BUTYL RUBBER

1. Introduction and Background

Isobutylene has been of interest since the early days of synthetic polymer research when Friedel Crafts catalysts were used to prepare elastic materials. Isobutylene polymers of commercial importance include homopolymers and copolymers containing small amounts of isoprene or *p*-methylstyrene. Currently, chlorinated and brominated derivatives of butyl(poly[isobutylene-*co*-isoprene]) have the highest sales volume.

Isobutylene was first observed to polymerize in 1873 but high molecular weight polymers were not made until work at I. G. Farben in Germany established that molecular weight increases with decreasing polymerization temperature. Polyisobutylene was synthesized at $-75°C$ using BF_3 as a catalyst. However, as the polymer was saturated, it could not be cross-linked into a rubbery network and no commercial uses were found (1).

Poly[isobutylene-*co*-isoprene] or butyl rubber was synthesized in 1937 at the Standard Oil Development Co., forerunner of ExxonMobil Chemical Co. (2). The first sulfur-curable copolymer was prepared in ethyl chloride over an aluminum chloride catalyst with 1,3-butadiene as the comonomer; however, it was soon found that isoprene was a better comonomer and that methyl chloride was a better polymerization diluent. During World War II, the natural rubber supply to the United States was drastically curtailed, boosting the production of synthetic rubber. The commercial production of butyl rubber in 1943 was an enormous scientific and engineering achievement given the very early state of the art and complexity of this technology.

The discovery of butyl rubber was, in fact, the discovery of the limited-functionality elastomers. Unlike natural rubber and polybutadiene, which have reactive sites on every monomer unit, the unsaturation in butyl rubber is widely spaced along a saturated, flexible hydrocarbon chain. The principle of limited functionality has been subsequently used in other elastomers, eg, ethylene–propylene terpolymers and chlorosulfonated polyethylene. Halogenated butyl rubber was first synthesized at Goodrich (3). A brominated butyl rubber was commercialized via a small-scale batch method in 1954 starting from *N*-bromosuccinimide and butyl rubber. The product was withdrawn in 1969. Following the withdrawal of Goodrich bromobutyls from the market, Polymer Co. of Canada developed the commercial process using elemental bromine, which is the currently used commercial process. Chlorinated butyl rubber was developed at ExxonMobil and commercialized in 1961. It is made by the continuous chlorination of a solution of butyl rubber (4). Currently, brominated butyl rubber is also manufactured by a similar continuous-solution process.

The first use for butyl rubber was as inner tubes, whose air-retention characteristics contributed significantly to the safety and convenience of tires. Good weathering, ozone resistance, and oxidative stability have led to applications in mechanical goods and elastomeric sheeting. Automobile tires were manufactured for a brief period from butyl rubber, but poor abrasion resistance curtailed this development.

Halogenated butyl rubber greatly extended the usefulness of butyl rubber by providing much higher vulcanization rates and improving the compatibility with highly unsaturated elastomers, such as natural rubber and styrene–butadiene rubber (SBR). These properties permitted the production of tubeless tires with chlorinated or brominated butyl innerliners. The retention of air pressure (5) and low intercarcass pressure (6) extended tire durability.

Polyisobutylene is produced in a number of molecular weight grades and each has found a variety of uses. The low molecular weight liquid polybutenes have applications as adhesives, sealants, coatings, lubricants, and plasticizers, and for the impregnation of electrical cables (7). Moderate molecular weight polyisobutylene was one of the first viscosity-index modifiers for lubricants (8). High molecular weight polyisobutylene is used to make uncured rubbery compounds and as an impact additive for thermoplastics.

2. Process Chemistry

Butyl rubber is prepared from 2-methylpropene [115-11-7] (isobutylene) and 2-methyl-1,3-butadiene [78-79-5] (isoprene). Isobutylene with a purity of >99.5 wt% and isoprene with a purity of >98 wt% are used to prepare high molecular weight butyl rubber. Water and oxygenated organic compounds are minimized by feed purification systems because these impurities interfere with the cationic polymerization mechanism. Copolymers of isobutylene can also be prepared from mixed C_4 olefin containing streams that contain *n*-butene. These copolymers are generically known as polybutenes.

2.1. Isobutylene Polymerization Mechanism.

The carbocationic polymerization of isobutylene and its copolymerization with viable comonomers like isoprene and *p*-methylstyrene is mechanistically complex (9–11). The initiating system is typically composed of two components: an initiator and a Lewis acid coinitiator. Typical Lewis acid coinitiators include $AlCl_3$, (alkyl)$AlCl_2$, BF_3, $SnCl_4$, $TiCl_4$, etc. More recently uncommon Lewis acid such as methylaluminoxane

(MAO) (12,13) and specifically designed weakly coordinating Lewis acids such as $B(C_6F_5)_3$ (14,15) have been used as Lewis acids in initiating systems for isobutylene polymerization. Common initiators include Brønsted acids such as HCl, RCOOH, H_2O, alkyl halides, eg, $(CH_3)_3CCl$, $C_6H_5(CH_3)_2Cl$, esters, ethers, peroxides, and epoxides. More recently, transition-metal complexes, such as metallocenes and other single-site catalyst systems, when activated with weakly coordinating Lewis acids or Lewis acid salts, have been used to initiate isobutylene polymerization (16). In the initiation step, isobutylene reacts with the Lewis acid coinitiator–initiator pair to produce a carbenium ion. Additional monomer units add to the formed carbenium ion in the propagation step. Temperature, solvent polarity, and counterions affect the chemistry of propagation. These reactions are fast and highly exothermic. The propagation rate constant has been determined to be around 108 L/(mol · s), essentially diffusion-limited (17,18). Polymerizations at low temperature give extremely high polymerization rates in either hydrocarbon or halogenated hydrocarbon solvents. Isoprene is copolymerized mainly by trans-1,4-addition (>90%), and to a lesser extent by either 1,2-addition (19,20) or as a branched 1,4-addition product (21). The propagation proceeds until chain transfer or termination occurs.

In the chain-transfer step, the carbenium ion chain end reacts with isobutylene, isoprene, or a species with an unshared electron pair, ie, RX, solvents, counterion, and olefins. Reaction with these species terminates the growth of this macromolecule and permits the formation of a new chain. The activation energy of chain transfer is larger than propagation, thus the molecular weight of the polymer is strongly influenced by the polymerization temperature. Lower temperatures lead to higher molecular weight polymer. As comonomers exhibit their own chain-transfer characteristics, the presence of comonomer can also influence the final molecular weight of a copolymer. Higher isoprene contents typically lower the molecular weight of prepared butyl rubber (22,23). Termination results from the irreversible destruction of the propagating carbenium ion and discontinuance of the kinetic chain. Termination reactions include the collapse of the carbenium ion–counterion pair, hydride abstraction from comonomer, formation of dormant or stable allylic carbenium ions, or by reaction of the carbenium ion with nucleophiles, eg alcohols or amines. The reactivity ratios are strongly affected by the polymerization conditions (Table 1). A laboratory procedure for the preparation of butyl rubber is described in Reference 34

Fundamental rate constants for the initiation, propagation, chain-transfer, and termination steps in the polymerization process are difficult to measure because of the rapid rate of reaction. However, recent work (35) has shown that the propagation rate constant is of the order of 6 × 108 L/(mol · s).

Studies of the living cationic polymerization of isobutylene and copolymerization with isoprene have begun (36,37). The living copolymerization of isobutylene and isoprene has so far produced a random copolymer with narrow molecular weight distribution and a well-defined structure. For example, the BCl_3/cumyl acetate polymerization system in methyl chloride or methylene chloride at $-30°C$ provides for copolymers with 1–8 mol% trans-1,4-isoprene units and M_n between 2000 and 12,000 with a M_w/M_n of under 1.8. The advent of living polymerization of isobutylene has brought about the preparation of a large number of new isobutylene-based materials.

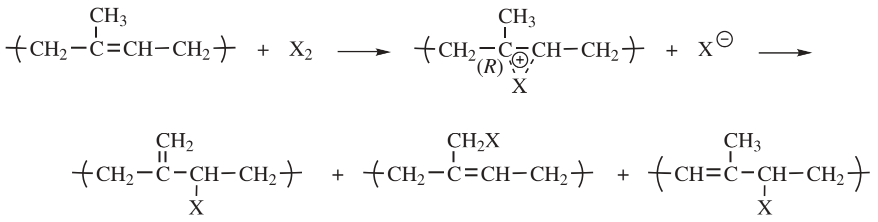
Table 1. **Copolymerization Reactivity Ratios of the Isobutylene/Isoprene System**[a]

Initiating system	Solvent	T,°C	r_1	r_2	Reference
$AlCl_3$	CH_3Cl	−103	2.5 ± 0.5	0.4 ± 0.1	24
$EtAlCl_2$	CH_3Cl	−100	2.17	0.5	25
$AlCl_3$	CH_3Cl	−90	2.3		26
$EtAlCl_2 + Cl_2$	CH_3Cl	−35	2.5		27
$AlCl_3$	EtCl	−95	2.26	0.38	28,29
$EtAlCl_2$	EtCl	−90	2.27	0.44	28,29
$EtAlCl_2$	CH_3Cl 88%/hexane 12%	−80	2.15	1.03	30
$EtAlCl_2$	CH_3Cl 50%/hexane 50%	−80	1.90	1.05	30
$EtAlCl_2$	CH_3Cl 12%/hexane 88%	−80	1.17	1.08	30
$EtAlCl_2$	Hexane 100%	−80	0.80	1.28	30
$AlCl_3$	C_5/CH_2Cl_2	−70	1.56 ± 0.19	0.95 ± 0.17	31,32
$AlCl_3$	CH_3Cl	−80	1.6		33

[a] Ref. 24.

High molecular weight copolymers of isobutylene and isoprene have been prepared at temperatures 40–50°C higher than is commercially practiced using metallocene and single-site initiators (12–16). Newer Lewis acids like methylaluminoxane and weakly coordinating anions or their salts like $B(C_6F_5)_3$ or $R^+[B(C_6F_5)_4]^-$ also prepare high molecular weight copolymers at these higher temperatures (12–16).

2.2. Modification of Butyl Rubbers. *Halobutyls.* Chloro- and bromobutyls are commercially the most important derivatives. The halogenation reaction is carried out in hydrocarbon solution using elemental chloride and bromine (equimolar with the enchained isoprene). The halogenation is fast and proceeds mainly by an ionic mechanism. The structures that may form include the following:



1 2 3

Normally structure 1 is dominant (>80%) (38,39). More than one halogen atom per isoprene unit can also be introduced. However, the reaction rates for excess halogens are lower and the reaction is complicated by chain fragmentation (40).

Other Derivatives. Various other derivatives have appeared on the market or reached the market development stage. Conjugated-diene butyl is obtained by the controlled dehydrohalogenation of halogenated butyl rubber

(41). The product can be cross-linked with peroxide or exposure to radiation. Free-radical grafting with vinyl monomers, eg styrene, can be used in a graft cure, leading to a transparent rubber with a T_g of about −59°C. Carboxy-terminated polyisobutylene useful in forming networks with epoxies or aziridine has been prepared from high molecular weight butyl rubber or a poly(isobutylene-*co*-piperylene) [26335-67-1] copolymer (42). The resulting carboxy-terminated polymers are viscous liquids. High molecular weight isobutylene−cyclopentadiene rubbers containing up to 40% cyclopentadiene were produced and developed by ExxonMobil (43) and were recently reexamined by Daelim (43). Highly branched polyisobutylene are prepared by use of an appropriately designed initiator that is also a comonomer in the polymerization (44).

Isobutylene−Isoprene−Divinylbenzene Terpolymers. A partially cross-linked terpolymer of isobutylene, isoprene, and partially reacted divinyl benzene is commercially available from Rubber Division, Bayer Inc., Canada. The residual vinyl functionality may be cross-linked with peroxides, a treatment that would normally degrade conventional butyl rubbers. This material is used primarily in the manufacture of sealant tapes and caulking compounds (45).

Liquid Butyl Rubber. Degradation of high molecular weight butyl rubber by extrusion at high shear rates and temperatures produces a liquid rubber with a viscosity average molecular weight (M_v) between 20,000 and 30,000. The relatively low viscosity aids in formulating high solids compounds for use in sealants, caulks, potting compounds, and coatings. Resulting compounds can be poured, sprayed, and painted.

2.3. New Materials. *Star-Branched (SB) Butyl.* Butyl rubbers have unique processing characteristics because of their viscoelastic properties and lack of crystallization of compounds on extension. They exhibit both low green strength and low creep resistance as a consequence of high molecular weight between entanglements. To enhance the strength of uncured traditional butyl rubber a relatively high molecular weight is required. Increasing molecular weight also causes an increase in relaxation time along with high viscosity. In such situations it is usually helpful to broaden the molecular weight distribution, but this is difficult to accomplish in conventional butyl rubber polymerization. Physical blending of low and high molecular weight polymer can also provide broader molecular weight distributions, but it results in other processing problems such as high extrudate swelling in flow-through shaping dies.

SB butyl has a bimodal molecular weight distribution with a high molecular weight branched mode and a low molecular weight linear component. The polymer is prepared by a conventional carbocationic copolymerization of isobutylene and isoprene at low temperature, but in the presence of a polymeric branching agent. The high molecular weight branched molecules are formed during the polymerization via a graft-from or a graft-onto mechanism. A graft-from reaction takes place when a macroinitiator/macrotransfer reagent, such as hydrochlorinated poly(styrene-*co*-isoprene) or chlorinated polystyrene, is used. A graft-onto reaction takes place when a multifunctional terminating agent, eg, poly (styrene-*co*-butadiene), is employed as the branching agent. In general, the SB butyl has 10−20% high molecular weight branched molecules, which have a random comb-like structure with 20−40 butyl branches. Although this is not a true star topology, it approaches a star structure since the branching agent is relatively short and the branching density is relatively high, ie, the molecular weight between branching points is low compared to the segment length of the butyl branches. SB butyl rubbers offer a unique balance of viscoelastic properties, resulting in significant processability improvements. Dispersion in mixing and mixing rates are improved. Compound extrusion rates are higher, die swell is lower, shrinkage is reduced, and surface quality is improved. The balance between green strength and stress relaxation at ambient temperature is improved, making shaping operations such as tire building easier. Several grades of ExxonMobil SB butyl polymers including copolymer, chlorinated, and brominated copolymers are commercially available.

Brominated Poly(isobutylene-co-p-methylstyrene). *para*-Methylstyrene [622- 97-9] (PMS) can be readily copolymerized with isobutylene via classical carbocationic copolymerization using a strong Lewis acid, eg, $AlCl_3$ or alkyl aluminum in methyl chloride, at low temperature. The copolymer composition is very similar to the feed monomer ratio because of the similar copolymerization reactivity ratios, ie, $r_1 = 1$ and $r_2 = 1.4$, under commercial polymerization conditions. These new high molecular weight copolymers encompass an enormous range of properties, from polyisobutylene-like elastomers to poly(*p*-methylstyrene)-like tough, hard plastic materials with T_g's above 100°C, depending on monomer ratio. A highly reactive and versatile benzyl bromide functionality, $C_6H_5CH_2Br$ can be introduced by the selective free-radical bromination of the benzyl group in the copolymer. The brominated copolymer can be cross-linked with a variety of cross-linking systems. This new functionalized copolymer preserves polyisobutylene properties, low permeability, and unique dynamic response, while adding the behavior of inertness to ozone, a property similar to ethylene–propylene rubbers. Copolymers with PMS below 10 mol% are most useful for elastomeric applications because the T_g's are near -60°C. Several grades of the brominated copolymer (Exxpro^{TM} Specialty Polymers) are available from ExxonMobil (46,47).

The benzyl bromide in the brominated copolymer can also be easily converted by nucleophilic substitution reactions to a variety of other functional groups and graft copolymers as desired for specific properties and applications (47). Ionomers (48), grafted copolymers (49), radiation-cured rubbers (50), and rubber-toughened nylons (51) are a few examples of the derivatives and functions that modification of brominated poly(isobutylene-*co*-*p*-methylstyrene) can offer.

Thermoplastic Elastomers. With the structural control inherent in living polymerization, new block copolymers containing polyisobutylene are possible (36). ABA triblock copolymers (A = polymethyl vinyl ether, B = polyisobutylene) that provide morphologies capable of exhibiting properties of an elastomer at use temperature, while processing like a thermoplastic, have been made from polyisobutylene and several styrenic derivatives (52–58). As thermoplastic elastomers, these materials offer other advantages owing to the intrinsic properties of polyisobutylene, namely low permeability and low dynamic modulus. More recently, star block copolymers of the A_2B_2 type have been prepared and exhibit unique physical properties (59). Many more architecturally designed polyisobutylenes are possible through living polymerization techniques. Kuraray Inc., Japan, commercially manufactured polyisobutylene–polystyrene block copolymers. Also, Kaneka Inc., Japan, produce Epion, a functionalized polyisobutylene.

3. Manufacturing

Most of the butyl polymers made commercially are produced by copolymerizing isobutylene and isoprene in precipitation processes that use methyl chloride as the diluent and a catalyst system comprising a Lewis Acid and an alkyl halide. The Lewis acid used in many of the commercial butyl rubber plants is aluminum chloride, which is low cost, a solid, and soluble in methyl chloride. Aluminum alkyls are now becoming popular because they simplify catalyst preparation and have been shown to increase monomer conversion.

The manufacture of butyl rubber, poly(isobutylene-*co*-*p*-methylstyrene) (Exxpro backbone) and high molecular weight polyisobutylene (Vistanex) requires a complex manufacturing process consisting of feed purification, feed blending, polymerization, slurry stripping, and finishing. A schematic flow diagram (Fig. 1) shows the major units in a butyl plant.

An alternative solution process, developed in Russia, uses a C_5–C_7 hydrocarbon as solvent and an aluminum alkyl halide as the initiator. The polymerization is conducted in scraped surface reactors at −90 to −50°C. The solution process avoids the use of methyl chloride, which is an advantage when butyl rubber is to be halogenated. However, the energy costs are higher than for the slurry

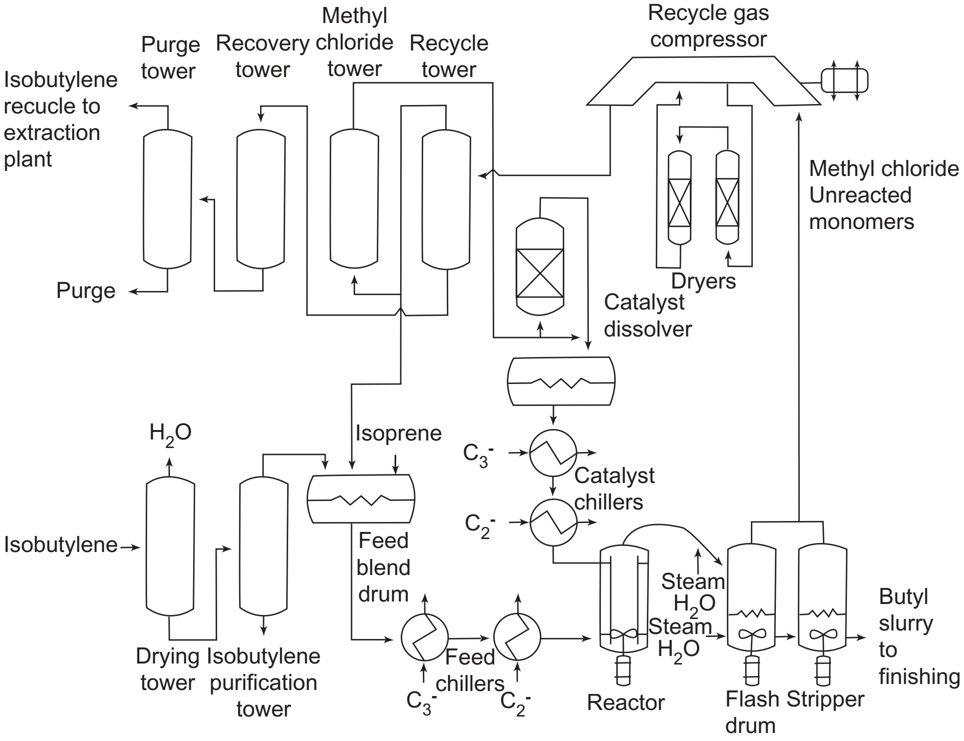


Fig. 1. Butyl plant flow plan.

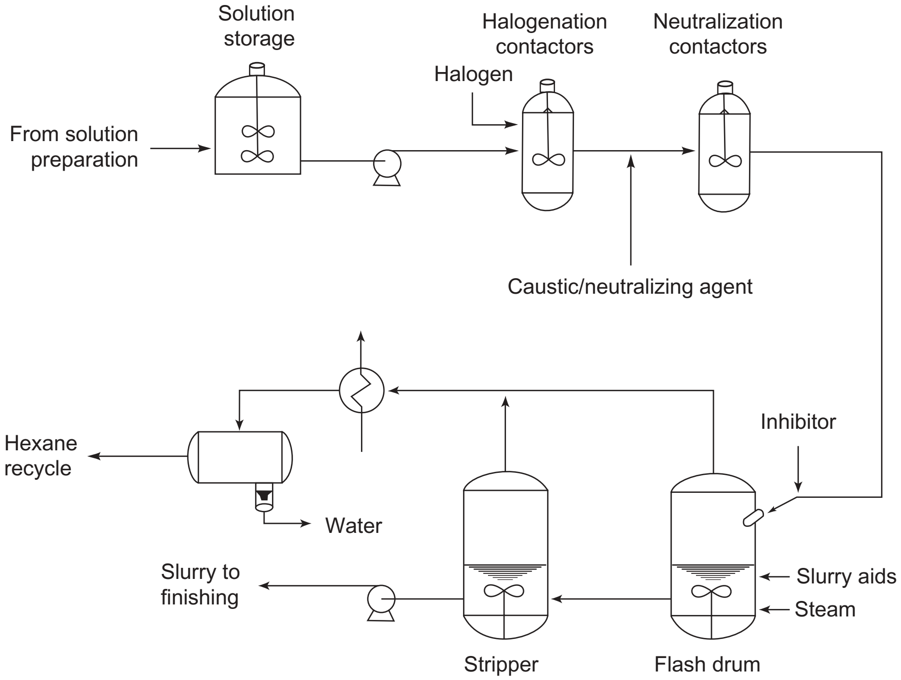


Fig. 2. Block diagram of halogenation.

process because of the higher viscosity of the polymer solution. Consequently, it is unlikely that the well-established slurry process will be displaced.

The manufacture of halobutyl rubbers such as Bromobutyl, Chlorobutyl, and Exxpro [bromopoly(isobutylene-*co*-*p*-methylstyrene)] requires a second chemical reaction: the halogenation of the polymer backbone. This can be achieved in two ways, the finished polymer produced in the butyl plant can be dissolved in a hydrocarbon solvent such as hexane or pentane, or a solvent replacement process can be used to dissolve the polymer from the slurry leaving the reactor. A schematic flow diagram of the halogenation process is shown by Figure 2.

3.1. Monomer Purification. To make high molecular weight polymers with good isobutylene conversion and good reactor service factor, the feed must be pure and dry. We must start with high quality isobutylene ($>99\%$), dry it, and remove other olefins, eg butene-1, butene-2, propene, and oxygenated hydrocarbons such as dimethyl ether and methanol. A number of commercial processes are available for production of the required high purity isobutylene. An extraction process based on sulfuric acid has been developed by several companies (60,61) and is used extensively. Significant quantities of isobutylene are also produced by dehydration of *tert*-butyl alcohol (62). The highest purity isobutylene is produced by MTBE (methyl-*t*-butyl ether, [1634-04-4]) decomposition plants. This process starts with the selective reaction of dilute isobutylene in a C_4 stream with methanol over an acid ion-exchange resin, eg, Amberlyst 15, to form MTBE. This ether is produced mainly as a high octane blending component for low lead gasoline. Catalytic decomposition at 170–200°C and 600 kPa

(5.9 atm) over a fixed-bed acid catalyst, eg, $SiO_2Al_2O_3$ or Amberlyst 15, produces high purity isobutylene (63–65).

The isobutylene is then dried by azeotropic distillation and purified in a super-fractionating distillation column to reduce the butenes to less than 1000 ppm. Note that if water is not removed it will cause icing in the feed chillers and this will lead to a poor reactor service factor.

The purified isobutylene is then blended with a recycled methyl chloride stream containing a low level of isobutylene (∼5%). Finally, the comonomer, isoprene or *p*-methylstyrene, is added. In this blending process, control of the ratio of comonomer to isobutylene is very important. This is because it has a significant impact on the composition of the polymer produced, the conversion of monomer, and the stability of reactor operation. For these reasons, a combination of both an analyzer and a mass balance control can be used to maintain the composition of the feed blend. The feed blend contains 20–40 wt% of isobutylene and 0.4–1.4 wt% of isoprene or 1–2 wt% of *p*-methylstyrene, depending on the grade of butyl rubber to be produced; the remainder is methyl chloride.

3.2. Polymerization. Catalyst solution is produced by passing pure methyl chloride through packed beds of granular aluminum chloride at 45°C. The concentrated solution formed is diluted with additional methyl chloride to which a catalyst activator is added and the solution later stored. The feed blend and catalyst solutions are chilled to −100 to −90°C in a series of heat exchangers before entry to the reactor.

The cold feed and catalyst are introduced continuously to a reactor comprising a central vertical draft tube surrounded by concentric rows of cooling tubes. The reactors have an aspect ratio of 28 (length) to 8 (diameter) and contain an axial flow pump located at the bottom of the draft tube that circulates the slurry through the cooling tubes. The reactor is constructed with 3.5 or 9 wt% nickel steel, or alloys that have adequate impact strength at the low temperature of the polymerization reaction. The production of high molecular weight butyl requires a polymerization temperature below −135°F (−90°C) and the reaction is exothermic, generating 0.82 MJ/kg (350 Btu/lb) of polymer. This requires a two-stage refrigeration system that uses boiling propylene or propane and ethylene as the refrigerants. In some plants ammonia is used in the first stage of the refrigeration process.

The reactors are the epicenter of all butyl plants and are mechanically complex. The operation of the remainder of the plant is dictated by the reactors. Essentially, the reactors are stirred tanks that contain a heat exchanger to keep them cold.

In the reactor, polymer chains are initiated by the catalyst and propagate in solution. Chain propagation occurs in microseconds but the overall reaction rate is controlled by the slower initiation sequence. As individual polymer molecules are formed they precipitate to produce a fine milky slurry of sub–micron-size particles. These particles grow in the reactor by accreting new polymer chains and by agglomeration.

The polymer slurry circulates through the reactor tubes, and boiling liquid refrigerant in the reactor jackets keeps the reactor contents cold. The butyl polymerization process is complex because of the combination of low temperature operation, polymer slurry formation, and difficulty in directly measuring polymer quality. To achieve high molecular weight, the reaction temperature must be kept low to reduce the amount of chain transfer. In the slurry process, the viscosity is relatively low, and good heat transfer can be achieved. To maintain a stable slurry, the temperature must be kept below the glass-transition temperature, T_g, of polyisobutylene (-68°C) and, as the slurry is shear-thinning, there must be a high level of shear. The axial flow pump that provides a high degree of circulation in the reactor achieves this.

One of the common theories to explain fouling in a butyl reactor is that rubber particles in the reactor slurry are not completely glassy because of diluent and monomers in the surface layer. This causes them to be sticky as well as agglomerating, and the particles will stick to the heat-transfer surfaces in the reactor. This causes the heat-transfer resistance to increase and the slurry temperature to warm. Eventually, this warming can cause the slurry to destabilize and the viscosity to increase rapidly. Ultimately, this could lead to plugging, which requires extended solvent washing to clean the reactor. Therefore, production in a reactor is stopped every 2–4 days for solvent washing. This forces a cyclical multireactor operation in which some reactors are producing polymer while others are being washed to remove rubber fouling. Typical runs are from 18 to 60 h, depending on feed purity, slurry solids concentration, and production rate.

The production rate is 2.0–4.5 t/h, depending on feed rate, monomer concentration in the feed, and monomer conversion. The conversion of isobutylene and isoprene typically ranges from 75–95% and 45–85%, respectively, depending on the grade of butyl rubber being produced. The molecular weight of the polymer produced is set by the ratio of chain-making to chain-terminating processes. In commercial plants the molecular weight and composition of the polymer formed are controlled by the concentration of monomers in the reactor liquid phase and the amount of terminating or transfer species present to interrupt chain growth. The slurry composition depends on the monomer content of the feed stream and the extent of monomer conversion. In practice, the flow rate and the composition of catalyst to the reactor is the principal operating variable; reactor residence time is often in the range 30–60 min.

The original reactor design, known as the draft tube reactor, has been used commercially since the initial development of butyl in the 1940s. An improved design in which the draft tube is replaced by additional tubes and the circulation pump is redesigned has recently been proposed (66).

In addition to these changes to the mechanical design of the reactor, improvements to the polymerization chemistry and diluent have been investigated in the last decade. Examples are the use of supercritical carbon dioxide (67) and the use of aluminum alkyls in the catalyst system (68).

3.3. Halogenation. Chlorinated and brominated butyl rubber can be produced in the same plant in blocked operation. However, there are some differences in equipment and reaction conditions. A longer reactor residence time is required for bromination because of the slower reaction rate compared to chlorination. Separate facilities are needed to store and meter the individual halogens to the reactor. Additional facilities are required because of the complexity of stabilizing bromobutyl rubber.

The halogenation process begins with the preparation of a hexane solution of butyl rubber with the desired molecular weight and unsaturation. Slurry from a butyl polymerization reactor is dissolved (69–71) by transferring it into a drum containing hot liquid hexane that rapidly dissolves the fine slurry particles. Hexane vapor is added to flash methyl chloride and unreacted monomers overhead for recovery and recycle. The solution of butyl in hexane passes to a stripping column where the final traces of methyl chloride and monomers are removed. The hot solution is brought to the desired concentration for halogenation, typically 20–25 wt% in an adiabatic flash step.

Alternatively, bales of finished butyl rubber are chopped or ground to small pieces and conveyed to a series of agitated dissolving vessels or to a large vessel divided into multiple stages. Solutions containing 15–20% polymer can be prepared in 1–4 h depending upon temperature, particle size, and agitation. This method has the advantage of being independent from the butyl polymerization process but requires storage and careful inventory control between the two stages of the process. This process also requires two finishing operations: one to produce dry butyl backbone, the second to finish the halobutyl product. Investment costs for the two dissolving processes are similar, but energy costs for the dissolving process can be higher.

Halogenation is the second major chemical reaction in the production of halobutyl polymers. It is usually carried out by adding bromine liquid or chlorine vapor to a solution of rubber in hydrocarbon solvent (hexane or pentane), which is often referred to as cement. The cement must be essentially free of monomers, or low molecular weight toxic species will be formed during the chlorine or bromine reactions. The halogenation of the butyl backbone is an ionic-substitution reaction in which the halogen is added to the cement stream in a well-mixed reactor (eq. 1). This reaction is unusual for polymers where it's more typical for the bromine to add across the double bond.

Insufficient mixing will lead to poor distribution of the halogen on the polymer, which can cause the product cure characteristics to be unsatisfactory. Another potential problem is the vigorous reaction of liquid chlorine with hydrocarbon. This leads to complete breakdown of some of the polymer, producing carbon and HX. This causes the polymer to be gray rather than the normal off-white and the product properties to be adversely affected.

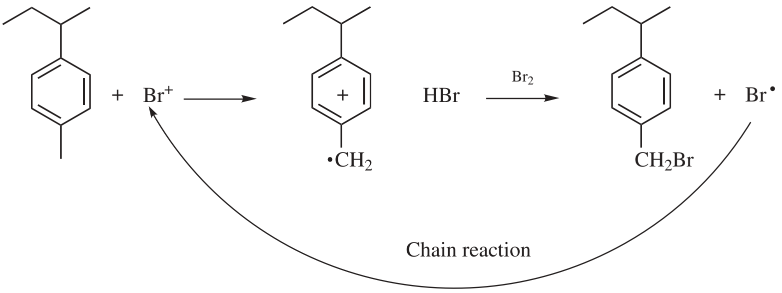
For both chloro- and bromobutyl rubber two isomers are formed as shown in equation 1. The ratio of these isomers must be carefully controlled in order to keep consistent product properties.

The by-product from this reaction, HX, is normally reacted with aqueous caustic solution to give a soluble salt. Incomplete neutralization will leave HX in the rubber, and subsequent reactions during the drying process can destabilize the polymer. The key to good neutralization is good mixing of the halogen and cement. Further improvements to the neutralization process can be achieved by the addition of a surfactant (72).

Because of the generation of HCl or HBr, the maximum efficiency for halogen usage in this process is 50%. An improvement in efficiency can be achieved by adding hydrogen peroxide to the process to convert the acid back to halogen (73).

The bromination reaction required to produce Exxpro requires a free-radical reaction because there is no unsaturation in the backbone. The bromine and a free-radical initiator are added to the cement, mixed well, and then passed through a series of stirred tank reactors where the chain reaction shown by equation 2 occurs.

$$I_2 \xrightarrow{\text{Heat}} 2I^{\bullet} \xrightarrow{Br_2} IBr + Br^{\bullet}$$



An alternative process is bulk-phase halogenation (74–76). Dry butyl rubber is fed into a specially designed extruder reactor and contacted in the melt phase with chlorine or bromine vapor. By-product halogen acids are vented directly, avoiding the need for a separate neutralization step. Halogenated rubbers comparable in composition and properties to commercial products can be obtained.

3.4. Finishing. The halogenated rubber solution then passes into a vertical drum where the solvent is flashed and stripped by steam and hot water. Calcium stearate is added to the slurry in this drum to prevent polymer agglomeration. A second vessel in series provides additional residence time for the solvent to diffuse from the rubber and be vaporized. The final solvent content and the steam usage for solvent removal depend on the conditions in each vessel. Typically, the lead flash drum is operated at 105–120°C and 200–300 kPa (29–43.5 psi). Conditions in the final stripping stage are 101°C and 105 kPa (15 psi). The hexane can be reduced to 0.5–1.0 wt% with a steam usage of 2.0–2.5 kg/kg rubber.

The resultant polymer/water slurry is kept agitated and then screened to separate the bulk water from the rubber. The polymer is then dried in a series of extrusion dewatering and drying steps to a final moisture content of <0.3 wt%. Antioxidants and stabilizers, eg, BHT and epoxidized soybean oil, protect against dehydrohalogenation and are added in the final extrusion step. Fluid-bed conveyors and/or airvey systems are used to cool the product to an acceptable packaging temperature. The resultant dried product is in the form of small "crumbs," which are subsequently weighed and compressed into 75-lb bales for wrapping in polyethylene film and packaged into wooden or metal crates or cardboard containers.

4. Structure, Properties, and Product Applications of Isobutylene-Based Polymers

4.1. Molecular Structure. *Polyisobutylene.* Isobutylene polymerizes in a regular head-to-tail sequence to produce a polymer having no asymmetric carbon atoms. The two pendant methyl groups bonded to alternative chain atoms in polyisobutylene (PIB) produce steric crowding, for which a partial relief is achieved by a distortion of the methylene carbon to 124° as compared to 110° for the tetrahedral carbon (73,74). Methyl crowding is further alleviated by distorting the dihedral angle, leading to a splitting of the trans-rotational isomer by about 25° (73–75). The splitting of the trans isomer in two equivalent states is a special feature of PIB, not observed in its vinyl analogue, and has significant impacts on its local chain-segment dynamics (76). The additional fast trans-to-trans skeletal relaxation process in PIB results in a faster segmental motion and a lower glass-transition temperature despite the fact that PIB is a sterically strained and crowded macromolecule (76). The glass-transition temperature of PIB is about −70°C (77). It is an amorphous elastomer in the unstrained state. On extension at room temperature, PIB of high molecular weight crystallizes into crystals of an 8/3 helix with an alternating distorted trans-gauche structure (78). One chain end of PIB is typically unsaturated because of chain-transfer and termination mechanisms. Molecular weights could range from several hundred to several millions. There is no long-chain branching unless special synthesis methods are employed. The molecular weight distribution is commonly the most probable with $M_{\mathrm{w}}/M_{\mathrm{n}} = 2.0$.

Polybutenes. Copolymerization of mixed isobutylene and 1-butene containing streams with a Lewis acid catalyst system yields low molecular weight copolymers, from several hundreds to a few thousand, that are clear, colorless, and viscous liquids. The chain ends are unsaturated and are often chemically modified to provide a certain functionality (79,80).

Butyl Rubber. In butyl rubber, isoprene is enchained predominantly (90–95%) by 1,4-addition and head-to-tail arrangement (81–84). The remaining minor isoprene species may be interpreted spectroscopically either as 1,2-enchained (83,84) or as branched species from 1,4-addition (85). Depending on the grade, the unsaturation in butyl rubber is between 0.5 and 3 mol%. The glass-transition temperature of butyl rubber is about −65°C (86). With the low content of isoprene and a near-unity reactivity ratio between isoprene and isobutylene (87), a random distribution of enchained isoprene monomer in butyl rubber is achieved. The molecular weight distribution in butyl rubber is mostly with $M_{\mathrm{w}}/M_{\mathrm{n}}$ of 3–5.

Halogenated Butyl Rubber. Halogenation at the isoprene site in butyl rubber proceeds by a halonium ion mechanism leading to the formation of a predominated exomethylene alkyl halide structure in both chlorinated and brominated rubbers (88,89). Upon heating, the exo allylic halide rearranges to give an equilibrium distribution of exo and endo structures (90–92). Halogenation of the unsaturation has no apparent effects on the butyl backbone and on the butyl glass-transition temperature. However, cross-linked halobutyl rubbers do not crystallize on extension as a result of the backbone irregularities introduced by the halogenated isoprene units.

Star-Branched (SB) Butyl. Introduction of a branching agent of styrene–butadiene–styrene (SBS) block copolymer during cationic polymerization of butyl leads to a SB butyl that, in general, contain 10–15% of star polymers, with remaining linear butyl chains (93,94). SB butyl is a reactor blend of linear polymers and star polymers, where the star molecules were synthesized during polymerization by cationic grafting of propagating linear butyl chains onto the branching agent (95). In the solid state, these star polymers aggregate to form ~30-nm-diameter spherical domains separated by about 90 nm and covered by about 6 vol% (96,97). It was proposed that these domains consist of predominantly the styrene–butadiene–styrene branching agent (96). A much broader molecular weight distribution is achieved in SB butyl with M_w/M_n greater than 8. Halogenation of SB butyl results in the same halogenated structure in the linear butyl chains and in the linear butyl chain arms of the star fraction as that in the halogenated butyl. Unreacted butadiene blocks of the SBS branching agent were 100% brominated and 60% chlorinated after halogenation (98).

Brominated Poly(isobutylene-co-p-methylstyrene). Copolymerization of isobutylene with *para*-methylstyrene (PMS) produces a saturated copolymer backbone with randomly distributed pendant *para*-methyl-substituted aromatic rings. During radical bromination after polymerization, some of the substituted *para*-methyls are converted to bromomethyls for vulcanization and functionization (99,100). Brominated poly(isobutylene-*co*-*p*-methylstyrene) polymers are saturated terpolymers containing isobutylene, 1–6 mol% PMS, and 0.5–1.5 mol% BrPMS (brominated *para*-methylstyrene). Their T_gs increase with increasing PMS content and is around −60°C. The molecular weight distribution of brominated poly(isobutylene-*co*-*p*-methylstyrene) is narrow, with M_w/M_n less than 3 (99).

4.2. Physical Properties.

Permeability. Primary uses of polyisobutylene and isobutylene copolymers of butyl, halobutyl, SB butyl, and brominated poly(isobutylene-*co*-*p*-methylstyrene) in elastomeric vulcanized compounds rely on their properties of low air permeability and high damping. In comparison with many other common elastomers, polyisobutylene and its copolymers are notable for their low permeability to small-molecule diffusants as a result of their efficient intermolecular packing (101–103) as evidenced by their relative high density (density of 0.917 g/cm3). This efficient packing in isobutylene polymers leads to their low fractional free volumes and low diffusion coefficients for penetrants (101). In combination with the low solubilities of small-molecule diffusants in isobutylene polymers, low permeability values for small molecules, such as He, H_2, O_2, N_2, CO_2, and others, are observed in isobutylene polymers as compared with other elastomers (104).

As shown in Figure 3, diffusion coefficients of nitrogen in both various diene rubbers and in butyl rubber increase with increasing differences between the measurement temperature and the corresponding rubber's glass-transition temperature. However, although the rate of increase in diffusion coefficient with $T-T_g$ is about the same between diene rubbers and butyl rubber, the absolute values of diffusion coefficient in butyl rubber are significantly less than that of diene rubbers. Considering isobutylene, copolymers discussed contain only small amounts of comonomers besides isobutylene, their temperature-dependent permeability values follow the same curve in Figure 3 for butyl rubber. With brominated poly(isobutylene-*co*-*p*-methylstyrene) having the highest T_g among isobutylene copolymers, it has the corresponding lowest permeability value at room temperature among isobutylene copolymers (105).

Dynamic Damping. Polyisobutylene and isobutylene copolymers are high damping at 25°C, with loss tangents covering more than eight decades of

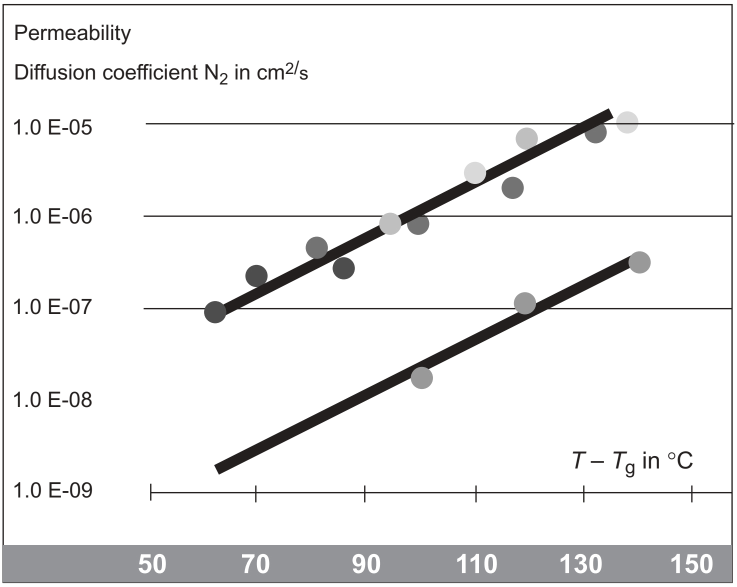


Fig. 3. Diffusion coefficients of nitrogen in diene rubbers and in butyl rubber as a function of $T - T_g$ (Data from Ref. 104). ● Chloroprene rubber (neoprene); ● styrene butadiene rubber; ● natural rubber; ● nitrile butadiene rubber; ● butyl rubber.

frequencies even though their T_gs are less than $-60°C$ (106,107). This broad dispersion in PIB's dynamic mechanical loss modulus is unique among flexible-chain polymers and is related to its broad glass–rubber transition (108). The narrowness of the glass–rubber transition, as defined by the steepness index, for PIB is 0.65, which is much smaller than most polymers. In addition, PIB has the most symmetric and compact monomer structure among amorphous polymers, which minimizes the intermolecular interactions and contributes to its unique viscoelastic properties (109,110). As a result, a separation in time scale between the segmental motion and the Rouse modes is broader in glass–rubber transition, leading to the appearance of the sub-Rouse mode (108,109). In Rouse's theory, a polymer chain is represented as a sequence of equivalent Gaussian submolecules. The Rouse mode refers to motions of these submolecules, and sub-Rouse mode involves motions of chain units smaller than these submolecules. Considering the differences in temperature dependencies of these motions, the glass transitions of PIB and its copolymers are thermo-rheological complexes and they do not follow time–temperature superposition (108,111). PIB and its copolymers have high entanglement molecular weights (112) and corresponding low plateau moduli which, in turn, contribute to their high tack or self-adhesion in the uncross-linked state. Entanglement molecular weight of PIB is about 9000 as compared with 1300 for polyethylene, 1700 for ethylene–propylene copolymer, 2000 for 1,4-polybutadiene, 3000 for styrene–butadiene copolymer, and 6100 for hevea rubber.

Chemical Properties. PIB is a saturated hydrocarbon where the unsaturated chain ends could undergo reactions typical of a hindered olefin. These end groups are used, particularly in low molecular weight materials where plenty of chain ends are available, as a route to functionization, such as the introduction of amine groups to PIB for producing dispersants for lubricating oils. As for butyl rubbers, their in-chain unsaturations could be attacked by atmospheric-ozone-leading degradation and, hence, require protection by antioxidants (113). Chlorobutyls are thermally more stable than bromobutyls. Upon thermal exposure up to 150°C, no noticeable decomposition took place in chlorobutyl except for some allylic chlorine rearrangement, whereas the elimination of HBr occurred in bromobutyl concurrently with isomerization to produce conjugated dienes that subsequently degrade (91,92). Brominated poly(isobutylene-*co*-*p*-methylstyrene), without any unsaturation, is the most thermally stable isobutylene copolymer. In addition, the strong reactivity of the benzylic bromine functionality in brominated poly(isobutylene-*co*-*p*-methylstyrene) with nucleophiles allows functionization and grafting in addition to its uses for vulcanization (99,100). Polyisobutylene and its copolymers, including butyl, halobutyl, and brominated poly(isobutylene-*co*-*p*-methylstyrene), are readily soluble in nonpolar solvents where cyclohexane is an excellent solvent, benzene is a moderate solvent, and dioxane is a nonsolvent (114).

4.3. Elastomeric Vulcanizates.

As with almost all rubbers, the applications of isobutylene copolymers in rubber goods require compounding and subsequent vulcanization, or cross-linking. During compounding, various fillers, processing aids, plasticizers, tackifiers, curatives, and antidegradants are added.

Fillers. Filler addition is a common practice in rubber industries to stiffen and strengthen amorphous rubbers. In addition to the reinforcement, fine and particulate fillers, most notably carbon black, suppress elasticity of gum rubbers and render better processability, such as less die swell, less shrinkage, less melt fracture, and less nerve (or less elastic spring-back in uncured state) (115). Physical interactions between carbon blacks and rubber are strong but can yield upon stressing. The effects of carbon black on properties of butyl, halobutyl, and brominated poly(isobutylene-*co*-*p*-methylstyrene) rubbers are similar to that of other elastomers. As particle size decreases with a corresponding increase in specific surface area, the strength, modulus, hardness, viscosity, and damping of carbon-black-filled vulcanized rubbers increase (116,117). Tensile strength, in general, is raised to a maximum with carbon black content and then decreases at higher loading. For butyl rubber, this maximum tensile strength is obtained at 50–60 phr (part per hundred of rubber) of carbon black.

Beyond filler addition in rubbers, elastomeric behavior can be tailored by proper blending of filled elastomers. Major reasons for the usage of blends are to reduce compound cost, to improve processability, and to enhance final product performance (118). But, in this case, selective filler partition may alter the blend morphology and produce significant changes in blend properties. Elastic and fracture properties, such as resilience, tear strength, and fatigue resistance, of rubber blends have been found to depend strongly on filler phase distribution (119,120). Carbon aggregates were known to preferentially reside in the polymer with higher unsaturation, lower viscosity, and higher polarity, generally in that order of significance (121). Hence, a preferential filler partition into the diene rubber phase, such as BR and SBR, in diene rubber blends with butyl rubber was found (122,123). However, with the strong interactions between allylic bromine or benzylic bromine in bromobutyl and in brominated poly(isobutylene-*co*-*p*-methylstyrene), respectively, and carbon blacks (124), the opposite in terms of preferential filler partition into the bromobutyl or brominated poly (isobutylene-*co*-*p*-methylstyrene) phases in their blends with high diene rubbers was indicated (125,126).

Mineral fillers are used for light-colored rubber compounds for cost reduction and physical improvement. In butyl and halobutyl, alkaline fillers, such as calcium silicates, and hygroscopic fillers can strongly retard cure, while acid clays can accelerate cure. Silicas provide maximum reinforcement among mineral fillers but they promote compound stiffness and strongly affect cure rates by their absorption of curatives. Clays are less reinforcing and calcined clay is particularly suited for pharmaceutical stopper applications for its purity, low water content, and particle size uniformity. Talc is semireinforcing and improves resistance to fragmentation during needle penetration and withdrawal in pharmaceutical closures. Nonreinforcing fillers, such as calcium carbonate, are added to lower compound cost without affecting cure. Strong reductions in permeability in black or light-colored compounds of isobutylene copolymers could be achieved by adding small percents (less than 5 wt%) of exfoliated high-aspect-ratio atomic-thickness sheets of layered mineral, such as organonanoclays, without significant compromises in flexibility (127–129). The alignment of the nanoclay leads to a nematic-phase morphology and introduces torturosity for the diffusants, resulting in the lowering in permeability (130).

Plasticizers and Processing Aids. Petroleum-based oils are commonly used as plasticizers to lower compound viscosity and to improve processability and low temperature properties but with an increase in compound air permeability. Plasticizers are selected for their compatibility with isobutylene polymers and for their low temperature properties. Butyl rubber has a solubility parameter that is similar in value to that of polybutene, and paraffinic and naphthenic oils for which they are preferred. Although not to be considered as solvating agents, paraffin waxes and low molecular weight polyethylene are added for improved processing. For an improvement in low temperature flexibility, ester-type plasticizers, such as adipates and sebacates, can be used. In addition to functioning as a plasticizer, Struktol 40 MS can enhance filler dispersion and cure adhesion to high diene rubber substrates. Materials such as mineral rubber and asphaltic pitch have also been used for this dual function.

Other Ingredients. Other compound ingredients include tackifiers, flame retarders, odorants, and lubricants. Hydrocarbon tackifier resins improve the tack of unvulcanized compounds without any side reactions but are less effective than the phenolic type. However, phenol-formaldehyde tackifier resins react with halobutyl through their methylol groups, leading to premature cure. Hindered phenolic antioxidants added during manufacture of butyl and halobutyl prevent oxidation during their finishing, storage, and usage. These antioxidants also improve the resistance of vulcanized butyl and halobutyl compounds to ozone cracking. Additional stabilization against dehydrohalogenation at elevated temperature is required for halobutyls (26,131). Calcium stearate is used in chlorobutyl and a combination of calcium stearate and an epoxidized soybean oil is applied in bromobutyl to prevent dehydrohalogenation. No antioxidants or other stabilizers are added in brominated poly(isobutylene-*co*-*p*-methylstyrene).

4.4. Vulcanization.

Vulcanization or curing in isobutylene polymers introduces chemical cross-links via reactions involving either allylic hydrogen or allylic halogen in butyl or halobutyl, respectively, or benzylic bromine in brominated poly(isobutylene-*co*-*p*-methylstyrene) to form a polymer network. In butyl and halobutyl, most vulcanizates have about $1 \times 10{-}4$ mol of cross-links per cm^3, or about 250 backbone carbon atoms between cross-links.

Butyl. The basic curing agent for butyl rubber is elemental sulfur, with the formation of sulfide cross-links. Because of the low unsaturation in butyl rubbers, sulfur accelerators, such as thiurams or dithiocarbamates, are required to obtain acceptable rates and states. To activate accelerators and to stabilize cross-links already formed, butyl compounds require zinc oxide. Sulfur cross-links rearrange at elevated temperatures as a result of their low bonding energy that could lead to creep and permanent set in strained butyl at high temperatures. The resin cure in butyl rubber is based on the reaction of the methylol groups in the phenol-formaladehyde resin with allylic hydrogen in butyl, usually with a Lewis acid catalyst, to yield carbon–carbon cross-links that are thermally stable. Resin cure is preferred in butyl tire-curing bladders for their required thermal fatigue stability.

Halobutyl. The basic curing agent for halobutyl is zinc oxide, with the formation of carbon–carbon cross-links by alkylation catalyzed by a zinc halide produced after dehydrohalogenation of halobutyl (90,91,132). The ease of halogen elimination is the main difference between chlorobutyl and bromobutyl during curing where the bromobutyl cures faster (133). Esterification occurs at the halogen site in the presence of stearic acid. As a result, stearic acid accelerates cure rate and lowers the cure state. The zinc oxide cure is sensitive to acidic and basic compounding ingredients. In general, acids accelerate cure while bases retard. Water is a strong retarder because it complexes with reactive intermediates. In some applications, such as special pharmaceutical stoppers, the absence of zinc is mandatory. On the basis of the strong reactivity between amine and allylic halogen (134), diamines can be used as the curative. While regular butyl undergoes molecular weight breakdown in the presence of peroxide, halobutyl can be cross-linked with organic peroxides. The best cure rate and optimal properties are achieved with a suitable co-agent, such as *m*-phenylene bismaleimide, at high temperatures.

Brominated Poly(isobutylene-co-p-methylstyrene). Using mainly zinc oxide and stearic acid, the cross-linking of brominated poly(isobutylene-*co*-*p*-methylstyrene) involves the formation of carbon–carbon bonds through Friedel–Crafts alkylation coordinated by a zinc complex (135,136). Unlike halobutyls, brominated poly(isobutylene-*co*-*p*-methylstyrene) cures extremely slowly with zinc oxide alone. A nucleophilic agent, such as zinc stearate, is needed to promote rapid displacement of benzyl bromide. The zinc stearate can be added directly or can be formed during vulcanization through the reaction of zinc oxide and stearic acid. In cases where faster cure is desired, dinucleophilic substitution using dinucleophiles, such as diamines, is the method of choice.

Table 2. **Annual Butyl and Halogenated Butyl Rubber Production Capacity (YE 2002)**

Producer	Products	Capacity, 10^3 t
ExxonMobil Chemical Co.		
Baton Rouge, La.	Halobutyl rubbers	143
Baytown, Tex.	Butyl rubber	27
	Halobutyl rubbers and Exxpro	75
Notre Dame de Gravenchon, France	Butyl rubber	54
Fawley, U.K.	Halobutyl rubbers	97
Japan Butyl Co., Ltd.[a]		
Kawasaki, Japan	Butyl rubber	78
Kashima, Japan	Halobutyl rubbers	52
Bayer (152)		
Sarnia, Ontario, Canada	Butyl, halobutyl rubbers	140
Zwijndrecht, Belgium	Butyl, halobutyl rubbers	115
CIS (152)		
Nizhnekamsk, Russia	Butyl rubbers	60
Togliati, Russia	Butyl rubbers	35
Sinopec (152)		
Yanshan, P.R. China	Butyl rubbers	30

[a] Jointly owned with Japan Synthetic Rubber Co., Ltd.

5. Economic Aspects

Table 2 shows the manufacturing capacity for the world's major butyl and halobutyl polymers manufacturers. In addition to ExxonMobil Chemical and Bayer, during the last 10 years, butyl rubber produced at both Nizhnekamsk and Togliati has been sold throughout the world. Also, in the last 5 years, Sinopec has started to produce butyl polymers at its Yanshan plant in the People's Republic of China. All of the world's butyl plants use the more efficient slurry process except for the Togliati plant, which uses the solution process.

Manufacturing capacity has continued to expand in the last decade to keep up with the increasing demand due to expanding car sales and the growth in popularity of sports–utility vehicles, particularly in the United States. Apart from the economic downturns in 1992 and 2001, Figure 4 shows the worldwide sales of halobutyl polymers increasing steadily at approximately 4% per year. The widespread use of halobutyl innerliners in the tires of both passenger cars and light trucks accounts for most of these sales, although there is a small market for pharmaceutical stoppers. For most of the decade, halobutyl manufacturing plants have been running well above 85% capacity.

In the 1990s, sales of regular butyl polymers have not seen the same rate of growth as halobutyl. The majority of sales are to inner tube and tire bladder applications and, except for trucks and in some developing countries, these markets have been overtaken by the more popular tubeless tire. The introduction of the Russian and Chinese manufacturers has also dampened demand and not until the early 2000s has there been significant growth. Figure 5 shows the sales of regular butyl polymers during the past decade.

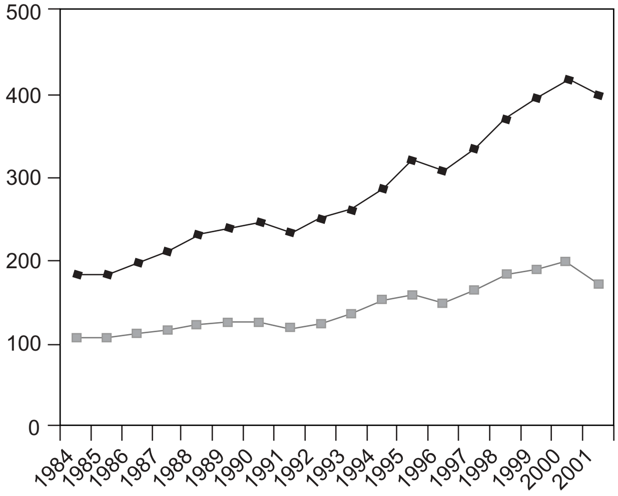


Fig. 4. Worldwide halobutyl sales. —◆— Halobutyl, worldwide; —■— Halobutyl, Americas.

6. Health and Safety Factors

Polyisobutylene, isobutylene–isoprene copolymers, and isobutylene-*p*-methylstyrene copolymers are considered to have no chronic hazards associated with exposure under normal industrial use. Some grades can be used in chewing-gum base and are regulated by the FDA in 21 CFR 172.615. Vulcanized products prepared from butyl rubber or halogenated butyl rubber may contain small

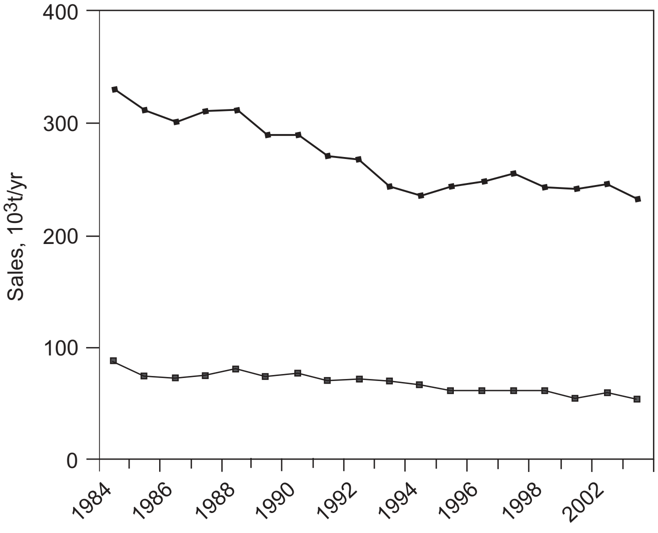


Fig. 5. Worldwide butyl sales. —◆— Regular butyl, worldwide; —■— Regular butyl, Americas.

amounts of toxic materials as a result of the particular vulcanization chemistry. Although many vulcanizates are inert, eg, zinc oxide cured chlorobutyl is used extensively in pharmaceutical stoppers, specific recommendations should be sought from suppliers.

7. Uses

The polyisobutylene portion of the isobutylene copolymers, such as butyl, halobutyl, and brominated poly(isobutylene-*co*-*p*-methylstyrene), imparts chemical and physical characteristics that make them highly useful in a wide variety of applications. The low degree of permeability to gases accounts for the largest uses of butyl and halobutyl rubbers, namely as inner tubes and tire innerliners. These same properties are also of importance in air cushions, pneumatic springs, air bellows, accumulator bags, and pharmaceutical closures. The thermal stability of butyl rubber makes it ideal for rubber tire-curing bladders, high temperature service hoses, and conveyor belts for hot material handling. With the added thermal stability in brominated poly(isobutylene-*co*-*p*-methylstyrene), it has made inroads in applications of bladders and curing envelopes.

Isobutylene-based polymers exhibit high damping and have uniquely broad damping and shock absorption ranges in both temperature and frequency. Molded rubber parts from butyl and halobutyl find wide applications in automobile suspension bumpers, exhaust hangers, and body mounts.

Blends of halobutyl or brominated poly(isobutylene-*co*-*p*-methylstyrene) with high diene rubbers are used in tire sidewalls and tread compounds (137–139). In sidewalls, ozone resistance, crack cut growth, and appearance are critical to their performance. Properly formulated blends with high diene rubbers that exhibit phase cocontinuity yield excellent sidewalls (140). The property balance for tire tread compounds can be enhanced by the incorporation of a more damping halobutyl or brominated poly(isobutylene-*co*-*p*-methylstyrene) rubber phase (141). Improvements in wet-, snow-, and ice-skid resistances and in dry traction without compromises in abrasion resistance and rolling resistance for high performance tires can be accomplished by using bromobutyl or brominated poly(isobutylene-*co*-*p*-methylstyrene) up to 30 phr in tread compounds (142).

Blends of isobutylene polymers with thermoplastic resins are used for toughening of these compounds (143,144). High-density polyethylene and isotactic polypropylene are often modified with 5–30 wt% of PIB. In some cases, a halobutyl phase is cross-linked as it is dispersed in the plastic phase to produce a highly elastic compound that is processable in thermoplastic molding equipment (145,146). The strong reactivity of the benzylic bromine group in brominated poly(isobutylene-*co*-*p*-methylstyrene) with amines during blending of brominated poly(isobutylene-*co*-*p*-methylstyrene) with polyamides results in surface-reactive compatibilization that suppresses coalescence and leads to extremely fine dispersions in these blends (147). Combining the low permeability values of both polyamides and brominated poly(isobutylene-*co*-*p*-methylstyrene), dynamic vulcanized thermoplastic blends of polyamides with brominated poly (isobutylene-*co*-*p*-methylstyrene) have been demonstrated to be suitable for tire innerliner applications (148–151).

Polybutenes enjoy extensive uses as adhesives, caulks, sealants, and glazing compounds. They are also used as plasticizers in rubber formulations with butyl, SBR, and natural rubber. In linear low density polyethylene (LLDPE) blends, they induce cling to stretch-wrap films. Polybutenes when modified at their chain-end unsaturations with polar functionality are widely employed in lubricants as dispersants. Blends of polybutene with polyolefins produce semisolid gels that can be used as potting and electrical-cable filling materials.

It should be noted that proper compounding and formulation are critical to the successful uses of all elastomer materials. It is recommended that the suppliers be contacted for information.

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