1

Introduction

The purpose of this book is to improve understanding of the chemical nature of the global rubber industry in a context of commercial and political forces. These forces have often resulted in higher prices and periodic shortages in the supply of raw materials and intermediates necessary for the continued production of rubber products. Both the 20th and 21st centuries have witnessed numerous raw material shortages that have seriously impacted the global rubber industry. In all probability, these shortages and disruptions will continue for the foreseeable future.

The rubber industry today is based on the mixing of batches of rubber compounds. This industry is basically a batch industry where raw rubber(s), filler(s), and other compounding ingredient(s) are mixed together using either a two-roll mill or an internal mixer to prepare batches of rubber compounds (Figure 1.1). These uncured batches are further processed “downstream” through capital-intensive processes involving extruders, calenders, injection-molding machines, continuous vulcanization units, and curing presses. The continuity of these processes relies on a consistent, steady supply of rubber compounding ingredients and base polymers (natural and synthetic rubbers); see Figure 1.2 for how these topics are arranged in this book.

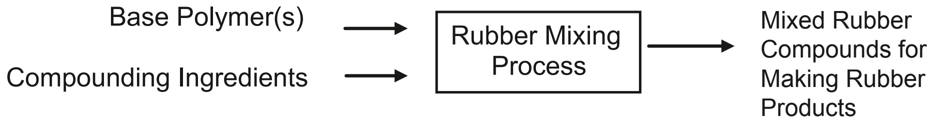


Figure 1.1 Rubber mixing process

There are three types of material shortages that have occurred and can occur in the rubber industry. These three types of shortages or material disruptions are as follows:

1. Shortage or supply disruptions in base materials from earth extraction or agriculture.
2. Shortage or supply disruptions in chemical intermediates.
3. Shortage or supply disruptions in supply of compounding ingredients or base polymers (rubbers).

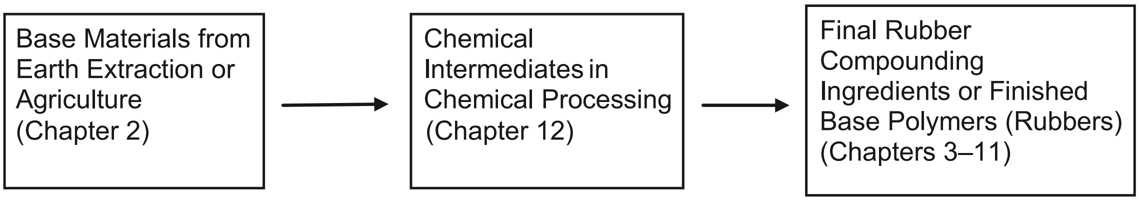


Figure 1.2 Organization of this book

Examples of shortages of extracted base materials from the earth were seen with the oil embargo of 1973 and extraction of cobalt ore in the 1980s. Shortages of the monomer styrene or butadiene needed for the polymerization of styrene butadiene rubber (SBR) are examples of chemical intermediate shortages in the 1980s and the last decade as well. Examples of rubber compounding ingredient or finished base polymer shortages are seen when the United States was cut off from its sources of natural rubber supply during World War II, shortages of zinc oxide and titanium dioxide in the 1970s and 1980s, as well as shortages of various raw elastomers in the recent past.

1.1 Rubber Industry's Place in the World Economy

The worldwide rubber industry totaled about $220 billion in 2010, which is about one-quarter of one percent of the world GDP. About two-thirds of the rubber industry is tire related with one-third being non-tire related.

1.2 The Structure of the Tire Industry

There are over 70 active tire manufacturers in the world (Table 1.1). In 2012, the big three tire companies (Bridgestone, Goodyear, and Michelin) represented about 46% of all tire sales. Bridgestone, Michelin, Goodyear, and Continental represented about 50% in 2010 of all tire sales. If Pirelli, Sumitomo, Yokohama, Hankook, Cooper Tire, Cheng Shin, Hangzhou Zhongce, Kumho Tire, Toyo Tire and Triangle are added as well, these top 14 firms represent a total of 75% of world tire manufacturing.

Table 1.1 Seventy Tire Manufacturers in Approximately Descending Order by Size

Tire Company	Headquarters Location
Bridgestone Corp.	Tokyo, Japan
Michelin	Clermont-Ferrand, France
Goodyear Tire and Rubber Co.	Akron, OH, USA
Continental AG	Hanover, Germany
Pirelli SpA	Milan, Italy
Sumitomo Rubber Industries Ltd.	Kobe, Japan
Hankook Tire Co. Ltd.	Seoul, South Korea
Cooper Tire and Rubber Co.	Findlay, OH, USA
Kumho Tire Co.	Seoul, South Korea
Toyo Tire and Rubber Co.	Osaka, Japan
Cheng Shin	Yuanlin, Taiwan
Giti Tire Co.	Singapore/China
Triangle Group Co.	Shandong, China
MRF Ltd.	Chennai, India
Noklan Tyres PLC	Nokia, Finland
Sibur-Russkie Shiny	Moscow, Russia
Apollo Tyres Ltd.	Kerala, India
Shanghai Tyre and Rubber Co. Ltd.	Shanghai, China
Amtel-Vredestein N. V.	Moscow, Russia
J. K. Industries Ltd.	New Delhi, India
Hangzhou Zhongce Rubber Co.	Hangzhou, China
Shandong Chengshan Tire Co.	Chengshan, China
Nexen Tire Corp.	Seoul, South Korea
Ceat Ltd.	Mumbai, India
Nizhnekamskshina	Nizhnekamsk, Russia
Aeolus Tyre Co.	Jiaozuo, China
BRISA/Bridgestone Sabanci Tire	Izmit, Turkey
P. T. Gajah Tunggal	Jakarta, Indonesia
GPX International Tire Corp.	Malden, MA, USA
Qingdao Doublestar Industrial Co.	Qingdao, China
Kenda Rubber Industrial Co.	Yuanlin, Taiwan
Matador AS	Puchov, Slovakia
Trelleborg AB	Trelleborg, Sweden
Carlisle Companies, Inc.	Charlotte, NC, USA
South China Tire and Rubber Co.	Cuangzhou City, China
Nankang Rubber Tire Corp.	Taipei, Taiwan
JSC Belshina Belarus Tyre Works	Bobruisk, Belarus
Dunlop Tyres International Pty. Ltd.	Durban, South Africa

Table 1.1 Seventy Tire Manufacturers in Approximately Descending Order by Size *(continuation)*

Tire Company	Headquarters Location
Marangoni, S. p. A.	Verona, Italy
FATE S. A. I. C. I.	San Fernando, Argentina
Hwa Fong Rubber Ind. Co. Ltd.	Taipei, Taiwan
CGS Ceske Gumarenska Spol.	Prague, Czech Republic
GTY Tire Co.	Mount Vernon, IL, USA
Federal Corp.	Tao Yuan, Taiwan
Alliance Tire Co.	Hadera, Israel
Cia. Hulera Tornel S. A. de C. V.	Mexico City, Mexico
Inoue Rubber Co.	Ikeda, Japan
Kerman Tire and Rubber Co.	Tehran, Iran
JSC Dneproshina	Dnepropetrovsk, Ukraine
Vredestein NV	Enschede, Netherlands
Balkrishna Industries Ltd.	Maharashtra, India
Loadsar Pvt. Ltd. / Solideal Co.	Colombo, Sri Lanka
Guangzhou Pearl River Rubber Tyre	Guangzhou, China
Denman Tire Corp.	Leavittsburg, OH, USA
Dena Tire and Rubber Mfg. Co. Ltd.	Tehran, Iran
Beijing Shouchuang Tyres Co.	Beijing, China
Metro Tyres Ltd.	Ludhiana, India
Qingdao Yellow Sea Rubber Co., Ltd.	Qingdao, China
Shandong Zhongce Tyre Co.	Shouguang City, China
Silverstone Corp.	Kuala Lumpur, Malaysia
Double Happiness Tyre Industries	Taiyuan, China
Liaoning Tyres Group Co.	Liaoning, China
Xuzhou Tyre Group	Xuzhou, Jiangsu, China
Casumina (Southern Rubber Industry)	Ho Chi Minh City, Vietnam
TVS Srchakra Ltd.	Chennai, India
Specialty Tires of America	Indiana, PA, USA
Societe Tunisienne des Pneumatiques	Sousse, Tunisia
J. V. Matador-Omskshina	Omsk, Russia
General Tyre and Rubber Co. of Pakistan, Ltd.	Karachi, Pakistan
Falcon Tyres Ltd.	Mysore, India

The tire industry sales consist of about 60% passenger tires and 30% truck and bus tires, with the remaining 10% represented by farm service, aircraft, motorcycle, bicycle, and earth-moving tires (also called off-the-road or OTR tires).

The world tire industry produced over 1 billion tires of all types in 2010. By the numbers of tires (not sales figures), about 80% of all tires are passenger tires. There are about eight passenger tires made for every truck tire produced. According to the Rubber Manufacturers Association (RMA), a typical passenger tire weighs about 25 pounds and contains about 3.5 pounds of natural rubber, about 6.8 pounds of synthetic rubber, 7 pounds of carbon black, and 3.7 pounds of steel tire cord and bead wire. Likewise, the typical truck tire weighs about 120 pounds and contains about 32.4 pounds of natural rubber, 17 pounds of synthetic rubber, 33.5 pounds of carbon black, and 17.4 pounds of steel tire cord and bead wire.

■ 1.3 The Structure of the Nontire Industry

There are numerous nontire rubber fabricators in the world today (Table 1.2). A far larger number of different rubber fabrication plants exist for the nontire than for the tire sector. The economies of scale are different for tire manufacturing compared to fabrication of rubber articles and products for the nontire sector. Achieving effective economies of scale for a tire plant requires a certain minimal size of perhaps 25,000 tires per day. On the other hand, the minimal capital and size requirements for production plants in the nontire sector are considerably less. Therefore, the nontire sector is populated with a larger number of production plants, representing a broader mix of large, medium, and small plants.

Table 1.2 Some of the Largest Nontire Rubber Companies in the World in Approximate Descending Order of Their Annual Sales of Nontire Rubber Products

Company	Country of Origin
Continental AG	Germany
Hutchinson	France
Bridgestone Corp.	Japan
Freudenberg Group	Germany
Trelleborg	Sweden
Tokai Rubber Industries	Japan
Tomkins PLC	United Kingdom
Cooper Standard Automotive	USA
Parker Hannifin Corp.	USA
NOK Inc.	Japan
New Balance Athletic Shoe	USA
Veyance Technologies	USA
Mark IV Industries	USA
Federal-Mogul Corp.	USA
Eaton Corp.	USA

Table 1.2 Some of the Largest Nontire Rubber Companies in the World in Approximate Descending Order of Their Annual Sales of Nontire Rubber Products *(continuation)*

Company	Country of Origin
Wolverine World Wide	USA
Carlisle Companies	USA
Metzeler Automotive Profile Systems	Germany
Yokohama Rubber Co.	Japan
Ansell Ltd.	Australia
Toyo Tire and Rubber Co.	Japan
Semperit AG	Austria
Fenner PLC	United Kingdom
Dana Corp.	USA
Bando Chemicals Industries	Japan
ZF Boge Elastmetall	Germany
Sumitomo Rubber Industries	Japan
SKF AB	Sweden
West Pharmaceutical Services	USA
WOCO Industrietechnik	Germany
ElringKlinger AG	Germany
Kinugawa Rubber Co.	Japan
Cardinal Health	USA
Veritas AG	Germany
Saar Gummi Group	Germany
Zodiac SA	France
Fukoku Co.	Japan
Avon Rubber p.l.c.	United Kingdom
Mitsuboshi Belting Ltd.	Japan
Nishikawa Rubber Co.	Japan
SSL International PLC	United Kingdom
Okamoto Industries	Japan
Lord Corp.	USA

The top four nontire companies are Freudenberg, Hutchinson, Bridgestone, and Continental, each with about three billion dollars in annual sales. Therefore, in 2010 these top four firms represented at least one-fifth of the entire nontire rubber industry.

This nontire rubber industry is about 38% dependent on the automotive industry, 32% industrial, 12% construction, 12% aerospace and other transportation, and 6% other application areas.

1.4 Sectors of the Nontire Rubber Industry

The major sectors of the nontire industry include the following:

- Hoses
- Conveyor belts
- Transmission belts
- Seals and gaskets
- Blowout preventers
- Single-ply roofing
- Bushings and motor mounts
- Molded rubber goods
- Tank lining
- Wire and cable insulation
- Shoe heels and soles
- Sponge rubber
- Weatherstripping
- Latex products
- Rubber rollers
- Rubber tiles
- Rubber bands

1.4.1 The rubber *hose* industry is one of the two largest segments of nontire rubber fabricators. Worldwide, the hose industry had about $6 billion dollars in total sales in 2010. Automotive and industrial are two very large market areas for hose. Some hose processes, for machine-made and hand-built hose, are very labor intensive. Processes for braided and spiral hose are less labor intensive. Hoses constructed in the factory are commonly cured in autoclaves.

1.4.2 The *belt* segment is approximately the same size as the hose segment, $6 billion dollars worldwide in 2010. Conveyor belts (or large belts) are used as an efficient conveyance system for ores and mineral deposits for both surface and underground mining. Power transmission belts are used extensively in the automotive and industrial equipment markets. Light belts are used in such applications as food cafeterias.

1.4.3 *Seals and gaskets* are another multibillion dollar industry. Modern machinery requires many seals and gaskets, which are used everywhere in industry. There are static seals such as traditional O-rings and gaskets. Also, there are dynamic seals used under reciprocating conditions such as radial lip seals. Dynamic seals are also used under rotary conditions. These rotary seals can be either contacting or noncontacting. Contacting rotary, dynamic seals are represented by radial shaft seals, axial slingers, mechanical face seals, and packings. Noncontacting, rotary, dynamic seals are represented by viscoseals, fluid seals, labyrinths, and bushings. Seals are usually manufactured by either injection or compression molding.

1.4.4 *Blowout preventers and packers* are adjustable sealing devices made of rubber and metal that are used extensively in oil drilling operations (called “downhole”). These devices are relatively large and critical to successful oil exploration and production. Because of the increasing need for more oil, this market has been growing significantly. About 5% of the available nitrile rubber goes into BOP (blowout preventer) production. Significant quantities of fluoroelastomers, HNBR and XNBR, are also used in this area. Much of the manufacture of these devices is carried out in the states of Texas and California.

1.4.5 *Single-ply roofing* is one of the largest single uses for EPDM rubber. It is the preferred roofing material for most commercial buildings, especially in the United States. Warranties are very important in this market. These roofing materials must function as an effective barrier for many years.

1.4.6 *Bushings and motor mounts* are components used in virtually all motorized vehicles. Here dynamic performance is critical. Rubber is compounded to impart specific, targeted dynamic property characteristics to these components. Rubber compounds in these components can be formulated to function as “isolators,” which pass mechanical energy through the component with only a minimal amount of heat generation. Or, rubber compounds can be formulated as “dampers,” which deliberately absorb energy being passed through the component and dissipate that energy as heat. Dynamic targets are set up for the quality assurance of these products, so they can function in the field as they were designed. Usually, injection or compression molding is used to manufacture these rubber-metal components.

1.4.7 Besides seals and dynamic rubber components (bushings and motor mounts), other *molded rubber goods* represent a sizable market. Products are manufactured through compression molding or the more productive injection molding. Also, liquid injection molding (LIM) has been gaining a larger market share. In fact, many molded rubber goods for the medical industry are made from liquid silicone rubber (LSR) through LIM. Some other common examples of molded rubber goods include bumpers, grommets, end stops, buffers, diaphragms, and bellows (cylindrical extendable vessels).

1.4.8 *Tank lining* is a relatively small market where rubber is specially formulated and cured to make an effective barrier to contain various liquids for transportation and storage. Worldwide, there are just a few rubber fabricators serving this market. Rubber lining is also used as a wear layer, protecting steel pipe from highly abrasive mining slurry.

4

Specialty Elastomers

Unlike the general-purpose elastomers just discussed, specialty elastomers have lower volumes of use. Except for butyl and halobutyl rubbers, most of the rubbers in this group have some degree of oil resistance. On the other hand, butyl and halobutyl rubbers possess good aging resistance properties.

The following specialty elastomers in Table 4.1 are discussed in this chapter.

Table 4.1 Speciality Elastomers

Name	Official ASTM Abbreviation	Alternate Name
Butyl Rubber	IIR	
Halobutyl Rubber	BIIR, CIIR	Chlorobutyl Rubber, Bromobutyl Rubber
Isobutylenepara-methyl Styrene Rubber	BIMSM	BIMS
Acrylonitrile Butadiene Rubber	NBR	Nitrile Rubber
Hydrogenated Acrylonitrile Butadiene Rubber	HNBR	Hydrogenated Nitrile Rubber
Curable PVC/NBR Polyblends	None	
Acrylic Rubber	ACM	Polyacrylate Rubber
Polychloroprene	CR	Neoprene
Chlorinated Polyethylene Rubber	CM	CPE
Chlorosulfonated Polyethylene	CSM	
Epichlorohydrin Rubber	CO, ECO	Chlorohydrin Rubber
Ethylene Acrylic Elastomer	AEM	
Ethylene Vinyl Acetate	EVM	EVA
Fluoroelastomers	FKM, FEPM	Fluorocarbon Elastomer
Perfluoroelastomer	FFKM	Perfluorocarbon Elastomer
Silicone Rubber	MQ, PMQ, PVMQ, VMQ, FMQ, FVMQ	

Reference: ASTM D1418; ASTM D2000

The following discussion gives a classification of these specialty elastomers based on their relative oil vs. heat resistance, in accordance with ASTM D2000 testing (Figure 4.1).

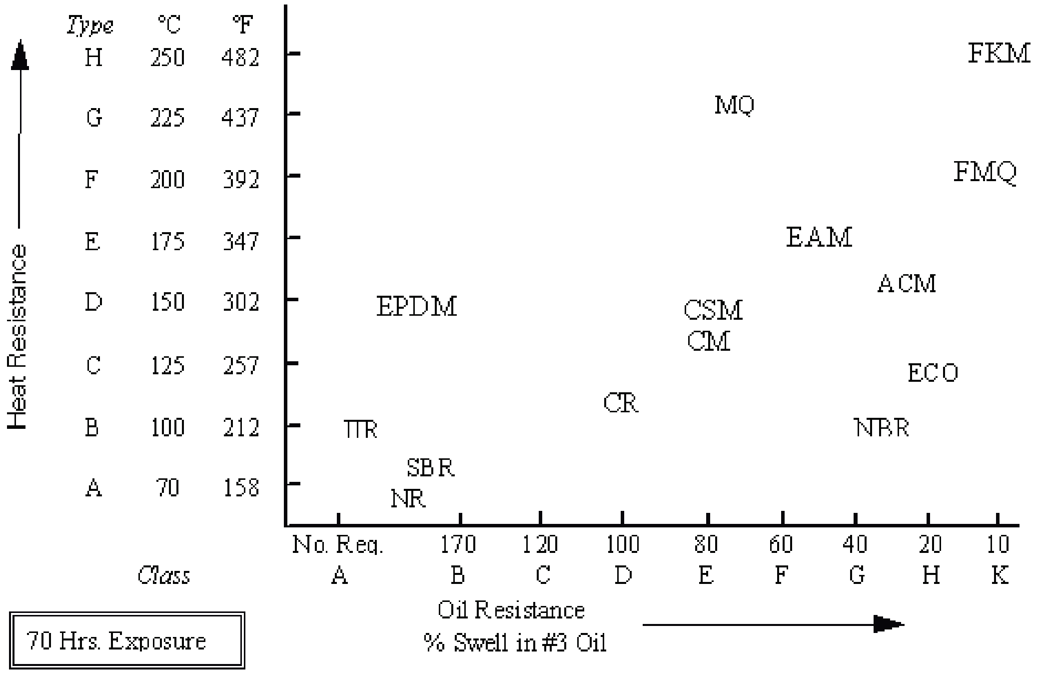


Figure 4.1 Classifying specialty elastomers by ASTM D2000

Except for butyl and halobutyl, these specialty elastomers are largely used in the nontire sector of the rubber industry. They typically provide differing degrees of heat aging and oil resistance.

4.1 Butyl Rubber

Butyl rubber is a copolymer of isobutylene and isoprene. It is a product of research carried out in both Germany and the United States in the 1930s.

Polyisobutylene rubber (IM) was a precursor to butyl rubber, which was first developed in Germany. However, this polymer had no unsaturation; it could not be cured with a sulfur-based system. In 1937 Standard Oil (now ExxonMobil) developed the copolymer version that is used today in high volume. A small amount of isoprene provides the unsaturation that enables conventional curing with sulfur or other crosslinkers.

The world productive capacity for butyl rubber (and its related “cousin” halobutyl) is about 2 billion pounds annually from over 12 production plants scattered around the world. This volume represents 7% of the world production of synthetic elastomers. It is the fifth largest volume rubber used today and the highest volume specialty elastomer. In fact, the consumption of butyl rubber is comparable in volume to that of the general-purpose elastomers discussed earlier.

ExxonMobil and Lanxess together have about 80% of the world capacity, with ExxonMobil possessing the larger market share in 2010. The demand for butyl grows about 1.5% annually. Some new capacity has been created in China and Singapore. However, because of the specialized nature of butyl rubber's manufacture, it is difficult for other companies to quickly acquire the "know-how" to break into this market.

While there are butyl rubber plants around the world, there appears to be a disproportionately high level of capacity in North America. However, because of the relatively higher prices for butyl rubber compared to general-purpose elastomers, the shipment costs are only a small fraction of the total costs. Therefore, a significant quantity of butyl rubber is exported from North America to many other countries worldwide.

Butyl rubber (Figure 4.2) is made from a cationic vinyl polymerization of isobutylene, with a relatively smaller quantity of isoprene, carried out at very low temperatures (to prevent the reaction from proceeding too quickly and getting out of control). This polymerization reaction is very exothermic.

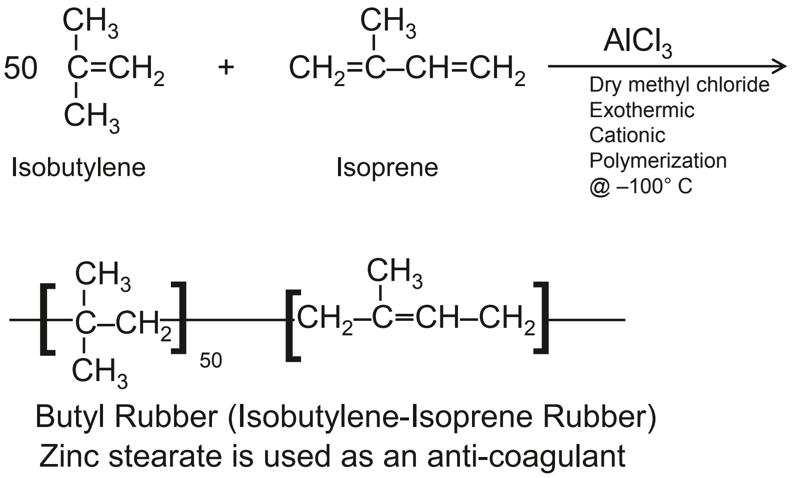


Figure 4.2 Butyl rubber synthesis

Synonyms

IIR

Butyl rubber

Feedstock Dependency

Isobutylene is obtained from fractionation of refinery gases see Figure 4.3.

Figure 4.3 The fractionation of refinery gases to obtain isobutylene

Isoprene can be obtained from three different processes shown in Figure 4.4.

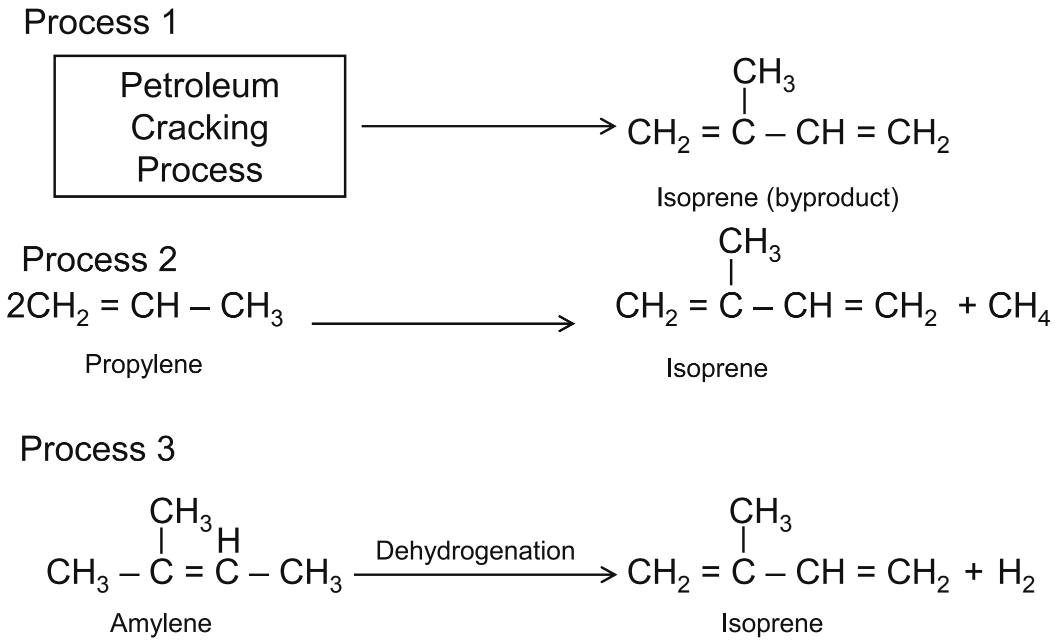


Figure 4.4 Three processes for obtaining isoprene

Standard Classifications

There is no official standard classification for butyl rubber. These elastomers are classified usually by their Mooney viscosity (ASTM D1646), and the mole percent unsaturation (which is proportional to the amount of the second monomer (isoprene) is generally not greater than 3%. Higher mole percent unsaturation will increase the cure rate but can hurt the ozone resistance imparted to the cured rubber compound.

Some Producers

ExxonMobil

Lanxess

Japan Butyl Co. (JSR/ExxonMobil)

JSR (Japan)

Nizhnekamskneftekhim (Russia)

Socabu (ExxonMobil) (France)

Sibur (Russia)

Reliance Industries (India)

Sinopec (China)

Zhejiang Cenway New Synthetic (China)

Why Used in Rubber Industry

The major reason that butyl rubber is used in the tire industry is its superior resistance to air permeability, as well as other gases. Butyl has approximately 13 times greater resistance to air permeability than natural rubber. This makes it ideal for use in making tire innerliners and inner tubes. While some polar specialty elastomers can also provide good air permeability resistance, they are far more expensive and generally do not possess the right combination of other needed properties.

Butyl rubber, because of its chemical structure, imparts high damping properties in dynamic applications where energy absorption is needed in automotive and other applications. In addition, certain grades of butyl are used in medical applications.

Alternate Nonrubber Uses

Butyl is also used in the manufacture of sealants and caulking materials. Special FDA-approved grades of butyl rubber are used in chewing gum.

Substitutability and Technical Alternatives

Because of butyl rubber's unique resistance to air permeability, its use is very important. It is very difficult to substitute with another elastomer, especially when those elastomers cost more.

Tight Supply Situations in the Past and Future Supply Outlook

There have been tight supply situations for butyl and halobutyl in the past. The demand for regular butyl rubber is decreasing in developed countries because it is chiefly used in tire inner tubes, which are in declining use in developed economies. (The innerlining of tires today uses halobutyl rubber, which will be discussed next.) Because of this decline in use of tire inner tubes, ExxonMobil will be eliminating its production of regular butyl but increasing production of bromobutyl at its Baytown, Texas, plant. Also, Lanxess has announced a similar increase in production of halobutyl rubber at its Sarnia, Canada, plant and built a new plant in Singapore.

■ 4.2 Halobutyl Rubber

The halogenated form of butyl rubber, which was developed in the 1950s, has replaced a significant amount of regular butyl consumption over the last few decades. It is the only form of butyl that can be used in tubeless tire innerliners, which now represents over 60% of all forms of butyl rubber use. Halobutyl rubber has partially replaced the use of regular butyl because it is compatible in blends with general-purpose elastomers such as natural rubber. Since zinc oxide is a vulcanizing agent for halobutyl rubber, it can be covulcanized with general-purpose elastomers as well. This was not possible with regular butyl rubber, which cannot be cocured. Also, halobutyl imparts adhesion to general-purpose elastomers where regular butyl rubber does not.

There are two variants of halobutyl: chlorobutyl and bromobutyl rubbers see Figures 4.5 and 4.6, respectively. These halobutyl rubbers are made directly from regular butyl rubber.

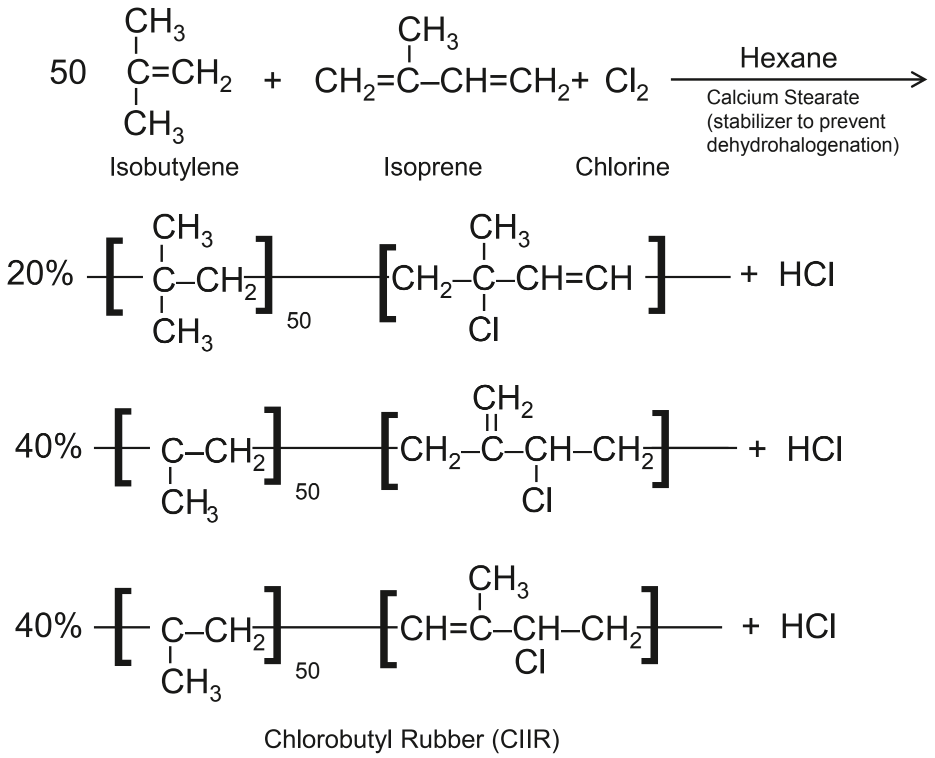


Figure 4.5 The process for chlorobutyl rubber (CIIR)

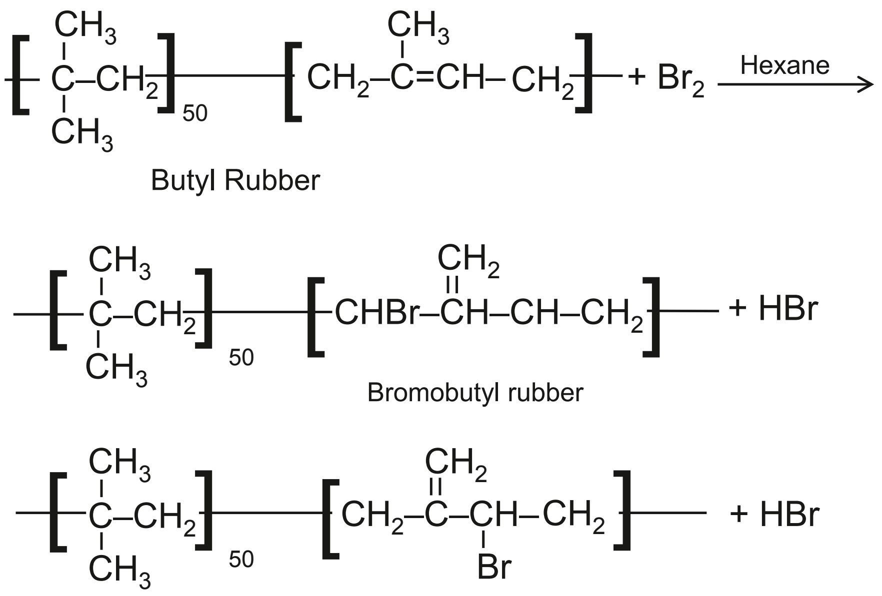


Figure 4.6 The process for bromobutyl rubber (BIIR)

Bromobutyl rubber is a little more expensive to produce than chlorobutyl rubber; however, it will sometimes give better adhesion than chlorobutyl rubber to other elastomer-based compounds. Also, bromobutyl rubber cures a little faster than chlorobutyl. However, bromobutyl rubber may also have a greater tendency than chlorobutyl rubber to impart scorch problems to a compound during processing.

Synonyms

Chlorobutyl rubber

CIIR

Bromobutyl rubber

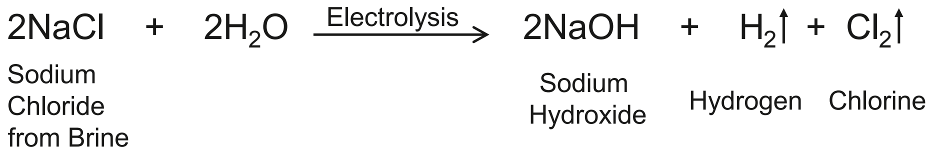
BIIR

XIIR

HIIR

Feedstock Dependency

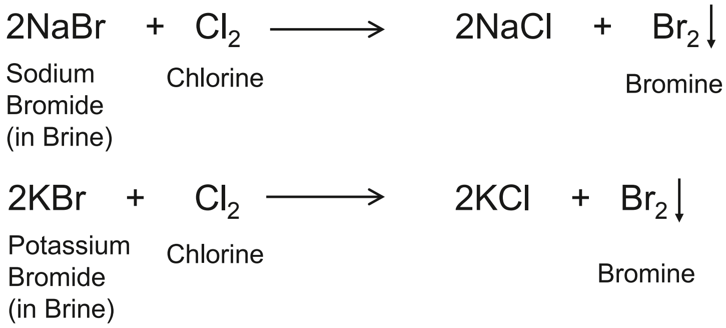
With chloro- and bromobutyl rubbers, regular butyl rubber is considered a "raw material" that is being halogenated with either chlorine or bromine from the following sources, see Figure 4.7.



$$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + H_2\uparrow + Cl_2\uparrow$$

Figure 4.7 The preparation of chlorine for the chlorination of butyl rubber

Bromine can be obtained by a simple substitution reaction of sodium bromide with elemental chlorine shown in Figure 4.8.



$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2\downarrow$$

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2\downarrow$$

Figure 4.8 Elemental chlorine reacts with sodium bromide and yields bromine

Standard Classifications

Just as with regular butyl rubber, there is no official classification system for halobutyl rubber. However, these polymers are commonly classified by their Mooney viscosity value (ASTM D1646), and amount and type of halogenation and unsaturation.

Some Producers

ExxonMobil

Lanxess

JSR (Japan)

Chinopec (China)

SIBUR (Russia)

Zhejiang Cenway New Synthetic (China)

Why Used in Rubber Industry

Halobutyl rubber is used mostly to make the innerliner compound for today's modern tubeless tires. This is because halobutyl rubber is compatible with general-purpose rubbers, can be covulcanized with them, and can impart good adhesion to them. Virtually all tubeless tire innerliners use halobutyl rubber.

Alternate Nonrubber Uses

There are not as many nonrubber applications for halobutyl rubber as there are for regular butyl rubber.

Substitutability and Technical Alternatives

The technical alternatives to halobutyl rubber in tire innerliner applications are very poor, in the short term. However, with the development of new innerliner compounds based on BIMS (see below), a substitution could be achieved long term with much development work.

A new BIMS/nylon thermoplastic vulcanizate innerliner is being investigated for possible use as a tire innerliner.

Tight Supply Situations in the Past and Future Supply Outlook

There have been tight supply situations and even customer allocations of halobutyl rubber that from time to time have limited its availability. Sometimes, the problem has been limited productive capacity. Sometimes, the problem has been a shortage of isobutylene feedstock. These problems should be alleviated somewhat with announced capacity improvements by ExxonMobil and Lanxess. ExxonMobil announced that it has increased its productive capacity for halobutyl rubber at its Baytown, TX, plant, and its joint venture in Japan has been expanded. Lanxess has increased the halobutyl rubber capacity at its plants in Sarnia, Canada, and Singapore.

4.3 Brominated Copolymer of Isobutylene and *para*-Methylstyrene (BIMSM)

Brominated copolymer of isobutylene and *para*-methylstyrene (BIMS) is the latest new class of synthetic rubber that has been developed for the rubber industry. The sole producer of this new class of elastomer is ExxonMobil, which commercialized it successfully under the trade name Exxpro in the first decade of this new century. The advantage of this new polymer class vs. bromobutyl rubber is that this new elastomer possesses a completely saturated backbone and possesses more reactive benzylic bromine functionality than the bromine sites on the conventional bromobutyl backbone. This means that BIMS reportedly gives superior performance in service vs. BIIR. This superiority is shown as better high-temperature resistance, better aging stability than either BIIR or EPDM, better weathering resistance, and better ozone resistance. Also, BIMS provides the potential of imparting superior air permeability resistance.

This new commercial rubber is produced from the carefully controlled bromination of the copolymer of isobutylene and *para*-methylstyrene, which forms a terpolymer as shown in Figure 4.9.

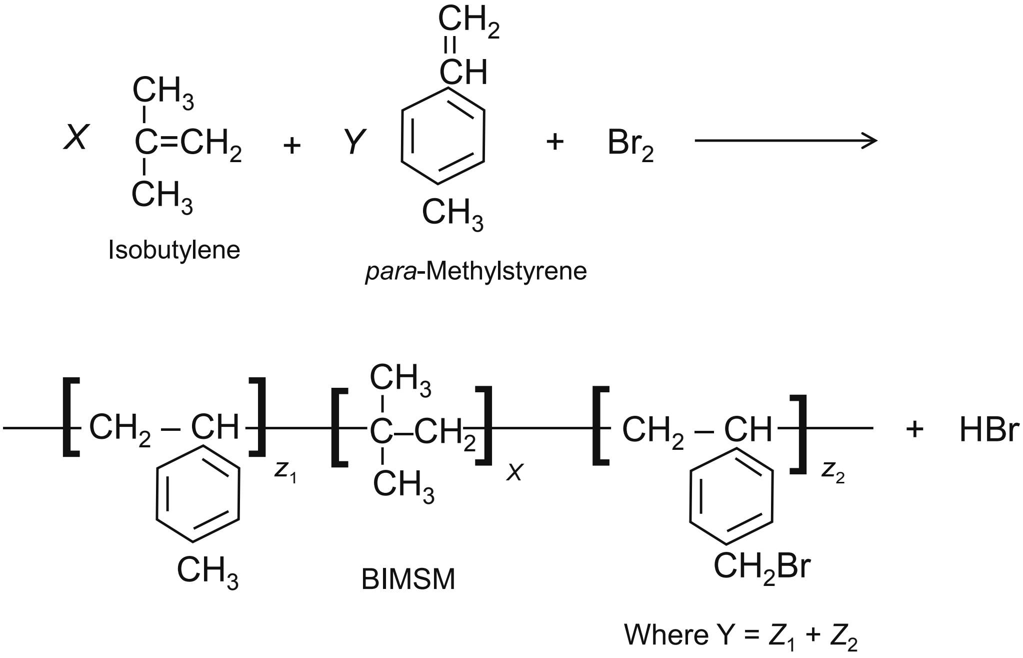


Figure 4.9 Copolymerization of isobutylene and *para*-methylstyrene to give BIMSM

The quantity of *para*-methylstyrene (PMS) used in this polymerization is small relative to the isobutylene (maybe only 2 to 20 weight percent PMS depending on the grade) while the bromine is even less, perhaps 0.2 to 3 mole percent. The ratio of feedstocks has a great influence on the performance of the BIMSM in rubber compounding.

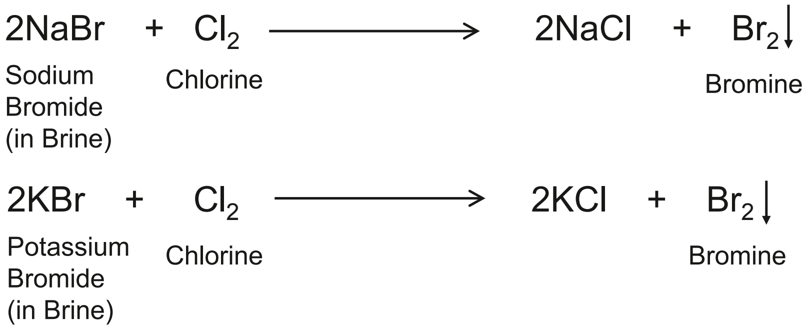
Synonyms

BIMS

BIMSM (official ASTM abbreviation where all rubbers with saturated backbones must end the abbreviation with M)

Feedstock Dependency

The production of BIMSM depends on the availability of bromine, isobutylene, and paramethylstyrene, as shown in Figure 4.10 through Figure 4.12.



$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2\downarrow$$

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2\downarrow$$

Figure 4.10 Optional paths to synthesis of bromine

Figure 4.11 The manufacture of isobutylene

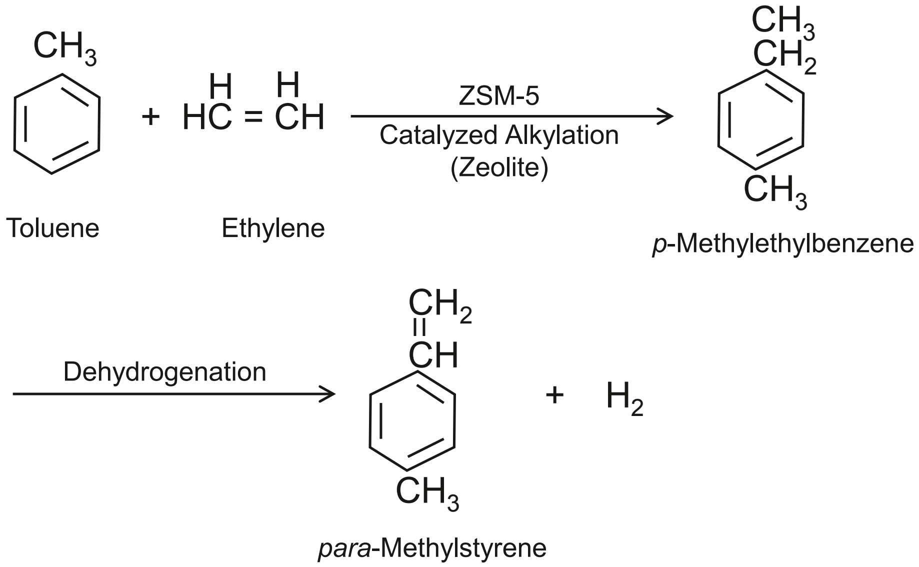


Figure 4.12 Derivation of *para*-methylstyrene

Standard Classifications

There is no formally accepted method of classifying the different grades of BIMSM. However, an informal classification could be based on the amounts of *para*-methylstyrene and the level of bromination that determines the different grades of BIMSM.

Some Producers

ExxonMobil Chemical Company

Why Used in Rubber Industry

BIMSM may be used instead of halobutyl rubber because it possesses a saturated backbone that imparts a heat aging resistance superior to XIIR. Also, tires can be constructed with a BIMSM-based innerliner that will hold air longer than conventional innerliners based on XIIR.

Alternate Nonrubber Uses

Unknown

Substitutability and Technical Alternatives

Of course, before BIMSM was invented, XIIR (halobutyl rubber) was (and still is) extensively used for tire innerliners. If there were a shortage of BIMSM, the tire industry should be able to return to XIIR-based innerliners.

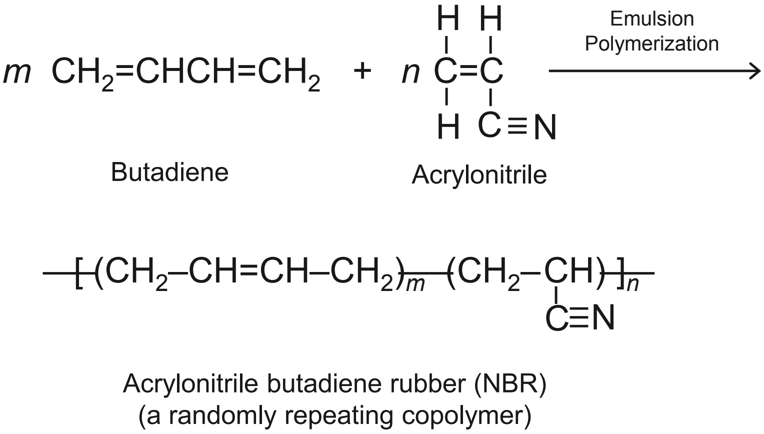
ExxonMobil in 2005 announced that it was increasing its productive capacity for manufacturing BIMS. How successful BIMS will be at partially replacing XIIR is currently being determined. The use of BIMS to make an “alloy” TPV with nylon may actually have a better chance at replacing traditional XIIR innerliners through a new blow molding process. Also, BIMS is being considered for medical applications.

■ 4.4 Nitrile Rubber

Nitrile rubber is a copolymer of acrylonitrile and butadiene (BD) with the standard abbreviation of NBR. NBR is produced by emulsion polymerization, and it dates back to the 1940s. The emulsion polymerization process developed for NBR is somewhat similar to the emulsion process developed for SBR in the same time period.

As a specialty elastomer, a rather large quantity of nitrile rubber is consumed. About one billion pounds of NBR are manufactured in the world each year, almost 4% of the total production of synthetic elastomers. The reason for its relatively large worldwide use is simply that this polymer is a relatively inexpensive rubber for use whenever good oil resistance is needed, for example in hose applications, belting, “under the hood” automotive applications, and “downhole” oil drilling applications.

The chemical process for manufacturing NBR is shown in Figure 4.13.



$$m\ CH_2{=}CHCH{=}CH_2 + n\ \overset{H\ \ H}{C{=}C}\underset{H\ \ C\equiv N}{} \xrightarrow[]{\text{Emulsion Polymerization}} -\!\!\left[(CH_2{-}CH{=}CH{-}CH_2)_m\,(CH_2{-}\underset{C\equiv N}{CH})\right]_n\!\!-$$

Figure 4.13 Chemical process for nitrile rubber (NBR)

Synonyms

Nitrile rubber

Acrylonitrile butadiene rubber

NBR

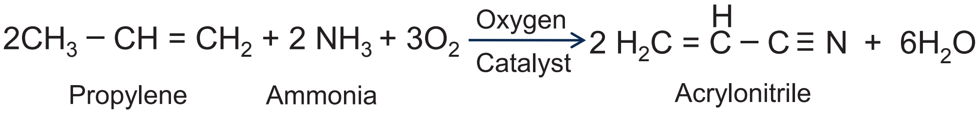
Buna N

Paracril

Nitrile butadiene rubber

Feedstock Dependency

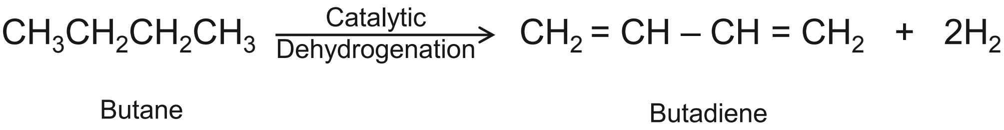
The basic feedstocks for NBR are shown in Figures 4.14 and 4.15. For acrylonitrile, propylene can be reacted with ammonia to produce acrylonitrile (ACN).



$$2CH_3 - CH = CH_2 + 2\ NH_3 + 3O_2 \xrightarrow[\text{Catalyst}]{\text{Oxygen}} 2\ H_2C = \overset{H}{C} - C \equiv N + 6H_2O$$

Figure 4.14 Production of acrylonitrile (ACN)

Butadiene, on the other hand, is derived as shown in Figure 4.15.



$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{Dehydrogenation}]{\text{Catalytic}} CH_2 = CH - CH = CH_2 + 2H_2$$

Figure 4.15 Derivation of butadiene (BD)

Today more butadiene is produced from butene (another C4) through steam cracking of naphtha gas oil as a byproduct from ethylene/propylene production. Through extractive distillation of this C4 cracker stream, butadiene is obtained. Commonly, the yield achieved for BD is dependent on the quality of the feedstocks used for ethylene production. Usually, the heavier the feedstock, the greater the BD production. Reportedly, the "light" feedstock only yields about one-fifth the yield of butadiene compared to the "heavy" feedstock.

One major problem with the availability of NBR in 2007 and 2008 was the availability of butadiene monomer. Because of the gradual switchover from petroleum-based naphtha feedstocks to ethane natural-gas-based feedstocks in the production of ethylene for the plastics industry, there are fewer C4 streams available for butadiene production. Ethylene plants are gaining significant economic savings by making this feedstock conversion from naphtha to ethane. This has resulted in significant shortages of butadiene to the rubber industry during the last decade. However, there is optimism now that butadiene will be more available than previously because of the emergence of hydraulic fracturing (or "fracking") for natural gas (especially "wet" natural gas), which has resulted in a new abundance of butane. With all these new reserves of butane, there should be no problem in the future in building "on purpose" cracking units for the sole purpose of converting butane into butadiene.

Standard Classifications

There is no official standard classification system for different grades of nitrile rubber. Commonly the percent acrylonitrile (ACN) and the Mooney viscosity value (which crudely relates to average molecular weight by ASTM D1646) are used to classify an NBR. Even with this, however, it is very possible that two sources of NBR with the same ACN content and the same Mooney viscosity will still process very differently and impart quite different physical properties to a rubber compound.

NBR grades that possess higher bound ACN content will usually impart higher oil resistance to a rubber product while in service. However, a higher percent ACN content will also hurt the products low-temperature properties and resiliency.

Some Producers

Zeon Chemical Co.

Lanxess

DSM Copolymer

Nitrilo

INSA, LLC

Nitriflex (Brazil)

Kumho

Nantex (Taiwan)
Synthos (Poland)
Sibur (Russia)
JSR
Polimeri
Insa Gpro (Nanjing) Synthetic Rubber Co. (China)
Girsa (Mexico)
PetroChina
Hyundai (Korea)

Why Used in Rubber Industry

NBR is commonly selected where good oil resistance is needed but high-temperature service conditions are not required. If high protection against heat is not needed, then the price of NBR is usually quite reasonable.

About 20% of NBR is used in the molding of rubber seals and O-rings that will be exposed to engine oil, lubrication oil, and so on.

Another 30% is used in hose and belting stock, again for oil resistance.

About 5% is used in making blowout preventers or packers in the so-called "downhole" applications in drilling for oil

Another 10% is used in molding miscellaneous parts.

About 12% is used in making rubber latex products, while another 5% goes into sponge applications.

Maybe 3% is used in footwear (such as in the soles of work shoes and military footwear).

Alternate Nonrubber Uses

About 15% of NBR is used by the sealant and adhesives industry.

A significant quantity of NBR is used as an impact modifier in the plastics industry for ABS plastic and NBR/PVC plastic blends.

Substitutability and Technical Alternatives

Certainly, other specialty elastomers can be substituted for NBR to achieve even better oil resistance. However, most of these alternatives currently have a significantly higher price than NBR. For oil resistance per se, NBR is very price effective.

Tight Supply Situations in the Past and Future Supply Outlook

In the 1980s there were approximately 10 NBR plants in North America and many others in Europe, Asia, and South America. Now there is only one nitrile rubber plant left in the United States (Zeon's Louisville, KY, plant). Also, there is the nitrile rubber plant in Altamira, Mexico, which exports into the United States. (The Lanxess Canadian NBR plant has been shut down.) The NBR polymerization technology is mature. The "barriers to entry" are small compared to some other types of polymer plants. Thus other countries are increasing their NBR productive capacities while developed countries such as the United States have been decreasing theirs. However, in 2008 Lanxess modernized their Lawantzenau, France, NBR plant, which increased its output by 30%. Lanxess invested $15 million in this upgrade. Also, significant, new productive capacity of NBR is being created in Asia.

In the last twenty years the demand for NBR has been rather flat (or even declining in some locations) because many of the newer specialty elastomers have substituted for automotive "under the hood" applications that traditionally went to NBR. The operating temperatures "under the hood" have been getting progressively higher. Regular NBR does not have very good heat aging resistance.

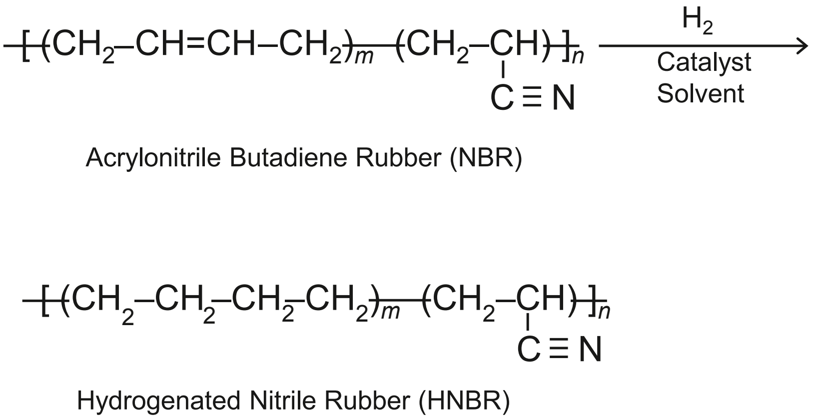
Worldwide demand for NBR is projected to grow about 3% annually on average even though the growth in the United States has been declining about –1.2% annually. The largest growth in emerging producers of NBR can be found in mainland China and Taiwan.

There have been some shortages from time to time of available NBR in the last twenty years.

4.5 Hydrogenated Nitrile Rubber (HNBR)

HNBR has significant advantages over NBR in that it imparts superior heat and oxidative resistance compared to the less-expensive NBR, without loss in oil resistance. Also, the hydrogenation to convert NBR to HNBR changes the butene backbone to a methylene backbone, which improves the strength of an HNBR compound as measured by ultimate tensile strength and tear-resistance tests. However, converting the butene backbone to a more flexible, saturated methylene backbone can hurt low-temperature properties because of crystallization. So in order to prevent this sacrifice in low-temperature properties, a second generation of HNBR polymers was developed using proprietary third monomers in order to break up crystallinity tendencies and restore good low-temperature properties. Not only do HNBR elastomers retain their oil-resistant properties, but they possess superior dynamic properties vs. NBR, which explains why HNBR is the preferred polymer for use in the production of automotive timing belts.

HNBR is manufactured from specially prepared NBR elastomers. By using a proprietary precious metal catalyst (which selectively saturates the olefinic rather than the nitrile unsaturation, with a catalyst cost of more than $500 per ounce), this NBR feedstock is converted into HNBR, which is marketed at a much higher price than NBR. Because of HNBR's specialized applications and higher cost, only about 50 million pounds are used each year worldwide.



$$\left[(CH_2{-}CH{=}CH{-}CH_2)_m {-} (CH_2{-}\underset{\displaystyle C \equiv N}{CH}) \right]_n \xrightarrow[\text{Catalyst Solvent}]{H_2}$$

$$\left[(CH_2{-}CH_2{-}CH_2{-}CH_2)_m {-} (CH_2{-}\underset{\displaystyle C \equiv N}{CH}) \right]_n$$

Figure 4.16 The manufacture of hydrogenated nitrile rubber (HNBR) from NBR

As seen in Figure 4.16, the HNBR possesses no unsaturation in the backbone if it is fully saturated. However, many grades are produced where the NBR is only partially saturated, leaving a relatively small level of unsaturation in order to sulfur cure the HNBR polymer. Sulfur cures can impart less heat buildup during dynamic flexing of a given product; however, peroxide cures of a fully saturated HNBR-based compound can give greater strength and heat resistance.

Complete saturation of the polymer backbone as shown above imparts much better resistance to ozone attack, extended service temperature range, and improved hot air resistance, compared to compounds based on conventional NBR. In other words, compounds based on HNBR are much more resistant to heat than those based on regular NBR elastomers. HNBR compounds have better thermo-oxidative aging resistance, qualifying them for automotive "under the hood" applications.

Synonyms

Hydrogenated nitrile

Hydrogenated NBR

Hydrogenated acrylonitrile butadiene rubber

HNBR

Highly saturated nitrile (HSN)

Index

Symbol

1,1,1-trichloroethane 523
1,1,1-trimethylolpropane (TMP) 524
1,1'-azobisformamide 361
1,2-dichloroethane 437
1,3-ethylene-2-thio-urea 289
1,4-BD 190, 191
1,4-bis-(*t*-butylperoxyisopropyl)benzene 323
1,4-butanediol 190, 191, 381, 401, 406, 446, 464
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