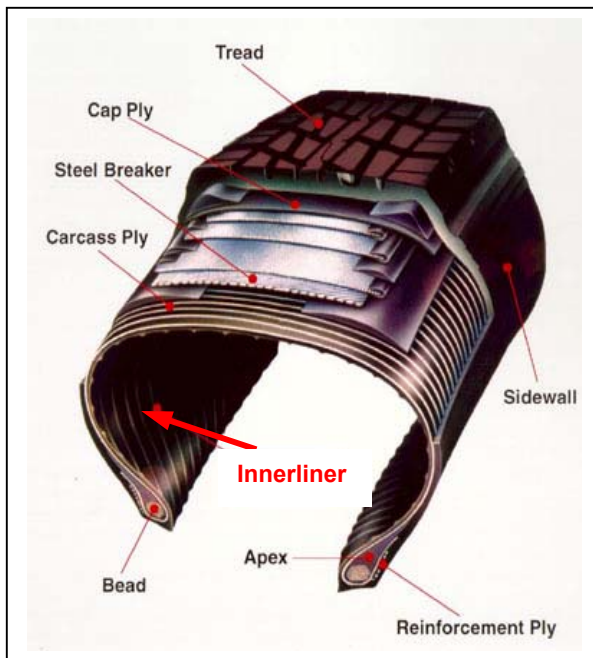


BUTYL RUBBER

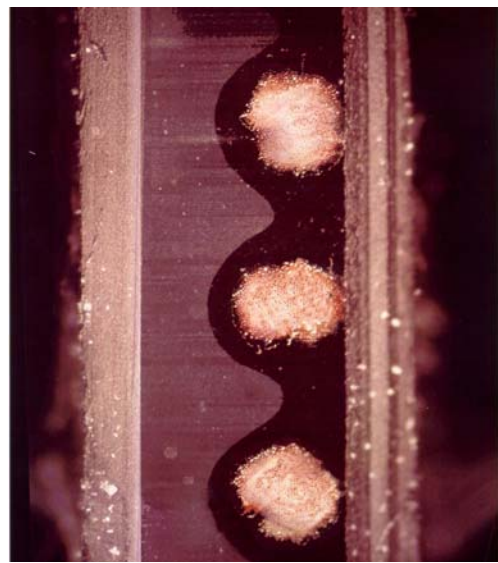
Properties and Applications

Butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene. First commercialized in 1943, the primary attributes of butyl rubber are excellent impermeability/air retention and good flex properties, resulting from low levels of unsaturation between long polyisobutylene segments. Tire innertubes were the first major use of butyl rubber, and this continues to be a significant market today.

The development of halogenated butyl rubber (halobutyl) in the 1950's and 1960's greatly extended the usefulness of butyl by providing much higher curing rates and enabling co-vulcanization with general purpose rubbers such as natural rubber and styrene-butadiene rubber (SBR). These properties permitted development of more durable tubeless tires with the air retaining innerliner chemically bonded to the body of the tire. Tire innerliners are by far the largest application for halobutyl today. Both chlorinated (chlorobutyl) and brominated (bromobutyl) versions of halobutyl are commercially available. In addition to tire applications, butyl and halobutyl rubbers' good impermeability, weathering resistance, ozone resistance, vibration dampening, and stability make them good materials for pharmaceutical stoppers, construction sealants, hoses, and mechanical goods. The total annual demand for Butyl Polymers is ~650,000 Metric Tons.



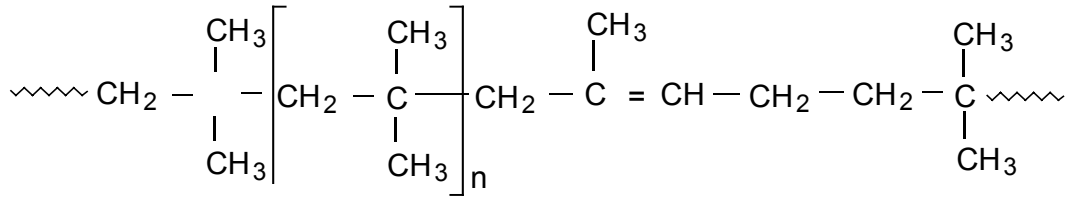
Photomicrograph of Tire Innerliner



Chemistry and Manufacturing Process

Butyl Rubber typically contains about 98% polyisobutylene with 2% isoprene distributed randomly in the polymer chain. To achieve high molecular weight, the reaction must be controlled at low temperatures (-90 to -100 degC). The reaction is highly exothermic. The most commonly used polymerization process uses methyl chloride as the reaction diluent and boiling liquid ethylene to remove the heat of reaction and maintain the needed temperature. It is also possible to polymerize butyl in alkane solutions and in bulk reaction. A variety of Lewis acids

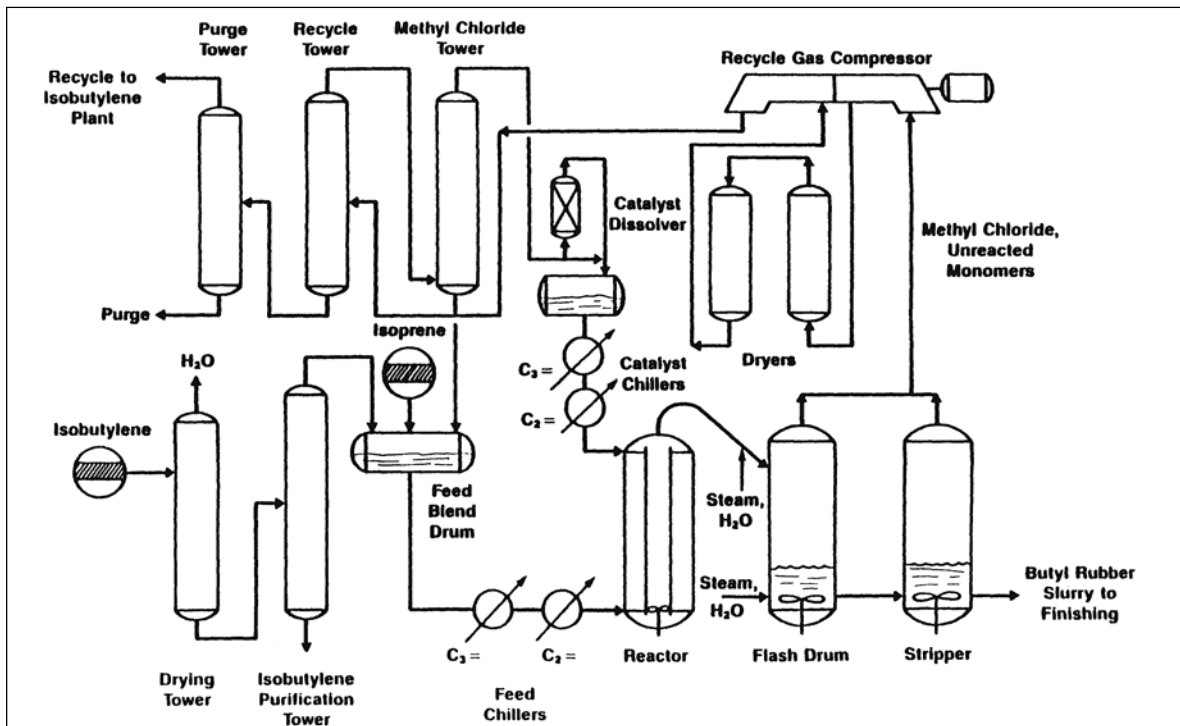
can be used to initiate the polymerization. The molecular weight of butyl is set primarily by controlling the initiation and chain transfer rates.



Butyl Molecule

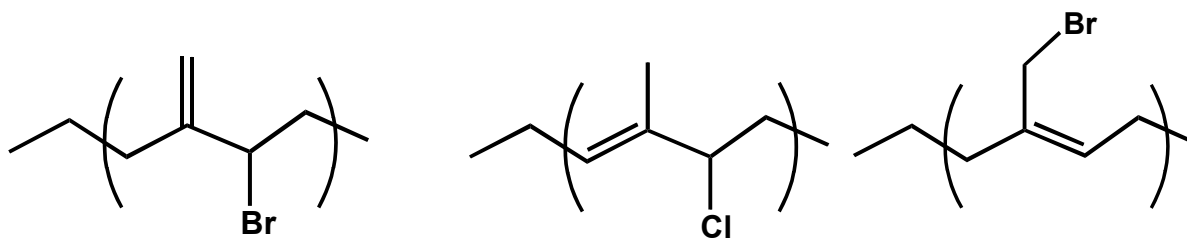
In the most widely used manufacturing process, a slurry of fine particles of butyl rubber (dispersed in methyl chloride) is formed in the reactor. The methyl chloride and unreacted monomers are flashed and stripped overhead by addition of steam and hot water, and then they are dried and purified in preparation for recycle to the reactor. Slurry aid (zinc or calcium stearate) and antioxidant are introduced to the hot water/polymer slurry to stabilize the polymer and prevent agglomeration. Then the polymer is screened from the hot water slurry and dried in a series of extrusion dewatering and drying steps. Fluid bed conveyors and/or airvey systems are used to cool the product to 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 PE film and packaging.

Commercial Butyl Slurry Polymerization Process



The polymerization process for halobutyl is exactly the same as for non-halogenated butyl. Prior to halogenation, the butyl must be dissolved in a suitable solvent (hexane, pentane, etc...) and all unreacted monomer removed. Several different processes are currently used to prepare butyl solution for halogenation. Either reactor effluent polymer, in-process rubber crumb, or butyl product bales may be dissolved in solvent in preparation for halogenation.

Bromine liquid or chlorine vapor is added to the butyl solution in highly agitated reaction vessels. One mole of hydrobromic or hydrochloric acid is released for every mole of halogen that reacts, therefore the reaction solution must be neutralized with caustic (NaOH). The solvent is then flashed and stripped by steam/hot water, with calcium stearate added to prevent polymer agglomeration. The resultant polymer/water slurry is screened, dried, cooled, and packaged in a process similar to that of unhalogenated butyl.



Most Abundant Halobutyl Isomer

Minor Halobutyl Isomers

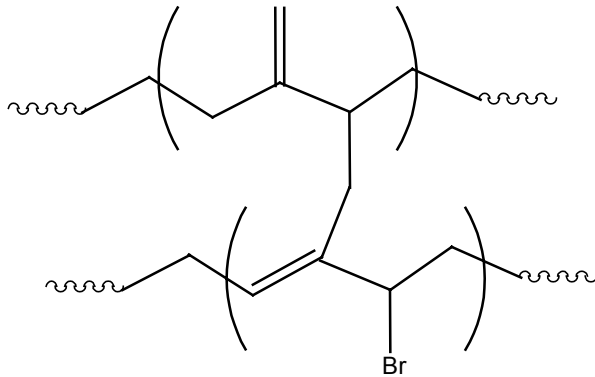
Processing and Vulcanization

Like other rubbers, for most applications, butyl rubber must be compounded and vulcanized (chemically cross-linked) to yield useful, durable end use products. Grades of Butyl have been developed to meet specific processing and property needs, and a range of molecular weights, unsaturation, and cure rates are commercially available. Both the end use attributes and the processing equipment are important in determining the right grade of Butyl to use in a specific application. The selection and ratios of the proper fillers, processing aids, stabilizers, and curatives also play critical roles in both how the compound will process and how the end product will behave.

Care must be taken when processing Halobutyl that premature dehydrohalogenation does not occur due to high temperature. Stabilizers (calcium stearate alone for chlorobutyl, supplemented with an epoxy compound such as epoxidized soybean oil in the case of bromobutyl) are required to prevent dehydrohalogenation during processing.

Elemental sulfur and organic accelerators are widely used to cross-link butyl rubber for many applications. The low level of unsaturation requires aggressive accelerators such as thiuram or thiocarbamates. The vulcanization proceeds at the isoprene site with the polysulfidic cross links attached at the allylic positions, displacing the allylic hydrogen. The number of sulfur atoms per cross-link is between one and four or more. Cure rate and cure state (modulus) both increase if the diolefin content is increased (higher unsaturation). Sulfur cross-links have limited stability at sustained high temperature. Resin cure systems (commonly using alkyl phenol-formaldehyde derivatives) provide for carbon-carbon cross-links and more stable compounds.

In halobutyl, the allylic halogen allows easier cross-linking than does allylic hydrogen alone, because halogen is a better leaving group in nucleophilic substitution reactions. Zinc oxide is commonly used to cross-link halobutyl rubber, forming very stable carbon-carbon bonds by alkylation through dehydrohalogenation, with zinc chloride byproduct. Bromobutyl is faster curing than chlorobutyl and has better adhesion to high unsaturation rubbers. As a result, its volume growth rate has exceeded that of chlorobutyl in recent decades as tire plants have driven to higher productivity operation.



Crosslinked Halobutyl Rubber

Conclusion

Butyl (and its primary derivative, halobutyl) is and will continue to be a high value polymer particularly well suited for its primary application of air retention in tires. Its unique combination of properties (excellent impermeability, good flex, good weatherability, co-vulcanization with high unsaturation rubbers, in the case of halobutyl) make it a preferred material for this application. As miles driven, tire size, and market sensitivity to pressure retention are all increasing, the demand for butyl rubber (specifically halobutyl) will continue to grow.

All of the material here is either paraphrased or verbatim from the public sources:

- 1. Encyclopedia of Polymer Science and Engineering (Vol 8)*
- 2. The R. T. Vanderbilt Rubber Handbook (13th Edition)*
- 3. Kirk-Othmer Encyclopedia of Chemical Technology (4th Ed, Vol No. 8)*