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Synthesis of Brominated Poly(isobutylene-co-isoprene)-Based Ionomers and Their Applications

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Abstract

Reactive bromobutyl rubber and its modification have been studied in detail. These reactive bromobutyl rubber was converted to ammonium and phosphonium functionalized bromobutyl rubbers using triphenyl phosphine (PPh3) and 4-dimethylaminopyridine (4-DMAP). Mechanical properties of synthesized ionomers are found to be comparable to butyl rubber. Pharma stopper was made from a synthesized phosphonium ionomer that may be useful for pharma industries due to its self-healing characteristics, which can help to preserve the properties of drugs that are sensitive in nature. Polypropylene impact copolymer and phosphonium ionomer-based bromobutyl rubber blend shows improved impact strength with the addition of 10 wt% % phosphonium ionomer. The improvement in impact strength shows the suitability for automotive applications like auto bumpers and other applications. Ammonium bromobutyl ionomer was also made using DMAP nucleophile shows potential application for elastomeric fibers, etc. This study presents the synthesis and characterization of brominated poly(isobutylene-co-isoprene) ionomers, focusing on phosphonium and ammonium functionalized derivatives. The phosphonium ionomer, synthesized using triphenyl phosphine, exhibits self-healing properties and enhanced adhesion, making it suitable for pharmaceutical stoppers and automotive impact modifiers. Ammonium ionomer, prepared with 4-dimethylaminopyridine (4-DMAP), demonstrates potential for elastomeric fiber applications. Polypropylene blends with phosphonium ionomer show significant improvements in impact strength, highlighting their utility in automotive components. The study underscores the promising mechanical and functional properties of these novel ionomers for diverse industrial applications.

Keywords: Butyl rubber, bromobutyl rubber, ionomer, blend, mechanical properties

INTRODUCTION

Butyl rubber is a random copolymer made of isobutylene and isoprene through the polymerization technique. It is prepared by the slurry process by randomly copolymerizing isobutylene with a small amount of isoprene (1–4 mol%). The presence of unsaturation in the form of isoprene units in butyl rubber provides the probability of enhancing its properties by incorporating a reactive functionality, such as halogens, epoxides, esters, ions, etc. Bromobutyl rubber mainly contains endo microstructure. Endo-microstructure contains easily replaceable bromine molecules, making it ideal for chemical modification, i.e., ionomer synthesis and living polymerization. There is a significant reactivity difference between the two isomers. Elastomers having ionic functionality are suitable for a wide range of applications in polymer composites and blends due to their improved adhesion. Endo-bromobutyl rubber can be used to synthesize ionomers. Ionomers with cationic functionality, i.e., ammonium, phosphonium, and imidazolium groups, are preferred due to anti-

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microbial activity. The substitution reaction of bromide by triphenyl phosphine is an irreversible process, whereas the reaction of amine nucleophiles and endo-bromobutyl rubber is equilibrium-guided. In toluene solution, high conversion of ammonium ionomer can never be achieved as dilution shifts the equilibrium position towards reactants. Solvent-free synthesis of phosphonium ionomer of bromobutyl rubber is reported by Parent et al. (2011) [1]. But literature dealing with the synthesis of phosphonium ionomer in the solution phase is rather scant. The synthesis of phosphonium ionomer in hexane has also been reported earlier also. The process involves the dissolution of bromobutyl rubber in hexane and the reaction with triphenyl phosphine at 100°C for 60 minutes followed by coagulation in ethanol and drying [2].

The phosphonium ionomer demonstrates improved adhesion with fillers, such as nano clay and silica, which enhances green strength due to its ion-pair aggregation while retaining the oxidative stability and impermeability of butyl rubber. The phosphonium ionomer synthesized by halobutyl rubber exhibits better adhesion to steel, glass, and polyethylene terephthalate compared to bromobutyl rubber. The antimicrobial property exhibited by this ionomer is maintained for a longer time compared to polymers with antimicrobial additives, and it is non-volatile and chemically stable. The preparation of isobutylene-based ionomers through the displacement of halide from brominated poly(isobutylene-co-isoprene) (BIIR) using triphenylphosphine (PPh3) and N, N-dimethyl-octylamine (DMOA) is demonstrated, which possess dynamic mechanical properties that are comparable to thermoset vulcanizates. The elastomeric network is the result of ion-pair aggregation [3]. Triphenyl phosphine salt and N, N-dimethylaminoethanol are used to synthesize butyl rubber ionomer by solution polymerization and subsequent bromination of butyl rubber [4]. A new class of isobutylene-rich imidazolium bromide ionomers is prepared using N-alkylation of a range of imidazole nucleophiles by the allylic halide functionality within BIIR [5]. The patent described novel ionomers, processes for preparing ionomers, and processes for curing ionomers. The ionomers are obtained by reacting a halogenated iso-olefin copolymer with a nucleophile comprising a pendant vinyl group [4].

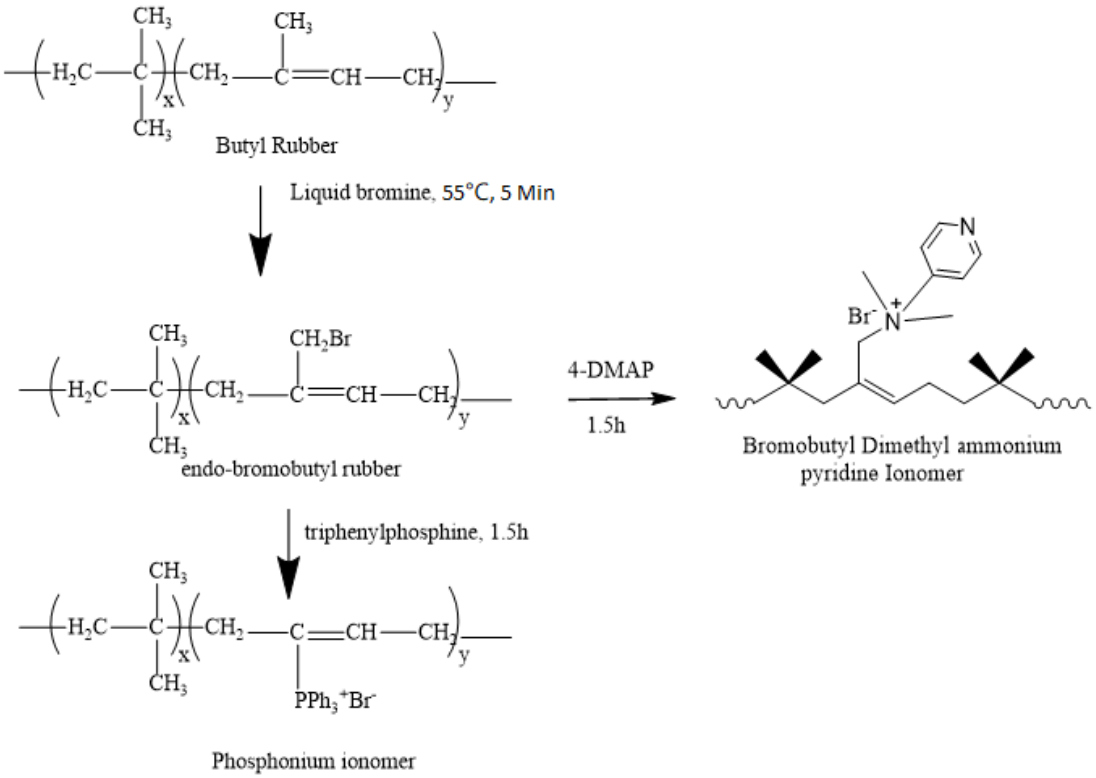
In the present work, a direct method to the synthesis of endo-bromobutyl is developed along with the conversion of bromobutyl rubber to phosphonium and ammonium ionomers using suitable nucleophiles. Phosphonium bromobutyl rubber can be used as an impact modifier additive for automotive applications. Only 10 wt% blending of ionomer with polypropylene would improve the impact strength. This ionomer has the potential to be used as an impact modifier in formulations for pharmaceutical closures and high strength adhesives. The ammonium ionomer has been synthesized using p-dimethylaminopyridine as a nucleophile. The futuristic application for this ionomer includes elastomeric fibers and high-temperature (hot melt) adhesive.

MATERIALS AND METHODS

Lanxess 301 butyl rubber with unsaturation of 1.85 ± 0.2 mol% & Mooney viscosity of 52; ML (1+8) 125°C is used. Hexane (HPLC grade), Toluene (AR grade) & acetone (AR grade) with 99% purity from SD Fine Chemical were used. Triphenyl phosphine (PPh3) is used from SD Fine Chemicals with a 98% purity level. 4-Dimethylaminopyridine (4-DMAP) is procured with a 99% purity level from Spectrochem. The blended samples were evaluated by SEM (FEI-NOVA NANOSEM 650). The mechanical properties of samples were analyzed using UTM (Llyod-EZ 20). Air permeability was evaluated by a gas permeability analyzer.

60 g of commercial butyl rubber was mixed in 400 ml of hexane to dissolve completely, and further rubber solution was further heated at 50°C. After reaching the desired temperature, 4 wt% liquid bromine diluted with 50 mL hexane was added to it, and the bromination was continued for a desired time with continuous stirring at 500 rpm. After completion of the reaction, the reaction media was neutralized with 1 N NaOH solution, and the product was washed with water to neutral pH. The aqueous phase was separated and discarded. The rubber was isolated by coagulating the organic phase in acetone and then washing it with acetone twice. The isolated product was dried at 50°C to constant weight in a vacuum oven to obtain an off-white color solid bromobutyl rubber.

Lab-scale synthesized bromobutyl rubber is used for the preparation of ionomer. 50 gm bromobutyl rubber is dissolved in 500 ml of toluene under stirring at 275 rpm. Triphenyl phosphine (5 gm, 2.5 mol equivalent, 10 wt%) is added to the rubber solution heated at 50°C. Then the temperature of the reaction mixture is raised to 100 °C and the reaction is continued in the temperature range of 100–102°C for 1.5 hours. After 1.5 hours, the reaction mixture is cooled down to room temperature. The reaction mixture is precipitated in acetone, and then the rubber is coagulated in hot water to remove residual toluene and acetone, and finally dried in a vacuum oven at 70°C. Ammonium ionomer is also prepared in similar processes and conditions using lab-scale synthesized bromobutyl rubber and 4-dimethylaminopyridine nucleophiles. The final product is characterized by ^{1}H NMR, DSC, TGA, and Mooney viscosity. Both ionomer synthesis process from bromobutyl rubber is given in Scheme 1.



Scheme 1. Schematic of phosphonium and ammonium ionomer from bromobutyl rubber.

Lab-synthesized phosphonium ionomer was mixed in different proportions with polypropylene to make blends. The commercial polypropylene grade (ICP B220MN) was taken from Reliance Industries Limited and blended with lab-synthesized 5 and 10 wt% bromobutyl phosphonium ionomer in the presence of thermal stabilizer Irganox 1010. Mixing was carried out using a twin screw microcompounder (Micro 15, DSM) at temperature range 190–210°C and 100 rpm. Mixing time was kept at 10 min. Sample specimens were prepared using a mini-injection moulding machine connected to the twin screw micro compounder. Injection molding temperature and cooling time were kept at 210 °C and 3 min, respectively. Thermal analysis is carried out using Differential Scanning Calorimetry (DSC-Q2000, TA Instruments). Tensile, Impact, and flexural properties were evaluated using different ASTM methods, i.e., ASTM D 238 for impact strength, ASTM D-790 for flexural properties, and ASTM D-638 for tensile properties.

RESULTS AND DISCUSSION

Two bromobutyl ionomers have been synthesized using two different nucleophiles, which is triphenyl phosphine (PPh3) and 4-Dimethylaminopyridine (4-DMAP). 1H NMR analysis as shown in

Figure 1, confirms the formation of phosphonium and ammonium ionomers, and the same is confirmed by ^{31}PNMR also. The product phosphonium ionomers were characterized by NMR, both ^{31}P & ^{1}H NMR to confirm the formation of ionomers. The ^{31}P NMR of triphenyl phosphine nucleophile showed a signal at –5 ppm, whereas in the product it shifts to 19 ppm, thereby, confirming the formation of phosphonium ionomer.

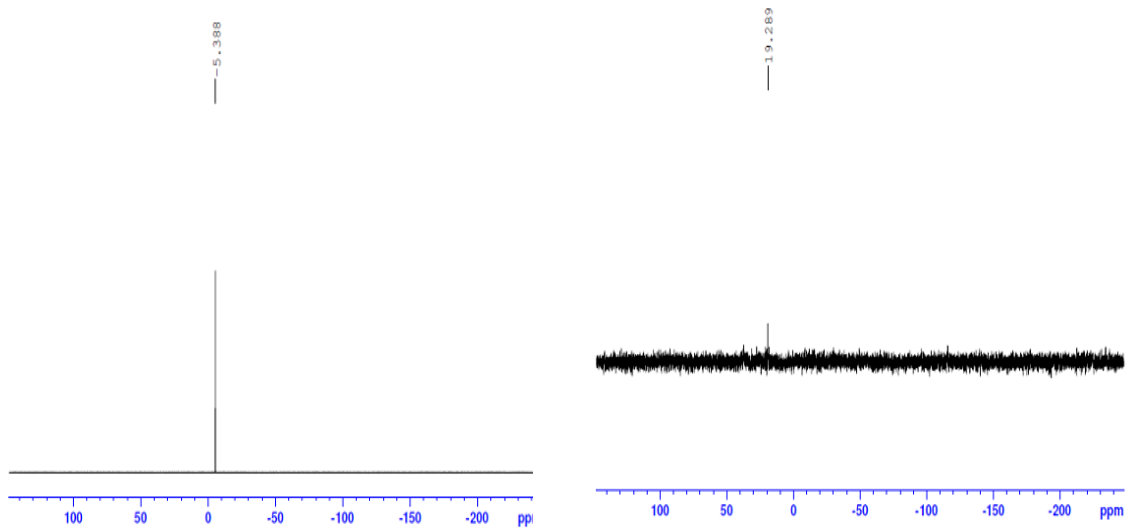


Figure 1. 31P NMR of PPh3 and lab-synthesized phosphonium bromobutyl rubber ionomer.

From Figure 2 also the peaks of 1H NMR at 4.51 (S, CH2-PPh3Br, Z), 4.77 (S, CH2-PPh3Br, E), 5.35–5.45 (m, =CH, Z), 5.5–5.61 (m, =CH, E) presented the formation of phosphonium ionomer. ^{1}H NMR showed the presence of broad aromatic protons in the region of 7.5–7.7 ppm in the ratio of 2:2:1 from the phenyl group of PPh_3; thereby further confirming the formation of phosphonium ionomers. Phosphonium butyl ionomer shows 1.8–2% allylic bromide, assuming the absence of conjugated diene side product. The endo & exo isomer in the ionomer was found to be 75–81% & 15–19%, respectively.

From Figure 3, the 1H NMR spectra of 4-DMAP-based ionomers show the representative peaks at 6.8 ppm for aromatic protons (n) attached next to the amine group and at 8.2 ppm for aromatic protons(o)next to ring nitrogen. The characteristic peaks at 4.1 ppm (C) and 5.8 ppm (D) confirm endo-microstructure. At 5.4 ppm, a multiplet (D') is present, indicating the isomers of endo-microstructure. A new peak at 4.8 appeared, which is due to the shift of allylic protons from 4.1 ppm (C) to 4.8 ppm (C') after the reaction with 4-DMAP. This observation supports the success of the reaction, and it is evident in the NMR spectra. The conversion is calculated from the peak intensities at 4.8 ppm and 4.1 ppm. 77% conversion is achieved for 4-DMAP ionomer. Starting material has a Mooney viscosity of 25–34, a glass transition temperature of –63°C, and a bromine content is 1.2%.

Table 1. Characterization of phosphonium and ammonium ionomer.

S.N.	Nucleophiles	Tg (°C)	Mooney Viscosity ML (1+8@125°C)	Ionomer Content (Mol%)	Br Content (wt%)
1	PPh3	–64	44	0.65	1.2
2	4-DMAP	–63	49	0.71	1.1

The phosphonium and ammonium ionomer has a Mooney viscosity of 44 and 49, respectively, thereby showing higher inter-chain interactions due to the presence of ionic groups on the bromobutyl rubber backbone, as shown in Table 1. This has been correlated with NMR, which shows a quantitative reduction in endo microstructures with a simultaneous appearance of new peaks due to ammonium Ionic functionality [6].

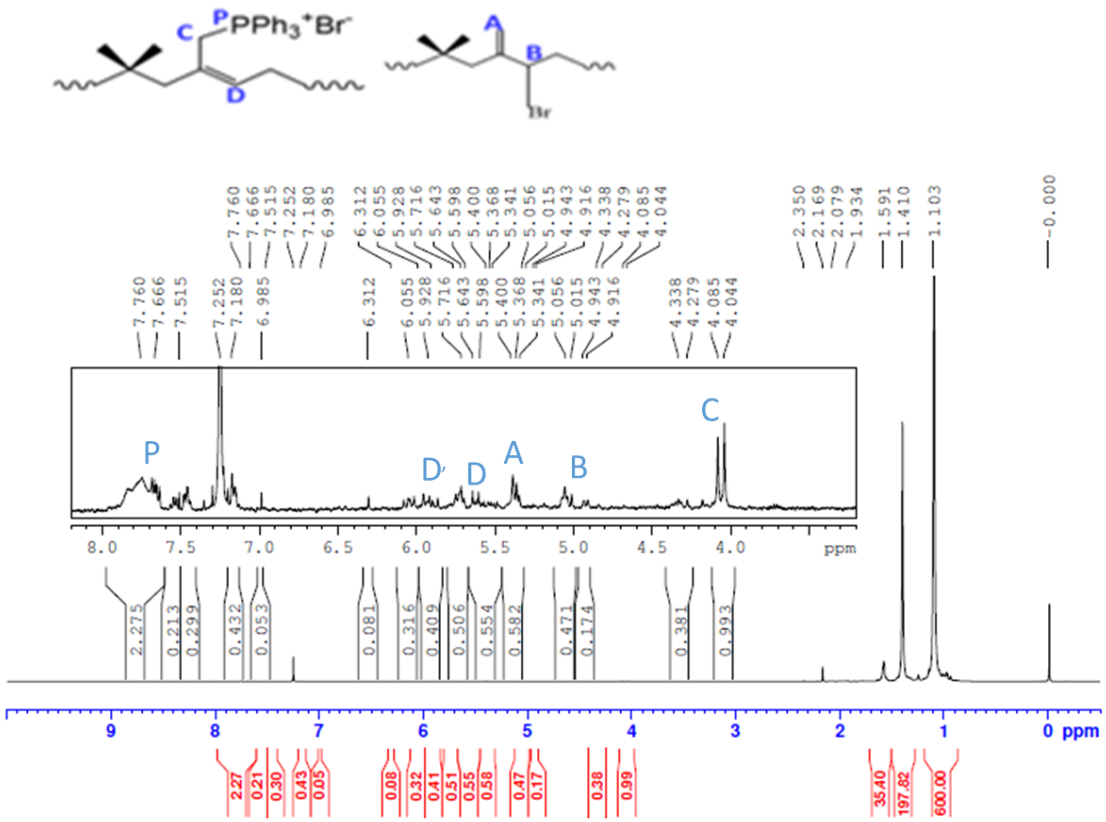


Figure 2. [1]H NMR of synthesized phosphonium bromobutyl rubber ionomer.

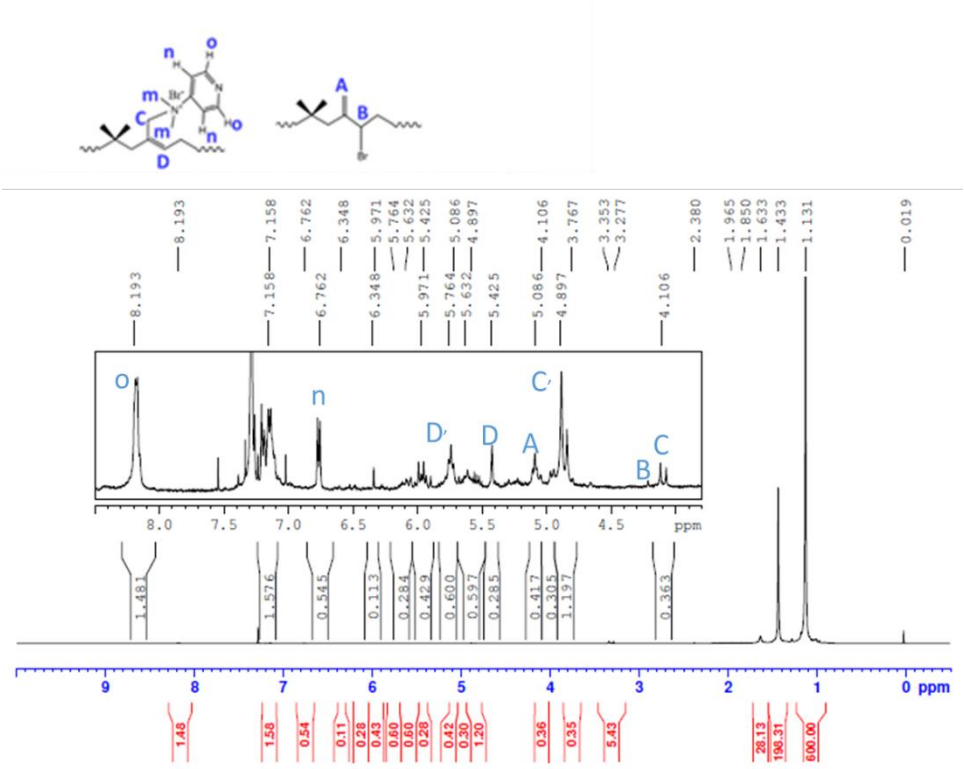


Figure 3. [1]H NMR of 4-DMAP ammonium ionomer.

Phosphonium Ionomer Applications: Self-Healing Properties

Bromobutyl Phosphonium ionomer depicted a self-healing phenomenon. The self-healing experiment was conducted by cutting a rubber sample into two pieces, bringing them together in contact with gentle pressing, and leaving them to heal for 12 hours at 35℃. The rubber sheet was subsequently stretched, and no fracture was seen in the cut region [7] as shown in Figure 4.

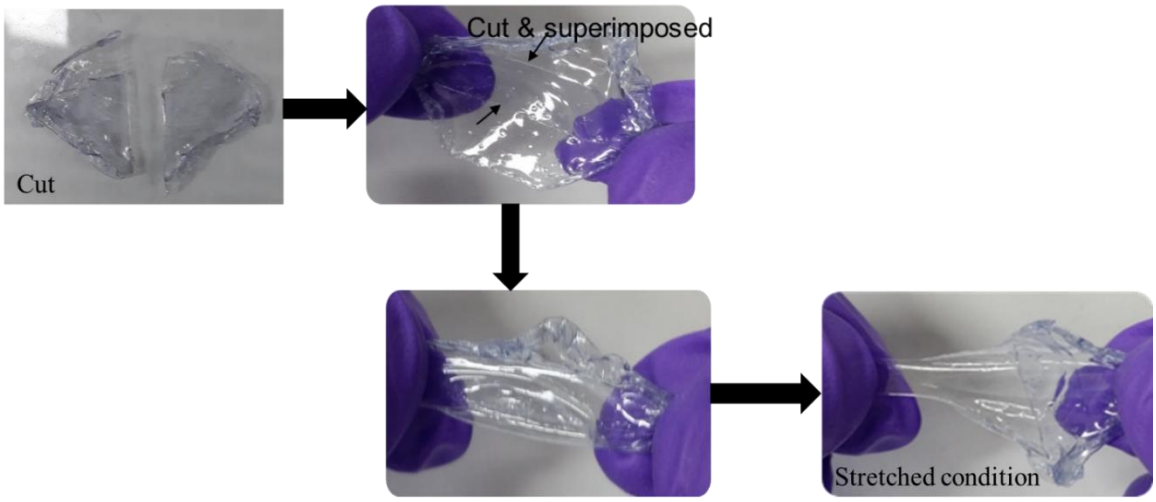


Figure 4. Self-healing behavior of bromobutyl phosphonium ionomer.

Pharma Stopper Application

Lab-synthesized bromobutyl phosphonium ionomers processed to make a stopper for pharma applications. The pharma stopper, as shown in Figure 5, is prepared as per the formulation given in Table 2 using the compression molding technique at 160℃ for 10 min. The mechanical properties of bromobutyl phosphonium ionomer and commercial BIIR formulations are shown in Figure 6(a). Higher elongation at break, tensile strength, modulus, and shore A hardness were observed for bromobutyl phosphonium ionomer as compared to commercial BIIR pharma stopper properties due to may be the better crosslinking in the presence of PPh3. There is a significant improvement seen in the case of air permeability of bromobutyl phosphonum ionomer as compared to commercial butyl rubber, as shown in Figure 6(b), which may be due to network formation. This product will be useful where air retention is important [8].

Table 2. Formulations for pharma stopper application using bromobutyl rubber and lab-synthesized phosphonium bromobutyl ionomer.

S.N.	Formulation-1	Amount (phr)	Formulation-2	Amount (phr)
1	Commercial BIIR	100	Bromobutyl phosphonium ionomer	100
2	Calcined clay	40	Calcined clay	40
3	Silane talc	40	Silane talc	40
4	oil	7	oil	7
5	MgO	3	MgO	3
6	Sulphur	1.5	Sulphur	1.5

Figure 5. Pharmaceutical stopper made of bromobutyl phosphonium ionomer.

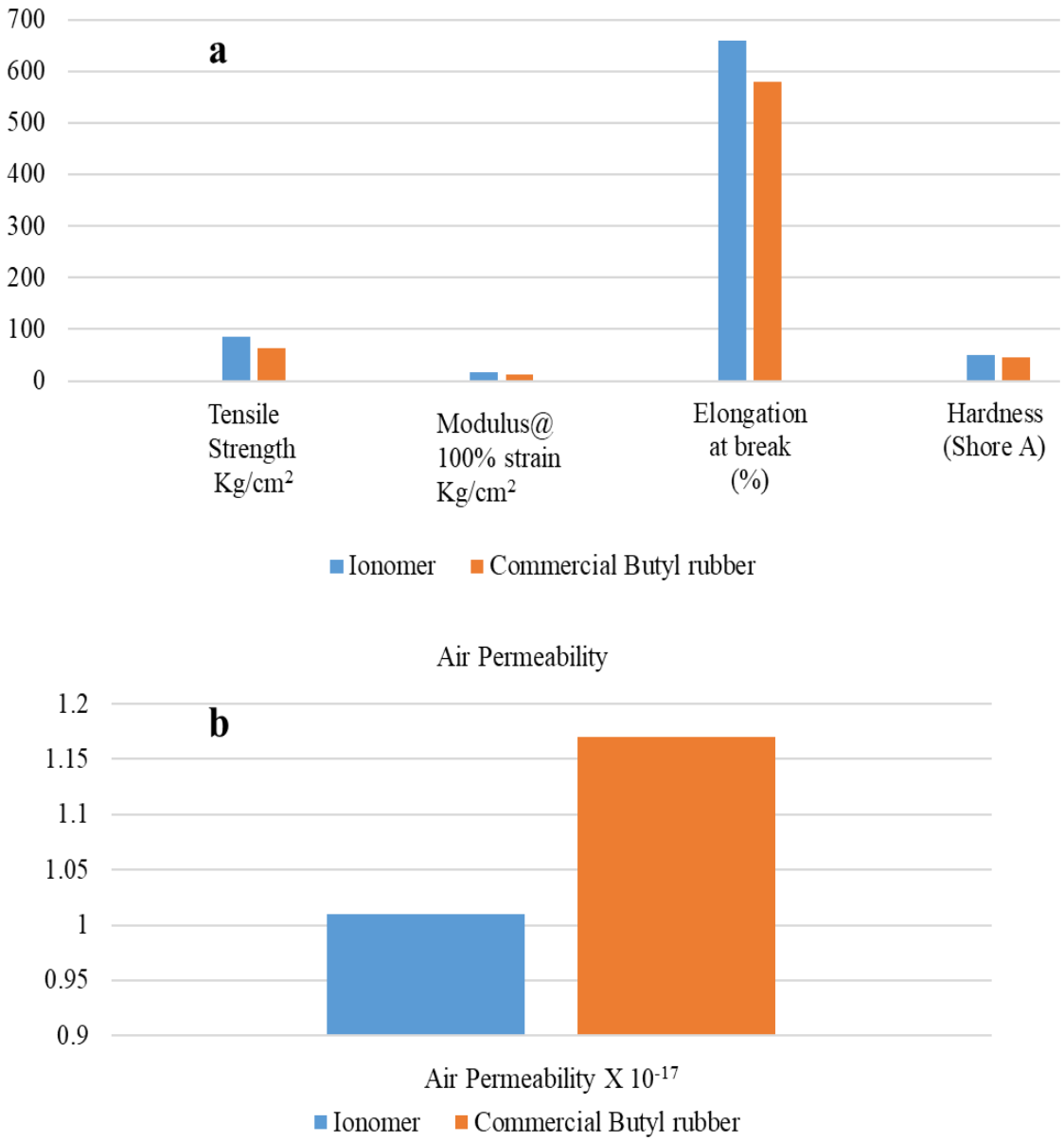


Figure 6. (a) Mechanical properties of compounded commercial BIIR and lab-synthesized bromobutyl phosphonium ionomer; (b) Air permeability of commercial BIIR and lab-synthesized bromobutyl phosphonium ionomer.

Impact Modifier Additive for Automotive Applications

Lab-synthesized phosphonium ionomer in different proportions was mixed with polypropylene copolymer (ICP B220MN) and samples have been prepared using a melt mixing technique in a twin screw microcompounder. The mechanical properties are evaluated and mentioned in Table 3. Polypropylene impact copolymer (ICP) and 10% bromobutyl phosphonium ionomer (PI) blend showed very good impact strength as required by the auto industry and better than a commercial grade, as shown in Table 3. The tensile strength of ICP+PI10% was found comparable with the commercial grade. Flexural modulus of 10% added bromobutyl phosphonium ionomer showed slightly lower values as compared to ICP and commercial grade. The SEM image showed better dispersion of bromobutyl phosphonium ionomer in polymer matrix as shown in Figure 7(a, b), which resulted in better mechanical properties. In conclusion, ICP-10% bromobutyl phosphonium ionomer blend shows promising results, which can be used as an impact modifier additive for automotive applications [9, 10].

Table 3. Composition of bromobutyl phosphonium ionomer (PI) and polypropylene (ICP B220MN) blend and its mechanical properties.

Sample	Notched Izod Impact Strength (J/m)	Flexural Modulus (MPa)	Tensile Strength (MPa)
ICP B220MN	131	1200	25
ICP+ PI5 wt %	183	860	23
ICP+ PI10 wt %	606	800	20
Commercial grade-PP based	500	980	20

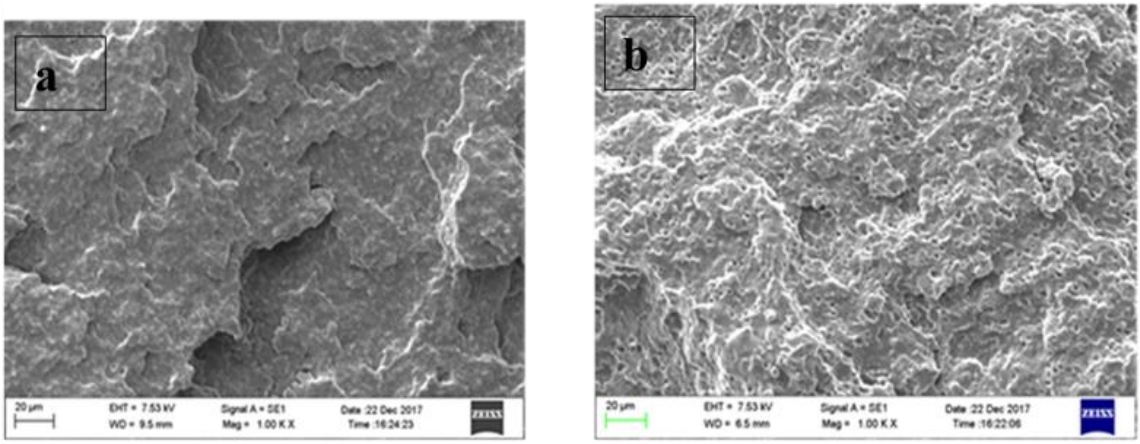


Figure 7. Morphology of ICP (a) and ICP+PI10wt% (b) by scanning electron microscope (SEM).

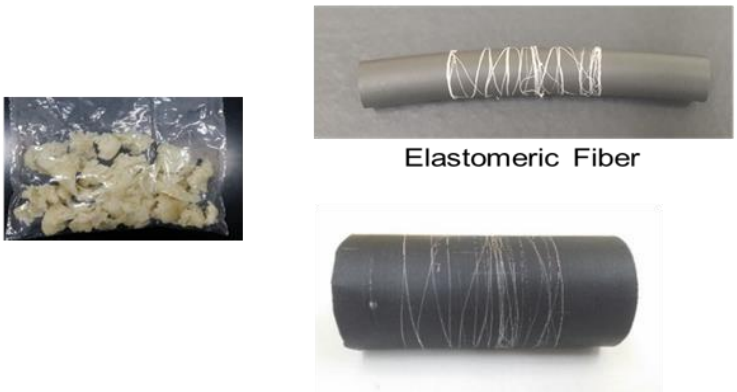


Figure 8. Elastomeric fibers from ammonium ionomer based on 4-DMAP.

Ammonium Ionomer Application

The product ammonium ionomer is obtained from using 4-DMAP nucleophile, which has excellent fiber-forming capabilities, with very high elongation, and can be useful for stretchable fabrics, especially for sportswear, undergarments, bandages & diapers. These fibers can be converted into several useful forms, like fibers, yarns, spun fibers, and multi-filaments. DMAP fiber has been drawn manually in the lab from the solution phase as shown in Figure 8.

CONCLUSIONS

Synthesis of phosphonium and ammonium ionomers using triphenyl phosphine (PPh3) and 4-Dimethylaminopyridine (4-DMAP) from lab-synthesized bromobutyl rubber has been studied. Phosphonium ionomer was synthesized from lab-synthesized BIIR. Synthesized phosphonium ionomer shows encouraging results in terms of mechanical properties, which are found to be better than commercial BIIR 2211. Pharma stopper is made from phosphonium ionomer and can be used in the

pharma industry due to its self-healing properties. Air permeability was found to be higher for the synthesised phosphonium ionomer. Polypropylene impact copolymer (ICP) and bromobutyl phosphonium ionomer blends have been developed using 5 and 10 wt% bromobutyl phosphonium ionomer. Significant impact strength increases at 10 wt% ionomer with no break. SEM shows uniform dispersion of rubber particles in the polymer matrix. Bromobutyl phosphonium ionomer showed self-healing properties and was demonstrated in the lab by cutting and overlapping in the presence of heat. This property will be useful in tire inner liner and coating applications. Ammonium ionomer is obtained by using 4-DMAP as a nucleophile, which has excellent fiber-forming capabilities and very high elongation.

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