Custom Molding of Thermoset Elastomers
A Comprehensive Approach to Materials, Mold Design, and Processing

Sample Chapter 3: Materials
3 Materials

This chapter will describe some of the unique differences between available TSE materials along with some important historical achievements in TSE development. Some descriptions of elastomers are taken in their entirety, or abbreviated from referenced sources. Described are only some of the most common materials used for custom molders. For more materials and greater detail, the reader should consider some of the references listed at the end of this chapter or material suppliers.

3.1 Natural Rubber (NR)

“The discovery of rubber dates back to when the Europeans started exploring South and Central America. They observed not only young children playing with balls that bounced, but also crude waterproofing methods for clothing and shoes. The material was called 'cachuc' which means 'weeping wood'. This mysterious elastic and waterproof substance was observed by the explorers as originating from the bark of a certain tree after being punctured. A milky substance secreted and was captured by the natives and poured onto clothing and shoes to form an elastic waterproofing.

The word spread in Europe about this fascinating material prompting all kinds of ideas for its commercial use. An English scientist, Priestley, discovered that this material would rub off pencil marks; he called it 'rubber'. That name stuck with the substance ever since. As interesting as this material was, it had no intrinsic value since the rubber turned stiff and brittle in cold temperatures and soft and sticky at warm temperatures. It was not until 1839 that Charles Goodyear discovered that when the rubber was heated with sulfur, it dramatically changed into a strong, elastic material in cold and warm temperatures. This coupled with Hancock's earlier discoveries on how to shape and process the material finally accelerated rubber into wide-spread use" [1].

Natural rubber, the same material seen by the early European explorers in a bouncy ball is made from the milky colored excretion (latex) from the Hevea Brasiliensis tree. It is the only commercially available non-synthetic rubber. Natural rubber is known chemically as cis-1,4 polyisoprene. Natural rubber is a strong material; its tensile strength makes it the standard bearer in the rubber family. It has a high molecular weight, giving it a high Mooney viscosity. Natural rubber's strength, abrasion resistance, and resistance to deformation make it an excellent candidate for tires and shock isolation devices.

Disadvantages of natural rubber include: poor resistance to oils, fuels, high temperature, ozone, and acids. Often additives and/or blends with synthetic rubbers make up for some of natural rubber’s shortcomings.

Natural rubber is considered a difficult to process material. Its high viscosity and high tensile strength resist flow, making injection molding natural rubber difficult. Natural rubber has
a long cure time when compared to most other materials. Its high tensile strength makes secondary removal of flash difficult. Natural rubber has an unmistakable odor when molding. It’s difficult to shape and break down in its uncured state (considered green strength) actually offers advantages in molding tires. The green strength allows the uncured rubber to stay in position and be layered with wire bands and other rubber materials.

### 3.2 Synthetic Polyisoprene (IR)

It was not until the 1950s that the long sought after synthetic version of natural rubber was discovered. It has long been understood that isoprene was the fundamental ingredient to natural rubber, and would be key in developing a synthetic version. With the advent of a new type of catalyst system called “stereospecific,” monomer units were able to be selectively joined in a well organized fashion. Initial commercialization of synthetic polyisoprene came in 1960 as Shell Isoprene Rubber, by the Shell Chemical Company. In 1962, Natsyn was introduced by the Chemical Division of Goodyear Tire, and in 1965 Goodrich-Gulf came out with Ameripol SN. These rubbers are all high cis-1,4 content type. There are other synthetic polyisoprene types, but the materials made by cis-1,4 addition best emulate natural rubber. Not surprising, synthetic polyisoprene is used as a replacement for natural rubber. Synthetic polyisoprene does slightly fall short of natural rubber’s physical properties in tensile and modulus, and particularly at elevated temperatures. It also has lower green strength, which may be an advantage or disadvantage depending on the molding process chosen. High green strength is a feature useful in layering materials in tire molding. Synthetic polyisoprene can have a longer cure time than natural rubber.

Synthetic polyisoprene does have advantages over natural rubber. Synthetic polyisoprene is much more consistent than natural rubber. Its lower molecular weight makes it easier to process. Ease and consistency may offset the added cost of synthetic polyisoprene over natural rubber.

Typical applications for synthetic polyisoprene are tires, motor mounts, vibration dampeners, footwear, and rubber bands. Recently, it has gained popularity in the medical industry because it does not contain the potential latex protein allergens found in natural rubber [2].

### 3.3 Styrene-Butadiene (SBR)

The copolymer of styrene and butadiene became the most important and widely used synthetic rubber ever produced. But is was not until the 1920s that the first emulsion systems using free radical catalysts to produce high polymerization rates and high molecular weight products were recognized. In the 1930s and the advent of WWII, developed countries wanted to rid their dependence on foreign sources of material. The German government promoted research in the development of synthetic rubber and the first butadiene-styrene copolymer from an emulsion system was produced by the research laboratory of I.G. Farbenindustrie and was known as Buna S. A butadiene-acrylonitrile copolymer (Buna N) followed shortly thereafter.
These first products were of very poor quality compared to natural rubber. However, the technology with considerable improvements and modifications formed the basis for synthetic rubber production in the United States.

As the United States entered WWII, their access to natural rubber became increasingly difficult, while the demand for rubber increased due to the industrial revolution and the need for rubber in military equipment. The US government in association with material companies prompted research on a replacement for natural rubber. In 1942 GR-S (known as SBR today) was launched into production in a government plant. By 1945 the US government financed 15 SBR plants, 16 butadiene plants, and 5 styrene plant which all eventually were sold to the private sector.

Polymerization is done through an emulsion or solution process. In emulsion the predominant ingredients, styrene and butadiene, are emulsified in a water-like solution with emulsifying agents such as soaps. Initial polymerization of SBR was considered a “hot” process and was performed at 41 °C. Later (1947), a “cold” process was developed which used a temperature of 5 °C, and offered superior physical properties over the hotter processed SBR.

The solution process is considered a cleaner process because it does not contain any soap residues common in the emulsion process. These residues can contain as much as 7% by weight of the polymer bale. This process utilizes a solution of hydrocarbons to produce better stereospecificity. Alkyl-lithium-based catalyst systems are used because they are the only stereo-specific catalysts that copolymerize styrene and butadiene.

Most of the SBR material finds its way to the automotive tire industry. However, SBR is also seen in products like: floor mats, shoe soles, cable insulation, food packaging, adhesives, caulks, military tank pads, and even common chewing gum [3].

### 3.4 Polybutadiene (BR)

Polybutadiene is only second to SBR in total synthetic rubber consumption. Nearly 70% of all BR is used for treads and sidewalls of tires. BR has excellent abrasion resistance and low temperature resistance. In fact, only silicone rubber has a lower temperature resistance. However, BR is difficult to process and exhibits poor wet traction properties and is therefore predominantly used in blends with natural rubber and SBR for tires.

BR is also used as an impact modifier for polystyrene and acrylonitrile-butadiene-styrene plastics. Polymerization is similar to SBR in that the process can be either emulsion or solution based. Typical cure systems for BR compounds are sulfur or peroxide cured [4].

### 3.5 Butyl (IIR)

Butyl rubber is a copolymer of isobutylene and a very small amount of isoprene (98% vs. 2%, respectively). By far, butyl’s greatest property is gas permeability resistance. Coupled with good flex resistance, and resistance to oxidation and ozone, butyl makes an excellent choice for inner tubes, and inner liners in tubeless tires.
Halogenated butyl, known as halobutyl, was developed in the early 1960s, which lead to better processability and allowed for copolymer blends with rubbers such as natural rubber and SBR. This significant event lead to the development of tubeless tires because the addition of the other rubbers allowed the excellent gas permeability resistance of butyl rubber to be bonded to the inner wall of a tire. There are two types of halogenated butyl rubbers: bromobutyl (BIIR) and chlorobutyl (CIIR). Butyl is made by low temperature cationic polymerization. Other applications for butyl are: vibration dampeners, bladders, steam hose, and pharmaceutical stoppers [5].

### 3.6 Ethylene-Propylene-Diene (EPDM)

EPDM is a terpolymer of ethylene, propylene and a small percentage of diene which provides unsaturation in side chains pendant from the saturated backbone [6]. EPDM's most appealing trait is that it has excellent ozone resistance. As such, EPDM is used as roofing material, automotive cooling system seals, wire and cable covers, high voltage boots, and other similar products.

EPDM can be sulfur or peroxide cured. Peroxide cure systems allow for better compression set and a higher temperature range. EPDM has good high temperature resistance, but is prone to attack from hydrocarbons. EPDM's non-polarity gives it excellent electrical resistance properties.

### 3.7 Nitrile (NBR)

NBR is a highly polar copolymer of butadiene and acrylonitrile. The acrylonitrile content offers NBR its oil resistance that improves as its content increases, but also worsens low temperature flexibility.

NBR has good hydrocarbon resistance, but moderate temperature resistance. As NBR can be cured with a variety of cure systems, peroxide should be used to increase its temperature range. For an even higher heat range, hydrogenated nitrile (HNBR) should be used. The hydrogenation process removes most of the unsaturation in the polymer making it less vulnerable to attack from heat, ozone, and oxygen. HNBR can be made for low, or high temperature resistance.

For improved strength and abrasion resistance, carboxylated nitrile (XNBR or CNBR) is available. For these versions, carboxylic acid groups are added to the polymer chain during the polymerization process. These groups provide additional crosslinking sites during the curing process.

NBR is the least expensive material in the oil resistant rubber category. There is a substantial cost penalty for hydrogenated and carboxylated versions [7].
3.8 Polyacrylic (ACM)

ACM found favor in the automotive industry because of its outstanding resistance to petroleum-based oils and fuels. ACM also has good ozone resistance and a high temperature range. However, it has inferior strength, water resistance, and low temperature resistance and as a result was displaced in many applications by ethylene acrylic rubber.

3.9 Ethylene Acrylic (AEM)

AEM is a terpolymer of ethylene, methyl acrylate, and a third monomer (carboxylic acid groups) in a very small amount to serve as a cure site for the resulting polymer. AEM has good high temperature resistance, good oil resistance and moderately low temperature resistance. AEM has replaced much of the ACM used in automotive applications because of better low temperature resistance [8].

Good low temperature properties are derived from its ethylene content, while the methyl acrylate co-monomer provides oil and fluid resistance. The completely saturated nature of the polymer backbone displays excellent resistance to oxidation, ozone, UV radiation and weathering [9].

3.10 Silicone (MQ, VMQ, and PMQ)

Silicones are synthetic rubbers but are derived from organic and inorganic materials. The element silicon, which does not exist naturally, is present in sufficient amounts to positively affect the material's physical properties. Silicon is the second most abundant element on earth. Silicon can be found in sand and rock. In fact, 28% of the earth's crust consists of silicon [10].

Silicones are a class of material that can vary in form from fluids and greases to resins and rubber. Silicone rubber can be purchased in pourable form or as a thick paste. Structurally, silicone relies on a form that is never found in nature. This structure relies on a polymer backbone of silicon and oxygen atoms arranged in the same fashion as sand and rock. However, the silicon atoms are also joined to organic groups arranged similarly to hydrocarbons found in petroleum and natural gas. Therefore, silicone exhibits the high temperature resistance and toughness known in the mineral world and flexibility and lubricity known in the organic world [10].

Silicones can be categorized into three classifications; polydimethylsiloxanes (MQ or VMQ), polydimethylsiloxanes with phenyl substitutes (PMQ or PVMQ), and polydimethylsiloxanes with 1,1,1 trifluoropropyl substitutes (FVMQ, better known as fluorosilicone) [11]. Phenyl-containing gums are more flexible at low temperature. Vinyl-containing gums offer better compression set resistance.

Organic polymers mainly have an unsaturated double bond in their backbone structure that is prone to attack from oxidation and ozone. The unique chemistry of silicone does not contain an unsaturation in its silicon-oxygen backbone and offers extreme resistance to these factors [12].
Silicone rubber compounds made from gums use inorganic fillers which are not affected by heat. Vulcanization catalysts are usually organic peroxides. Fluorosilicones are used in applications requiring resistance to fuels and better resistance to oils, but at a large cost penalty and a slightly worse high temperature resistance.

Liquid silicone rubber (LSR, or sometimes referred to as LIM-Liquid Injection Molding) is a pumpable silicone having very low viscosity. LSRs usually incorporate a platinum cure system which involves hydrosilylation with platinum catalysts. In addition to an extremely quick cure time, platinum cure systems offer exceptional toughness and tensile strength, but generally require a post cure. Platinum cures are sensitive to cure inhibition from contamination with trace quantities of certain chemicals such as sulfur, or amines commonly used in organic compounds [13].

Silicone applications include: automotive seals and gaskets, spark plug boots, electrical insulators, o-rings, medical seals and gaskets, dampeners, food related parts and similar applications.

### 3.11 Fluoroelastomer (FKM)

These materials have excellent high temperature resistance and excellent fluid and oil resistance. They are very expensive, but often are the only choice in harsh environments.

There are numerous types of fluoroelastomers, including the following:

- Tetra-fluoroethylene/propylene
- Vinylidene fluoride and hexafluoropropylene copoymers, which were among the first stable fluoroelastomers
- Terpolymers of vinylidene fluoride, tetrafluoroethylene, and perfluoro (methyl vinyl)ether, or PMVE
- Terpolymers of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene.

The primary suppliers for FKM in North America are DuPont Dow Elastomers L. L. C. (Viton); Dyneon (Fluorel and Aflas); and Ausimont USA (Tecnoflon).

FKMs have three cure systems available, and some material suppliers include these systems with the compound. Diamine cures were the original cure systems available and are best suited in applications where compression set is not critical and moderate resistance to steam and acid is required.

Bisphenol cures offer improved scorch and the best compression set properties. Bisphenol also offers improved steam and acid resistance.

Peroxide cures were originally introduced to improve steam and acid resistance. However, peroxide cures do not offer the compression set resistance of bisphenol.

Applications for FKM include: automotive shaft seals and valve stem seals, fuel related seals, oil field related devices, aerospace seals and gaskets, and related applications [14].
3.12 Polyurethane (AU and EU)

There are two types of polyurethane rubber used today: polyester-based (AU) and polyether-based (EU) products. Polyurethanes possess the best tear strength of any rubber and have excellent wear and abrasion resistance. Polyurethanes have a low threshold of heat tolerance, and therefore their applications are limited.

Millable PU is cured via peroxides, sulfur, or diisocyanates. There are also castable grades of PU that are poured or injected into molds. These products are often sold as prepolymer that consist of a polyol backbone reacted with diisocyanate.

Polyurethane applications include: roller skate wheels, casters, flex joints, dust boots, grommets, medical injection sites, and similar applications [15].

3.13 Epichlorohydrin (CO and ECO)

Epichlorohydrin has excellent resistance to fuels and is less expensive than fluoroelastomers. It has therefore gained popularity in automotive fuel related applications.

Epichlorohydrin exhibits poor low temperature flexibility, low temperature properties, and abrasion resistance. Applications include: fuel seals, intake manifold boots, and hose.

3.14 Conclusion

A variety of TSE materials exist which exhibit dramatic differences in physical properties, and may require unique processing. Custom molders should understand these differences, and more importantly, they should know how to tweak efficiencies by marrying the material to the molding process.

References