced these properties, lowered viscosity, and increased scorch time.

Smaller, lighter, hotter-running engines are a part of the changing conditions for radiator hoses [355]. Temperatures around automotive hose reach temperatures as high as 150 °C locally, with coolant temperatures ranging between 110 and 125 °C. Different curing systems provide relative advantages and disadvantages for the hose; for example, peroxide curing is generally more expensive than sulfur curing. Peroxide is used despite this and other disadvantages. Peroxide-cured hose generally has less electrical conductivity because it doesn't contain zinc-based chemicals.

CSM-based hose can be used at up to 140 or 150 °C when properly compounded [356]. It generally requires the use of lead-based compounds as an acid accepter. Where lead is objectionable, hydrotalcite (magnesium aluminum hydroxycarbonate) is a potential alternative.

Electrochemical failure is a potential failure mode for radiator hose [357]. It was found that lower conductivity was needed in hose compounds to reduce or eliminate this failure mode. Specific types of carbon black have been developed to alleviate this problem.

Hose and liquid coolant form an electrical path between metal connectors, that is, between the engine or radiator and the hose tube material [358]. This can cause microcrack formation within the hose tube, after which the coolant can attack and weaken the hose reinforcement. Changing the electrical properties of the hose can correct this problem [359].

Microcracks, formed by an electrochemical process, occurred in the inner tubes of EPDM radiator and heater hose used in automobiles [360]. The use of noncarbon filler electrically isolated the hoses and corrected the cracking problem.

Hoses on cars registered a voltage in the range of 20 to 200 mV when voltmeter probes were placed on a radiator hose and on the engine or radiator connections [361]. Raising the voltage to 15 V was found to greatly accelerate the formation of striations on the hose.

Cooling system failures earlier accounted for 25% of major failures on a large fleet of transit buses [362]. The use of maintenance-free silicone rubber greatly reduced these costs, and special hose clamps were developed to prevent mechanical damage caused by hose removal and reassembly.

A hydraulically driven torque feeder supplies a constant amount of silicone rubber for extruded rubber hose and provides consistent pressure to a die plate [363]. It is also said to eliminate air inclusions and to increase output by 5 to 10%. For certain hose applications, it may be desirable to design the hose braid angle to produce a length change to improve coupling retention [364].

Electrical properties of rubber are important in other rubber products such as silica-based tires [365]. Too-low electrical conductivity caused an electrostatic discharge problem. Complaints ranged from shocks to toll booth operators to excessive radio static. Increased conductivity corrected the problems. Conductive rubber feet are used for hospital stools [366]; conductive silicone and fluorosilicone rubber are also used in electromagnetic shielding for gaskets [367].

Balancing required properties such as physical properties, conductivity, and processing characteristics can be problematic [368]. Materials such as silicone ECS4 are said to provide a favorable combination of properties.

4.39.3 Fuel Hose

Increasing use is being made of multilayered fuel hoses that contain a thin fluoropolymer layer to retain vapors during circulation of fuel in engines [369]. Replacing two extrusion processes with one saves factory space and costs [370]. Concentric layers of rubber can be formed in a cylindrical complex body that is said to be easy to clean.

Nonlead cure systems can effectively substitute for an ETU/lead system for fuel hose based on epichlorohydrin [371]. A new fuel hose combines an 8 mm layer of fluoroelastomer on the inner surface of the hose and a thicker PVC/NBR layer [372]. The combination, which resists scuffing and mechanical damage, meets emission regulations at lower cost.

Compounds based on two classes of polyepichlorohydrin were tested by immersion in various fuels and ethanol-fuel blends [373]. ECO-based compounds, which showed no significant change in low-temperature performance before and after immersion, remained consistently flexible near or below −45 °C even after 1008 hours of exposure to fuel media. E15 blend was the more aggressive media examined.

4.39.4 Turbocharger Hose

It is expected that turbocharger hose use will increase because turbocharged engines are more efficient [374]. Vamac Ultra HT is a high-viscosity AEM terpolymer designed for use in turbocharger hose, and compounds made from it have high green strength and favorable scorch characteristics that favor good extrusion behavior, along with good dynamic properties.

Turbocharger hoses must operate under both increasingly harsh chemical environments and at higher temperatures and pressures [375]. To meet these demanding requirements, hose typically consists of a layered construction that incorporates several different rubbers, such as a fluoroelastomer liner and a silicone cover. A partially crystalline fluorothermoplastic material replaced FKM in a hose compound. It improved tear strength, low-temperature flexibility, and chemical resistance and halved fuel diffusion/permeation [376].

Special fiber-winding techniques are said to reduce cost by using a technique that allows each fiber to support its maximum load [377]. Deviation of a reinforcing fiber by just 5° from its optimum angle is said to reduce its load-carrying ability by one-half. Turbocharger hoses are a major application for this new technology.

Calendered strips are used to feed an extruder to improve gauge control of silicone turbocharger hose [378]. These are then wrapped around a mandrel with four plies of aramid that impart the required strength. The hose is cured in an autoclave, and a subsequent test sequence at a temperature of 400 °F minimum, accompanied by vibration, ensures satisfactory service.

Single or multiple layers of a high-temperature fabric such as aramid reinforce a hose assembly. The use of aramid fiber as reinforcement is an alternative to aramid fabric [379]. A proprietary technique produces a homogenous predispersion of aramid pulp in an elastomeric matrix. The technique produces hose with high-surface-area aramid reinforcement without the problems associated with incorporating or dispersing the raw pulp. Currently, aramid fibers withstand the heat and pressure to which hose is subjected [380]. When fabricating multipolymer hose layers of different composition, it is important to invest considerable time and effort to ensure satisfactory behavior [381].

Many turbocharger hoses that previously incorporated acrylic rubbers, such as AEM, have changed to silicone rubber, which can operate continuously at temperatures greater than 170 °C [382]. When fabricating multipolymer hose layers that differ in composition, it is important to determine that hose will perform satisfactorily in its intended application [383].

Hose liner in turbocharger hoses must survive extended contact with hot engine oils [384]. Synthetic oils that contain additives affect hose degradation, and a sulfur donor cure combined with effective antidegradants is said to provide extended hose life [385]. For maximum heat resistance, peroxide cure systems are favored [386].

4.39.5 Refrigerant Hose

A thin layer of plasticizer-free polyamide is said to virtually eliminate pollutant emissions from refrigerant hose [387]. The hose retains its flexibility with a 0.06 mm thick foil lining, and emissions from it are about 5% of the amount that escape through butyl hose without a foil lining.

4.39.6 Heating Hose

Hydronic hose, buried in or attached to flooring for heating, is often fabricated from NBR and operates best over a temperature range of 100 to 160 °F [388]. It is important that proper fluid, for example half water and half propylene glycol, scavenge trace metals from the heat transfer fluid. Entran II heating or snow-melting hose was the subject of considerable litigation [389].

4.39.7 Brake Hose

Different fabric weaves are available to meet specific hose requirements. Reinforcing wire is used in a range of hydraulic and industrial hose to satisfy high-pressure requirements. Even cotton fabric can impart substantial resistance to high pressure as evidenced by an air brake hose that withstood 900 psi pressure [390]. Other important brake hose properties include flexibility, bend radius, and electrical resistance.

Brake-by-wire systems could potentially replace brake hose used in conventional hydraulic brake systems [391]. Such systems would eliminate from every car a gallon or more of hydraulic brake fluid, about six yards of brake hose, the master cylinder, and the vacuum booster unit.

A vehicle patented brake hose consists of multiple layers, comprising an inner tube, first and second reinforcing layers, an adhesion layer, and an outer tube rubber layer [392]. An adhesion layer bonds the first and second braided fiber reinforcing layers to the outer tube rubber layer as shown in Figure 4.16.

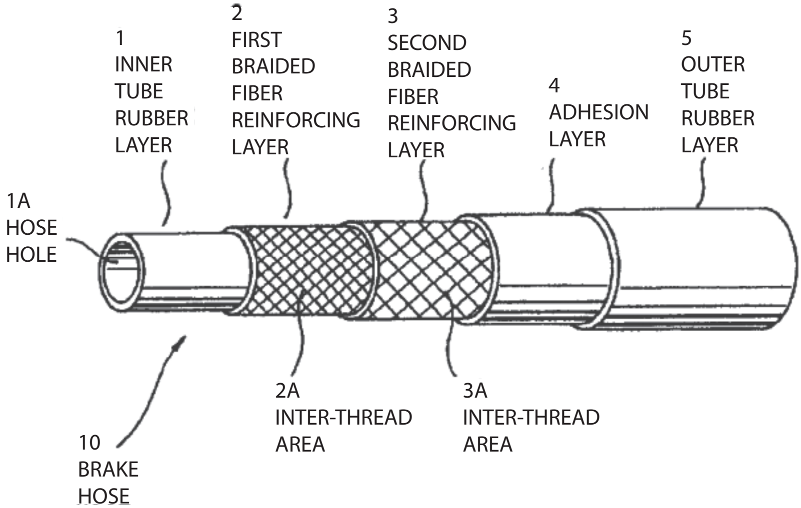

Figure 4.16 Multilayer brake hose [392]

4.39.8 Power-Steering Hose

Tearing energy values that correlated well with a previously developed model were involved in work to improve power-steering hose [393]. It was found that attack by molecular oxygen led to additional crosslinking in the hose cover. Initially, an additive in the power-steering fluid caused more crosslinking in the hose tube than oxygen did. However, after additive depletion, the fluid acted to protect the hose.

Ford had intended to incorporate 80% steer-by-wire systems by the year 2012 [394]. It further committed to fit electric power steering (EPS) on 80 to 90% of its Ford, Lincoln, and Mercury automobiles by 2012.

4.39.9 Hose Design

Hose should be capable of conforming to the smallest anticipated bending radius without becoming overstressed [395]. Static wires and conductive rubber components are used in some hose to dissipate electrical charges that could be hazardous around flammable liquids. In contrast, nonconductive hose is used around power lines for reasons of safety. It is critical to properly identify hoses used in these specific applications.

An important consideration with a lined hose is the relative age resistance of the hose lining and the hose cover [396]. The lining of an older hose can crack when bent, with the defect hidden.

Hose designers try to design the neutral angle (54°44') into the carcass of hose [397]. At this angle, assuming no elongation of the reinforcement, internal pressure does not change hose length or diameter. Departure from the neutral angle causes

- hose length to increase, and diameter to decrease, for braid angles greater than neutral
- hose length to decrease, and diameter to increase, for braid angles less than neutral.

However, in multilayer hoses, inefficient stress transfer within the hose wall causes the inner layer of reinforcement to carry most of the load [398]. Hence, to optimize efficiency, not every layer should be assembled at the neutral angle.

4.39.10 Hose Manufacture

Three principal methods of hose manufacture are nonmandrel, flexible mandrel, and rigid mandrel [399]. Nonmandrel hose, which is formed by extruding a tube and cover without a mandrel for support, is generally used at working pressures less than 500 psi.

Lubricants for hose mandrels must meet several requirements that include inertness to mandrel material and rubber, lubrication provided over a wide temperature range, low toxicity, and water solubility [400].

Flexible mandrels are used to manufacture hose with more accurate dimensions. These can be fabricated from rubber or with a wire core to minimize distortion. The rigid-mandrel method is used for larger size hose when flexible mandrels become difficult to handle. Rigid cores are usually made from aluminum or steel.

4.39.11 Hose Failure

Replacement of hydrocarbon fuels with nonhydrocarbon fuels such as ethanol (gasohol) can result in hose failure. The ethanol caused greater swelling of traditional hose compounds based on NBR and ECO [401].

4.39.12 Hose Abrasion

Abrasion resistance of hose is an especially important property in sandblast hose [402]. NR used in this application provides excellent abrasion resistance. NR's good electrical resistance causes static electricity to build up; use of a conductive carbon black in the hose compound can correct this problem. NR is used in concrete-spraying guns because of its excellent abrasion resistance [403]. For comparison, steel nozzles used in spraying operations lasted only one day; rubber nozzle tips lasted a week or more.

Hoses are also used to suck diamonds from the seabed, where both sand and diamonds are very abrasive to the inner tube of the hose [404]. The hose used in this application must have good abrasion resistance, bendability, and flexural strength.

4.39.13 Medical Hose

PVC has been used for many years for flexible medical tubing because of its favorable balance of functional properties and cost [405]. Although early TPEs did not match the functional properties of PVC, they have significantly improved over time. Factors involved in medical hose applications include kink resistance, clarity, sterilization stability, and the feel of the hose.

Hose used in medical applications requires close dimensional control [406]. While 90% wall thickness was accepted earlier, 95% is now more the norm. Phthalate plasticizer use in hose is now being reconsidered because of its potential adverse effects.

4.39.14 Hose Identification Technology

Radio frequency identification (RFID) tags can identify, log, and track hose during manufacture [407]. Additionally, RFID can provide a complete history of all hose assemblies in a production facility directed toward hose management.

Articles initially made from Tracer Viton T-1 will fluoresce a light blue color until exposed to high temperature in a postcure oven [408]. High temperature changes the blue color to a permanent green color, except for exposure to certain strong acids, bases, and amines. The information obtained is useful for quality assurance purposes.

4.40 Expansion Joints

These are flexible connectors used with piping systems to relieve stress caused by temperature changes that occur in rigid piping systems [409]. Expansion joints also minimize vibration, sound, and transmission caused by vibrating equipment such as pumps and compressors.

4.41 Color

Specifying and agreeing upon a desired color is a major problem associated with colored compounds [410]. Color visualization software should aid in overcoming color problems. Color used for identification should be a readily recognizable shade to prevent recognition problems [411]. This is especially important for wire bundles where there may be a rainbow of colors.

Colored compounds should be mixed in a separate area remote from black-mixed compounds [412]. Where this is not possible, a clean-out batch can be used that can be incorporated later in less-critical compounds. Very low concentrations (about 5 phr) of a highly conductive carbon black can substantially improve the conductivity of a rubber compound without turning a colored compound black [413].

Use of blended colors can result in an unusual outcome [414]. EPDM roofing membrane in Oregon incorporated blue and yellow colorants to obtain a final green color in the membrane. After lengthy exposure to the sun the yellow faded and caused the membrane to turn blue. Ducks in the area saw the blue membrane as a pond and landed on it with interesting results.

Mining cables should be brightly colored for visibility in dim light [415]. A patent describes a self-healing additive for wire insulation using microcapsules containing reactants [416]. The reactants are released when the insulation cracks. Another reference describes polymer healing by olefin metathesis [417]. A special catalyst in polymers such as BR and NR repairs cuts and cracks in them at temperatures as low as 5 °C.

■ 4.42 Rubber-Covered Rolls

Rubber-covered rolls are fabricated from many different elastomers. Produced in a wide range of hardnesses, they are used in such diverse industries as paper making, printing, graphic arts, steel fabricating, and metal coating [418].

Rubber rollers vary widely, with some being as large as four feet in diameter; they can rotate with surface speeds of 60 mph in abrasive and caustic environments [419]. Consideration has been given to using replaceable sleeves on rolls [420]. Doing so could avoid removing and shipping entire rollers.

Meeting specific roll requirements requires a range of elastomers, for instance SBR and NR for paper mill rolls, NBR for printing and textile applications, and CR for steel mill rolls. Rolls used to drive paper must be abrasive resistant, a consideration that may dictate the use of polyurethane [421].

TPE is another candidate for building rolls, and machines for building rolls using TPE have recently improved substantially [422]. The cost for producing a 100 pound, 50 inch TPE roller was 23% cheaper than a TPU roller of the same size made with liquid cast polyurethane.

Interior roll temperatures in some applications can be more than 55 °C higher than those on the roll exterior [423]. Water can cool the core of rolls that operate under heavy loads, high speeds, or high ambient temperatures. Cooling also helps maintain adhesion that can decrease at high temperatures. Pulp and paper mill roll coverings should always be protected from freezing because differential expansion between the rubber cover and the metal core can crack covers and reduce adhesion. Other adverse factors include swelling of a roll covering, which can cause pocking in extreme cases, and chemical attack on the roll covering. Extraction of plasticizers can cause an increase in roll hardness. Light surface grinding of rubber will usually remove a degraded layer and permit return of a roller to service.

It should be noted that a roller that is statically balanced may be out of balance dynamically, an effect that becomes worse with increasing roll rpm. Adding counterweights to one or both ends of a roll can minimize dynamic imbalance. Rolls that operate at low rpm typically need only static balancing.

Rollers in the paper industry operate under extremely high forces, for example 1000 to 1500 pli and even 2000 pli [424]. The use of a very hard rubber compound helps limit strain under extreme loads.

Roll construction generally involves covering an adhesive-coated steel core with rubber, which needs to bond well to its core. Large rolls are generally fabricated with built-up calendered sheet, wrapped with fabric, and vulcanized in a steam- or a water-filled autoclave. Grinding the roll follows fabric unwinding, and small rolls are often molded rather than being built up.

Rolls built from strip are replacing those built with calendered sheet; some strip-building advantages follow [425]:

- adaptable to automation
- labor efficient
- scrap reprocessing capability
- rubber straining capabilities.

Disadvantages of strip building include extrusion problems with some compounds and witness marks at the strip junctions.

Some important rules to follow in maintaining a smooth-running roller/web process follow [426]:

- Control the time that a roller is in service.
- Avoid excessive roller deflection.
- Avoid slippage between roller and web.
- Mount rollers rigidly.
- Properly balance and align rollers.
- Choose a roller appropriate to an application.

A roller that has a larger diameter in the middle (axially) is said to have a crown. The crown provides proper tracking for fabric, and it also compensates for deflection that occurs in long rollers under load.

Polyurethane printing rolls can be made by casting into tubes containing a concentric core; materials with lower viscosities can be poured from the top into the space between core and tube [427]. As viscosity increases and/or roller wall thickness decreases, it can be advantageous to fill the mold from the bottom.

A small piston pump can overcome back pressure on small rolls. Excessive release agents used on molds can puddle at the bottom of a mold and cause surface defects [428]. Drum heaters are not recommended for heating polyurethane prepolymers because excessive localized heating can cause a loss of isocyanates and therefore, a viscosity increase.

4.43 Wire and Cable Coating

Rubber compounds for wire and cable are mainly used as jackets and insulation [429]. Jackets provide resistance to abrasion and the elements; insulation provides high electrical resistance that is retained after aging and at elevated temperatures. Because spark plug wires can experience different temperatures at different locations in an engine compartment, more expensive silicone elastomers might be used in the region of the hottest cylinders [430].

A range of EPM and EPDM polymers are available for formulating wire and cable compounds [431]. Physical properties of these compounds can easily be tailored using simple binary blends of metallocene and conventional Ziegler-Natta EPDM polymers, which provide a cost-effective and practical approach to improving medium-voltage insulation applications. EPDM provides a desirable combination of properties in these applications, including serviceability over a range of high and low temperatures, ozone resistance, and superior wet or dry electrical properties [432].

Sylgard HVIG high-voltage insulation coating has been used for many years as an electrical insulator coating in high-voltage applications [433]. It protects insulators against industrial pollutants, salt spray, and even desert sand, which can lead to costly power interruptions in electrical distribution systems. It offers long-term cost advantages over other protection methods such as water washing and grease.

4.44 Cellular Rubber

Cellular rubber can be either an open cell or closed cell [434]. Sponge rubber is made by incorporating a gas-producing chemical (blowing agent) into a compound such as sodium bicarbonate that expands during crosslinking. The rates of crosslinking and blowing must be carefully balanced because crosslinks must support cell walls as they form. Fabric molded on either surface of sponge rubber allows gas to escape and imprints a sponge surface. Die-cut articles will have open cells on all cut edges.

Sponge molds are only partially filled with compound so as to provide for expansion of a compound. Trapped air, often a problem with this process, can be alleviated by generous use of an inert dusting agent such as talc, mica, or starch. However, removal of the agent from the article is a downside for this approach. Articles can be molded with a thin sheet of a solid rubber on the faces of the sponge rubber for some applications.

Zinc oxide, zinc stearate, and urea speed the decomposition of blowing agents such as azodicarbonamide [435]. Barium stearate, calcium stearate, citric acid, and triethanol amine are moderately effective for this purpose.

■ 4.45 Hard Rubber

Hard rubber (ebonite), used considerably less than in the past, still finds some markets. Reaction of rubber with about 25 to 45% sulfur for a long time produces hard rubber that should not be used at temperatures above about 70 °C [436]. Although hard rubber adheres naturally to iron and thus forms a good lining material for chemical plants, it has been largely displaced by other materials. Ebonite can be molded to shape or machined. Because of its high hardness, screw threads and undercuts can be readily formed on it [437].

■ 4.46 Rocket Insulation

NBR compounds are used in solid rockets to insulate a rocket case from the intense heat of burning propellant [438]. Because NBR typically has a nontacky surface, it is generally wiped with an appropriate solvent to improve tack prior to adhering it to the rocket case. It is important to allow sufficient time for the solvent to evaporate to avoid porosity formation that would adversely affect subsequent performance of the insulation in service. Figure 4.17 shows trowelable rocket insulation that fills the "V" grooves in prevulcanized NBR rocket insulation for large rockets [439].

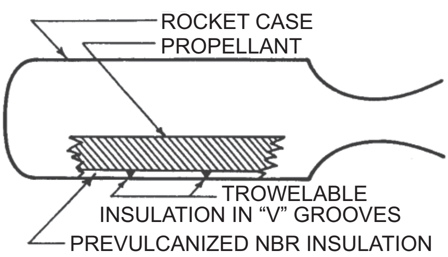

Figure 4.17 Rubber insulation installed in a rocket case [439]

Boric acid in the trowelable insulation permitted the insulation to function at 5000 °F in service; without it, the insulation rapidly ablated. Addition of hollow glass spheres to the composition significantly reduced the specific gravity of the insulation [440]; addition of a chemical blowing agent that expanded in service also improved performance [441]. Rubber that contains a conductive carbon black can be used in rocket insulation to detect a pending failure [442]. The carbon black can provide a range of resistivity of more than 16 orders of magnitude [443].

4.47 O-Rings

O-rings are used in wide-ranging applications that include seals for sprinkler heads [444]. Their use for this purpose resulted in a recall of several million sprinkler heads because the O-rings in the sprinkler heads may have corroded over time due to salt, corrosion, and other contaminants. These elements could potentially prevent activation of the sprinkler heads during a fire.

4.48 Earplugs

The silicone rubber earplugs shown in Fig. 4.18 illustrate the balance obtained among several factors [445].

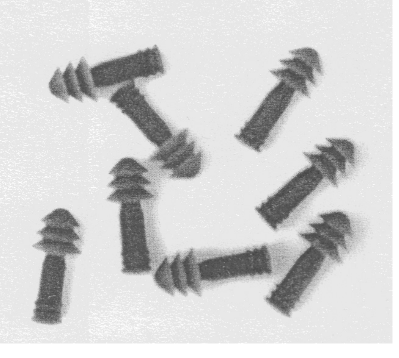

Figure 4.18 Soft silicone earplugs [445]

They are required to be soft (20 Shore A Durometer), have high tear strength, low scrap values, and short cycle times, and avoid mold fouling. Using Shin-Etsu KE2004-20 silicone, desired low scrap values were obtained without having to redesign the mold, which would have cost between $70,000 and $100,000.

4.49 Testing

Tensile tests, widely used to determine the effect of different compounding ingredients on the behavior of rubber compounds, are good for controlling product quality [446]. They are sensitive to changes in manufacturing and processing conditions that can cause undercure, overcure, or the presence of foreign matter.

However, tensile tests are overrated because they cannot be used in design calculations for rubber products. Many rubber products, for example O-rings, belts, mountings, and packings, are subjected to a maximum tensile stress in service of about 1 MPa. Further, the ultimate tensile strength of a compound depends as much on contamination and grit inclusion as it does on inherent compound design [447].

Ideally, tests chosen to characterize rubber would yield both functional and quantitative information that is readily useful to design engineers [448]. Rubber properties are often not well understood by engineers who are more familiar with steel and concrete properties. Purchasers of rubber products often overspecify tensile properties and unnecessarily increase product costs. Hence, rubber specifications should be performance based.

4.50 Dip Molding

By this technique, low-viscosity materials deposit on a form that is dipped in a suitable liquid polymer composition [449]. The thickness of material deposited can vary substantially and depends upon material and processing factors. Discussed here are two materials, latexes that produce thin coatings and plastisols that produce substantially thicker coatings. Dip-molded products include gloves, condoms, bellows, sleeves, balloons, boots, and coated handles.

4.50.1 Latex

Natural rubber and CR latexes are used to form a variety of products by dip molding. While NR latex is predominantly used in the manufacture of dipped gloves, HNBR is also used. An NR latex formulation for gloves could typically contain about seven or more ingredients, some that are incorporated in the latex as a dispersion. However, other ingredients such as ultra-accelerators might be water soluble.

Latex dipping represents nearly 50% of the worldwide consumption of NR latex that is used to produce a range of products. Three dipping methods are straight dipping, coagulant dipping, and heat-sensitive dipping.

In straight dipping, a clean, dry form is immersed in the formulated latex to the required depth, withdrawn slowly, and then dried [450]. This method is normally used for thin-wall articles such as condoms. Deposit thickness, which depends upon compound viscosity and total solids, is about 0.002 in. (0.05 mm) per dip. Repeated dipping increases film thickness before final drying and vulcanization.

Coagulant dipping increases thickness. A clean dry form is first dipped into a coagulant solution, withdrawn, and then dried. Subsequent insertion of the coagulant-coated form in the latex further increases film thickness up to 0.020 in. (0.5 mm) per dip. Coagulant dipping is used to produce thicker articles such as balloons, gloves, and catheters.

Heat-sensitive dipping consists of immersing a clean dry form heated to 60 to 80 °C in compounded latex to the required depth. Immersion is followed by slow withdrawal of the form and then drying and vulcanizing an article. Additives, such as polyvinyl methyl ether, cause the latex to gel at high temperatures to produce films that can be as thick as 0.080 in. (2 mm). Repeated introduction of hot forms into the latex raises latex temperature, and this can cause latex instability unless sufficient cooling is employed. Heat-sensitive dipping is used to produce thick-walled articles like footwear and electricians' gloves. Some latex products like gloves may be chlorinated or brominated after vulcanization to reduce their coefficient of friction.

Dipped articles are usually leached (washed with water) to remove water-soluble materials. Leaching is normally carried out on the unvulcanized wet gel using hot water at about 60 °C. A cold-water leach is used with some heat-sensitive formulations to thoroughly remove the heat-sensitizing agent. Leaching could also remove water-soluble proteins known to cause sensitizing reactions in some individuals.

Forms for dipping in latex are made from a variety of materials that include porcelain, glass, and metal. Copper must not be used in a form as it can promote rubber oxidation. Because the molded article must be stripped off its form, the open end of the article must stretch over the widest part of the form. As a general guide, the largest cross-sectional area of the form should be no more than six times that of the open end of the article, and manufacture of articles is made easier by limiting this ratio to three.

Defects in latex barrier articles such as condoms and gloves are of special concern because of the transmission of human immunodeficiency virus (HIV). Air bubbles that may have ruptured during leak testing appeared to be the most common defect in gloves. Careful control of process parameters can minimize defects associated with bubbles and inclusions. Further, careful handling procedures after dipping can minimize defects caused by abrasions.

4.50.2 Plastisol

Either cold or preheated forms can be dipped in a plastisol formulation to form an article, after which heating fuses the plastisol. Repeated dipping increases coating thickness, and the molded article is stripped from the form after fusion and cooling. Items such as wire and screening may be coated in a continuous process, and plastisol formulations can be modified to resist dripping.

Coatings can be retained on their forms by mechanical locking or by the use of an adhesive, as for example in the production of a tool handle. Inclusion of a crosslinkable epoxy resin in a plastisol can produce a strong bond to metal. Hot dipping, preferable for metal coating, can cause blobs of partially gelled (rubbery) materials to form because of repeated heating. Table 4.9 shows the effect of temperature on viscosity of a typical plastisol, after seven days at the indicated temperature [451].

Table 4.9 Effect of Temperature on Plastisol Viscosity

Temperature, °C	Viscosity, Pa · s
23	18
35	54
50	400
70	Gelled

4.50.3 Materials

Vinyl plastisol formulations usually contain fillers, stabilizers, and other additives that can provide a wide range of properties that include hardness from 40 to 93 Shore, weathering and cracking resistance, good dielectric strength, and gloss or matte surface.

Formulations can be adjusted to control other properties such as compression set, flexibility, density, odor, abrasion resistance, and stain resistance. Fillers in plastisols mainly reduce costs, but they can also reduce surface tack in some highly plasticized compositions. Various forms of calcium carbonate are the most common filler for plastisols. Oil absorption of fillers is an important factor because it affects viscosity of the formulation and therefore processing behavior.

4.50.4 Processing

The dipping process for plastisols is adapted from latex technology. Forms may be immersed in the plastisol at ambient temperature, or they may be preheated to a temperature of 100 to 160 °C. Too-rapid immersion of the forms can cause air entrapment and the formation of bubbles. The coating thickness deposited on a form depends upon factors that include

- viscosity of the plastisol formulation
- temperature, heat content, and the shape of the form
- immersion time
- rate of withdrawal of the form from the formulation.

Low shear rates occur during withdrawal, and associated viscosities are generally in a range of 1 to 15 Pa · s. Flow marks can result from withdrawing the form too rapidly. Shear thinning and associated lowered viscosity in a plastisol can cause the formation of teardrops. Shear thickening in a plastisol can be advantageous because it increases resistance to dripping.

4.50.5 Design, Products, and Applications

Dip-molded plastisol articles lend themselves to the production of hollow complex-shaped articles with undercuts. These articles are difficult to produce by other methods such as injection molding because of problems with removing articles from cores that form their interiors. Articles with wall thicknesses between 0.030 and 0.375 in. can be produced, and tolerances are normally ±0.010 in. Articles with internal diameters less than 0.125 in. are said to be impractical to produce in production quantities. The use of shallow rounded and properly spaced convolutions in a bellows results in more uniform wall thickness. These features also facilitate removal of a bellows from its form.

Dipped articles such as bellows do not have a parting line that is associated with injection-molded articles. Examples of other plastisol-based products are flexible ductwork, electrical outlet covers, power-tool covers, gear-shift boots, and grips for handles.

A knurled exterior surface can be incorporated on grips for handles by using a knurled form and then turning the molded grip inside out during stripping of the article from its form.

It should be kept in mind that even small variations in gelation and rheological characteristics could substantially affect plastisol thickness and uniformity. The troubleshooting guide in Table 4.10 addresses these and other issues [452].

Table 4.10 Dip Molding: Selected Problems, Likely Causes, and Solutions

Problem	Likely Cause	Solution
Nonuniform thickness	Incomplete drainage	Increase time for drainage
	Poor gelling behavior	Use faster solvating plasticizer
Variable coating weight		
Cold dip	Change in rheology of plastisol	Use higher MW resin or slower solvating plasticizers
Hot dip	Inadequate control of preheated parts	Heat parts to a uniform temperature
Sagging	Viscosity too low	Incorporate thixotrope
Bubbles	Inadequate deaeration	Improve deaeration process
Pinholes in thin coats	Poor wetting of mold surface	Lower viscosity of plastisol

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5 TPE Materials and Compounds

5.1 Introduction

Thermoplastic elastomers (TPEs) are rubbery, two-phase materials that can be fabricated like conventional thermoplastics but have the performance characteristics of a TSE [1]. TPEs are self-reinforcing, generally from two or more intermingled polymers that act as separate phases [2].

Among TPEs are thermoplastic vulcanizates (TPVs) and thermoplastic olefins (TPOs). TPVs contain a vulcanized phase; TPOs are a general class of unvulcanized olefinic TPEs [3]. They are defined as blends of various olefinic semicrystalline plastics and amorphous elastomers. Common among these are blends of polypropylene and ethylene propylene copolymer.

Invision®, a higher modulus TPO, provides 33% greater stiffness in sheet products, which favors a thinner gauge and associated lower cost [4]. It is said to possess the highest stiffness-to-ductility ratio available in a TPO material. A new high-efficiency PP impact modifier has been developed for TPOs that is said to improve ductility in TPOs based on either PP homopolymers or impact copolymers [5].

Lower processing costs are associated with TPEs relative to TSEs. TPE molding cycles are often measured in seconds while those for TSE are typically measured in minutes, with some TSE molding cycles being hours long. On the negative side, the thermoplastic nature of TPEs limits their ability to function at higher temperatures compared to TSEs. Process equipment for TPEs should be heated to a temperature at least 20 °C above the service temperature of the block polymer or the melting point of the polymeric additive, whichever is greater [6].

5.2 TPE Types

5.2.1 TPV (Thermoplastic Vulcanizate)

A wide range of TPVs is available and new ones are constantly becoming available; their annual growth rate is significantly higher than other TPEs [7]. Some provide heat resistance up to 150 °C, and these are used in applications such as vibration damping cuffs for automotive air ducts, industrial grips, and seals [8].

TPEs have been designed to comply with regulations aimed at preventing the transmission of "mad cow disease" [9]. They are available over a Shore A hardness range of 45 to 80 and are said to contain no animal-derived materials, such as lubricants based on beef tallow.

5.2.2 SBC (Styrenic Block Copolymer)

Some TPEs such as SBCs are compounded with oils, plastics (polystyrene and polyethylene), and fillers, thus reducing compound cost [10]. SBS (styrene butadiene styrene) is a widely used SBC that contains styrene end blocks and a polybutadiene center block that imparts rubbery behavior [11]. SBCs are very compatible with mineral oils, and compounds containing as little as 5% SEBS (see Section 5.2.3) have been used in several applications. The remaining 95% was 90% mineral oil and 5% wax. Some injection-moldable TPEs are remarkably soft—one is gel-like with a hardness of only 2 Shore A.

Midblock sulfonated copolymers are said to provide excellent performance in water transport, chemical resistance, and selective gas permeability [12]. They make it possible to desalinate water without removing the chlorine.

5.2.3 SEBS (Styrene Ethylene Butylene Styrene)

The central EB block provides improved polymer stability relative to SBS. It is important not only because of stability considerations, but also because it determines the SBC minimum use temperature [13]. Another difference is that SEBS hardens sufficiently to demold without distortion at a temperature of about 100 °C, whereas SBS has to cool to about 70 °C to reach this condition [14].

Olefinic TPEs originally consisted of rubber-modified PP and TPV [15]. More recently, new types of olefinic elastomers that can be used independently have supplemented these. For example, olefinic elastomers are replacing costlier and heavier TPUs in automotive applications.

Ultrasoft, gel-like TPE based on SEBS is used in medical applications [16]. Too soft to be measured on the Shore A scale, the polymers are measured on the Shore OO scale. Pellets of the material are said to flow freely even at this extremely low hardness. Both size and shape of pellets are important in processing operations such as extrusion and injection molding [17]. It is said that a general-purpose screw will melt almost any polymer if the pellets are the same size, shape, and cut. Pellets provided by a supplier should be inspected for uniformity.

5.2.4 TPU (Thermoplastic Polyurethane)

A typical TPU consists of crystalline (hard block) and amorphous (soft block) phases [18]. The hard segments determine the modulus, hardness, upper use temperature, and tear strength; soft segments determine the elastic and low-temperature properties. TPUs demonstrate very low coefficients of friction against other surfaces [19]. Since TPUs contain ester or ether linkages, they are subject to hydrolysis, with the ester-based materials being the most sensitive to hydrolysis. Carbodiimides that act as acid acceptors effectively minimize hydrolysis for ester-based TPUs [20].

Injection molding of soft TPU can be difficult because softer TPUs were earlier developed as hot-melt adhesives, and these typically contained plasticizers [21]. Estane TPU that is free of plasticizers can be used for overmolding articles. It is said to adhere to common substrates like ABS and polycarbonate.

When molding TPUs (and other polymers), lower-tonnage injection-molding machines can be advantageous [22]. For example, a bad cavity in a four- or eight-cavity mold means shutting down 10% or less of productive output. Shutting down a much larger mold containing a bad cavity can shut down the total molding operation.

5.2.5 TPO (Thermoplastic Polyolefins)

In contrast to the TPVs that contain a vulcanized phase, TPOs are a general class of unvulcanized olefinic TPEs. They are defined as blends of various olefin semicrystalline plastics and amorphous elastomers. Common among these are blends of polypropylene and ethylene propylene copolymer. TPOs are reportedly preferred materials in automotive applications because of their overall cost-performance advantages and versatility in meeting customer needs. They are said to provide better design flexibility and low-temperature performance than thermoplastic alloys.

TPO automotive fascia and bumpers represent a large segment of injection-molded automotive articles. Thinner cross section TPOs permit reduced weight; however, they can result in higher scrap levels because some TPOs have higher-than-desirable viscosities, which can make mold filling more difficult. Carbon filler produces a conductive surface that permits painting without a primer or an adhesion promoter.

5.2.6 COP (Copolyester)

Copolyester TPEs commonly contain blocks of alkylene terephthalate that crystallize to form hard domains. Long chain poly(alkylene oxide)s, esterified to phthalates, form the soft or elastomeric segments [23]. The alternating hard and soft blocks result in higher-hardness TPEs (about 80 to 90 Shore A) relative to conventional TSEs.

Design of blow-molded CVJ boots significantly affects their performance [24]. Reducing wall thickness of a boot by 50% and relocating hinge points can substantially improve boot performance.

Improved TPE performance is expected today [25]. The trend away from paint has produced new metallic-pigmented TPOs that are beginning to appear on smaller articles. Molded-in color is now preferred.

■ 5.3 Drying

TSEs, because they are typically processed at temperatures well above 100 °C, do not require drying before extrusion, molding, and so on. The need for drying different types of TPE varies, but when needed, drying of pellets is important from both a safety and a functional standpoint [26]. TPOs, while generally not hygroscopic, may require drying, which should be conducted according to supplier instructions. TPVs can absorb sufficient moisture to cause processing problems such as porosity and a rough surface appearance.

With hot-runner injection molding, discussed next, moisture can cause a dangerous buildup of high pressure. Dry TPVs can rapidly pick up moisture, depending upon the specific TPV.

Among several polymer combinations that should be avoided are [27]

- PVC and soft-touch materials such as TPV
- Acetal and some TPV
- Alcryn TPE and TPV or acetal.

Both the rate of moisture absorption and the equilibrium moisture content differ substantially for different elastomers. To minimize moisture pickup during shipment and storage, TPEs are placed in bags with a built-in moisture barrier. The bags should be stored in a cool environment, and they should be sealed or securely closed to control or prevent moisture absorption.

Moisture in TPEs can cause porosity, poor integrity, rough surface appearance, and poor dimensional control. It can cause a dangerous buildup of high-pressure steam during hot runner injection molding [28]. When drying TPEs such as TPUs and TPVs with desiccants, the condition of the desiccant should be checked every six months because these materials can emit volatiles that can render the desiccant ineffective [29].

5.4 Cost

Although the cost of precompounded TPVs might be higher than their TSE counterparts, the cost difference might be offset by shorter molding cycle times, increased recycling of scrap, and lower costs for quality control [30].

5.5 Service Temperature

TPVs provide excellent resistance to high-temperature aging for temperatures below their crystalline melting point. The thermoplastic phase of a TPV determines susceptibility to oxidative attack, which could be about 125 to 135 °C for polypropylene [31]. Polypropylene homopolymers melt at about 160 °C [32].

Zeotherm 110-70 B engineered TPV is said to provide heat resistance up to 150 °C along with damping of noise and vibration [33]. Potential applications include automotive air ducts, vibration mounts, fasteners, industrial grips, and pass-through plugs.

5.6 Color

Color can be incorporated in EPDM-based TPVs over a wide range of hardness with the exception of appliance white [34]. A solid pellet with about 50% pigment in a carrier resin compatible with TPV is preferred, with polypropylene being a desirable choice. Polystyrene, PVC, and polar resins are unacceptable. The low level of colorants typically used does not affect physical properties. Metallic stearates or stearic acid should not be used in the preparation of color concentrates for TPUs [35].

Even color concentrates can be difficult to uniformly disperse, and it is said that machine builders have done very little to investigate newer screw-design technologies directed toward more uniform dispersion [36]. Consequently, processors continue to struggle with defects caused by poor melt uniformity.

Ingredients can interfere in colored rubber compounds, especially TSE compounds. Age protection systems are among the worst offenders, with nearly all amine antioxidants causing significant staining. Phenolic antioxidants minimize this problem but are less effective antioxidants. Blending rubbers such as SBR and NR with EPDM and CR can improve degradation resistance and reduce the need for antidegradants. Curatives can cause color problems similar to those associated with protective systems. Because of these factors, coloring of TSEs is generally more problematic than coloring TPEs.

Titanium dioxide is probably one of the most common coloring materials for rubber compounds because it imparts excellent hiding power and is frequently used with other fillers to brighten color [37]. It is available in two crystalline forms, rutile and anatase, with the anatase providing 20% better initial whiteness. However, vulcanizates containing rutile show improved weathering.

It is unnecessary to start with a stark white base when compounding colored compounds [38]. For example, when a bright green color is needed, first incorporate a low-cost green oxide and then add an expensive organic green color masterbatch. Doing this is said to cause the sunlight-faded color to change from a bright green to a dull green rather than to white.

Both processing and curing temperatures can critically affect colored compounds that incorporate organic color pigments [39]. Temperatures above 325 °F are not recommended; however, higher temperatures can be used when color pigment is carefully selected and tested. Color pigments are usually incorporated at 2 to 5% based on total compound weight. Organic pigments provide brighter cleaner colors but are more expensive.

Dry colorants are not recommended for Kraton TPEs [40]. When using liquid carriers for colorants, paraffinic carriers are compatible, but aromatic carriers and DOP affect Kraton.

Synthetic polyisoprene is said to maintain a more uniform color and to be less sensitive to discoloration from heat during processing [41]. Some SMR and SIR types of NR may contain stabilizers that turn pink upon aging.

Other recommendations for the use of color include [42]:

- Use pale crepe in NR compounds.
- Avoid the use of high sulfur levels.
- Avoid or minimize the use of sulfenamide base accelerators.
- Use oil that has a minimum content of polar compounds.
- Clean molds regularly to avoid surface discoloration caused by mold fouling.

Yellowing of latex examination gloves commonly occurs as a result of copper contamination during handling in the factory [43]. Contamination can occur through handling of copper coins before wearing the gloves. Thorough hand washing is suggested to avoid the problem.

D.A. Smith provides an excellent in-depth review of color in rubber, and he highlights some of the reactions that can occur among compounding ingredients [44]. For example, zinc stearate can exchange zinc ions with calcium in a toner such as calcium lithol red, resulting in a bluish color. Additional useful references for color are 45 and 46.

Incorporation of color in some rubber articles can be problematic [47]. San Francisco considered a ban on colored tires because they can deposit colored skid marks.

5.6.1 Painting

Because of inventory considerations, it may be desirable to color an article by painting or coating rather than to impart color in an article [48]. The surface of a TPE article typically must be altered to improve its adhesion to paint or a coating. This can be done by treatment of the surface with a benzophenone solution, followed by UV irradiation; treatment with plasma; or flame treatment (if permitted in the workplace) [49].

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6 TPE Processes and Equipment

Among the substantial differences between processes and equipment for TPEs and TSEs are the thermal profiles for the two materials. During molding, a TPE increases in viscosity as it cools in its mold. In contrast, higher temperature first decreases viscosity of a TSE in its mold, and then crosslink formation increases its viscosity.

After a TSE extrudate exits its die, increasing temperature decreases both viscosity and dimensional stability. Then, with further heating, crosslinks form and stabilize TSE dimensional stability. After a TPE extrudate exits its die, temperature decreases, accompanied by increasing viscosity that stabilizes profile dimensions.

This is why TSEs are only rarely blow molded; the extruded hot TSE parison is dimensionally unstable relative to a TPE. The two major processes for shaping TPEs are injection molding and extrusion.

6.1 Injection Molding

Shortening an injection cycle for a TSE by 1 s is typically insignificant; however, the same change for a TPE can be significant because of the much shorter cycle time for a TPE [1].

In contrast to TSEs where compression and transfer and injection molding are all important, injection molding dominates for TPEs [2]. However, compression molding can be used to prepare standard TPE test specimens. When doing so, it is recommended that pellets be heated for 40 min at 190 to 215 °C to generate a melt, which is then compression molded at 165 to 190 °C at a pressure of 200 to 400 psi. About 10 % excess TPE should be provided to ensure mold filling.

Injection-molding machines for TSEs and TPEs differ significantly. Hydraulic clamps dominate on TSE injection-molding machines. Those for TPEs include but are not limited to toggle, hydraulic, and combined hydraulic-mechanical clamps. Toggle clamp advantages are speed of operation, instantaneous locking force, lower initial cost, and reduced hydraulic cylinder size to activate the toggle relative to an all-hydraulic clamp [3].

6.1.1 Injection Molding Machines

Safety considerations are paramount in the operation of injection-molding machines and other rubber processing equipment [4]. Safety concerns in injection molding involve a multitude of factors that include materials, mold design, machine operation, part design, mold construction, maintenance, and housekeeping.

Safety problems with imported machinery are a current concern [5]. For example, 90% of imported rubber and plastics machinery didn't meet European safety standards, and about 10% of this machinery was returned to China. This problem may be partially due to China's rapid development relative to its ability to write standards.

Suppliers of TPEs provide safety guidelines, handling procedures, and processing precautions for their respective materials, for example Hytrel. Contact suppliers of TPEs and processing equipment for current safety information. Safety is a primary concern in a wide range of rubber-related operations [6]. Table 6.1 lists some safety problems and potential solutions to these problems.

Table 6.1 Safety Problems and Potential Solutions to These Problems

Safety Problem	Potential Solution
Lifting bales from pallets on floor	Use vacuum lifter
Handling sacks of powder from pallets	Lower sack weights; bulk deliveries; vacuum lifting; job rotation during shifts
Separating sheets of compounded rubber for further processing	Separate rubber sheets with reusable liners
Operating a two-roll mill using manual cutting and takeoff	Use stock blender to avoid cutting, lifting, and reaching
Repeated mold lifting in and out of presses	Use lifting tables
Repetitive injury caused by trimming flash	Trimless molding; cryogenic deflashing

Safety considerations for Santoprene include purging all PVC (polyvinyl chloride), acetal, and other polymers from an injection unit. Purging can be done using polypropylene or polyethylene. Check and ensure at least daily that all safety systems—hydraulic, electrical, and mechanical—are operating satisfactorily. Follow all safety recommendations from equipment manufacturers and wear eye protection and safety shoes in processing areas.

During hot-runner molding, moisture can cause severe problems if moisture is converted into steam [7].

Users of materials and equipment must satisfy themselves that operating procedures comply with current applicable government procedures, and further, they must provide a safe workplace. Handling and processing precautions for Hytrel consider oral toxicity, static electricity, burns, and fumes, along with other factors. For example, the incorporation of materials with a pH of less than 7, such as clays with a pH of 4.5 to 5.5, promote decomposition of Hytrel. Compounding activities must consider label directions and handling precautions from all ingredient suppliers.

Tetramethylthiuram disulfide (TMTD) has been documented to react with ethanol to provoke a number of unpleasant symptoms that include a feeling of difficulty in breathing, throbbing headache, nausea, and vomiting [8]. An unpleasant surprise could result from having a beer after exposure to TMTD.

Enzymes in human skin convert the rubber chemical diphenylthiourea into metabolites that can cause contact dermatitis [9]. This problem sometimes occurs with workers handling neoprene.

A number of considerations concerned with injection-molding machines include clamp design and operation, with a major consideration being the clamp capability to provide the closure force required to resist the mold-opening force caused by pressurized melt in the mold cavity. Inadequate clamp force results in flashing and other problems. For a TPV, the clamp should provide sufficient force to keep the clamp closed when a mold contains melt pressurized to between 6000 and 10,000 psi.

Toggle clamps, although less expensive to produce than hydraulic clamps, require adjustment of both alignment and clamp force. In addition, toggle clamps require more maintenance than hydraulic clamps. There are relative advantages and disadvantages to clamp systems that incorporate single- or double-toggle systems. A single-toggle clamp distributes clamp forces more evenly across the clamp face than a double toggle because it concentrates clamp force nearer the platen center, rather than toward the platen edges. The single toggle's design is simpler and is said to operate at up to twice as fast as a double toggle.

L/D and compression ratio are two important screw characteristics that were defined and discussed earlier for TSEs. The L/D ratio affects inventory of polymer in the barrel and therefore affects the time it takes for the polymer to progress from the hopper end of the screw to the nozzle. Use of higher L/D ratio screws with TPEs provides better mixing and a more uniform melt temperature. For these reasons and because TPEs do not scorch, L/D ratios for TPE screws are higher (12:1 and higher) than L/D for TSE screws; current trends are toward even higher ratios. Recommended L/D ratios for screws for Hytrel range between 18:1 and 24:1. Typical compression ratios range from about 2:1 to 2.5:1.

In a cold-runner TPE mold, the combined projected areas of cavities, runners, and gates, multiplied by the pressure, will yield the clamp force necessary to maintain mold closure [10]. Hence, a cold-runner mold for a plaque with combined projected areas of 40 in^2 (cavity 35 in^2 and runner 5 in^2), pressurized to 10,000 psi, would require a minimum clamp force of 400,000 pounds to keep the mold closed.

In contrast, in a TPE mold with hot runners, the pressure of the melt in the runner(s) does not tend to open the mold because cavity and runner areas are not additive. Hence, the force required to open a hot-runner mold with a cavity area of 35 in^2, pressurized to 10,000 psi, would be 350,000 pounds. Factors such as clamp force and melt viscosity affect product cosmetics.

Other factors, such as the maximum stress allowable in mold components without damage, determine maximum clamp force. Clamp pressures in excess of 20,000 psi or 10 tons per in^2 of contact area begin to crush steel molds [11].

As with TSEs, machine size and its effect on economics are important considerations. Contrasting in size are a 5000 ton injection-molding machine for TPE air dams for automobiles and a 34 ton machine used for molding extremely small parts. Articles are being molded that are as low in weight as 0.007 g, with the runner system weight being over 50 times that of the molded articles. The following criteria are suggested when selecting a machine for injection molding TPEs [12]:

- annual production requirements
- shifts per day and reject rate
- number of cavities
- total projected area, including the distribution system
- shot size and mold size
- cycle time.

Because the cycle time of TPE is so short, it is especially important. A simple calculation shows that a reduction in cycle time from 10 to 9 seconds can save 800 hours/year. At a machine-hour rate of $ 48.50 this represents a savings of $ 38,800, assuming profitable use of the saved time. Small machines are said to reduce molded-in stresses, improve dimensional stability, and reduce the hobbing of vents.

As additional advantages, smaller machines will

- reduce interference among important mold features (such as cooling channels and ejectors) that compete for space
- facilitate just-in-time production
- shorten time for disassembly of screw and barrel for cleaning
- shorten mold building time and make mold handling easier
- provide greater flexibility in production.

Location of cooling fluid channels in too-close proximity to the mold surface can cause cold spots that lead to molding faults, such as weld lines [13]. Mechanical considerations require that sufficient metal thickness be provided to withstand the considerable pressure of the melt in its cavity. However, too-thick metal can cause unacceptably long cooling times.

Factors concerned with mold design and cooling behavior follow [14]:

- An excessive numbers of bends in a cooling circuit require additional pumping power.
- Limit the number of bends in one circuit path to 15.
- Excessively high cooling velocities, for example, those greater than 2 to 3 ft/s cause undesirable pressure drops and higher pump pressure.
- Limit cooling line length to 4 to 5 ft.
- Use uniform cross-sectional areas for cooling lines.
- Clean coolant channels before plumbing them into the cooling system.
- Make the inside diameter of pipe fittings at least as large as the cooling system diameter to minimize resistance to flow.

Flow in coolant channels should nearly always be turbulent to minimize cycle times [15]. Turbulent flow is relatively easy to achieve in coolant channels with small diameters; higher flow rates are necessary to achieve turbulent flow in larger-diameter channels. The Reynolds (R_e) number is a measure of whether flow is laminar or turbulent:

- Laminar flow occurs when R_e is less than about 2100 to 2300.
- When R_e increases above 2300, flow transitions from laminar to turbulent.
- Flow can be considered turbulent at an R_e above 3500.
- For efficient heat transfer, R_e should be at least 4000.

6.1.1.1 Specialized Machines and Techniques

Conventional machines inject a single TPE into a mold to produce a molded article. Specialized machines inject two materials and offer certain advantages, such as overmolding a TPE onto hard plastic. This technology is especially useful when the two materials are compatible and form a natural weld. An example is a black Santoprene TPE that is injection molded around a white polypropylene base with raised lettering to form a brake pedal cover.

Two-shot molding requires a machine with two independent injection units, wherein each unit injects a different material or color. Materials are injected through their respective runner systems simultaneously to form a good junction at their confluence. Two-shot injection is one of three co-injection techniques, the other two are sandwich construction and multishot injection. These techniques permit molding of complex and functional articles. They also eliminate the need for complicated assembly processes.

Injection-molding machines for co-injection of TPV facilitate quick color changes and can provide problem-free processing of polymers. Machines with a higher clamp force capability are useful for articles with thin walls, with a barrel capacity limited to a range between 1.3 and 4 shots. Molded articles containing two polymers are more difficult to recycle.

Overmolding a thermoplastic like nylon with a TPE can be problematic [16]. Nylon is extremely hygroscopic, and it also goes through post-molding crystallization, with both factors adversely affecting bonding to a TPE. Because of this, it is best to overmold the TPE immediately after molding the nylon substrate.

Weak weld lines that occur at the junction of two flowing fronts are affected by design, tooling, and processing [17].

Some articles are more tolerant of weld lines than others, and weakness occurs when the flowing fronts do not meld appropriately. It is important to locate gates so that the weld line is remote from the area of the article that experiences high stress in service.

Oscillating polymer streams at low frequency at their junction can improve properties of molded thermoplastic articles using a specially designed injection-molding machine [18]. This machine, equipped with two cylinders and pistons, forces melt through gates on either side of the junction of the polymer streams in a mold. Alternating pressure from these cylinders oscillates the polymer at the weld line in a push-pull action that results in shear thinning and an associated reduction in viscosity. Improved properties and weld line strength result from this action.

6.1.2 Machine Operation

Processing conditions for styrenic TPEs, TPOs, COPs, TPUs, and polyamides should be obtained from TPE suppliers for safe materials handling and optimum machine operation. Special attention should be given to material safety data sheets that can be provided by TPE suppliers.

An overview of the injection-molding process for TPEs suggests that the process should be relatively simple (compared to TSEs) because of a need only to convert TPE pellets to a melt, shape the resulting melt in a mold, and then cool the melt in a mold to produce a molded article. As the saying goes, “the devil is in the details,” and the following sections discuss some important details, drying being the first.

Suppliers often provide recommendations for nozzles for use with their specific TPEs. Conventional nozzles, those with reverse taper, or nozzles that offer positive shutoff are said to be satisfactory for injection molding styrenic TPEs. General-purpose nozzles of a standard size, with a 3 to 6 mm orifice, are recommended for TPVs. The nozzle orifice is generally slightly smaller than the sprue diameter.

General-purpose nozzles are not recommended because their land is said to be too long and because of dead space just inside the tip [19]. A free-flow-type nozzle tip or, if necessary, a reverse taper design is recommended. A nozzle tip should contact its sprue bushing on the inside of the radius, not the entire radius. The smaller contact area results in less heat transfer from nozzle to sprue.

Nozzles for copolyester (COP) should have a spherical tip with a 0.75 in. (19 mm) diameter. Tip diameter should be slightly less, 0.031 in. (0.8 mm), than that of the sprue bushing. A free-flowing nozzle with a reverse taper is recommended for TPU, and it should be equipped with a separate temperature-controlled heater band to prevent the TPU from freezing or drooling.

6.1.3 Drying

Appropriate pellet drying is important from both a safety and a functional standpoint, and it varies for different types of TPE. TPOs, while generally not hygroscopic, may require drying, which should be done according to supplier instructions. TPVs can absorb sufficient moisture to cause processing problems such as porosity and a rough surface appearance. With hot-runner injection molding—discussed below—moisture can cause a dangerous buildup of high pressure.

Dry TPVs can rapidly pick up moisture, depending upon the specific TPV involved. To minimize moisture pickup during shipment and storage, some TPEs are placed in bags with a built-in moisture barrier. Bags should be stored in a cool environment and be securely closed to minimize or prevent moisture absorption.

COP, being hygroscopic, can absorb sufficient moisture from ambient air in one hour to degrade it during processing. Degradation of a COP by hydrolysis is a factor to consider in addition to the physical effect of moisture absorption. A two to three hour drying period at 100 °C is typical. While the use of 100% regrind is possible, the virgin-regrind ratio must take into account any degradation of the regrind material and its subsequent effect on properties.

6.1.4 Barrel and Screw

Although SBS (Kraton D) and SEBS (Kraton G) are both styrenic TPEs, their processing temperatures differ. For injection molding in a reciprocating screw machine, the recommended range of barrel temperatures for SBS is 300 to 400 °F (150 to 205 °C), while that for SEBS is 400 to 475 °F (205 to 245 °C). These differences result from the stronger phase separation in the SEBS relative to the SBS, wherein the SEBS flows as a gel with a yield point. Hence, phase separation plays an important role in molding behavior. In addition, the unsaturation in the polybutadiene in SBS makes the SBS more susceptible to degradation, favoring lower temperatures for processing SBS.

Typical injection-molding conditions for different molding grades of Santoprene TPV are

- rear barrel zone from 350 to 380 °F
- center zone from 360 to 390 °F
- front zone from 375 to 390 °F.

Electrical resistance bands are typically used to heat extruder barrels for TPEs. A disadvantage of these is that they heat the barrel surface from the outside to the inside [20]. In contrast, an induction-heated barrel heats the barrel from the inside to the outside. It incorporates a layer of thermal insulation between a contiguous, helically wound induction heating coil and the barrel. Induction heating is said to use up to 70% less power than heater bands.

Nozzle temperatures from 390 to 410 °F are suggested, and typical mold temperatures are 50 to 175 °F for a range of TPVs. Mold temperature is important because it affects both the cycle time and the appearance of a molded product.

Typical barrel temperature ranges for different grades of Hytrel are

- rear zone, 310 to 440 °F
- center zone, 340 to 470 °F
- front zone, 340 to 480 °F.

Typical nozzle temperature range is 340 to 480 °F. Some grades of Hytrel have a sharp crystalline melting point that increases with both hardness and degree of crystallinity; melt viscosity depends strongly upon melt temperature. The needle of a pyrometer inserted into COP as it exits the nozzle can accurately measure the melt temperature.

Table 6.2 lists selected troubleshooting suggestions for injection-molded Hytrel [21].

Table 6.2 Problems, Possible Causes, and Suggested Solutions for Injection-Molded Hytrel

Problem	Possible Cause	Suggested Solution
Nonfill	Shortage of polymer	Check injection stroke and increase as necessary
Flashing	Injection pressure too high	Reduce injection pressure
	Warped mold platens	Check and refurbish as necessary
Warpage of molded article	Excessive cavity packing	Reduce injection pressure
Excessive shrinkage	Gates not frozen off	Increase time injection ram is forward
Burning or black specks	Polymer too hot	Reduce temperature

Barrel temperatures for TPUs are affected by factors such as the grade of TPU, part design, cycle time, and the ratio of shot to barrel volume. Temperatures for processing TPUs range from 350 to 400 °F. TPO feed throat temperatures must remain below 250 °F to avoid bridging.

6.1.5 Injection Rate

Different factors such as flow behavior of a TPE affect the choice of injection rate, and rates vary both within and among TPE classes. Moderate injection rates are normally used with Kraton D because it does not require high shear rates to attain low viscosity and good flow. Faster injection rates are desirable with Kraton G to promote good processing. The reasons for this are two-fold:

- Viscosity of the “G” is higher than that of the “D” over a wide range of shear rates.
- Increased shear rate reduces the viscosity of the “G” faster than “D.”

Generally recommended flow rates for TPV are 10 to 50 g/s/gate, with a fill time of 0.5 to 1.5 s. Injection rates for this and other TPEs should be sufficiently fast to prevent premature freezing of polymer in the gate(s) during mold filling, and mold venting should be sufficient to prevent air entrapment.

Mold design affects the selection of injection rates for COP. Rapid injection rates facilitate filling thin cross sections (< 0.125 in.) before increased viscosity prevents mold filling. An injection rate slow enough to prevent jetting is recommended for cross sections greater than 0.25 in. Avoidance of jetting favors the formation of smoother surfaces on molded articles.

6.1.6 Injection Pressure and Mold Packing

Use minimum pressure consistent with uniform filling of cavities. Again, mold design affects the molding procedure, and injection pressure can range from 5000 to 20,000 psi. Excess pressure often causes increased orientation and overheating of the polymer.

Retractable cores in molds are often required to form voids in rigid plastics. Side-action methods could be required to release rigid plastic articles from molds with undercuts. TPE articles that incorporate undercuts, because they are flexible, release more easily than rigid plastics. High injection pressures during the molding cycle can cause problems with side actions on molds and can cause deflections in mold components that affect mold operation.

Underpacking of TPV in a mold reduces contact between the hot TPV and its cool mold walls. Poor contact reduces cooling efficiency and can cause the following:

- excessive shrinkage
- voids in thicker cross sections caused by shrinkage
- sink marks in large surface areas
- poor appearance and poor molded article performance.

Overpacking can adversely affect subsequent service performance of a molded article, and for long production runs it wastes a significant amount of polymer. When the clamp stays closed during the packing stage as intended, practically no movement of material occurs.

Too-high injection pressures can cause Hytrel to stick in its mold cavity. Holding pressure, generally 50 to 70% of the pressure at peak fill rate, should be maintained until the polymer in the gate freezes and seals the gate.

The low-pressure molding characteristics of Lomod thermoplastic polyester affect the choice of a mold material. Kirksite is an inexpensive zinc alloy that was used with low injection pressures of 8000 to 9000 psi. One Kirksite mold produced over 28,000 air dams for the front of an automobile.

A simple and useful test to show the cavity-filling progression in both single- and multiple-cavity molds is to partially fill a mold and then gradually increase the shot size until the mold fills. This test locates the junction of flowing polymer streams so that vents can be effectively located to minimize trapped-air problems. The test also reveals the filling sequence in multi-cavity molds, to facilitate balanced flow.

Gases must exit a mold cavity during injection to attain the desired quality of molded articles [22]. It is said that molds that breathe well will run well. To do so, vents must be appropriately sized and located, and they must be kept open.

6.1.7 Clamp Pressure

Injection-molded Kraton compounds seldom require high clamp pressure. A range of 3000 to 6000 psi is usually sufficient to lock the mold and prevent flashing. Mold design and size are additional factors to consider. For Santoprene, a higher clamping pressure of 6000 to 10,000 psi for the projected area is recommended.

Pressure-sensitive paper, for example Pressurex paper, can be used between a mold clamp and its mold to determine uniformity of force across a mold surface [23].

6.1.8 Nonreturn Valve

Among the several functions of a nonreturn valve is the formation of a seal at very high pressures that prevents back flow of polymer into the screw during the injection-molding cycle [24]. A valve and its seat that have identical angles do not seat as well as valves and seats with an angular difference in their mating surfaces. It is suggested that the difference in angles be greater than about 2° to improve sealing.

6.1.9 Mold Temperature and Cooling Time

Cooler molds shorten cooling cycles within limitations. Excessively low temperatures increase shrinkage of cooled melt from the mold wall, thus reducing cooling rate and lengthening cooling time. Mold temperatures of 50 to 105 °F (10 to 40 °C) are favored for Kraton D compounds, while those for Kraton G should typically be 95 to 150 °F (35 to 65 °C). Higher mold temperatures promote flow, permit cavity filling at lower pressures, and produce more uniform surfaces on molded articles without significantly increasing cycle times. Typical operating conditions resulted in cycle times of 20 s for Kraton D and 17 s for Kraton G.

Mold temperatures for different Santoprene grades depend upon the grade chosen. For general-purpose Santoprene grades, mold temperatures range from 50 to 175 °F (10 to 80 °C). Higher temperatures of 140 to 210 °F (60 to 100 °C) are suggested for Geolast®. It should be remembered that article design strongly influences the practical mold temperature. For articles with long flow paths, mold surface temperatures should be 100 °F (38 °C) minimum. Too-cool molds may adversely affect appearance of a molded article. Table 6.3 lists selected problems, possible causes, and suggested solutions for injected-molded Santoprene [25]. A significantly expanded table is in the original reference.

Heat flows from a molten TPV through the mold wall as the hot TPV cools in a mold cavity, and a stream of coolant flowing through the coolant channels in the mold removes heat. Factors that affect cooling time include molded article thickness, thermal diffusivity, heat distortion temperature, and barrel and mold temperatures.

Some problems that occur with cooling channels are difficult to detect. For example, a metal turning can lodge in a cooling channel and reduce the intended amount of coolant flowing through the channel [26]. Excessive rusting or buildup of lime can

Table 6.3 Problems, Possible Causes, and Suggested Solutions for Injected-Molded Santoprene

Problem	Possible Cause	Suggested Solution
Flash on parting line of molded article	Excessive injection pressure	Decrease final injection speed
		Decrease hold pressure
		Increase clamp force
Flow lines in molded article	Incorrect mold functioning	Increase number of gates
		Ensure adequate location and number of gates
		Remove debris from mold surface
Drool from nozzle	Nozzle too hot	Reduce nozzle temperature
	Front zone of barrel too hot	Reduce front zone temperature
Article dimensions are too large	Mold is overpacked	Decrease mold temperature
		Decrease final injection speed
		Decrease back pressure

have the same effect. Deposits can be removed by a chemical treatment such as acid. Deposits can reduce heat transfer by as much as 30% when they are only 0.004 in. (0.1 mm) thick [27].

Mold temperature ranges of 80 to 100 °F (27 to 38 °C) are suggested for different grades of Hytrel. Lower mold temperatures reduce cycle time and facilitate ejection; higher temperatures improve flow and surface finish. A mold temperature of 80 °F (27 °C) gives the maximum rate of crystallization for Hytrel 4056, resulting in rapid stiffening of the molded article.

In contrast to crystallization, SBS stiffens in a cold mold because a polymer domain—polystyrene in the case of SBS—is cooled below its T_g. While the polybutadiene also stiffens at lower temperature, polystyrene stiffening is the dominant factor. Over a temperature range of 80 to 160 °C, the viscosity of polybutadiene changes less than ten-fold; over the same temperature range, the viscosity of SBS changes by 100,000 times. Hence, while crystallization is a controlling factor with crystallizing COPs like Hytrel, T_g is the controlling factor for amorphous TPEs like SBS. Relative to amorphous TPEs, crystalline TPEs require extra cooling capacity to remove heat of crystallization.

6.1.10 Heat Transfer

When a long narrow pin forms a deep narrow hole in a molded thermoplastic article, the pin can be mounted in mold plates at one end or two ends. In either case, heat transfer is poor along the axis of the pin. Thermal pins can greatly increase the rate of heat transfer and shorten cycle time [28]. Basically, they are sealed copper-alloy tubes filled with a conductive gas mixture, and they are inherently many thousand times more thermally conductive than copper.

Injection-molding factors such as mold temperature affect both processing behavior and end-use properties of a TPE. Specific injection temperatures were required to obtain maximum tensile strength and fatigue life for a TPU. Differential scanning calorimetry proved an excellent technique to detect optimum mold temperature; a temperature that also affected dimensional stability of the TPU for some applications.

Avoid overheating a polymer melt because significant TPU degradation could occur above 230 °C; polyester-based TPUs are generally less sensitive to overheating than polyether-based TPUs. Tinuvin PUR 866 is said to improve the durability and functionality of TPU [29]. It improves visual appeal for both pigmented and nonpigmented applications.

6.1.11 Mold Fouling

Mold fouling by TPEs is significantly less problematic than with TSEs because TPE molds operate at a considerably lower temperature than TSE molds; high mold temperature is a major cause of mold fouling.

6.1.12 Regrind

Regrind derived from Kraton sprues, runners, and improperly molded articles is completely recyclable. It can be ground and blended in any proportion with virgin material. Grinding of soft flexible articles necessitates the use of very sharp grinder knives.

Santoprene regrind can be reprocessed with virtually no loss of material properties. Although regrind levels of up to 100% have been used successfully, 20% regrind is generally recommended to ensure easy handling. Minimizing fine particles reduces interference with handling of the regrind in vacuum-conveying systems. Sharp grinder blades minimize the occurrence of fines.

A typical flexible production line for microcellular articles can produce about 5 to 10% scrap in the form of rejects, flash, trimmings, and so on. Scrap, appropriately treated and incorporated in virgin TPU, was blended and then extruded and pelletized to produce an injection-moldable product that demonstrated good physical properties relative to other elastomers.

6.1.13 Injection Molds

TPE injection molds range from simple to quite complex construction, and they generally incorporate significantly more off-the-shelf components than do their TSE counterparts.

6.1.13.1 Mold Material

An ideal mold exhibits a number of properties that include durability, good heat transfer characteristics, corrosion resistance, and very high stiffness.

Remember that material thickness, modulus, and design factors affect stiffness. Assume two steel strips with identical moduli, one 0.001 in. thick, the other 0.025 in. thick. The thinner strip can be easily bent back on itself to a small radius, and upon release it will elastically return to its original shape. In contrast, the much stiffer thick strip when bent back on itself remains permanently deformed, having exceeded its elastic limit.

Aluminum alloys have a modulus of elasticity only about one-third that of carbon steel, and increases in their section thickness result in significantly higher overall stiffness. An aluminum mold with the same design as a steel mold, subjected to the same clamp force, deforms more and is less durable than a steel mold.

Specialized high-strength aluminum materials with an as-supplied hardness ranging from 160 to 170 Brinell have been developed for molds. Hardness of these materials is significantly lower than that of prehardened P20-type steel for molds. However, the aluminum materials are considered adequate for many molding applications that involve low wear.

Although thermal conductivity (*K*) is not the major determinant in selecting a mold material, it significantly affects the rate of heat transfer. Materials with a low *K* value require a more elaborate cooling system than those with a high value. A crystallizing TPE such as Hytrel requires additional cooling capacity because its latent heat of fusion must be removed from the melt before demolding.

Hytrel requires removal of about 150 Btu/lb (348 kJ/kg) in conjunction with recommended molding conditions. Cooling channels should be located to uniformly cool the melt in the mold cavity to avoid hot and cold spots. Core pins longer than three diameters should be cooled internally if possible to facilitate uniform cooling, and coolant hoses should be at least 0.5 in. (13 mm) in diameter to provide an adequate coolant flow rate.

For slender core pins where the pin is secured only at their mounted end, the fixed end should be held rigidly for at least 3D in length where D is the pin diameter [30]. The normal maximum length for an unsupported pin is 5D.

6.1.13.2 Mold Surface Treatments

Chrome and nickel coatings have been widely used to improve wear and corrosion resistance and to facilitate mold release. A newer coating such as electroless nickel can be applied within a tolerance of 0.0001 in. When thicker than 0.001 in., it is generally pore free and provides an extremely homogenous surface for polishing. The incorporation of materials such as Teflon, silicon carbide, and industrial-grade diamond in electroless nickel can significantly extend mold life.

6.1.13.3 Mold Maintenance

Diligent and timely maintenance of molding equipment pays off in the long term. Scheduled maintenance significantly increases productivity for both molding machines and molds. The traditional concept of maintenance is changing to include a hybrid of maintenance people who know how machines work and technicians who know how to maintain a molding process. Software can monitor the status of equipment and process, prioritize factors that require attention, and then suggest corrective action.

Vents deserve special attention during mold maintenance to ensure that gases leave the mold unimpeded at high flow rates during mold filling. Locating vents on an accessible side of a mold in a clamp makes it unnecessary to remove the mold for vent cleaning. Maintaining cleanliness of sliding mold components such as ejector pins, sleeves, and cores is also important and reduces problems with galling.

Ejector pins can cause high local stresses during ejection that could lead to distortion or damage to the molded article [31]. Use of an increased number of pins is desirable because they more evenly distribute the ejection force applied to the molded article, thus reducing the pressure on the face of the pin that ejects an article. However, an increased number of pins complicates mold design.

Judicious application of grease to sliding surfaces of mold components reduces galling, but molded medical articles could preclude the use of grease.

Maintaining cleanliness requires continuous attention. One company has a program to eliminate all wood pallets and cardboard for internal products, and no forklifts are allowed in the molding area [32]. Instead, overhead cranes and special pallet rollers are used.

Bad things can happen to good molds during mold storage. Different anticorrosion treatments can protect molds, and anticipated storage time and conditions are important considerations selecting an appropriate treatment. Materials applied to molds intended for short-term protection tend to be less viscous than those used for long-term storage. Some protectants are clear while others are colored to facilitate uniform application and easy recognition of the applied coating. Most anticorrosion treatments must be completely removed prior to returning a mold to service.

6.1.14 Mold Design

An early and important consideration in mold design is the establishment of who has responsibility for what—this makes for smoother sailing later. If total responsibility is given to the mold builder and communication is less than effective with the mold purchaser, factors such as material corrosion and flow properties may not be adequately considered. If the molder assumes total responsibility for design, specific machining knowledge that could significantly affect the design could be omitted. Hence, a team effort is advantageous.

Open and frank communication, from the beginning and throughout completion of a molding project, favors satisfactory design and fabrication of a mold. Nothing should be assumed or taken for granted. Project information should be specified, shared, agreed upon, and recorded. It is important that the molder supply to the mold maker critical factors that could affect end-use behavior.

The mold designer should be familiar with at least the general material characteristics involved. For instance, some softer TPOs can require draft angles of at least 3° to facilitate part ejection [33]. Some soft Kraton materials may also require a draft angle for easier release [34].

Software with varying capabilities can assist the mold designer. Software with 2-D capabilities could be more efficient for initial concept development, while 3-D software could be efficient for designing for production. Friendlier software helps automate the most repetitive aspects of mold design. Integrated software packages carry out broad functions that include updating changes made to different mold elements, materials, and production drawings.

Guidelines for injection-molding simulations that should improve predictions of shear-induced melt variations follow [35]:

- 3-D mesh, preferably with tetrahedral elements
- 12 to 10 elements through thickness of runners and gates.

Mold designs sometimes incorporate only a few of the many design factors that require consideration. A common example is maximizing the number of cavities without adequately considering space and location requirements for effective placement of cooling channels. Maximizing the number of cavities can force location of the outer row of cavities too close to the mold edge. It can also reduce mold durability and result in cracking of cavities if walls between cavities are too thin.

If a mold plate for an initial design is too large to fit between the tie bars of an injection press, selection of a smaller mold base is an obvious solution—but not necessarily the best one. This solution could result in an inadequate area of steel around cavities and inserts. Sufficient steel thickness should be provided between cavity walls and the outside edges of a mold plate to provide resistance to cavity cracking. Avoid sharp corners in the cavities and use proper welding techniques to provide the required mold durability. Larger radii in corners of mold cavities can significantly increase mold strength and thus improve resistance to breakage.

Pressurized injected melt stretches cavity walls and repeated stretching can lead to fatigue cracking that occurs at stresses less than the ultimate tensile strength of the mold material. In contrast, gross cracking is another mechanism that usually occurs suddenly or after a mold has been in service for a short time. Factors such as improper steel selection, defective steel, and incorrect heat treatment can lead to gross cracking.

Mold wear also needs to be considered, especially when compounds contain hard particles that cause abrasive wear by scouring a mold surface [36]. Filler hardness, type, shape, and level in a polymer affect the severity of abrasive wear; steels with increased hardness better resist abrasive wear. Adhesive wear occurs when mold materials of similar composition and hardness contact one another under pressure and tear away a portion of a mold or mold component surface. The use of tough mold materials with dissimilar surfaces alleviates adhesion wear, as can appropriate mold coatings.

Mold designs that simultaneously consider these and other requirements, and that use a systematic approach, are much more likely to be successful than those that use a piecemeal approach. A systematic approach initially considers a number of factors that include

- the number of molded articles, their costs, and delivery dates
- molded article geometry, material, appearance, tolerance, and so on
- injection machine data.

Then, a detailed flow chart considers specific design factors, some of which are

- number of cavities
- cavity layout
- cavity dimensions
- sprues, runners, and gates
- cooling and ejector system
- mold mounting options.

Obtaining balanced cavity filling in molds has been a problem for some time [37]. However, a new runner design called a “MeltFlipper” flips the melt orientation by 90° and eliminates asymmetrical distribution of hotter and cooler melt to diverging runner branches. This technology, applicable to both TPEs and TSEs, can be incorporated in both new and existing tooling [38]. The biggest advantage to this technology is that it potentially can double or quadruple production with larger cavitation molds [39].

A methodical design approach jointly considers each of the above factors in detail. Among the many mold designs available are two- and three-plate molds. Figures 3.20 and 3.21 respectively show examples of two- and three-plate molds.

Two-plate designs are generally used with edge-gated articles, wherein runners remain with the molded article after demolding. They are easier to maintain and cost less than three-plate molds that incorporate separate plates for the runner and cavity-core systems. Center gating evens the flow during filling and reduces problems with knit lines. Pins successfully eject molded articles if the face of the pins has sufficient bearing area to minimize stress at the interface between pin and molded article. As with TSEs, leader pins and bushings align mold plates.

Table 6.4 shows selected molding problems, potential causes, and corrections [40].

Table 6.4 Molding Problems, Potential Causes, and Corrections

Defect	Cause	Correction
Blisters	Moist TPE	Dry TPE and reduce barrel temperature
Flash	Overheated material	Reduce injection pressure
	Too-high injection pressure	Reduce injection pressure
	Too-low clamping pressure	Increase clamping pressure
Article sticks in mold	Too-high injection pressure	Reduce injection pressure
	Insufficient cooling	Increase cooling and/or cycle time
	Highly polished mold surface	Change mold surface
Reduced toughness	Moisture in material	Dry TPE
	Too-small gate	Increase gate size
	Gate land too long	Decrease gate land length
Sink or shrink marks	Too-low injection pressure	Increase injection temperature
	Polymer overheated	Reduce barrel temperature
	Insufficient feed	Increase feed
	Too-low mold temperature	Increase mold temperature
Underfilled mold	Insufficient feed	Increase feed
	Too-low barrel temperature	Increase barrel temperature
	Too-low injection pressure	Increase injection pressure
	Undersize nozzle orifice, runner, or gates	Adjust size of components

By numbering cavities in a mold, molded article problems can be assigned to a specific mold cavity [41]. As molded article defects occur and mold maintenance is tracked, repetitive problems in specific areas or quadrants of a mold can be identified, addressed, and corrected.

A problem called “splay” can result from bubbles in melt from moisture, trapped air, and degradation [42]. Splay has the appearance of splash marks or silver streaks.

■ 6.2 Blow Molding

Injection molding and blow molding differ in several important aspects. Wall thickness of a blow-molded article is typically less well controlled than its injection-molded counterpart [43]. Rigid metal components in an injection mold generally determine dimensions of an injection-molded article. For example, a rigid core in the mold for an injection-molded bellows determines the inside diameter of a bellows. In contrast, a pressurized gas determines the interior surface of a blow-molded bellows. Common to both injection-molded and blow-molded articles, a mold cavity forms the exterior surface dimensions.

The ability to blow mold articles that are nearly impossible or very difficult to injection mold is a significant advantage for blow molding. Because blow molds are subject to considerably less pressure than injection molds, aluminum blow molds provide adequate service. Figure 6.1 illustrates the blow molding of bellows [43].

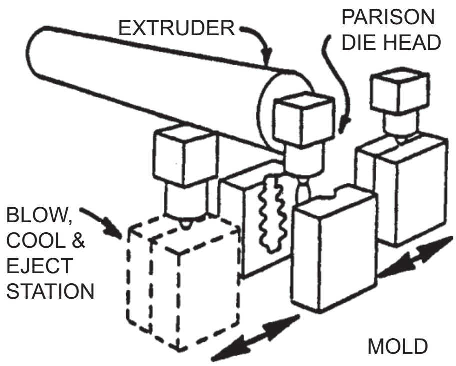

Figure 6.1 Blow molding of bellows [43]

During blow molding an extruder extrudes a hollow tube, called a parison, into an open blow mold. The mold then closes around the molten parison and advances it to the blow station. There air, injected into the parison through a blow pin, inflates and forces the parison against the cool mold walls to form a bellows. After sufficient cooling the bellows is ejected.

Conventional blow-molded bellows walls are thinnest at their maximum outer diameter. Wall thickness can be made uniform by programming the wall thickness of the parison to be thicker at a location that expands to become the maximum outer diameter of the bellows.

A melt temperature range of 300 to 400 °F (150 to 205 °C) is suggested for Kraton D compounds and a range of 375 to 475 °F (190 to 245 °C) for Kraton G compounds. Lower temperatures may produce rough surfaces on the extrudate, while higher temperatures increase extrudate sagging. Gas pressures of 35 to 120 psi are used to inflate the extrudate.

Recommended temperatures for extrusion blow molding of different grades of Santoprene range from 340 to 410 °F in the feed zone, 360 to 410 °F in the transition zone, and 380 to 410 °F in the metering zone. Recommended die zone temperatures range from 400 to 430 °F. Mold temperature should be slightly above the dew point of the air to prevent problems with condensation. Mold temperatures of 27 to 38 °C favor the best surface definition.

TPVs resist sagging under the influence of gravity during extrusion, except for the heaviest parison. The die swell of about 5 to 10% that occurs during extrusion is substantially less than that for rigid plastics. Although a typical wall thickness is 0.5 to 2.0 mm (0.020 to 0.080 in.), it can be as low as 0.25 mm (0.010 in.) or as heavy as 7.6 mm (0.300 in.). Predrying of TPV is necessary to achieve the desired blowing characteristics, and a drying cycle of 2 to 3 hours in a desiccant dryer at 75 °C (165 °F) is recommended. Regrind should be dried for four hours.

Among successful TPE blow-molded articles are vacuum connectors, clean air ducts, and boots for rack and pinion steering in automobiles. Blow-molded boots replaced more than 90% of the boots formerly molded from TSE because of major cost savings with TPE. TPE has replaced TSEs such as CR, NBR, and ECO in clean-air ducts. Use of TPV in a constant velocity (CV) joint represents a widespread automotive application for TPE.

While most TPE blow-molded articles incorporate a single material, multiple materials are also used. An example is the joining of a hard material and a rubbery material during sequential extrusion to form a parison that is then blow molded to form articles such as air ducts for automotive applications. Materials that are chemically similar bond most easily.

Extrusion blow molding proved most suitable for manufacturing bellows from TPEs. This method produces good quality articles with low energy use in short cycle times wherein bellows exit the blow-molding machine ready for use. Bellows are used to cover and protect struts in automotive suspension systems from dirt. Blow-molded TPEs replaced TSEs in this application because of major cost savings. Additional advantages are resistance to fluids, tear, and abrasion, and favorable low-temperature flexibility.

A seat belt sleeve has a complex shape that would require the use of an intricate core to form its interior if it were injection molded. Blow molding eliminates the need for a core because pressurized gas forms the interior of the sleeve. Even though a TPE replaced a lower cost thermoplastic material, the good TPE properties justified its use. Properties included good low-temperature flexibility, flex resistance, and excellent resistance to degradation by UV.

Requirements for rubber used in medical applications are understandably very strict [44]. Under current FDA regulations, a change in manufacturing method or material supplier necessitates a process re-evaluation after a mandatory notification. Most manufacturers in the U.S. require a two-year lead time for a change in polymer.

Special requirements apply to blow-molded articles that are used in some applications. For example, articles used in medical applications might require sterilization by steam, ionizing radiation, or ethylene oxide. TPEs in medical applications offer advantages that include colorability in addition to suitability for sterilization by gamma and electron beam [45]. They are also useful for cane and walker handles used by frail elders. Patients with osteoarthritis or rheumatoid arthritis can benefit from cushioned grips that put less stress on joints.

Suppliers of TPEs often provide troubleshooting help for their specific materials. Table 6.5 lists general problems that might occur with extrusion and injection blow molding.

Table 6.5 Blow Molding Problems, Causes, and Suggested Solutions

Problem	Cause	Suggested Solution
Parison blowout	Pinch-off too sharp	Increase land width of pinch-off
	Clamp pressure too low	Adjust clamp pressure
Excessive flash	Parison diameter too large	Change tooling
	Improper mold closure	Check for mismatch in mold
	Flash grooves too shallow	Increase groove volume

6.3 Extrusion

Efficient extrusion requires good instrumentation and appropriate control of the following three critical process variables: melt pressure, melt temperature, and motor load [46].

Rupture discs can protect extruders from excessive pressures that could blow out an extruder die and injure personnel or damage equipment [47].

Additional parameters for monitoring include barrel and die temperatures, moisture level of feedstock, and water inlet and outlet temperatures [48].

Extrusion can produce a wide TPE product range that includes sheeting, tubing, and complex profiles [49]. A crosshead die can apply TPV jacketing to electrical wire and cable. Two different hardness materials can be co-extruded.

Scrap from both molded and extruded products can be ground into pellets and recycled to save costs. Best grinding results are obtained with the use of grinder blades that are kept sharp and where clearances in the grinding machine are minimized. Table 6.6 shows that TPVs retain their properties after reprocessing five times [50].

Table 6.6 Processing Effect on Property Retention

Property	Retention, %
Viscosity	93
Tensile strength	100
Ultimate elongation	102

Extrusion has the greatest requirement for predrying of all TPV processing methods [51]. Drying in a desiccant dryer for two to three hours at 65 to 75 °C should be satisfactory.

6.3.1 Extrusion Equipment

Recommend ratios of screw L/D are 20:1, with 24:1 preferred. A recommended compression ratio is 2.7 to 3.5:1 [52]. The feed throat should be cooled with water to prevent bridging of pellets. To assure an even flow of TPE through a die, a screen pack of 20, 40, and 60 mesh screens should be incorporated between extruder barrel and die. Entrance to the die should be funnel-like (see Fig. 3.6) rather than abrupt, to promote streamline flow. As a general rule, there should be no dead areas to trap polymer that approaches a die.

Table 6.7 highlights general extrusion problems, potential causes, and possible solutions [53].

Table 6.7 Extrusion Problems, Potential Causes, and Solutions

Problem	Potential Cause	Solution
Surging	Incorrect barrel temperature	Change barrel temperature
	Screens plugged	Change screens
	Bridging in hopper	Cool hopper zone
	Wet material	Dry pellets
Rough extrudate surface	Wet material	Dry pellets
	Too-low die temperature	Raise die temperature
	Too-fast extrusion rate	Reduce extrusion rate
Voids	Wet material	Dry pellets
	Degradation of material	Adjust temperature and screw speed
	Shallow metering section	Use proper screw
Color streaking	Dirty hopper	Clean hopper
	Poor mixing	Use proper screw
	Extrusion temperature incorrect	Adjust extrusion temperature
Pitted extrudate surface	Extrudate improperly cooled	Improve cooling
	Wet material	Dry pellets

Relatively coarse screen packs of 20 to 60 mesh should provide a homogenous, nonsurging melt flow when extruding Santoprene [54]. A finer screen pack can improve melt quality and homogeneity when there are problems such as poor kitting, excessive output rates, and screw design limitations. Occasionally, higher back pressure can help homogenize the melt, particularly when operating an extruder at low rpm [55].

Table 6.8 describes some extrusion problems associated with Santoprene.

Table 6.8 Possible Causes and Corrective Action for Santoprene Extrusion Problems

Problem	Possible Cause	Corrective Action
Center keeps moving	Undersize wire	Change reel of wire
Extrudate rough surface	Improperly sized or worn die	Replace die with one of correct size
	Too cool die	Increase die temperature
	Low melt temperature	Increase extruder zone temperatures or shear rate
Porosity in extrudate	Improperly dried material	Ensure dryer system is operating properly
		Increase drying time
	Excessive shear	Use screw that produces less shear
Burned particles in extrudate	Contamination from previous runs	Clean screw, barrel, hopper, head, screen pack
	Extruder L/D is too short	Reduce screw rpm and/or raise barrel temperature

Areas of high extruder wear can reveal problems such as design issues or alignment problems [56]. A burr on the side of a screw trailing edge indicates a high, localized pressure that forces the screw to one side of the barrel, causing galling between screw and barrel.

A high-consistency, UV-curable silicone is said to be extrudable at room temperature [57]. The UV exposure time for curing can be as short as 0.5 s depending on line speed and UV intensity. Since the cure is initiated by UV radiation, the rate of cure is independent of the diameter and cross section of the extrudate.

As with other polymers, Santoprene TPE tends to flow more easily in the center of an extrusion die than in the thinner portions of the die [58]. Adjusting the land lengths behind the die face can correct flow imbalance. It is very important that Santoprene be properly dried. Moisture contents of 0.08 % and higher have been found to cause problems such as porosity, surging, low melt strength, and rough extrudate edges.

Adhesion is important, not only for bonding coatings but also for bonding TPEs and polyolefins to themselves and other materials. Induction can be used to heat a thermoplastic electromagnetic interlayer between surfaces to be bonded [59]. The interlayer incorporates a dispersion of fine micron-sized ferromagnetic powders such as iron or stainless steel that are heated by induction.

A magnetic rubber patch for repairing holes on damaged ships represents another application for magnetic technology [60]. It has been used in many ship rescue operations, including one in the Arctic where major damage was sustained and a repair was made in only six hours.

Design of adhesive joints affects adhesion results [61]. Overlap joints, regardless of the material, concentrate applied stress at the ends of the overlap. Three techniques that can reduce stress are:

- Taper the overlap to "move" the stresses back from the leading edge towards the center of the bond line.
- Use a flexible adhesive to distribute the stresses.
- Use a shiplap joint for a better fit.

TPV articles can be heat welded without the need for an adhesive [62]. Surfaces of the articles to be bonded can be heated by a hot metal surface, hot air, ultrasonic heating, or linear vibration heating wherein frictional heat fuses the surfaces.

In a study of adhesion of polyamide to NR, oxidation occurred and sulfur-bearing accelerators migrated to the boundary layer. This increased hardening at the boundary layer during flex testing of the NR-polyamide composite and contributed to bond failure [63].

6.3.2 General Design Guidelines for Extrusion

Among design guidelines that affect extrusion behavior, cost, and serviceability are wall thickness, ribs, radii, hollows, extrudate density, multilayer extrusions, welded joints, hinges, and occurrence of kinking [64].

Uniform or near uniform cross sections favor processing ease, lower costs, improved process control, superior finish, and successful extrusion of more complex shapes.

Too-abrupt changes in thickness and too-large thickness variations complicate the balancing of flow in an extrusion die. Hollow sections complicate die design and make shape retention more difficult; hence they should be used only when necessary. However, they effectively reduce the compression stiffness of an extrudate and are therefore widely used for seals that serve as weather strip for vehicles.

It is critical in the early design stage of weather strip to determine the behavior of a rubber section under loading conditions and also to judge how section changes will affect behavior [65]. FEA can analyze very complex geometries and provide flexibility that is difficult to obtain by other means.

EPDM materials were needed with improved formulation flexibility, extrusion flexibility, and better cure efficiency. XUS 51102, a grade of metallocene EPDM rubber, is said to meet these characteristics [66]. Although designed primarily for weatherstrip applications, it is also useful in hoses, roofing, wire and cable, and sports flooring.

Co-extrusion combines two extrudates into a single article in a single extrusion process. It uses two extruders that supply a die that channels and combines extrudates into a single extrudate. Co-extrusion is widely used to combine a plastic such as PP with TPV to form a composite.

Heat welding effectively bonds TPV extrudates by melting the surfaces of joining faces under slight pressure, followed by cooling. Surfaces can be heated by a hot plate, heater element, or hot air.

Hinges can relieve strains and make a seal more pliable or concentrate bending strains at the hinge to promote better elastic recovery. Judicious selection is necessary to determine the best hinge thickness and FEA can assist in this activity. Improvements in die design can be made for EPDM compounds using numerical simulation [67].

Kinking can occur when a dense extruded seal is formed around a radius; a cellular material allows an extrudate to compress on the inside radius with less kinking than a dense material.

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7 TPE Products

Copolyester TPEs are said to be easily extruded into blown films with a thickness less than 1 mm [1]. Both the extruder adapter and head should be as streamlined and as short as possible to minimize regions of low flow that can lead to polymer degradation and subsequent random release of degraded polymer.

Specifications for some TPE products such as wire and cable require them to be fire retardant, and an example is an SBC compound intended to meet requirements of UL 94 [2]. Improved flame-retardant properties are attributed to formulation techniques that modify melt viscosity and char formation.

The number of available TPE products keeps increasing as new materials, design capabilities, and process techniques increase. For example, the development of oil-resistant TPEs opened the market for a range of new products. Process techniques, such as blow molding, can produce hollow articles that are much more amenable to TPEs than to TSEs. The ability to form strong bonds between heated TPE surfaces without an adhesive is also an advantage relative to TSEs.

Joining materials can be problematic. Ingredients in a bonded TSE/TPE composite might migrate to the bondline and cause bond failures. Examples of potential migrating ingredients are excessive levels of paraphenylene diamine antiozonants and butyl carbitol formal-type plasticizers. Because bonding problems are time dependent, it is prudent to determine the bond strength after aging bonded assemblies for various times and temperatures to identify potential service problems.

Plastics with a heat-deflection temperature less than about 400 °F should typically be avoided when preparing rubber-plastic composites [3]. The high temperature and pressure of molding can distort the plastic in a composite.

Table 7.1 lists examples of products available today that incorporate TPEs [4].

Table 7.1 Some Products That Incorporate TPEs

Appliances	TPE Article
Clothes washer	Seals, drive wheels, bumpers
Electronic equipment	Bumpers, feet
Footwear	Soles, heels, composites
Architectural glazing	Windows, doors

7.1 Athletic Products

Athletic balls such as soccer balls must be extremely robust to perform satisfactorily over their intended service life [5]. Soccer balls fabricated from block copolymers of nylon 11 are said to be 1.6 times more durable than soccer balls made from conventional materials.

7.2 Hood Stops

Screw threads can readily be formed on TPEs for use in products such as hood stops for automobiles [6]. Hood stops (Figure 7.1 TPE hood stops for automobiles [6]) that were formerly produced as TSE-metal composites are now fabricated from TPE with weight and cost savings, along with simplified manufacture.

Figure 7.1 TPE hood stops for automobiles [6]

7.3 Food Trays

Food trays used in prisons are required to be sufficiently stiff to effectively hold food; however, they should be insufficiently stiff to be turned into weapons by inmates. TPE, appropriately designed, meets these requirements [8].

7.4 Rollers

Thermoplastics have been used for some time to mold small-diameter rollers. However, large-diameter rollers presented special problems because of uneven cooling [9]. TPU is considered favorable for replacing polyurethane-covered rollers.

7.5 Seals

A seal previously used in a windshield-washer assembly was fabricated from CR with a separate metal screen that functioned as a filter. The metal screen was used because the CR could not be molded to the required fine tolerances [10]. It was difficult to insert properly in the rubber seal, often leading to leakage and poor filtering of the windshield washer fluid. This two-piece seal was satisfactorily replaced with a one-piece seal molded from TPE that reduced the cost from 30 cents for the CR and brass screen assembly to 13 cents for the TPE seal.

Two primary categories of seals are static and dynamic [11]. Static seals deform only once, for example in a pipe seal buried underground. A dynamic seal is one that closes and opens intermittently, for example a glass run channel on an automobile. TPV foam has been tightly bonded to injection-molded corners for glass run channel and primary body seals [12].

7.5.1 Seal Design

Factors important in static seal design include

- seal specifications considering pressure and peak temperature requirements
- relevant compression stress relaxation level that would provide good seal performance for long-term service
- space for a seal to expand in service.

Factors to consider in dynamic seal design include

- gap dimension to be filled—average and extreme
- choice of bulb or lip design
- lip seal strain, which should be between 20 and 45% strain in the bending region
- occurrence of seal bending in the intended region
- use of FEA to assist seal design.

7.6 Hose

Thermoplastic hydraulic hose was successfully constructed by using TPV for its cover and intermediate layers [13]. The preferred tube assembly consisted of an impact-modified polyamide 6 or a pure polyamide 6 resin to resist migration and weeping of hydraulic oil. The hose performed well during extensive testing.

7.7 Prosthetics

Prompted by soldiers who returned home with hand and finger injuries, TPU was molded into prosthetic fingers that provided each finger with the dexterity to independently and gently conform to whatever is grasped [14]. Wrist motions actuate mechanical fingers by wrist inflections and molded-in fingernails enabled picking up small objects such as coins.

7.8 CVJ Boots

CVJ (constant-velocity joint) boots on vehicles protect rotating joints from the ingress of dirt and water, and they prevent loss of lubricant that is necessary for proper joint operation. They transmit torque from the gearbox to wheels while accommodating steering and suspension movements. Several factors are important in their successful operation, and consequently, COP boots replaced CR boots [15].

The high flexural modulus of COP provided increased dimensional stability during boot rotation. This feature reduced the required clearance around a rotating boot to avoid contact between the boot and the surrounding structure. Another advantage is the shorter molding cycle for rotationally molded consequently, COP boots relative to injection-molded CR boots.

Lubricants can extract antiozonants and antioxidants from CR boots, leaving only one-third of these protective agents after two years of service [16]. There are no antiozonants and antioxidants in COP to leach out. Better dimensional control favors CR boots because they are molded in closed-cavity molds. Attention should be given to the newer high-performance lubricants because they can attack polymers. Temperature conditions for CVJ boots in a vehicle vary [17]. Location of a boot near a catalytic converter necessitated the use of silicone rubber rather than CR to obtain the required high-temperature resistance.

7.9 Fish Lures

Transparent colorants and mini-LEDs are used in proprietary polymer mixtures to illuminate colorful iridescent lures at any depth and under any water conditions [18]. Lure specific gravity was adjusted to allow for floating or sinking to specific depths.

7.10 Design

Design considerations for TPV molding include [19]

- Maintain as uniform a wall thickness as possible to minimize warpage and sink marks.
- Incorporate strengthening members such as ribs and flanges to be about 50 % of the wall thickness of the sections they support.
- Minimum radius in TPV should be 0.5 mm (0.020 in.).
- Add surface texture to moldings by chemical etching, electric discharge machining, or sand blasting.

Design tips for static TPV seals include [20]

- For an article compressed by 25 % in a groove, limit the width of the TPV to 70 % of the groove width.
- Examine specifications for sealing in terms of pressure and peak temperature.
- Use softer grades of TPV to seal irregular mating surfaces.

7.11 Appearance

Splay is most often caused by bubbles in melt associated with moisture, trapped air, and gases caused by degradation [21].

7.12 Conductive SEBS

Conductive SEBS can be compounded with fillers such as silver-coated or nickel-coated glass [7]. Properties include low hardness (55 to 65 Shore A) and low compression set in a highly filled compound with low melt viscosity. Overmolding can often be achieved without the need for primers.

7.13 Safety

Safety concerns with injection molding and other polymer operations involve many factors that include materials, mold design, machine operation, maintenance, and housekeeping [22].

Contact suppliers of materials and equipment for relevant and current safety information. Users of materials and equipment must satisfy themselves that operating procedures comply with current applicable government procedures and that a safe workplace is provided.

Electrical considerations deserve special attention with respect to safety, for example junction box location and ratings [23]. SPI Moldmakers Division is developing guidelines for mold electrical interface practices.

Underwriters Laboratories have long been involved in safety issues [24]. A legitimate UL mark includes the following information:

- The UL trademark: The letters "UL" are arranged diagonally (descending left to right) within a circle, with a small ® symbol directly below the U.
- The word "listed" printed either below or beside the circle in all capital letters: LISTED.
- A four-character alphanumeric control number or a four- to six-digit issue number. In the case of the issue number, it may or not be preceded by the phrase "Issue No." as well as one or two letters. The reference provides additional information.

Building purchased molds directly from crude sketches is considered a bad practice. Rather it is desirable to describe a mold layout in a quote and have customer-approved current drawings on file because this action facilitates communication and helps to protect a moldmaker in the event of subsequent litigation. High pressures, the occurrence of pinch points, and so on demand particular attention to safety during injection mold design and operation.

As an example, high pressure in a manifold caused an ineffectively retained plug to blow out [25]. The plug penetrated the safety gate, passed through a person's abdomen, and caused permanent injury. An ensuing suit, settled for approximately two million dollars, named defendants that included the person's employer and the molding machine manufacturer. In other litigation, an ejector box crushed four fingers on an operator's hand. The injection machine manufacturer and the moldmaker were sued for "failure to warn" and "design defects."

Additional safety concerns include the attachment of heavy molds, such as fascia molds for automobiles, to large injection machines. All involved personnel should follow recommendations for safety and maintenance provided by equipment makers, and personnel should also follow good housekeeping practices such as keeping work areas free of oil.

The Mold Safety Committee of the Society of the Plastics Industry, Inc. is working to provide certain safety guidelines related to electrical and mold interface issues that include recommended wire sizes and their current carrying capability and the temperature rating of wires used in molds. Interface issues include mold wiring and cavity-numbering procedures and the location of junction boxes and connectors.

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Appendix I

Abbreviations

ABS	acrylonitrile-butadiene styrene
ACM	polyacrylic elastomer
ASTM	American Society for Testing and Materials
CBS	N-cyclohexyl-2-benzothiazolsulfenamide
COF	coefficient of friction
COP	copolyester
cP	centipoise
CPE	chlorinated polyethylene
CR	polychloroprene rubber
CSM	chlorosulfonated polyethylene elastomer
CTM	cavity-transfer mixer
CTP	cyclohexylthiophalamide
CV	constant viscosity
D	diameter
DOTG	di-o-tolyl guanidine
DPG	diphenyl guanidine
DPTT	dipentamethylene thiuram tetrasulfide
E	Young's modulus
EA	elastomeric alloy
EAM	ethylene-acrylic elastomer
ECO	epichlorohydrine rubber
EPDM	ethylene-propylene diene monomer
EU	European Union

EV	efficient vulcanization
EVA	ethylene vinyl acetate elastomer
FDA	Food and Drug Administration
FEA	finite element analysis
FIFO	first in first out
g	g-force, acceleration due to gravity
gpd	gram per denier
GR-S	government rubber-styrene
HCR	high-consistency silicone rubber
HFR	halogenated flame-retardant materials
HNBR	hydrogenated nitrile-butadiene rubber
hp	horsepower
hr	hour
I.D.	inside diameter
IIR	isobutylene-isoprene rubber
K	thermal conductivity factor
L	length
L/D	length/diameter ratio
LED	light-emitting diode
LIM	liquid injection molding
LSR	liquid silicone rubber
MBS	2-(4-morpholinyl) mercaptobenzothiazole
MDI	methylene diisocyanate
MBT	2-mercaptobenzothiazole
mph	miles per hour
mV	millivolt
MW	molecular weight
MWD	molecular weight distribution
NBC	nickel dibutyl dithiocarbamate
NBR	acrylonitrile-butadiene rubber
NR	natural rubber
O.D.	outside diameter
OR	operating region

Pa · s	Pascal-second
PC	polycarbonate
PDMS	polydimethylsiloxane
PLD	powder liquid dispersion
PEEK	polyether-ether ketone
pli	pounds per linear inch
PI	synthetic polyisoprene
PMMA	polymethyl methacrylate
phr	parts per hundred rubber hydrocarbon
PMVE	perfluoromethylvinyl ether
PP	polypropylene
6PPD	N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine antiozonant
pphm	parts per hundred million
psi	pounds per square inch
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
RAPRA	Rubber and Plastics Research Association
R_c	Rockwell C hardness
R_e	Reynolds Number
RFL	resorcinol formaldehyde latex
RIM	reaction injection molding
RMA	Rubber Manufacturers Association
rpm	revolutions per minute
rms	root mean square
SAE	Society of Automotive Engineers
SBR	styrene-butadiene rubber
semi-EV	semi-efficient vulcanization system
SIR	styrene-isoprene copolymer
SMR	Standard Malaysian Rubber
SPC	statistical process control
SPMRA	semipermanent mold release agent
SUV	sport-utility vehicle
t	time

TeDEC	tellurium diethyl dithiocarbamate
TBTD	tetrabutyl thiuram disulfide
TETD	tetraethyl thiuram disulfide
T_g	glass transition temperature
T_m	crystalline melting point
THQ	2,2,4-trimethyl-dihydroquinoline
TMQ	1,1-dihydro-2,2,4-trimethylquinoline
TMTD	tetramethyl thiuram disulfide
TPE	thermoplastic elastomer
TPO	thermoplastic olefin
TPU	thermoplastic polyurethane
TPV	thermoplastic vulcanizate
TSE	thermosetting elastomer
UV	ultraviolet
V	volt
VNB	5-vinyl-2-norbornene
XNBR	carboxylated acrylonitrile-butadiene rubber processed

Appendix II

Definitions

Bloom	the appearance of an undesirable material on the surface of a rubber article
Bushing	the tubular device in a mold plate that accepts a leader pin or dowel and aligns mold plates
CAD	computer-aided design
Damping	a system or material property that, when deflected, results in the conversion of mechanical energy into heat
Deflash	remove flash from a molded article
Flash	the excess material that forms on the edge of a molded article at the mold parting line
Gate	the restricted opening located between the runner and the cavity of a mold
Green tire	(1) an environmentally favorable tire (2) an uncured tire
Land	the small area of a mold surface that borders a mold cavity
Leader pins	pins in the plate of an open mold that enter bushings in an opposing mold plate during mold closing, directed toward accurately aligning mold plates
Marching modulus	a continuing increase in modulus with cure time, that is, no plateau modulus
Nerve	a measure of the elasticity of uncured elastomers and compounds
Pot life	a measure of the time available before crosslinking occurs, which usually applies to low-viscosity compositions
Reversion	a deterioration of elastomer properties that occurs with overcure

Runner	the portion of a rubber distribution system that is located between the gates and nozzle
Scorch	a measure of the time available before crosslinking occurs, which usually applies to high-viscosity compositions
Splay	splash marks or silver streaks
Sprue	the round, tapered channel that conveys compound from the transfer pot to the runner system or mold; also the cured compound that is formed in the channel
Stickiness	ability of uncured rubber to stick to other materials such as metals and textiles
Tack	ability of uncured rubber surfaces to stick to one another under limited pressure, after a short dwell time
Web	a strip of material conveyed, embossed, printed, or otherwise processed

Index

D

E

F

G

H

M

N

T

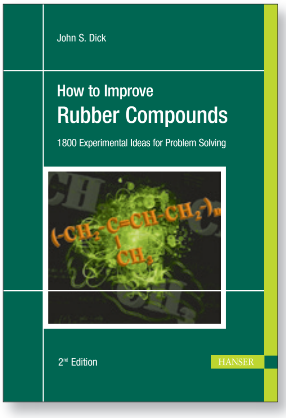
X

Y

Z

HANSER

Improve Your Rubber Compounds



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Rubber compounding is a very complex endeavor. There are many interactions and many ways to achieve the target properties and economic goals while maintaining an acceptable tradeoff for these characteristics. This book is dedicated to providing the reader with various experimental ideas which may guide him or her to developing better compounds and solving technical problems.

In a combined effort, 20 reknown industrial experts compiled a large number of diverse experimental suggestions for enhancing a specific compound property. By reviewing the suggestions in this book, the compounder may develop a better "feel" for how to best achieve a compromise or trade-off with compound properties when developing new or improving tested rubber recipes.