

Synthesis and characterization of thermoset imidazolium bromide ionomers



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ABSTRACT

Elastomeric ionomers are prepared via halide displacement from brominated poly(isobutylene-co-isoprene) (BIIR) with various imidazole-based nucleophiles. Reaction of BIIR with imidazole or 1,1'-(1,4-butanediyl)bis(imidazole) in a single-step, solvent-free elastomer compounding approach is used to synthesize thermoset derivatives, in addition to a two-step process involving reaction of BIIR with 1-vinylimidazole (VIm), followed by peroxide-initiated cross-linking. The physical properties of these ionomeric thermosets are the product of their covalent and ionic networks. Ion-pair aggregation contributes significantly to dynamic storage modulus and low-strain static tensile modulus, but extensive relaxation of this labile network minimizes its influence over timescales larger than 1 min. The adhesive properties and antibacterial activity against *E. coli* provided by these ionomers are also demonstrated.

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1. Introduction

The adhesion provided by the small amount of ionic functionality within ionomers makes them ideally suited for a range of polymer composite and blend applications. [1,2] Most commercial ionomers are thermoplastic materials containing carboxylate and sulfonate functionality [3,4], but materials bearing cationic functionality, including quaternary ammonium, phosphonium and imidazolium groups, have attracted recent attention [5,6], in part due to their anti-microbial activity [7,8] and their resistance to fouling by marine mollusks. [9] Unlike the small molecule ionic liquids or nanoparticle technology in present use, the polymer bound ionic functionality is not released into the environment, but retained in the thermoset indefinitely. [10,11].

Applications requiring oxidative stability and gas impermeability are well served by isobutylene-rich elastomers such as poly(isobutylene-co-isoprene) [12]. In addition to finding use in industrial sealants, tire inner liners [13] and pharmaceutical closures, these materials are suited to vibration dampening equipment and electrical insulating devices requiring a low dielectric constant [14]. The ionomer derivatives of present interest expand these fields of use by virtue of the influence of polymer-bound ion pairs on material properties. For example, triphenylphosphonium bromide functionality not only affects solution viscosity, [15] but enhances the dispersion of fillers such as precipitated silica and onium-ion exchanged montmorillonite clay [16].

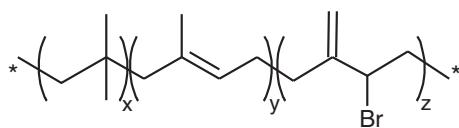
We have recently described a series of imidazolium ionomer derivatives of brominated poly(isobutylene-co-isoprene), or BIIR, that can be prepared through halide displacement by imidazole-based nucleophiles. [17,18] Although early research focused on quaternary ammonium ionomers, the reversibility of N-alkylation by BIIR resulted in incomplete nucleophile conversion, yielding a thermoset containing residual amine. [19] The air-instability of most phosphines, coupled with the challenges in preparing functional phosphine nucleophiles, [20] limits practical P-alkylation chemistry to PPh₃. [21] However, imidazole-based nucleophiles offer a versatile platform for generating ionomeric elastomers, since their N-alkylation is effectively irreversible, and a wide range of functionality can be introduced through imidazole derivatization.

BIIR is effectively a random terpolymer comprised of about 98 mol% isobutylene, 1 mol% isoprene and 1 mol% allylic bromide functionality (Scheme 1). Since only the latter is reactive toward imidazole-based nucleophiles, BIIR-derived thermosets are usually depicted according to their crosslink structure, showing allylic substitution products while omitting unconverted mers for the sake of clarity. Scheme 2 provide such illustrations for the three imidazolium bromides investigated in this work.

These thermoset elastomers are produced by two distinct synthetic approaches. IIR-ImBr and IIR-BisImBr are prepared by a conventional compounding process where BIIR is mixed with the desired nucleophile to create a compound that is subsequently cross-linked in a heated compression mold. Since ionic functionality is only generated during the cure, the mixed compound has a low viscosity, making this approach

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Scheme 1. Structure of BIIR.

attractive from an elastomer processing perspective. In contrast, IIR-VImBr contains imidazolium bromide bearing a peroxide-curable vinyl group. This benefits compounds of highly reinforced composites, who require heightened adhesion to assist with the incorporation and dispersion of finely divided fillers such as precipitated silica [22]. The reinforced compound can be mixed with peroxide initiator before curing in a heated compression mold to give IIR-VImBr-XL.

Although the chemical structure of these imidazolium ionomers is well characterized, the relative merits of each strategy have not been investigated, and important questions remain regarding their physical properties. Their characteristics are the product of an unusual combination of a covalent network and an ionic network. Alkylation of imidazole nucleophiles ultimately provides a covalent network that is creep resistant, while the aggregation of poorly-solvated imidazolium bromide groups gives a labile ionic network that is prone to stress relaxation. These hybrid networks have the potential to confer thermoset properties that are inaccessible using conventional, non-ionic cure technology. A complete understanding of these materials requires detailed knowledge of the covalent network density, the extent of ion pair aggregation in the solid state, and the interaction between covalent and ionic networks. This is a formidable challenge, especially since the ionic functionality within imidazolium bromide ionomers is not amenable to small

angle neutron scattering analysis in the manner of alkali metal sulfonate or carboxylate systems [23].

This report details experiments that improve our knowledge of these important structure-property relationships. The synthesis of each ionomer thermoset is demonstrated at a standard reaction condition, and the contributions of their hybrid ionic/covalent networks to material properties are discussed. A brief examination of cure dynamics is followed by comparisons of tensile, adhesive and stress relaxation properties to relevant benchmark materials. We conclude with a demonstration of the anti-microbial activity that imidazolium ionomers exert against an *E. coli* bacterial culture.

2. Experimental

2.1. Materials

Poly (isobutylene-co-isoprene) (IIR, RB301) and brominated poly(isobutylene-co-isoprene) (BIIR, BB2030, 0.15 mmol allylic bromide functionality/g BIIR) were used as supplied by LANXESS Inc. 1-Butylimidazole (Bulm, 98%), 1-vinylimidazole (VIm, ≥99%), imidazole (≥99%), tetra-*N*-butylammonium bromide (Bu_4NBr , ≥98%), acrylic acid (anhydrous, 99%), 1,8-bis(dimethylamino)naphthalene (Proton Sponge®, 98%) and dicumyl peroxide (DCP, 98%) were used as received from Sigma-Aldrich. IIR-BulmBr [17], IIR-VImBr [18] IIR-Acrylate [24], 1,1'-(1,4-butanediyl)bis(imidazole) [17] were prepared according to cited literature methods. Bacteriological Agar (15 g/L, Marine BioProducts) and Plate Levine EMB Agar (BD Becton Dickinson Canada) were used as received.

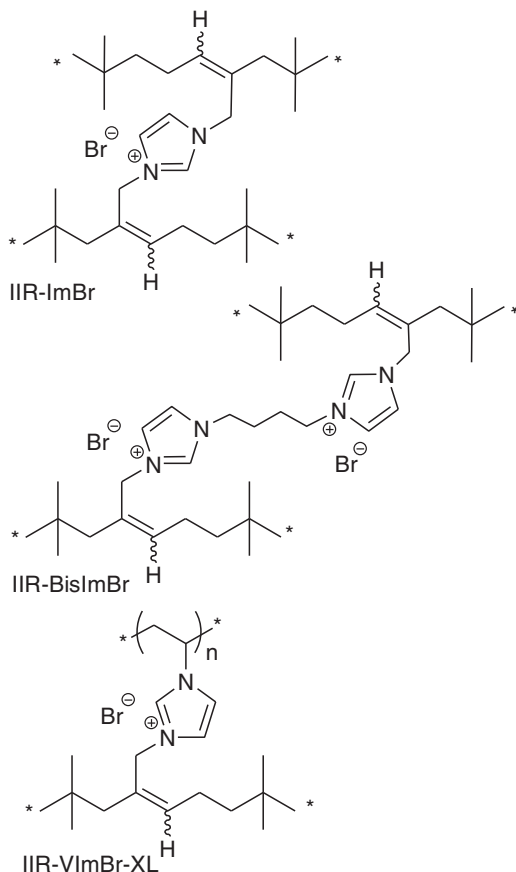
2.2. Compounding and physical testing

BIIR (40.0 g, 6.0 mmol allylic bromide) was mixed with 1,1'-(1,4-butanediyl)bis(imidazole) (0.58 g, 3 mmol) at 90 °C and 60 rpm using a Haake PolyLab R600 internal batch mixer equipped with Banbury blades. Similarly, a compound for IIR-ImBr preparation was prepared by mixing BIIR (40 g, 6.0 mmol) with 0.5 equivalents of imidazole (0.204 g, 3.0 mmol) and 0.5 equivalents of Proton Sponge (0.643 g, 3.0 mmol). IIR-VImBr (40 g) was coated with a solution of DCP (0.2 g, 0.74 mmol) in acetone (1 ml) and allowed to dry prior to mixing by passing through a 2 roll mill ten times.

Samples for tensile analysis were prepared by sheeting the desired compound (35 g) in a two-roll mill and compression-molding at 160 °C, 20 MPa for 25 min to yield a macrosheet of 2.00 ± 0.05 mm thickness. Dog bones were cut as described in ASTM D4482 [25] and analyzed at 23 ± 1 °C using an INSTRON Series 3360 universal testing instrument operating at a crosshead speed of 500 mm/min [26]. Reported results are the average of five replicate measurements.

Samples for adhesion measurements were prepared by placing sheeted compound on a Teflon sheet within the rectangular cavity of a preheated mold, and covering with a Mylar® film prior to fixing the top plate and compression molding at 20 MPa, 160 °C for 25 min. This Mylar film, made of polyethylene terephthalate, was used as a substrate from which cured elastomers were peeled, thereby providing a measure of polymer adhesion. The force required to separate a rectangular strip (25 mm wide) of cured compound from the Mylar sheet was measured at 23 ± 1 °C using a crosshead speed of 500 mm/min. Reported values are the average of 5 replicate measurements.

Samples for compression set analysis were prepared by curing the desired compound (2.5 g) in a cylindrical mold cavity (14.0 mm diameter, 12.5 mm depth) at 160 °C for 25 min. The resulting material was compressed from an initial height of 14.2 mm to a height of 6.44 mm (45% strain) for 18 h. Compression set was recorded 30 min after releasing the applied strain, with results reported as an average of four replicate experiments. This procedure was adapted from ASTM D395 – 03 (2008). [27].



Scheme 2. Cross-link functionality within imidazolium bromide thermosets.

2.3. Analysis

Rheological properties were measured with an Alpha Technologies Advanced Polymer Analyzer 2000 equipped with biconical disks. Crosslinking dynamics measurements were conducted at 160 °C with a 3° oscillation arc and 1 Hz frequency. Subsequent stress relaxation measurements were made at 100 °C and 2° static rotation, while temperature sweeps from 100 °C to 200 °C and back to 100 °C were conducted at 3° oscillation arc and 1 Hz frequency.

2.4. Critical surface energy measurements

Contact angles for sessile drops of a series test fluids (octane, dodecane, tetradecane, hexadecane, and cyclohexane) on thin polymer films were determined by digital imagery (VCA Optima, AST Products). Plots of the cosine of the measured contact angles against reported liquid-air surface tension were extrapolated to $\cos\theta = 1$, corresponding to incipient surface wetting, to give the reported critical surface energy [28].

2.5. Anti-microbial studies of cast elastomer films

Films of IIR, IIR-BuImBr, and IIR-VImBr were cast from solution (5-wt% polymer in THF) to the bottom of 10 cm diameter glass Petri dishes, air-dried at room temperature for 24 h, and heated to 50 °C to remove residual solvent. The resulting polymer-coated Petri dishes were autoclaved at 121 °C for 15 min, and the films were transferred aseptically to a sterile 125 ml Erlenmeyer flask containing 40 ml Tryptic Soy Broth. A suspension (1 ml at 0.2 OD640) of *E. coli* (K12, Strain SMG 123) was added, and the suspension was shaken at 37 °C for 2 h at 180 rpm. Once the bacterial suspension reached an OD640 of approximately 0.250, an aliquot (0.1 ml) was added to 5 ml deionized and autoclaved water. The resulting cell/water suspension was poured over a sterile cellulose acetate filter (0.45 μm pore size, Sartorius GmbH) by vacuum filtration. The membrane was placed into a sterile Petri dish containing Levine EMB Agar, and was covered with an elastomer film. The Petri dishes were sealed with Parafilm and incubated for 48 h at 37 °C. Photographs of the cellulose acetate filter after removal of the elastomer provided evidence of *E. coli* proliferation between the acetate filter and elastomer films.

3. Results and discussion

3.1. Cure dynamics and yields

Our study began with an examination of the dynamics of polymer network production. Note that an ideal thermoset formulation demonstrates three characteristics. It is inactive at 100 °C to facilitate the mixing of ingredients in a solvent-free polymer compounding device, it provides a short induction period at 160 °C to allow the compound to conform to the dimensions of a compression mold, and it crosslinks quickly to give a high, stable crosslink density. The standard means of quantifying elastomer cross-linking involves monitoring the compound's dynamic storage (G') and loss (G'') moduli at a fixed temperature, strain and frequency [29]. Fig. 1 presents the evolution of G' and the loss tangent ($\tan\delta = G''/G'$) for the synthesis of IIR-VIm-XL, IIR-ImBr, and IIR-BisImBr from their respective polymer compounds.

As illustrated in Scheme 3, the covalent crosslinks within IIR-BisImBr are generated through N-alkylation of both imidazole groups within 1,1'-(1,4-butanediyl)bis(imidazole) by the allylic bromide functionality within BIIR [17]. Although the reaction stoichiometry for polymer cross-linking is a 1:2 molar ratio of nucleophile:electrophile, selecting an appropriate amount of bisimidazole curative is complicated by BIIR dehydrohalogenation [30]. At the temperatures commonly used for elastomer cross-linking, HBr elimination is competitive with the desired nucleophilic substitution, leading not only to the loss of electrophile but

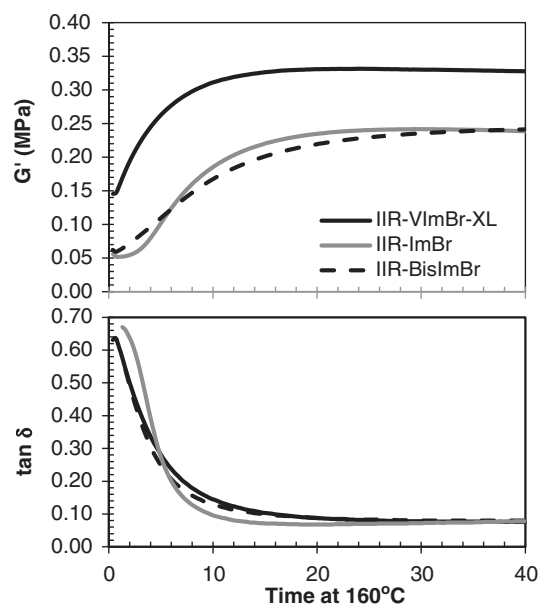
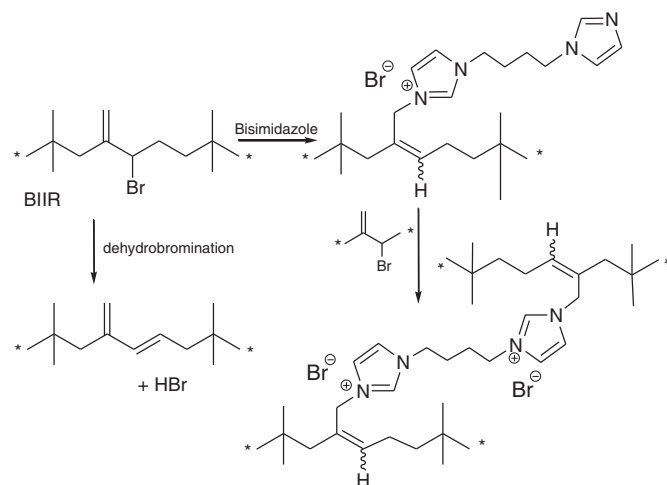


Fig. 1. Dynamics of ionomer thermoset preparation (3° arc, 1 Hz).

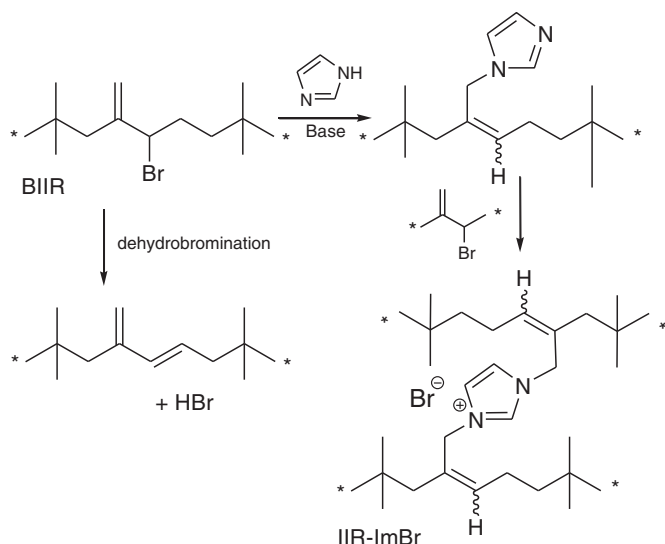
to loss of nucleophile to protonation of alkyl imidazole functionality. Both processes can reduce cross-link yields, but nucleophile protonation is a lesser concern, since acid scavengers such as epoxides and calcium stearate are added by BIIR manufacturers to sequester liberated HBr. Limited studies have indicated that dehydrobromination proceeds through an E1 mechanism involving the deprotonation of allylic cation intermediates, meaning that imidazole nucleophiles are not expected to accelerate HBr elimination [19].

The rheometry data plotted in Fig. 1 show the evolution of G' and $\tan\delta$ for a BIIR formulation containing 0.5 M equivalents of 1,1'-(1,4-butanediyl)bis(imidazole) relative to the 0.15 mmoles of allylic bromide functionality per gram of polymer. Over 40 min at 160 °C, the compound's storage modulus increased from an initial value of 0.06 MPa to a maximum value of 0.24 MPa, giving a change of $\Delta G' = 0.18$ MPa. This ultimate modulus value did not revert significantly over 60 min at 160 °C, indicating the hybrid ionic/covalent network established in the thermoset is robust at this temperature.

An alternate route to an imidazolium thermoset involves the repeated alkylation of imidazole by BIIR in the presence of a suitable base (Scheme 4) [17]. Bromide displacement from the elastomer yields an



Scheme 3. Alkylation and dehydrohalogenation reactions of BIIR to yield IIR-BisImBr.

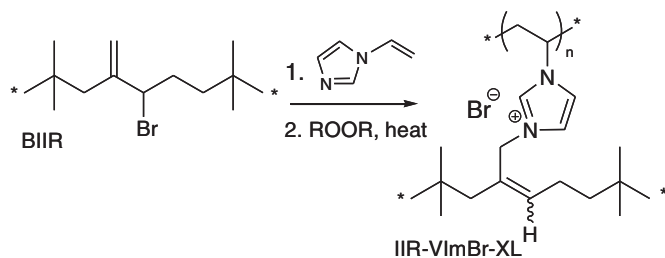


Scheme 4. Imidazole alkylation and HBr elimination reactions yielding IIR-ImBr.

imidazolium salt, whose deprotonation by a moderate base gives an N-allyl imidazole intermediate. Alkylation of this intermediate by a second allylic halide generates the desired ionomer cross-link. As was the case for the bisimidazole example described above, the ideal stoichiometry for this process is a 1:2 ratio of nucleophile:electrophile. However, the maximum yield of imidazolium bromide functionality is 0.075 mmol/g, one-half of the allylic bromide content of BIIR. Therefore, for ionomer applications that are sensitive to ion-pair concentration, this synthetic approach may present limitations. We elaborate on this issue below, where adhesive and surface energy properties of the various ionomer thermosets are described.

Fig. 1 illustrates the crosslinking of an IIR-ImBr formulation containing 0.5 equivalents of imidazole and 0.5 equivalents of Proton Sponge® relative to the allylic bromide functionality within BIIR. The non-nucleophilic organic base was used to deprotonate the initial imidazole alkylation product, as well as to scavenge any HBr released through BIIR dehydrohalogenation. It is interesting to note that crosslinking did not occur immediately, as the onset of the G' increase was delayed by several minutes. This induction delay is useful for some applications, since thermoset articles must be first molded and/or extruded into a desired shape before crosslinking renders them incapable of being processed. Presumably, differences in the alkylation rate of imidazole and N-allylic imidazole functionality underlies this induction phenomenon. The final state of cure is indicated by $\Delta G' = 0.19$ MPa, which is on the order of that observed for its IIR-BisImBr counterpart.

IIR-VImBr is distinct amongst the three ionomer thermosets studied in this work, since it is produced by a two-step synthesis involving the alkylation of N-vinylimidazole with BIIR, followed by peroxide-initiated cross-linking through radical oligomerization of pendant vinyl functionality (Scheme 5) [18]. This approach affords several advantages. Since



Scheme 5. Vinyl-imidazolium bromide ionomer synthesis and radical cross-linking to yield IIR-VImBr-XL.

the vinylimidazolium bromide ionomer can be prepared at temperatures below those that promote BIIR dehydrohalogenation, ion-pair yields can approach the full 0.15 mmol/g provided by the starting material. Moreover, the thermoset is free of residual HBr salts and unconverted imidazolium nucleophile, thereby providing a cleaner product than either IIR-BisImBr or IIR-ImBr. Thirdly, the thermal stability of vinylimidazolium bromide functionality [31,32] supports a wide range of radical initiator and cure temperatures, allowing greater control over reaction conditions than the one-stage, N-alkylation-based processes described above. [33].

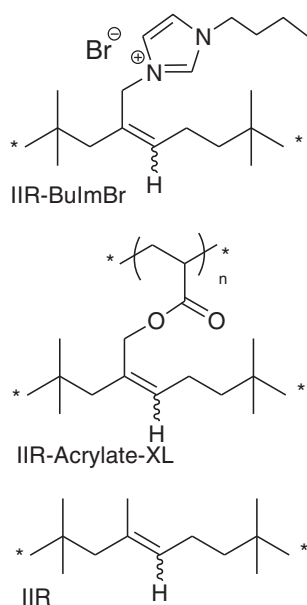
Fig. 1 provides cure rheology data for an IIR-VImBr formulation containing 7.5 μmol of dicumyl peroxide per gram of elastomer. The initial storage modulus and elasticity of this compound was substantially greater than that observed for the other two materials, owing to the ionic network established by the aggregation of imidazolium bromide functionality. This ionic network is, in general, an unfavourable characteristic of elastomeric ionomers, as it renders the material more difficult to process. However, as discussed above, the presence of ionic functionality can improve adhesion to siliceous and other mineral fillers, thereby improving dispersive mixing during the compounding process. Therefore, the two general methods described in this work are complementary, in that the single-stage N-alkylation methods provide low viscosity compounds that generate the ionomer thermoset in the curing mold, while the IIR-VImBr approach provides ionic functionality that can be advantageous for mixing elastomer composites.

Despite having a higher initial storage modulus, the IIR-VImBr formulation cured to nearly the same degree as IIR-BisImBr and IIR-ImBr, with $\Delta G' = 0.19$ MPa (Fig. 1). Crosslinking dynamics were typical of an IIR-based macromonomer cure, in that the rate of initiator thermolysis can dictate crosslinking rates [34]. Since the half-life of dicumyl peroxide at 160 °C is 5.4 min, radical activity is essentially complete at the 25 min mark. Unlike cross-linking by nucleophilic substitution, the rate of this radical chain reaction can be adjusted by selecting peroxides with different decomposition rates. However, the final modulus is dictated by the amount of macromonomer functionality grafted to the polymer backbone [24], so while the cure rate is easily adjusted, the cure yield of an IIR-VImBr-XL formulation is fixed. If lower crosslink densities are desired, the peroxide curable functionality can be diluted using a mixture of N-vinylimidazolium and N-butylimidazolium in the BIIR modification step of the synthesis, the latter being relatively unreactive to peroxide activation [35].

3.2. Rheological properties of hybrid ionic/covalent thermosets

Our interest in thermoset ionomers stems from a labile network of imidazolium bromide ion-pair aggregates that acts in combination with a stable network of covalent bonds to affect material properties. The following is a comparison of the rheological properties of IIR-BisImBr, IIR-ImBr, and IIR-VImBr-XL, with two control materials establishing proper context (Scheme 6). IIR-BuImBr is an uncross-linked ionomer that contains only an ionic network, while IIR-Acrylate-XL is a peroxide-cured acrylate ester derivative of BIIR containing a covalent network but bearing no ionic functionality. All materials share the same polymer backbone and random distribution of pendant functional groups, by virtue of their common origin.

Fig. 2 is a plot of storage modulus and $\tan\delta$ measured from 100 °C and ascending to 200 °C, then descending back to 100 °C. This temperature sequence had little to no effect on four of the five materials, with only IIR-ImBr showing significantly different dynamic properties between heating and cooling measurements. The storage modulus loss incurred by IIR-ImBr was irreversible, indicating that the polymer network established by the imidazole-based cure is unstable above 170 °C. Although few thermoset elastomers are subjected to this severe a service temperature, the instability of IIR-ImBr makes it a less attractive thermoset ionomer technology.



Scheme 6. Functional groups within physical property control materials.

The behaviour of the control materials was consistent with expectations based on their network structures. The storage modulus of IIR-BulmBr declined sharply with increasing temperature, due to a loss of ionic network strength [2]. In contrast, the storage modulus of IIR-Acrylate-XL increased significantly over the recorded temperature range. This is consistent with standard models of covalent thermoset behaviour, whose entropically driven elasticity generates a greater restorative force as temperature is increased. [36] The responses of IIR-VImBr-XL, IIR-ImBr and IIR-BisImBr are notable for their relative insensitivity to temperature. Irrespective of the ion-pair concentration and the covalent crosslink concentration created during thermoset production, the storage modulus and elasticity of the thermoset ionomers did not vary

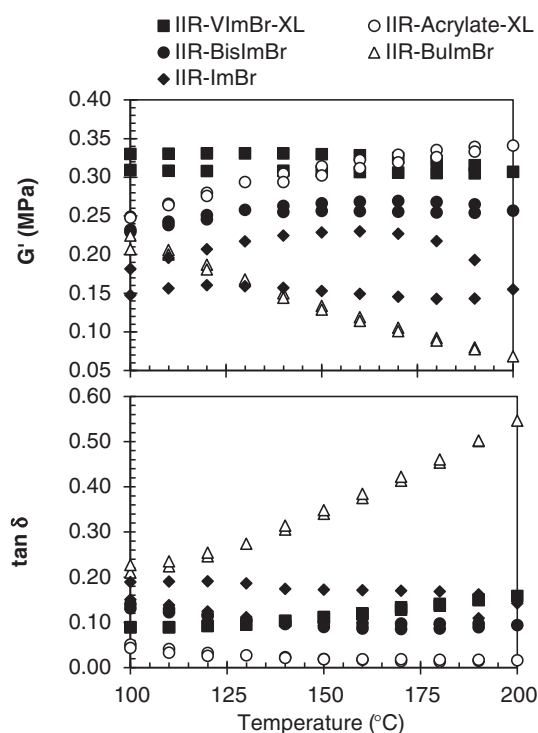


Fig. 2. Dynamic rheological properties of BIIR derivatives (100–200 °C, 1 Hz, 3° arc).

strongly with temperature, indicating that losses in ionic network strength are offset by increases in covalent network strength.

Fig. 3 illustrates the stress relaxation of our materials when subjected to a constant shear strain at 100 °C. As expected, the labile ionic network within IIR-BulmBr relaxed extensively, as polymer chain segments were capable of large-scale motion. After 5 min, the static modulus was near zero as the uncured material approached a fully relaxed state. The opposite behaviour was observed for IIR-Acrylate-XL, whose purely covalent network was so robust as to support a constant equilibrium modulus of 0.25 MPa. In keeping with their hybrid structure, the response of the thermoset ionomers to constant strain was intermediate to the control materials. Initial static modulus values paralleled the dynamic storage modulus measurements taken during the cure yield studies, with IIR-VImBr-XL providing higher values than either IIR-BisImBr or IIR-ImBr. In each case, extensive relaxation was limited to the first minute, beyond which the static modulus approached a stable plateau. This is consistent with ionic network relaxation acting in combination with a stable covalent network. Note that the static modulus of IIR-VImBr-XL declined to the value of IIR-Acrylate-XL, suggesting that long-term static properties are dictated by the entropic response of the covalent network.

3.3. Physical properties

Developing a thermoset formulation is typically a trial and error process that optimizes a range of physical properties. While specific test methods depend on the application, most compounding and physical testing regimens involve tensile and compression set analysis, and ionomer formulation development is often concerned with adhesive strength. Therefore, measurements of these physical properties are listed below and discussed in terms of ionic/covalent network contributions.

Compression set data are complementary to the stress relaxation measurements presented above, in that both tests quantify the response to a static strain. Compression of cylindrical samples for 18 h at room temperature resulted in permanent deformation, reported in Table 1 as a percent of the applied strain. The data reveal a heightened resistance to permanent deformation for peroxide-cured thermosets, with IIR-acrylate-XL and IIR-VImBr-XL providing the lowest compression sets, owing to the stability of their extensive covalent networks. As expected, the labile nature of ion pair aggregates resulted in a significant compression set for the uncross-linked control material, IIR-BulmBr. IIR-BisImBr produced a surprisingly low compression set result, providing further evidence of the superiority of this approach over IIR-ImBr,

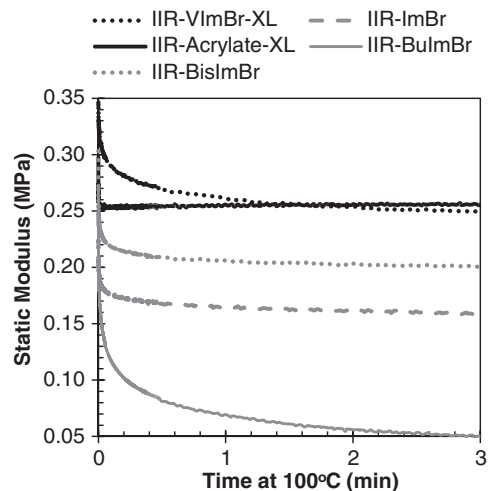


Fig. 3. Stress-relaxation of various BIIR derivatives at a fixed strain.

Table 1
Tensile, Compression set, Surface Energy and Adhesion Measurements.

Elastomer	Compression set (%)	5% modulus (MPa)	Tensile strain at break (%)	Tensile stress at break (MPa)	Peel strength (N)	Surface energy (mJ/m ²)
IIR	–	–	–	–	6.1 ± 2.7	20 ± 1
IIR-BulmBr	60 ± 2.0	0.72 ± 0.05	2300 ± 190	8.1 ± 1.1	10 ± 0.2	19 ± 1
IIR-VImBr-XL	6 ± 0.2	0.78 ± 0.04	300 ± 70	2.1 ± 0.2	7.2 ± 0.5	20 ± 1
IIR-BisImBr	7 ± 0.04	0.64 ± 0.02	900 ± 90	1.9 ± 0.3	23 ± 1.7	20 ± 2
IIR-ImBr	30 ± 1.0	0.64 ± 0.03	690 ± 40	1.4 ± 0.4	19 ± 2.1	19 ± 2
IIR-Acrylate-XL	2 ± 0.2	0.45 ± 0.03	250 ± 20	0.7 ± 0.1	5.6 ± 1.3	20 ± 1

given it is mechanically more robust at room temperature and, as described above, is more thermally stable.

The tensile data are noteworthy, in that they demonstrate an interesting attribute of imidazolium ionomers. Modulus values recorded at 5% elongation show the four ionomers to be stiffer at low elongation than IIR-Acrylate-XL. Even IIR-BulmBr, the control material with no covalent network, produced a 5% modulus of 0.72 MPa; 68% greater than that recorded for the non-ionic thermoset. IIR-BulmBr and IIR-VImBr produced the highest values, likely because their imidazolium bromide functionality is generated by a high yield, solution-borne N-alkylation process as opposed to a high temperature, solvent-free compounding approach that is adversely affected by BIIR dehydrobromination. Since most thermoset elastomer applications do not involve large strain amplitudes, the tensile strength conferred by the ionic network may have practical importance. Given the susceptibility of the ionic network toward stress relaxation, the high initial modulus will not withstand a static load, but under dynamic loading conditions the contribution of ion-pair aggregates to thermoset stiffness is significant.

Although ionic functionality had no measurable effect on the critical surface energy of the bulk polymer, it had a pronounced effect on

adhesive properties (Table 1). Peel strength measurements of the force per unit surface area needed to remove the polymer from a Mylar® film showed significant differences between the non-ionic controls (IIR, IIR-Acrylate-XL) and the ionomers. They also differentiated the ionomers into two classes, materials containing ionic functionality prior to forming the adhesive bond (IIR-BulmBr, IIR-VImBr-XL), and materials in which imidazolium bromide functionality was generated during the adhesive bond making process (IIR-BisImBr, IIR-ImBr).

These differences reflect the sensitivity of adhesive strength to the bond formation process, which requires displacement of air from the adherend (i.e. wetting) and relaxation of residual strain within the adhesive. [37] Ideally, compression molding the elastomer against a Mylar® film should allow the compound to make intimate contact with the film and relax fully before the compound is rendered thermoset. IIR-BisImBr and IIR-ImBr are low viscosity compounds that generate their covalent and ionic networks simultaneously through relatively slow N-alkylations, thereby allowing the material to produce an adhesive bond with low residual strain. On the other hand, IIR-VImBr is a high viscosity material that cures rapidly. As such, ionomer thermosets prepared by a single-step BIIR compounding techniques may provide

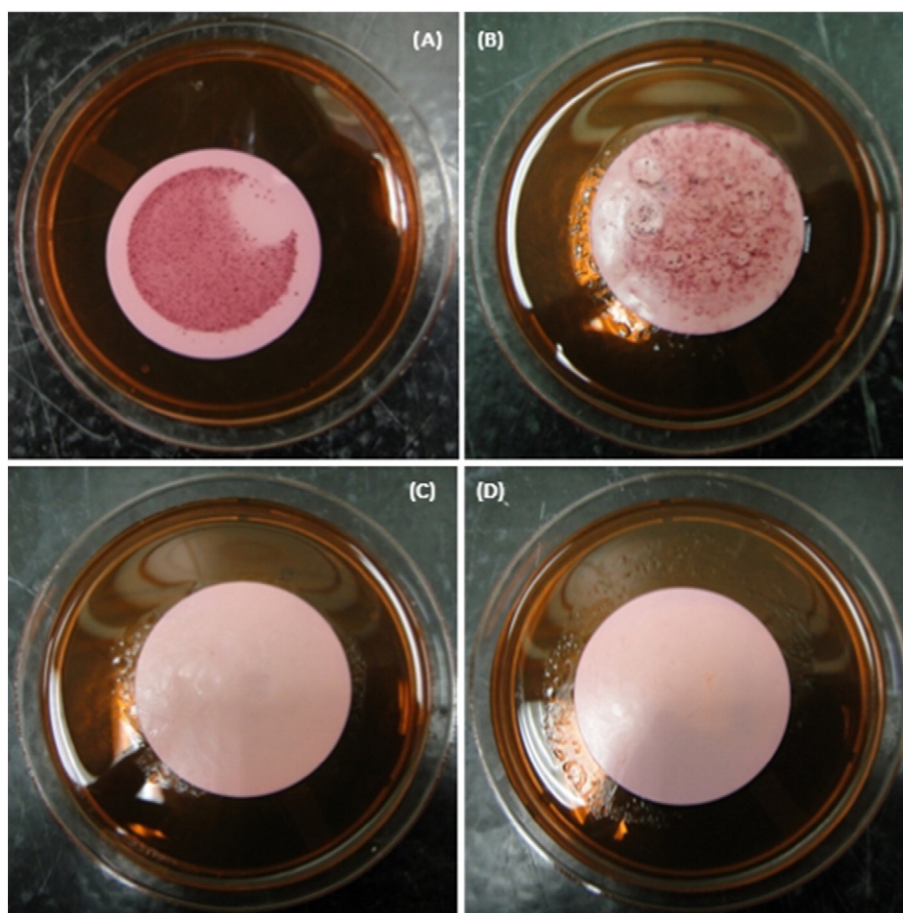


Fig. 4. Images of cellulose acetate filters after *E. coli* culture incubation under elastomer films (a) control sample (b) IIR, (c) IIR-BulmBr, (d) IIR-VImBr.

superior peel strength compared to those generated by the two-step macromonomer approach.

3.4. Anti-microbial properties

The potential of water insoluble ammonium, phosphonium and imidazolium ionic liquids (ILs) to improve the productivity of enzymatic and whole cell transformations has been demonstrated in which ILs sequester and/or deliver toxic substrates or bioproducts to/away from the biocatalysts. [38] However, despite some successful applications [39], many ILs have also caused enzyme denaturation and/or microbial cytotoxicity. [40] The mechanism for IL cytotoxicity has generally been ascribed to direct, destructive interactions with cell walls or cytoplasmic membranes [10], with antimicrobial activity varying across microbial species [41] and being IL structure dependent. [39,42].

Such cytotoxic properties, while being a constraint in potential bio-transformation applications, can be favourably exploited in the formation of antimicrobial surfaces. Bactericidal surfaces, potentially useful in healthcare devices (e.g. stents catheters, bandages) can be advantageously exploited to prevent the proliferation of pathogenic microorganisms and, because they can kill on contact [7], they can reduce or eliminate the need for antiseptic/antibiotic treatments that can lead to the proliferation of resistant organisms. “Tethering” cytotoxic functionality to polymer backbones has provided such directed antimicrobial activity across a wide range of pathogenic organisms including bacteria and yeast [10], while reducing the release of resistance-causing agents into the environment.

Our studies of anti-microbial activity against *E. coli* focused on IIR, IIR-BulmBr and IIR-VImBr, since these materials did not contain cure residues derived from un-alkylated nucleophile and/or HBr elimination. The apparatus consisted of a cellulose acetate filter coated with *E. coli*, laid face-up in an agar Petri dish. The size of the membrane's pores, 0.45 μm , allowed cells to absorb agar nutrients from the nutrient agar below, yet prohibited cell migration down through the pores. After covering the *E. coli*-coated filter with an elastomeric film, sealing the Petri dish and incubating the systems for 72 h and removing the polymer film, an examination of the bacterial colony growth on the membrane surface was performed.

Fig. 4 illustrates four independent experiments involving different elastomeric films. Fig. 4a is a control experiment in which no elastomer film covered the membrane, and these conditions produced the greatest extent of bacterial cell growth. Fig. 4b shows the cellulose acetate membrane that had been covered under an IIR film with significant cell proliferation on the membrane, as well as on the polymer film (not shown). Fig. 4c and d for IIR-BulmBr and IIR-VImBr films, respectively, demonstrate no evidence of bacteria colony growth on the cellulose acetate filter.

4. Conclusions

N-alkylation of imidazole-based nucleophiles by BIIR can be used to prepare isobutylene-rich ionomer thermosets using conventional elastomer compounding methods. Single-step processes employing imidazole and bis-imidazole reagents provide low viscosity compounds that produce ionic functionality during the curing process, thereby promoting adhesion between the thermoset and adjoining surfaces. A two-step process involving the N-alkylation of vinylimidazole, followed by peroxide-curing provides ionic functionality during the compounding process, potentially enhancing polymer-filler adhesion during mixing. Both technologies provide hybrid ionic-covalent networks whose physical properties are affected by the labile nature of ion-pair aggregates and the stable nature of covalent crosslinks. Over long timescales, such

as experienced in compression set and stress relaxation tests, the covalent network confers stability to the thermoset after a period of ionic network relaxation. However, properties measured over shorter timescales, such as encountered in static tensile testing and dynamic oscillatory rheology, are strongly influenced by ion-pair aggregates. In addition to affecting material properties, imidazolium bromide functionality provides antibacterial properties to these thermoset elastomer derivatives.

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