MODIFICATION OF POLYBUTADIENE RUBBER: A REVIEW

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ABSTRACT

Developments in modification of polybutadiene rubber (PBR) using various reagents and catalysts have been reviewed. Hydrogenation and functionalization occurring at the site of unsaturation along chain length are discussed. Hydrogenation involving various metal catalyzed processes is discussed. Suitable conditions that are effective during hydrogenation and functionalization are mentioned in this article. Reactivity ratios associated with microstructures of polybutadiene rubber and possible mechanisms involved are described in the review. The importance of reaction conditions during reactivity and their impact on product properties are highlighted. A specific method that needs to be adopted in order to achieve expected product properties is discussed. Various industrial applications of modified PBR and their commercial products in the global market are discussed. [doi:10.5254/rct.21.79892]
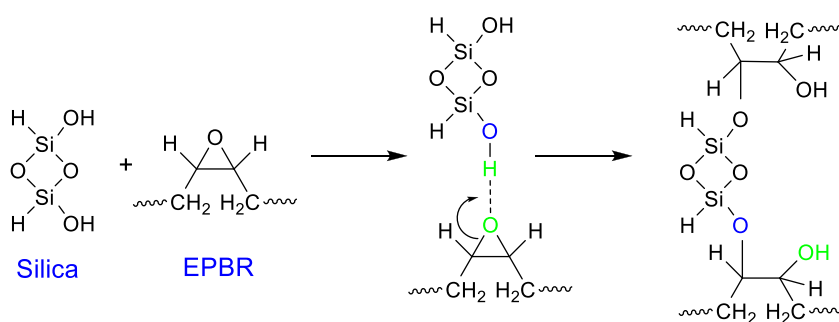
CONTENTS

I. INTRODUCTION

Rubber modification through chemical reaction has become an important technique to alter rubber properties. Polybutadiene rubber has unsaturation along the length of the backbone chain

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SCHEME 1. — Silica filler and epoxidized rubber interaction mechanism.[3]

and thus permits polybutadiene rubber to undergo several structural and functional modifications. Using hydrogenation or functionalization, it is possible to fine tune properties of rubber products according to desired applications. Hydrogenation of polybutadiene rubber is an important method to modify polybutadiene rubber at the molecular level. Depending on the extent of hydrogenation, rubber properties of polybutadiene rubber can be transformed into a plastic form. Functionalization at the site of the double bond is another important synthetic tool to modify polybutadiene rubber properties at the molecular level. Since polybutadiene rubber is non-polar in nature, functionalization with the polar functional group enhances the overall polar nature of the resultant rubber, which can be well used in the tire industry. Minimizing the polarity barrier between rubber and polar fillers improves their compatibility, which in turn enhances the tire's performance.

Green tires are an emerging trend in the automobile industry, which offers low fuel consumption and low carbon emission. The green tire system mainly uses dispersed silica, which is polar in nature, and its compatibility with rubber is highly significant in order to benefit low rolling resistance properties. Functionalization at double bonds of diene rubbers along polymeric chain, which includes hydroxylation, halogenation, epoxidations, aromatizations, and so on,[1,2] can be the most promising method to improve compatibility of resultant rubber products with polar fillers. Such functional groups in polymers can produce a strong dipole–dipole interaction, hydrogen bonds, and also covalent bonds between polymer and filler, which are essential features for green tires. A representative example of epoxidized polybutadiene rubber and silica filler interaction is shown in Scheme 1.

The presence of polar functional groups in base rubber improves the physical properties with inorganic polar fillers. Additionally, while maintaining the mechanical properties of the rubber, significant improvements in resistance of the functionalized rubber to thermal and oil can be achieved.[4] Functionalized groups in rubber were found to increase surface energy considerably, which allows their use as compatibilizers, between silica fillers and rubber chains.[5]

Technologies related to polybutadiene rubber modifications are successfully implemented at commercial scale around the globe. Important modified PBR is available at commercial scales; their major global producers with specifications and applications are mentioned in Table I.

In view of their potential applications, modifications in polybutadiene rubbers are gaining significant industrial interest. Various methods are available to modify or introduce functionality in polybutadiene rubber. Furthermore, a specific synthetic approach is necessary to alter double bonds or to introduce functionalization in polybutadiene rubber depending on their end applications. In view of this, techniques available to modify polybutadiene rubber, applications, and commercial relevance have been discussed comprehensively in this review.

TABLE I
MODIFIED POLYBUTADIENE PRODUCTS AT COMMERCIAL SCALE AND APPLICATIONS

Modified PBR products	Specifications	Commercial producer	Applications[a]
Hydrogenated PBR	a.[6] M_n: 2200 Iodine value (I₂/100 g): ≤ 21 Viscosity (poise/45 °C): 50–100 b.[6] M_n: 3300 Iodine value (I₂/100 g): ≤ 21 Viscosity (poise/45 °C): 100–300	Nippon SCL[6]	Resin modifiers, plasticizers, adhesives, paints, electrical insulating materials, cast resins[6]
Epoxidized PBR	a.[6] Epoxy eq. wt (g/eq): 190–210 Viscosity (poise/45 °C): 220 b.[7] Epoxy eq. wt (g/eq): 1500 Viscosity (poise/25 °C): 15,000	Nippon SCL,[6] Nagase[7]	Resin modifiers, adhesives, paints, encapsulants, epoxy curing[6]
Hydroxyl terminated PBR	a.[6] M_n: 1400 Hydroxy value (KOH mg/g): 68–78 Viscosity (poise/45 °C): 75 b.[6] M_n: 3000 Hydroxy value (KOH mg/g): ≥27 Viscosity (poise/45 °C): 310	Total, Evonik, Nippon SCL, Idemitsu Kosan, CRS Chemicals, Zibo Qilong Chemical Industry, Aerocon Systems Co., Emerald Performance Materials[8,9]	Rocket fuel, waterproof coatings and membranes, adhesives, sealants, electricals, and electronics[8]

[a] Detailed applications are discussed in Section IX.
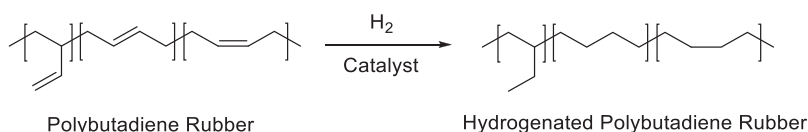
SCHEME 2. — Hydrogenation of polybutadiene rubber in presence of catalyst.[10]

II. HYDROGENATION

Polybutadiene rubber containing double bonds along the chain length has key advantage in controlling the rubber properties. Its elastic nature can be converted to a more plastic behavior by reducing double bonds through hydrogenation reactions. Upon hydrogenation as shown in Scheme 2, high *cis*-polybutadiene rubber can be reduced to a high density polyethylene-like product.[10]

Control over hydrogenation can be achieved depending on the catalyst system and its concentrations. Further, nearly every double bond in the chain can be hydrogenated. Hydrogenated polybutadiene rubber shows a number of advantages compared to standard polybutadiene rubber. At the microstructural level, double bonds are prone to undergo oxidation, thus, by reducing double bond concentrations, resistance to ageing and thermal and UV degradations can be enhcanced.[11,12] Product property of hydrogenated polybutadiene rubber results in improved wear resistance, better conservation of rubber elasticity after thermal heating, and also visco-elastic properties.[10,11] Higher tensile strength and low glass transition temperature (Tg) are displayed by vulcanized hydrogenated rubber.[12]

Hydrogenation reaction of diene rubber was first reported by H. Staudinger and J. Fritschi in 1922, and the method was effectively implemented to hydrogenate natural rubber.[13,14] In the report, the hydrogenation reaction of natural rubber was conducted catalytically using platinum at 270 °C and hydrogen pressure of 93 bar. At 10 h, complete saturation was achieved with a high molecular weight solid product, which resembles paraffin wax. In the following decades various catalytic and non-catalytic hydrogenation systems were developed, and important systems are described in the following sections.

A. HYDROGENATION BY PALLADIUM CATALYST

Hydrogenation of unsaturated compounds can be performed using various metal catalyst systems. In contrast to heterogenic catalysts, homogeneous catalysts can often remain in the final product, and therefore homogeneous processes are less preferred for the hydrogenation reaction. Heterogenic catalysts Pd/CaCO$_3$ and Pd/C can reduce diene unsaturation of high *cis* and *vinyl*-polybutadiene rubber at different reaction conditions. Rosedale and Bates achieved about 85% of hydrogenation, which is quite satisfying; however, work up was found to be a tedious process.[15,16]

B. HYDROGENATION BY COBALT AND NICKEL BASED CATALYST SYSTEM

Hydrogenation of polybutadiene rubbers with cobalt(II) 2-ethylhexanoate yields nearly complete saturated product in about 30 minutes at moderate conditions of 50 °C and 3.4 bar of hydrogen pressure. Reactivity of double bonds for cobalt based catalyst are in the order vinyl-1,2 > *cis*-1,4 > *trans*-1,4.[17–19] The order can be explained based on sterical hindrance of double bonds, as *vinyl* groups tend to expose, making it better access to catalyst compared to corresponding *cis* and *trans* forms, thus showing higher reactivity by *vinyl* groups.
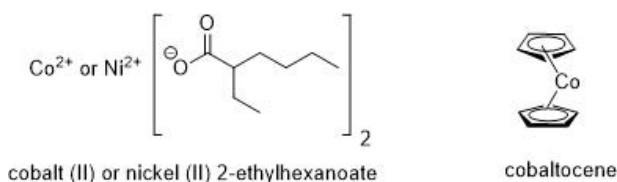
SCHEME 3. — Cobalt and nickel based catalyst system for hydrogenation.[17,18,23]

In nickel catalyst systems, depending on hydrogenation conditions, both homogenous and heterogenic catalysts are practiced. Heterogeneous catalysts include Raney-nickel or elementary Ni adsorbed on aluminum or silicon oxides.[20–22] They are used during the hydrogenation that requires higher temperature over 120 °C and hydrogen pressures up to 60 bar. In contrast, homogenous catalyst like nickel(II) 2-ethylhexanoate (Scheme 3) are used for milder conditions at temperatures of 10–35 °C and hydrogen pressures of 0.72–1.78 bar as described by Sabata and Hetflejs.[23]

They have observed that cobalt(II) 2-ethylhexanoate polybutadiene rubber shows highest reactivity for 1,2 double bond (*vinyl*) but with opposite reactivity of 1,4 double bonds toward hydrogenation (*trans*-1,4 > *cis*-1,4). At milder conditions cobalt and nickel catalysts show a high degree of hydrogenation, making them suitable catalysts for partial hydrogenation applications at moderate conditions.
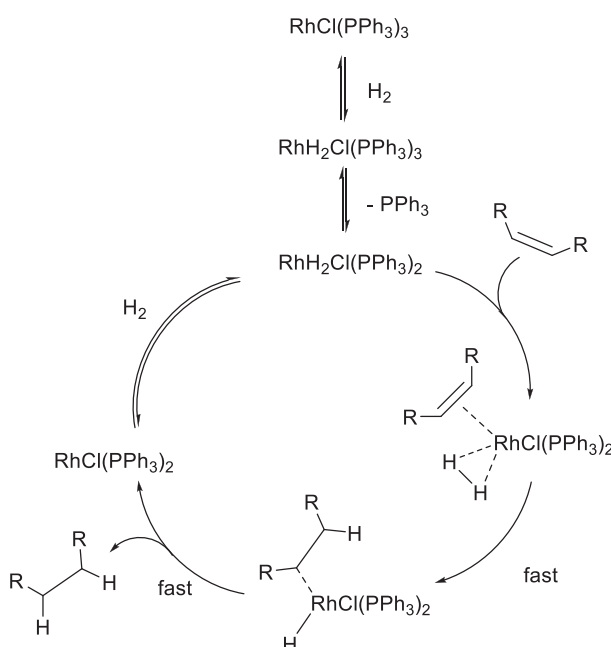
C. HYDROGENATION BY RHODIUM CATALYST

Hydrogenation by rhodium catalysts is one of the most prominent catalytic systems that uses (triphenylphosphine)rhodium(I) chloride. In the 1960s Wilkinson described the catalytic hydrogenation of unsaturated molecules like 1-hexene.[24] Birch and Walker performed hydrogenation of various unsaturated compounds, which includes the reduction of polybutadiene rubbers,[25] followed by various ruthenium-based analogous catalysts, which were invented for the rubber hydrogenation process.[26]

High *vinyl* butadiene rubber can be hydrogenated with tris(triphenylphosphine)rhodium(I) chloride over several days at 60 °C to yield up to 94% hydrogenation.[27] Prolonged hydrogenation reaction times can be reduced by adding triphenylphosphine (PPh$_3$), which assists with the diffusion of the catalyst in reaction mixture. In such case, hydrogenation is performed in 10 h with reaction temperature between 40 and 70 °C and hydrogen pressure below 1 bar.[28] Similar to cobalt and nickel catalysts, Wilkinson catalysts showed higher reactivity for 1,2 double bonds (*vinyl*) compared to 1,4 double bonds (*cis* and *trans*).[29]

Pan and Rempel, Guo and Rempel, and Martin et al.[29–31] proposed a mechanism to explain the hydrogenation process by Wilkinson catalyst (Scheme 4). Initially a hydrogen molecule is added to the catalyst in a reversible process. Then a PPh$_3$ group leaves the catalyst to allow subsequent coordination of an olefin molecule. Thus, active species for hydrogenation enters the process wherein hydrogen from rhodium dislocates to olefin, and hydrogenation with faster kinetics thus begins. The hydrogenated olefin leaves the initial complex, and a further complex readies itself for the next hydrogen acceptance. During the cycle, initial addition can either be an olefin or a hydrogen molecule.

Hydrogenation by a Wilkinson catalyst is generally performed in non-polar organic solvent system. A combination of organic solvents and ionic liquids further enhances the hydrogenation process. A solvent mixture containing toluene and the ionic liquid BMI(BF$_4$) and butadiene rubber containing about 40% of 1,2-*vinyl* groups can be hydrogenated up to 94% within 4 h at hydrogen pressure of 31 bar and at 100 °C.[10] Further, by using a micellar system containing water,

SCHEME 4. — Proposed mechanism of hydrogenation by Wilkinson catalyst RhCl(PPh$_3$)$_3$.[29–31]

dodecyltrimethylammonium chloride (DTAC) as detergent, and *n*-hexane, butadiene rubber containing a high *vinyl* ratio can be hydrogenated up to 91% at 20 bar hydrogen pressure within 20 min at a temperature of 100 °C.[32] Although rhodium catalyst based hydrogenation is successful, due to its high cost, commercial applications are limited.
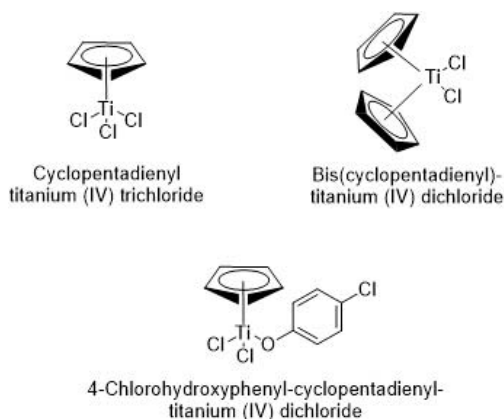
D. HYDROGENATION BY TITANIUM CATALYST

The discovery of a titanium-based Ziegler catalyst[33] for the ethylene polymerization has led to the development of titanium-based catalyst systems with a wide spectrum of applications. Titanium-based catalysts are compatible and soluble in most organic solvents, which allows hydrogenation of double bonds at moderated conditions.

Sloan et al. reported the overnight hydrogenation of short alkenes such as *n*-octene using TiCp$_2$Cl$_2$ with a hydrogen pressure of 4.4 bar at room temperature.[34] Then several titanium catalysts are developed containing basic structures of Cp (Scheme 5) and effectively used for hydrogenation purposes.[35–44]

E. HYDROGENATION BY IN SITU FORMED DIIMIDE

Hydrogenation through non-catalytic and homogenous route can be performed by diimides. Active species involved in the process can be generated by decomposition of hydrazine precursor or thermal decomposition of *p*-toluenesulfonylhydrazide (TSH) (Scheme 6).[45–48] The advantage of this method over expensive precious metal based catalysts has led to the extension of the process to polybutadiene rubber. Harwood et al.[49] elucidated hydrogenated high *cis*-polybutadiene and natural rubber using fivefold excess amount of TSH at temperatures of 135–140 °C and observed quantitative conversion of rubber after 8 h. Hahn[50] further improved the process and achieved

Cyclopentadienyl
titanium (IV) trichloride

Bis(cyclopentadienyl)-
titanium (IV) dichloride

4-Chlorohydroxyphenyl-cyclopentadienyl-
titanium (IV) dichloride

SCHEME 5. — Different hydrogenation catalyst based on titanium.

quantitative conversion of rubber at 4 h by using twofold excess of TSH. At similar conditions high *trans* polybutadiene rubber can be hydrogenated with a conversion of 74% at 6 h.[51]

Higher reactivity of 1,4-*cis* is observed compared to 1,4-*trans* double bond of polybutadiene rubber in diimide based hydrogenation process.[50–52] TSH that generated in reaction (Scheme 6) as a byproduct seems to cause degradation of high molecular weight polybutadiene rubbers.[50,51] The byproducts, degradation, and necessity of higher quantities of TSH makes the diimide method an unfavorable choice for the rubber hydrogenation process.

The relevant hydrogenation method is chosen depending on desired degree of hydrogenation and microstructural modifications. Methods and comparative analysis of catalyst mediated hydrogenation of polybutadiene rubber are summarized in Table II.

III. END GROUP FUNCTIONALIZATION

The end group modified rubbers technique is a new method to improve the affinity of rubber to filler or to enhance filler dispersity in the rubber matrix. Various methods are available to introduce functional groups at the terminating end of the polymer, namely, anionic polymerization,[53] living polymerization,[54] cross metathesis,[55] and so on. The cross metathesis approach to introducing terminal functionalized polybutadiene rubber is gaining more attention due to the simplicity of the reaction. The metathesis reaction with polybutadiene rubber results in the formation of telehelic
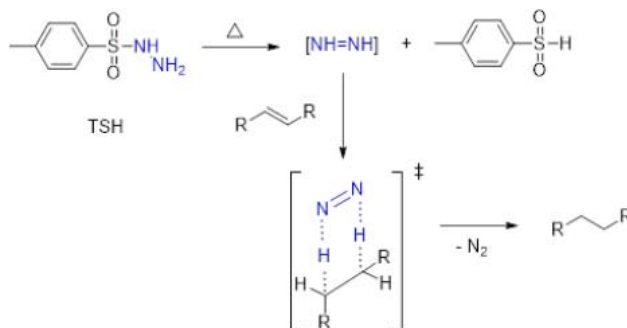
SCHEME 6. — Thermal decomposition of *p*-toluenesulfonyl-hydrazide (TSH) to form diimide (blue) and hydrogenation.[47]
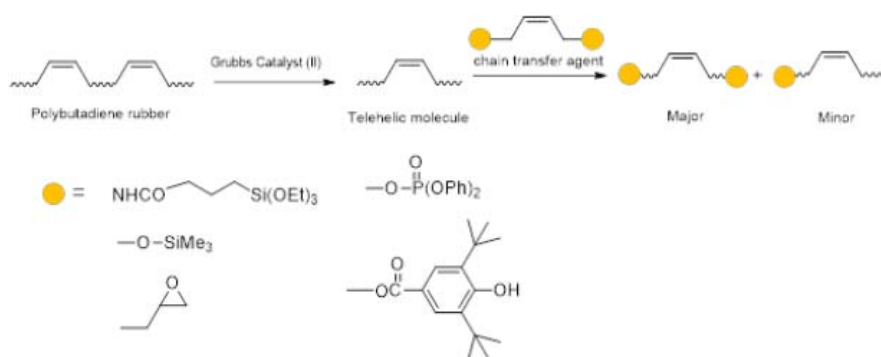
SCHEME 7. — End group functionalization of polybutadiene rubber via depolymerization and cross metathesis.[57]

compounds, that is, polymers with low molecular weight due to chain break down. The reaction of telehelic compounds with a suitable functionalized chain transfer agent results in end functionalized polybutadiene rubber products. Cross metathesis was used to prepare polybutadiene rubber bearing alkoxysilyl, alkyloxyl, hydroxyl, and amino ended polymers.[56]

Ying et al.[57] used the cross metathesis approach to prepare end functionalized polybutadiene rubber with higher polarity. Butadiene telehelics are prepared using Grubbs catalyst and end functionalized using chain transfer agents bearing functional groups of silane, phenol, oxirane, and phosphates. In order to prevent intramolecular cyclization during metathesis, a two step process is adopted (Scheme 7). The initial step involves depolymerization of polybutadiene in the presence of a catalyst, and in a subsequent step, chain transfer functional agents are added to produce a functional polymer.

Polybutadiene rubber synthesis by Ziegler–Natta catalysts is the best commercial production process that is known to date. Catalyst systems have come out as a powerful tool for controlling polymer microstructure through a regioselective and/or stereospecific approach, whereas control of molecular weight and molecular weight distribution is still limited.[58] Ozawa and Takata[59] describe the polymerizing butadiene to high *cis*-polybutadiene rubber by employing neodymium-based catalyst systems, followed by functional termination through several functional moieties. Further, the effective interaction results of polymer with silica filler indicates this as a favorable approach to green tires.

IV. HALOGENATION OF PBR

A. BROMINATION

Halogenation and, in particular, bromination reaction is a simple method to halogenate butadiene rubbers due to its higher reactivity and clean reaction process. Depending on the requirement, the introduced bromine group can be made to undergo a substitution or elimination reaction. On substitution, different nucleophilic groups can be attached to the rubber chain, and elimination results in introduction of double bonds depending on reaction conditions (Scheme 8).

Electrophilic bromination involved in the formation of the bromonium ion as active species and mechanisms was proposed by Roberts and Kimball (Scheme 9).[60] Heterolytic cleavage of the bromine molecule catalyzed by either a neighboring bromine molecule or a solvent molecule results in formation of the bromonium ion. Protic solvents like methanol catalyze the reaction by being able to stabilize the formed bromonium ion and, in the case of halogenated or non-protic solvents, a driving force is either by solvation or formation of tribromide species.
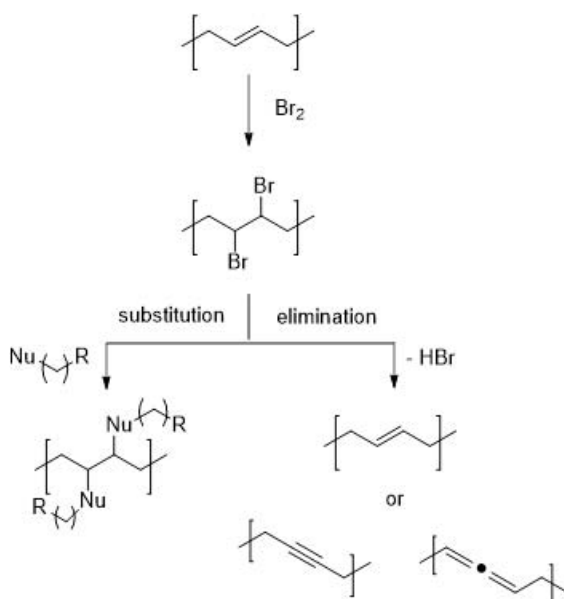
SCHEME 8. — Bromination of butadiene rubber followed by substitution or elimination reactions.[62]

The nucleophilic bromide ion adds on to the double bond in anti-addition fashion. In case of a *cis* double bond, a racemic mixture of R,R and S,S conformations is possible and a diastereomer can occur in case of a *trans* double bond, which leads to a meso compound.[61,62]
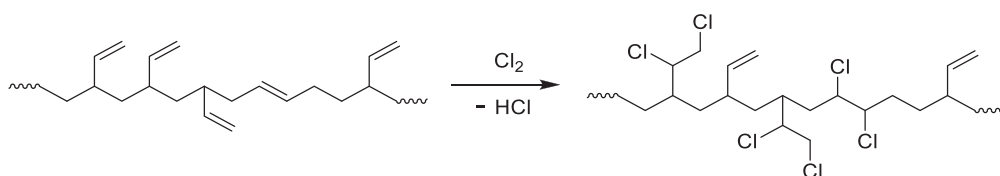
B. CHLORINATION

Polymer chain modification through chlorination is known to alter product properties of certain resinous polymers, natural rubber, and polypropylene.[63] Abdullin et al. functionalized low molecular weight 1,2 polybutadiene rubber by incorporating chlorine and hydrogen chloride to the unsaturated double bonds units.[64] Chlorination was conducted by two methods, addition of gaseous hydrogen chloride or chlorine to reaction mixture. In a polymer solution of 1,2 butadiene in chloroform, hydrochlorination was performed by bubbling dry hydrogen chloride at 3–50 °C, and chlorination was performed by bubbling chlorine gas at 20–24 °C. The reaction yielded chlorinated polymer products containing up to 56 wt % chlorine content. The reaction involved electrophilic addition of chlorine to unsaturated double bonds of polybutadiene (Scheme 10).

Chlorination was performed in a suspension mixture of polybutadiene and water using a sequential process of irradiation and heat treatment. Initially, partial dissociation of chlorine molecules occurs during irradiation, and complete dissociation is achieved by employing the heat treatment step. Radiation wavelengths in the range of 250 to 550 nm with intensities of 3–10 watt/kg of polymer are used. Then irradiation at a temperature of 70–100 °C is applied for 1 to 8 h.
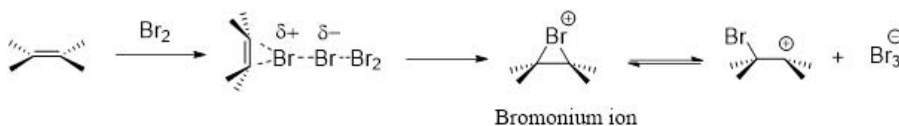
SCHEME 9. — Bromonium ion formation during bromination reaction.[60]

SCHEME 10. — Electrophilic addition of chlorine to polybutadiene.[64]

Chlorination proceeds through homolytic fission of Cl–Cl, and the process produces product with chlorine content of 40–70% depending on the intensity of radiation.[65]
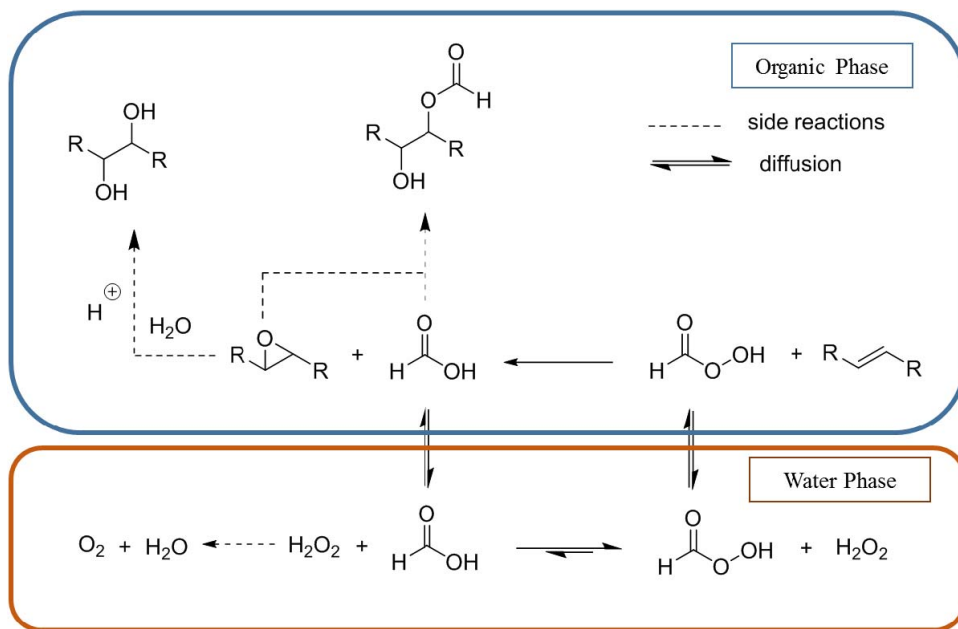
V. EPOXIDATION

Polyols, which have more than one or multiple hydroxyl groups within a molecule, are the key raw material in preparing polyurethane. PBR based polyols can be prepared through epoxidation of PBR followed by ring opening reactions. Epoxidized PBR also finds its major application in preparing green tires due to its enhanced polar interaction with silica filler. The epoxidation was first reported by Prileschajew[66] by epoxidizing double bonds with various organic peroxides. Epoxidation of diene rubbers is conducted by peroxides or peracids.[67] Epoxide functionality can be introduced by the reaction between nucleophilic double bonds and electrophilic oxygen (Scheme 11). Epoxidation follows a concerted mechanism wherein oxygen bond breaking and bond formation with double bonds occurs simultaneously, and thus by retaining stereo information in the resultant molecule (Scheme 11).[68]

In polybutadiene rubber, reactivity of double bonds toward the epoxidation depends on the extent of substituents along the length of the chain. Double bonds along the chain length are a result of 1,4 addition, and pendent vinylic double bonds are generated due to 1,2 addition. Carbon substituents increase the positive inductive effect of carbon, which in turn increases electron density and hence its nucleophilicity. As a result, 1,4 addition double bonds, that is, in-chain double bonds, show significantly higher reactivity toward epoxidation than 1,2 addition double bonds, *vinyl* group. The difference of nucleophilicity between these two types of double bond is so large that vinylic double bonds do not take part in epoxidation reactions.[69–71]

Stoichiometric peracids are required to obtain a quantitative epoxidation. Aliphatic or aromatic peracids can be used as oxidizing agents. At the end of the reaction, corresponding acids are formed followed by epoxidized products. Formation of the acidic reaction mixture due to acid and higher reaction temperatures results in various side products containing ring opened epoxide groups.[72] Such side products can be avoided by preferring aromatic peracids such as perbenzoic acid[73] and meta-chloro perbenzoic acid,[74,75] as these peracids are found to produce corresponding acids having lower acidity and are not strong enough to open the epoxide ring.
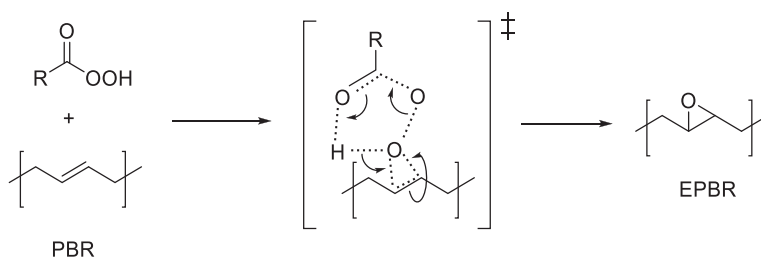
SCHEME 11. — Mechanism of PBR epoxidation by organic peracids.[61,62]

SCHEME 12. — Two phase catalytic system for epoxidation of PBR.[79,80]

At industrial scale these organic peracids are rather expensive, and hence alternate aqueous reagents are used wherein active species for epoxidation are in situ generated. Such active species are generated using combinations of oxidizing agents such as hydrogen peroxide and catalytic acid. In addition to being cost effective at industrial scale, the aqueous reagent method reduces the possibility of side reactions during the epoxidation process.[69,76–78] Higher acidity favors the formation of peracids and since formic acid has higher acidity, performic acid can be easily generated without any further additives.[78] Epoxidation through in situ generated active species uses a two phase system of polymer dissolved in organic solvent and the water phase containing acid and hydrogen peroxide (Scheme 12). Peracid generated at water phase migrates into an organic layer and initiates the epoxidation process.

Peracid formed during epoxidation is an endothermic process is considered to be a rate determining step,[79] and the epoxidation step is an exothermic process and therefore occurs faster.[80] Peracid, after completing the epoxidation process, converts to acid and migrates back to the water phase, where it again gets re-oxidized to peracid, and the process continues until all the hydrogen peroxide is used. Occasionally migration can become so slow that it becomes the rate determining step. To improve the ease of migration between the layers, detergents which lower the surface tension and increase transition can be used, resulting in enhanced diffusion rates.[78]

Epoxidized polybutadiene rubber can be further functionalized through nucleophilic reactions. A variety of nucleophiles are used to open the epoxide ring, and alcohols and amines are used more commonly.[61,62] Although epoxide groups in polybutadiene rubber chains are quite reactive, nucleophilic reaction requires either a strong nucleophile or acid catalyst.

During the ring opening reaction, regioselectivity is dependent on degree of substitution at the reaction site. If the ring opening reaction is acid catalyzed, the nucleophile is bound to proceed to the higher substituted carbon atom. Since the acid initially protonates the epoxide oxygen and generates a carbo cation, the cation stabilization is greater at the site where higher substituted carbon is present and allows the nucleophile to attack at that site (Scheme 13).
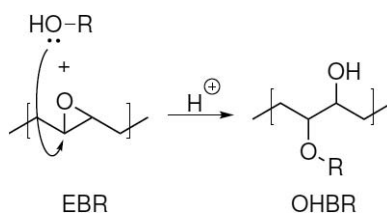
SCHEME 13. — Acid catalyzed epoxide ring opening of epoxidized polybutadiene rubber.[81]

The reaction with basic conditions favors an S_N2 (bimolecular nucleophilic substitution) pathway, and this guides the nucleophile to attach predominantly on the less substituted carbon. For the partial epoxidized polybutadiene rubber such regioselectivity has a minor role, since they mainly comprise epoxide groups on a polymer backbone. Thus, the epoxide group at 1,4 double bonds has uniform substitution on both the sides and therefore the influence of regioselectivity is very negligible.

Ring opening reactions of epoxidized PBR are challenging processes, since even strong bases such as *t*-BuOK are not able to open an epoxide ring.[82] Strong acids such as sulfuric acid can perform ring opening reactions at elevated reaction rates and at long reaction hours; however, polymer degradation under such conditions is a concern.[83] Super acids like trifluoromethane-sulfonic acid can open up an epoxide ring in reasonable time and at low temperatures.[82]
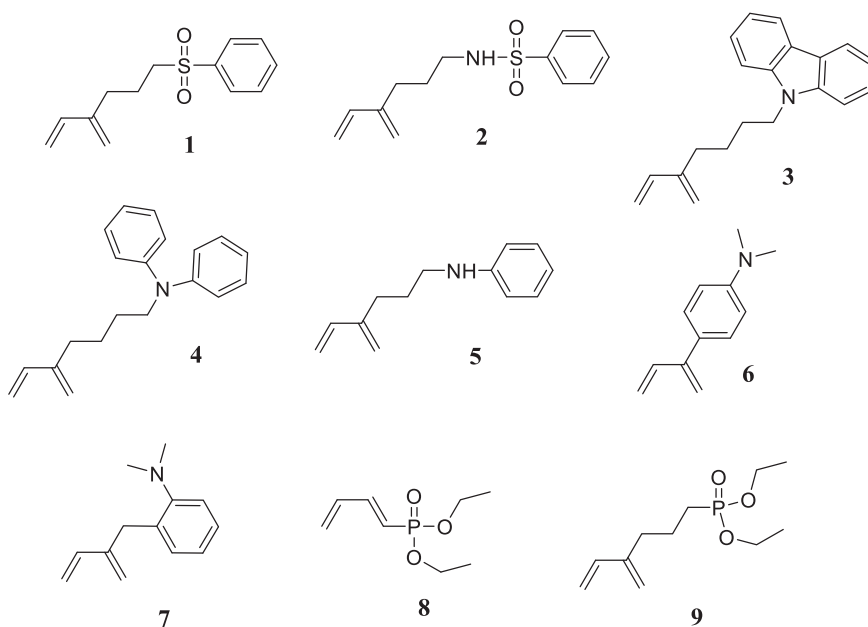
VI. FUNCTIONALIZATION THROUGH COPOLYMERIZATION

Incorporation of monomers bearing a functional group to 1,3 butadiene polymerization can be achieved by anionic or free radical polymerization techniques.[84–87] However, these polymerizations have drawbacks, since microstructural control cannot be achieved. Tire technology demands functionality along the polymer chain length to increase filler rubber interaction without compromising on microstructural properties of rubber. To achieve these, additional steps after polymerizations are practiced in general, and in contrast to this Leicht et al. developed a method to incorporate functionalities by commencing polymerization with a mixture of modified and original monomers.[88] They reported insertion copolymerization of simple butadiene monomers with various polar functionalized butadiene based co-monomers and more interestingly with stereo selective mode.

Silyl based functional monomers are developed through Grignard reactions between chloroprene and iodosilanes (Scheme 14). Copolymerization is performed using a nickel based catalyst system with high co-monomer conversions.

In addition to silyl monomers, several other polar group bearing monomers are prepared for copolymerization (Scheme 15). Copolymerization was found to be unsuccessful with monomers bearing amides, amines of primary, secondary, and aliphatic tertiary types, but successful copolymerization was observed in primary and tertiary aromatic amines. Copolymerizations are given identical molecular weight with a 95% *cis* content pattern at similar polymerization
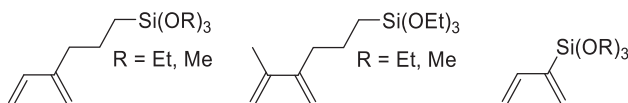
SCHEME 14. — Silyl based co-monomers used in 1,3 butadiene copolymerization.[88]

SCHEME 15. — Co-monomers bearing polar groups.[87]

conditions. *Cis* content is completely reversed to 85% *trans* content in cases of co-monomers containing a phosphonate functional group (Scheme 15).

VII. FUNCTIONALIZATION THROUGH ALLYLBORATION

Leicht et al. further extended monomer functionalization by using an allylboration reaction with aldehyde compounds that contain several active polar groups.[89] Initially model experiments were designed with allyl boronic acid and pinacol ester to understand the behavior of the reactions under the conditions suitable for the desired application (Scheme 16). Results of these model reactions showed that allylboration reactions are a potentially robust and simple method to introduce desirable functional groups on to the poly-diene backbone.

Both aromatic and aliphatic aldehydes are active toward allylboration reaction and by using nuclear magnetic resonance techniques, it is observed that nucleophilic substitution is proceeded through a highly selective S_N2' manner without S_N2 mechanism or any side reaction (Scheme 17).

Aromatic aldehydes bearing amine functionality are interesting in this part, since by virtue of amine groups, further polarity of resultant polymer products can be enhanced. Such amine functionality has the advantage of reacting with polymers bearing cross linkable sites.

VIII. HYDROXYL TERMINATED PBR

Hydroxyl terminated polybutadiene (HTPB) and modified HTPB are viscous oligomeric liquid rubbers that are extensively used in the binder system of composite solid propellants.[90] Also due to their temperature flexibility, electrical insulation properties, and elastic recovery, HTPB finds applications in membranes, adhesives, coating, sealants, newer materials, and so on. HTPB can be prepared by free radical polymerization, anionic polymerization, or by oxidation processes.
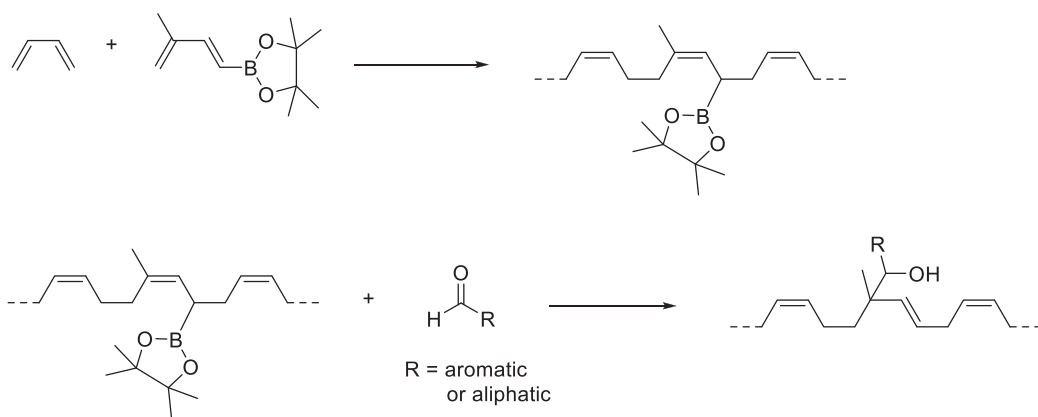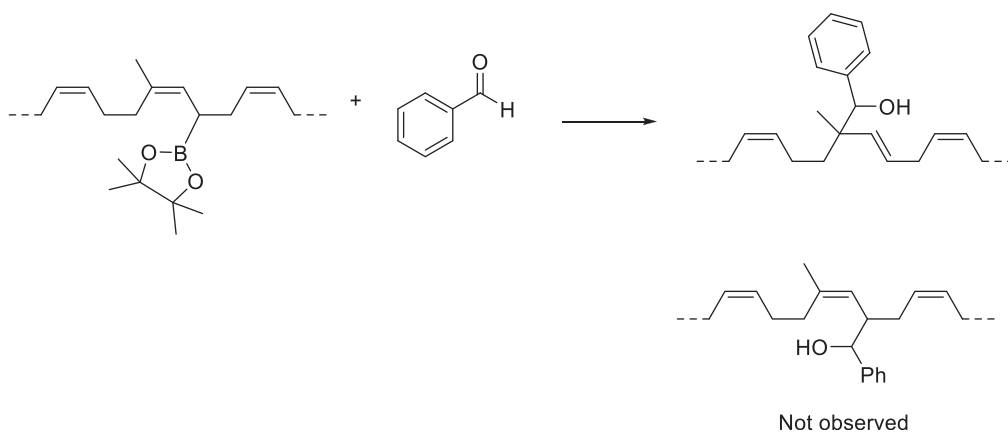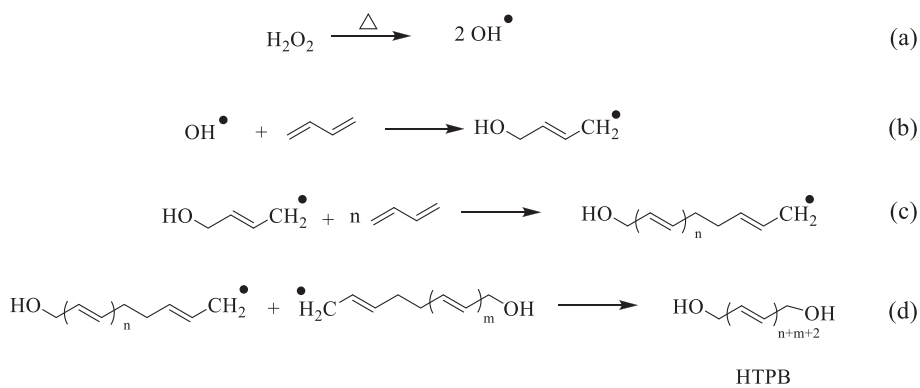
SCHEME 16. — Copolymerization of allyl borane monomer and functional group introduction[89]

SCHEME 17. — Allylboration reaction with aldehydes.[89]

SCHEME 18. — Free radical based HTPB reaction mechanism.[93]

TABLE II
COMPARATIVE CATALYTIC HYDROGENATION PROCESS

Catalyst	Catalyst composition and reaction conditions	Hydrogenation (%)	Advantages	Challenges
Palladium	Pd/CaCO$_3$ and Pd/C 70 °C and 35 bar	85[15]	Heterogeneous catalyst can be easily recovered	Expensive catalyst system; partial hydrogenation at milder conditions
Cobalt	cobalt (II) 2-ethylhexanoate 50 °C and 3.4 bar	>95[17]	Higher reactivity at mild conditions	—
Nickel	Nickel (II) 2-ethylhexanoate 35 °C and 1.7 bar	>90[23]	Higher reactivity at mild conditions; both homogeneous and heterogeneous catalyst system available	—
Rhodium	Tris (triphenylphosphine) rhodium (I) chloride 60 °C and 7 bar	95[27]	Higher reactivity at milder conditions; wide options of solvent medium	Expensive catalyst system
Titanium	Titanium cyclopentadienyl system; 30–50 °C and 3–5 bar	70[34]	Milder process condition	Lower conversion
In situ diimdie	p-toluenesulfonylhydrazide 140 °C, 4–6 h	74[51]	Economical process as no precious metal catalyst involved	Reduction in molecular weight by diimide species

HTPB made by radical polymerization occurs with non-defined hydroxyl group distribution in reaction to medium leading to cross linked network and with inferior mechanical properties.[91,92] The reaction mechanism involves (a) thermal decomposition of H_2O_2, (b) initiation, (c) propagation, and (d) chain termination to generate HTPB (Scheme 18).

On the other hand, HTPB prepared by anionic polymerization provides high 1,4-unit content of 90% and narrow molecular weight distribution and in principle well defined hydroxyl distributed product.[94] Solvent plays a very important role in acquiring desired microstructures. Anionic based HTPB prepared in polar solvent like tetrahydrofuran using naphthalene lithium as initiator results mainly in a 1,2 configuration.[95,96] Difunctional initiators such as 1,3-bis(1-lithio-methylhexyl) benzene soluble in non-polar solvent provides high 1,4 HTPB; however, association of di-initiators and polar additives could not provide expected polymeric microstructures.[97–99] Schulz et al. used hydroxyl-carrying mixed acetals as protected monofunctional initiators to synthesize anionic HTPB.[100] Tanna et al. prepared random hydroxyl functionalized polybutadienes by grafting mercaptoethanol to the polybutadiene backbone. As the grafting concentration increases, the resultant product is obtained with decreased molecular mobility, which leads to higher glass transition temperature (Tg).[101]

IX. APPLICATIONS

A. HYDROGENATED PBR

Hydrogenation lowers degrees of unsaturation in PBR and as a result, products possess both thermoplastic and elastomeric behavior. For this reason, noticeable changes in product properties occur, which includes decreased solubility in many common solvents, increased tensile strength, and resistance to ozone deterioration. Presence of rubber characteristics makes material flexible and non-brittle at lower temperatures; this makes them especially valuable for arctic service and for use in aircraft applications, which requires products with low temperature resistance properties.[102] Owing to thermoplastic characteristics, they are well suited for the preparation of articles by conventional extrusion or compression molding processes. The ability of hydrogenated butadiene products to undergo vulcanization allows them to be processed by either molding or vulcanizing techniques. Special properties of hydrogenated polybutadiene rubber are well used in making fibers, filaments dish fibers, filaments, dishes, containers, films, sheetings, toys, gaskets, tubing, coating materials, protective coverings, and white sidewalls for tires.[102]

Thermoplastic engineering material is prepared by blending partially hydrogenated polybutadiene rubber with polycaprolactams (nylon 6) to produce ultra–high-impact rubber-toughened polycaprolactams.[103] Hydrogenated polybutadiene containing hydroxyl ends are used to prepare hydrogenated polybutadiene diacrylate, which finds application as liquid photopolymer in three-dimensional (3D) printing. Elastomeric diacrylate systems provide increased molecular weight network between cross links, which permits one stage 3D printing processes without requiring a post–print processing step.[104]

B. END GROUP FUNCTIONALIZED PBR

Attaching functional groups at polymer chain ends significantly improves polymer affinity to fillers, which is an important factor in performance of tires or any other rubber goods.[105] High *cis*-polybutadiene rubber functionalized with epoxy-containing alkoxysilane showed remarkable improvements of silica dispersity in the rubber matrix. Owing to high functionalized polymer and silica filler interaction, reduction in hysteresis loss observed.[106] Silica based high performance

rubber compounds prepared by cross metathesis exhibit improved vulcanizate properties, namely, elongation at break, tensile strength, and loss factor.[57]

C. HALOGENATED PBR

High impact polystyrene modified with brominated polybutadiene rubber exhibits superior self-extinguishing properties. Hence this polymer can be used for fire retardant applications.[106] Blending of brominated polybutadiene rubber with other elastomers yields flexing foam product with improved insulation properties. Blending includes other advantageous properties like excellent flexibility, superior steam barrier, and adhesive properties.[107] Brominated polybutadiene polymers and copolymers are identified as potential flame retardants. Flame proof articles, which require high thermal stability, can be prepared by blending brominated polybutadiene with other base polymers.[108] The incorporation of chlorine atoms into macro molecules improves the adhesive properties of polymer products. Mixing chlorinated 1,2 polybutadiene with polyvinyl chloride (PVC) results in a substantial improvement in adhesion of the PVC film to metal components. At a constant amount of halogenated 1,2 polybutadiene in the adhesive composition, the adhesion tendency of PVC film to metal increases significantly with the chlorine content.[64]

D. EPOXIDIZED PBR

Compatibilizers or coupling agents which reduce the difference in polar characters of fillers and rubbers are necessary to improve rubber–filler interactions during tire manufacturing.[109,110] Polar epoxy group functionalization enhances the polarity of PBR, thus providing strong interaction between rubber and silica. Epoxidized polybutadiene rubber is effectively used as an alternate compatibilizer for a silica-based green-tire composite preparation. On increasing degree of epoxidation (to 30%), the compatibilization effect increased and then decreased at higher epoxidation level (50 mol%). Dynamic mechanical properties of rubber composition containing epoxidized polybutadiene exhibited improved rolling as well as wet skid resistance.[5] Rheological studies confirmed that during the mixing process, there are strong chemical interactions between epoxy units of epoxy polybutadiene polymer and the silanol groups of silica.[111] Epoxy resins have a major drawback of brittleness during cure state, which limits their applications in many fields requiring higher ductility of applied materials. Such limitation is overcome by modifying epoxy resin with epoxy functionalized polybutadiene, which yields engineering epoxy resin material with higher flexibility.[112]

E. HYDROXYL TERMINATED PBR

Major application of hydroxyl terminated polybutadiene rubber (HTPB) is in high performance composite propellants. Owing to its unique physico-chemical properties, such as excellent flow characteristics and storage capacity compared to other known binders, HTPB is considered a modern propellant composite.[113] Hydroxyl groups of the polymer are used as polyols to react with diisocyanates, which yields mechanically strong polyurethanes, which provides a matrix for inorganic oxidizers and other dispersed solid components of propellants.[114] HTPB based PU exhibits high gas permeability, low tensile strength, and breaking strength at room temperature. Owing to the excellent shock absorbing capacity of polyurethane made from HTPB, it is used in the field of explosive applications.[115] Hydroxy-carboxy-terminated polybutadiene synthesized from HTPB is successfully used to prepare a highly stretchable and self-healing hydroxy-terminated polybutadiene elastomer. Self-healing material was found to have remarkable properties,

elongation at break is 877.8%, and the self-healing efficiency can reach 92% after healing at 80 °C for 10 h after damage.[116]

Further, HTPB is used in various other applications, which includes sealants,[117] waterproofing membranes,[118] drug capsules due its excellent biodegradable properties,[119] bioengineering applications,[120] and air-dry coatings because of its ability to undergo autooxidative crosslinking.[121]

X. COMMERCIAL IMPORTANCE OF MODIFIED PBR

Polybutadiene rubber is the second largest commodity synthetic rubber produced worldwide next to styrene-butadiene rubber. Functionalized polybutadienes are emerging as an important industrial product due to their potential applications in specialty and engineering plastics as discussed in the above sections. Although not all the modified polybutadienes could make their place at commercial scale, technological solutions are continuously improving to produce them commercially. Hydrogenated,[5] end group functionalized,[5] epoxidized,[6] hydroxyl terminated[5,7,8] polybutadiene rubbers are successfully produced as commercial products.

The green tire concept that was introduced in the early 1990s has emerged as a paradigm shift in the automobile sector to improve the wet grip (safety) and rolling resistance (fuel efficiency) of tires simultaneously.[122,123] Any factor that enhances rubber and filler interaction contributes to a major improvement in tire performance. Polar functionality introduction to polybutadiene, in particular epoxy, hydroxy, and carboxy are found to be the most suitable techniques to enhance the rubber and filler interactions.[4,5] Thus, the automobile sector plays a major role in making functionally modified polybutadiene rubber, an industrially significant product in the near future.

XI. CONCLUSION AND PATH FORWARD

Numerous chemical methods are available to modify PBR structurally, and their potential applications make modified PBR a commercially valuable product. A detailed survey on modification of PBR at the molecular level has been made in this review. Hydrogenation of PBR involving various metal catalyst based reactions and the effect of microstructural properties on reactivity toward hydrogenation are discussed. Different methods involving functionalizing polybutadiene rubber have been mentioned. Multiple methods, catalysts, and reagents available for introducing similar functionalities are discussed. The effect of reaction parameters during functionalization and their impact on the final product are described. Reaction mechanisms involved during different functional group insertions are highlighted. Incorporation of functionality to polybutadiene rubber using modified co-monomers of silane and allylborates are described. Applications of modified polybutadiene rubber based on key functional groups are discussed in detail, and their futuristic aspects are presented. Commercial products of modified PBR offered by industries in the global market are summarized in brief.

Modified PBR has promising futuristic aspects due to its potential applications. Functional PBR and silica filler leads to environmentally friendly composites with low rolling resistance and better abrasion properties. Such properties are highly essential for future automotive sectors to develop green tires that enhance vehicle fuel efficiency. Halogenated PBR can be further explored as an elastomeric flame retardant material, and development of halogenated PBR product can be an alternate to chloroprene rubber. Partial or completely hydrogenated PBR is a thermoplastic elastomer product with improved product properties that are suitable for various flexible applications. Hydroxyl terminated polybutadienes are increasingly finding newer applications due to their unique properties. Further technology development is essential to bring several lab scale products to commercial products. It is evident from the above discussion that modified PBR is an emerging elastomeric specialty product that finds applications in various sectors ranging from

automobile to spacecraft. Exploring further modifications in PBR and their application developments can create potential opportunities in the future.

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