



Quaternary ammonium elastomeric ionomers by melt-state conversion

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Abstract

Quaternizations of benzyl bromide units in brominated poly(isobutylene-*co-p*-methylstyrene), or BIMS, elastomers with tertiary amines can be readily accomplished either by solution techniques or by melt reactive mixing. At temperatures of 130 °C and above, the nucleophilic substitution of benzyl bromide with ammonium bromide occurs instantaneously in an internal mixer. The conversion is around 95% for both dimethyl alkyl and dialkyl methyl amines. Suppressions in loss tangent measured in dimethyl alkyl amine melt quaternized BIMS indicate that molecular weight amplifications as a result of ionic association in these ionomers are in line with that obtained from solution quaternized BIMS. These melt quaternized BIMS ionomers become gels when their molecular weight amplification factors are greater than 1.5. Viscosity of BIMS can be raised significantly through quaternization to facilitate its mixing with thermoplastics. BIMS ionomers can also be added into bromobutyl innerliner compounds to enhance their green strengths. The efficiency in promoting ionic associations during melt mixing of BIMS with only 0.1 mol equiv. of dimethyl alkyl amines allows residual benzyl bromide units for subsequent curing.

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1. Introduction

An ionomer, or ionic polymer, is an ion-containing polymer with limited ionic bonds in its backbone or network structure [1–4]. These ions could be cationic, such as quaternary ammonium, sulfonium or phosphonium ions, or anionic, such as carboxylic, sulphonic, or phosphonic ions. Ionomers differ from water swellable or soluble polyelectrolytes with their low ionic contents, typically containing 10% or lower ionic groups. By definition, ionomers exist in either the salt or ionized form. Hence, a metal salt of poly(ethylene-*co*-methacrylic acid) is an ionomer, but a poly(ethylene-*co*-methacrylic acid) is not. Ions in ionomers are covalently bonded to the polymer backbone or network balanced with mobile counter-ions where their mobility depends on the ionic bond strength, the temperature, and the presence of preferential plasticizers. Since these limited ionic groups are typically surrounded by low dielectric-constant non-ionic co-monomers, the aggregation of ions in ionomers is commonly observed, if their chain conformation could accommodate.

Depending on the chain conformational freedom and

ionic contents, the ion aggregation in bulk ionomers varies from simple ionic pairs, to ionic multiplets, and to ionic clusters [5]. The multiplets are presumed to act as small physical crosslinks whereas the formation of clusters imparts a phase separated domain morphology. Cluster formation with corresponding failure of time–temperature superposition was indicated in poly(styrene-*co*-sodium methacrylate)s containing greater than 6 mol% methacrylate. Below 6 mol%, multiplets were assumed to be present in these polymers that observed thermorheological simplicity [6]. It is because of these ionic associations that enhancements in mechanical properties were obtained in ionomers. These ionic aggregates in ionomers have been found to be thermally stable until the polymer decomposes [7]. Ionomers flow by a hindered ion-hopping mechanism, where ions are transported between aggregates, resulting in significantly increased viscosity values [8]. This increase in ionomer viscosity depends on the difficulty in ion hopping which, in turn, is related to the cohesive strength of the ionic aggregate [2].

The first patent for a carboxylic elastomer was issued to I.G. Farben-industrie in 1933 [9]. Ionic interactions, or ionic crosslinks, are present in carboxylated rubbers vulcanized by metal-oxides in the presence or absence of sulfur [10]. These ionic associations raised the strength of the based

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rubber (without carboxyl groups), at the expense of elasticity, improved its hardness, abrasion resistance, film forming properties, and adhesion [11]. Most widely used commercial carboxylated rubber products are those based on diene rubbers, including butadiene, butadiene–acrylonitrile, and butadiene–styrene, copolymerized with acrylic or methacrylic acid. Ionic groups have been incorporated in other elastomers and rubbers, such as chlorosulfonated polyethylene metal salts (Hypalon), perfluorosulfonated ionomers (Nafion), sulfonated poly(ethylene-*co*-propylene-*co*-5-ethylidene 2-norbornene), or sulfo-EPDM [12], and polyurethane ionomers [13]. In isobutylene-based elastomers, sulfonated polyisobutylene telechelic elastomers have been synthesized with sulfonic end groups [14,15] by cationic polymerization using a di- or trifunctional initiators. However, these telechelics are not commercially available.

An isobutylene-based elastomer with improved green strength was obtained by melt compounding of brominated poly(isobutylene-*co*-isoprene), i.e. bromobutyl rubber (BIIR), with tertiary aliphatic amines, resulting in quaternary ammonium ionic associations through quaternization of the halogen in BIIR [16,17]. Similarly, melt conversion of allylic bromine in BIIR with dimethylaminoethanol in an internal mixer could promote reactive compatibilization between BIIR and poly(styrene-*co*-maleic anhydride) leading to rubber-toughened polystyrene with controlled small rubber dispersions and excellent mechanical properties [18]. According to the solution conversion study using a model compound [19], nucleophilic amines undergo N-alkylation reaction readily and preferentially by *endo* substitution. During the melt conversion at 140 °C for 10 min using BIIR with a tertiary amine, *exo*-allylic bromide, *endo*-allylic bromide, and conjugated diene structures were also present in addition to the *endo* substituted quaternary ammonium bromide [19]. Although exomethylene allylic bromide is a preferred structure in BIIR, it undergoes isomerization, to an *endo*-isomer, and HBr elimination to yield conjugated dienes [20,21] at high temperatures. These conjugated dienes could subsequently be crosslinked or β -scissioned resulting in BIIR degradation at high temperatures.

It may be due to the concern for the BIIR thermal stability, melt quaternization of BIIR with tertiary amines was done at 90 °C in an internal mixer at extended times, greater than hours, in the original patents [16,17] for BIIR green strength enhancements. All commercially available isobutylene-based random copolymers have only limited amounts of comonomers, less than 5 mol%, beside isobutylene to take the advantages of the low permeability, high damping coefficient, and oxidative stability of polyisobutylene. These comonomers could be isoprene, as in butyl rubber (IIR), chlorinated or brominated isoprene, as in chlorobutyl or bromobutyl (CIIR or BIIR), or brominated *para*-methylstyrene, as in brominated poly(isobutylene-*co*-*para*-methylstyrene) (BIMS), with the main purpose of providing curing sites. BIMS, which contains no unsaturation,

has the best thermal stability. Additionally, the versatile and reactive benzylic bromides in BIMS allow its ease for functionalization [22].

In this study, melt quaternization using an internal mixer of thermally stable BIMS is examined and compared with that from solution conversion. Reaction rates during melt conversion were monitored by the rise in torque and the conversion was determined using FTIR. Extent of ionic associations was estimated based on $\tan \delta$ suppression and strength of ionic associations was measured by the increase in capillary viscosity. Additionally, it was demonstrated that the viscosity of BIMS is raised sufficiently through quaternization to facilitate its mixing with thermoplastics. It was further demonstrated that the resulting BIMS ionomers can be added into BIIR innerliner compounds to enhance their green strengths.

2. Experimental

2.1. Materials

The BIMS polymer used was Exxpro™ 3745, a 45 Mooney (ML 1 + 8 at 125 °C) elastomer from ExxonMobil Chemical. It has 1.2 mol% brominated *para*-methyl styrene (or benzylic bromine), BrPMS, and 2.4 mol% unbrominated *para*-methylstyrene, or PMS. Its number average molecular weight is 210,000 g/mol with a polydispersity index of about 2.5 measured by size exclusion chromatography (SEC) using THF as an eluent. The reference BIIR polymer examined was Bromobutyl 2222, a 32 Mooney (ML 1 + 8 at 125 °C) elastomer from ExxonMobil Chemical. All tertiary amines were provided by Akzo Nobel Surface Chemistry. The dimethyl alky amines evaluated were DMCD, DM16D, DMHTD, DMHR, and DMHED. The ‘DM’ stands for dimethyl and C, 16, HT, HR, and HE refer to C12 alkyl, C16 alkyl, hydrogenated tallow, hydrogenated rapeseed, and C22 alkyl, respectively. The terminal suffix ‘D’ means distilled. Hydrogenated tallow contains 3.5% C14, 0.5% C15, 31% C31, 1% C17, and 61% C18 whereas hydrogenated rapeseed has 0.5% C14, 3.5% C16, 38% C18, 8% C20, and 50% C22. The two dialkyl-methyl amines studied were M2C, dicocoalkyl-methylamine, and M2HT, dihydrogenated tallowalkyl-methylamine. Cocoalkyl has 6% C8, 7% C10, 51% C12, 19% C14, 9% C16 and 2% C18.

Detailed methods for the nucleophilic substitution of BIMS in solutions have been reported previously [22]. Only one solution converted BIMS ionomer was prepared in this study for comparison purposes. BIMS was dissolved in THF/methanol mixture (95/5 v/v) with a twofold molar excess of DMCD. This 7-wt% solution was then refluxed for 4 days. The final reaction product was precipitated in an excess of methanol to remove unreacted amine and dried under vacuum at 60–70 °C for more than 1 month. Solution ¹H NMR, using a Varian Gemini FT 300 MHz, confirmed the completion of quaternization of BrPMS.

2.2. Mixing and melt quaternization

Melt quaternizing reactions were conducted in a Brabender internal mixer at 130 °C for 5 min at 60 rpm. Both blank BIIR and BIMS were sheared in the Brabender mixer without amine addition for 5 min for stability evaluations. No changes were found in BIMS whereas viscosity values, at shear rates from 30 to 1000 s⁻¹, showed an increase in BIIR after Brabender mixing, suggesting thermally induced crosslinking in BIIR. All amines were added 1 min after the polymer introduction and with concentrations of 0.1, 0.25, 0.5, and 0.75 bromine molar equivalents. The bromine in bromine molar equivalent refers to the benzylic bromine in BIMS and the allylic bromine in BIIR. An attached torque meter measured the onset of torque increase after amine addition, which, in turn, was used to determine the onset of ionic associations. Onset times could only be determined for dimethyl alkyl amines in BIMS. No changes in torque could be detected in BIIR with DMCD amines with all concentrations evaluated. Torque values were actually lowered in BIMS with dialkyl methyl amines due to plasticization. All mixes were not washed after mixing, thus no attempt to remove any residual unreacted amines was made.

All BIMS blends containing tertiary amines cannot be completely dissolved either in THF solvent (for SEC) or in deuterated chloroform (for solution NMR). Based on the SEC measurements of soluble fractions of these blends, reductions in molecular weight and molecular fraction were indicated as compared with that of unmodified BIMS. An instantaneous reaction between amines and benzylic bromine in BIMS in the mixer at 130 °C was indicated from the torque response. During the initial addition of amines in the mixer, this super-fast reaction may have prevented the added amine from being fully distributed and dispersed, leading to the formation of micro-gels. Although the micro-gels in these blends hinder analysis by solution techniques, these blends could still be characterized by solid-state analytical methods and, as will be illustrated in the results and discussion section, they still can be processed and utilized.

2.3. Solid state NMR and infrared spectroscopy

Two BIMS blends containing 0.5 mol equiv. of amines, one with DM16D and the other with M2HT, were evaluated for their quaternization by ¹H MAS (magic-angle spinning) solid state NMR using a Bruker DSX-500 spectrometer at 4.5 kHz spinning speed. Although spectra collected at elevated temperatures of 120 and 150 °C suggested the quaternization of BrPMS, their poor signal to noise ratios prevented their quantitative analysis. Considering the strong BrPMS peak at around 615 cm⁻¹ in FTIR (Fourier Transform Infrared Spectroscopy) spectra of BIMS compounds, the FTIR peak reduction in BrPMS was applied as a measure of the BrPMS conversion. Since there were no

distinct FTIR peaks that could be assigned to the quaternization product, this absence of BrPMS in BIMS was assumed to be equal to the quaternization of BrPMS. Only BIMS blends with 0.1 mol equiv. amines were examined by FTIR. Blends with higher amine contents were difficult to press into good quality films due to their high viscosities. Blends examined were compression molded at 100 °C into 0.6-mm thick films and subsequently evaluated with a Perkin–Elmer GX-2000 FTIR spectrometer.

2.4. Dynamic mechanical analysis

Due to the inability to measure the molecular weight of these BIMS-amine blends using SEC, molecular weight amplifications in these blends were determined according to their tan δ minimum suppressions. In accordance to the Marvin–Oser theory, the tan δ minimum, or tan δ_m, for a polymer is given by [23]

$$\tan \delta_m = 1.04(M/M_c)^{-0.80} \quad (1)$$

Here, *M* is molecular weight or number average molecular weight [24] and *M_c* is the critical molecular weight for influencing steady flow viscosity by entanglement coupling [25]. It needs to be emphasized that this *M_c* is different from *M_e*, or average molecular weight between entanglements. According to the theory of Grasseley [26], *M_c/M_e* = 2.5. By assuming that *M_c* stays constant in quaternized BIMS, an increase in molecular weight as a result of ionic associations would lead to lower tan δ_m according to Eq. (1).

An Advanced Rheometric Expansion System, ARES, from Rheometrics was applied to measure dynamic mechanical properties of all blends in shear using plate geometry at 0.1% strain. Four to five decades of frequency, from 0.06 to 390 rad/s, were used at each of the seven temperatures, -25, 0, 25, 50, 75, 100, and 125 °C, prescribed. Time–temperature superposition was then applied to obtain a master curve for each blend and, in turn, used to determine its tan δ_m value. All blends evaluated in this study satisfied the time–temperature superposition suggesting no ionic clusters formed even in blends with highest molar equivalent of amine. For DM16D modified BIMS, ARES was also utilized to examine the thermal stability of BIMS ionomers by cycling the temperatures from 100 to 250 to 100 to 250 °C at 5 °C/min at 1 s⁻¹ shear rate. Viscosity values of these ionomers at each temperature remain relatively unchanged during thermal excursion demonstrating the thermal stability of ionic association in quaternized BIMS.

2.5. Capillary viscosity

Capillary viscosity values of all blends at 100 and 150 °C and at shear rates of 30, 100, 300, and 1000 s⁻¹ were measured using a Monsanto Processability Tester, or MPT,

with a 20/1 length to diameter capillary die. MPT rheometer requires only a 10-g sample with 5 min thermal equilibrating time. No corrections for entrance pressure losses, i.e. the Bagley correction, and for the presence of non-Newtonian velocity profile, i.e. the Rabinowitsch correction, were applied to the data. The viscosity curves for polypropylene, PP4292 (1.5 MFR) from ExxonMobil Chemical, and for BIMS-A, Exxpro™ 89-4 (0.75 mol% BrPMS, 45 Mooney), were determined based on rheological measurements on an ARES rheometer and on a Rosand capillary rheometer at various temperatures followed by time–temperature superposition. The PP4292 and BIMS-A were used for the mixing study. The Rosand capillary rheometer was equipped with a 30/1 capillary that requires 25–30 g of sample and 15 min of thermal equilibration. Both Bagley and Rabinowitsch corrections were applied to all data from Rosand rheometer.

2.6. Applications in mixing and in green strength enhancement

A blend comprising 60 wt% PP4292 and 40 wt% BIMS-A melt quaternized with 0.5 mol equiv. DM16D was prepared by mixing components using a Brabender mixer at 80 rpm and 220 °C for 5 min. An otherwise identical control blend was prepared except that BIMS-A was not modified. Morphologies of these blends were examined using a NanoScope Dimension 3000 scanning probe microscope from Digital instrument in tapping phase AFM (Atomic Force Microscopy) mode. Blends were prepared for AFM analysis by being cryo-faced with a diamond knife at –150 °C in a Reichert cryogenic microtome. All tapping phase morphological images were processed using PHOTOSHOP, from Adobe Systems Inc., and an image processing tool kit, from Reindeer Games Inc., to determine the number average dispersion sizes, in terms of equivalent diameters, of BIMS-A in PP4292.

Although the green strength of BIMS is significantly enhanced upon tertiary amine addition, the corresponding increases in viscosity and in elasticity reduce its processability. As will be shown in the results and discussion section, the direct addition of a tertiary amine in BIIR during BIIR innerliner compounding has little or no effects on the liner's green strength. Instead, innerliner model compounds were prepared in an internal mixing using 80/20 BIIR/BIMS-B blends with the addition of tertiary amine for liner's green strength enhancement without compromising liner's processability. As shown in Table 1, a series of tire innerliner model compounds were mixed in a Banbury mixer using BIIR, brombutyl 2222, and BIMS-B, Exxpro™ 3035 (0.5 mol% BrPMS, 45 ml) at 100 rpm and 150 °C dump temperature (about 3–4 min total). The 0.5-phr, part per hundred of polymer in weight, DM16D corresponds to 0.1 bromine mole equivalent of BIMS-B. During Banbury mixing, polymers were added first followed by all other ingredients except DM16D, which was added just before dump. The curative package consisting of 3-phr zinc oxide

Table 1
Model innerliner compounds

Compound	1	2	3	4
BIIR	100	100	80	80
BIMS-B	0	0	20	20
Paraffinic oil	10	10	10	10
N660 black	50	50	50	50
Stearic acid	2	2	2	2
MgO	0.15	0.15	0.15	0.15
DM16D	0	1	0	0.5

(Kadox 930C from Zinc Corporation), 0.5-phr sulfur (from R. E. Carroll, Inc.), and 1.5-phr MBTS (Altax from R. T. Vanderbilt, Inc.) was added in all mixes on a 2-roll rubber mill after Banbury mixing. Calendered sheets were tested for green strength and cured for evaluations of cured compound properties. Test procedures are available elsewhere [27].

3. Results and discussion

3.1. Melt quaternization

During the Brabender mixing of tertiary amines with BIMS and BIIR, torque increase was only found in blends of BIMS with dimethyl alkyl amines. The onset time for torque increase after amine addition, which is an indication of ionic associations, for a dimethyl alkyl amine of various concentrations is similar. The average onset times, averaged over blends with amines of 0.1, 0.25, 0.5, and 0.75 bromine molar equivalents, for the five dimethyl alkyl amines studied are tabulated in Table 2. The torque ratios, ratios of equilibrium torque after amine addition to that of BIMS without amine, for these amines at four addition concentrations are also listed in Table 2. Considering the alkyl length of these amines follow DMCD (C12) < DM16D (C16) < DMHTD (61% C18) < DMHR (50% C22) < DMHED (C22), it appears that the onset time increases with alkyl length. Since the onset of torque increase requires both the BrPMS quaternization and ionic associations, it suggests that the combined rate of reaction and association is faster in BIMS functionalized with a dimethyl alkyl amine with shorter alkyl length. To minimize the formation of micro-gels during solid-state quaternization of BIMS using an internal mixer, it may be desirable to use dimethyl alkyl amines with longer alkyl length. The increase in torque, as a relative measure of the strength of ionic association, is highest in DMHTD-quaternized BIMS. Corresponding high increases in capillary viscosity were also found in these blends containing DMHTD. There is an apparent optimal alkyl length for maximizing viscosity and ionic association in dimethyl alkyl amine-quaternized BIMS. No changes in torque were detected in BIIR with DMCD amines and lower torque values of BIMS blended

Table 2
Brabender torque increase onset and torque ratio

Amine	Onset time (seconds)	Torque ratio (0.1 ^a)	Torque ratio (0.25 ^a)	Torque ratio (0.5 ^a)	Torque ratio (0.75 ^a)
DMCD	8	1.1	1.5	2.2	2.5
DM16D	14	1.1	1.4	1.7	2.5
DMHTD	18	1.2	1.8	2.8	3.4
DMHR	21	1.2	1.5	2.4	2.7
DMHED	21	1.2	1.8	2.4	3.0

^a Molar equivalent of amine addition.

with dialkyl methyl amines were measured. Hence, onset times and torque ratios for these blends cannot be determined.

BrPMS conversion, as measured from the reduction in its FTIR peak, was calculated and is listed in Table 3 for each of the five tertiary amines. Both dimethyl alkyl and dialkyl methyl amines react efficiently and almost completely, 95–100%, with benzyl bromides leading to the formation of quaternary ammonium bromides at 130 °C in an internal mixer. Considering that all amines were added 1 min after BIMS introduction to the mixer and that the measured torque values stabilized 3 min after amine addition, this melt quaternization with tertiary amines in BIMS requires less than 3 min at 130 °C. It was found that this high conversion, above 90%, in melt quaternization of BIMS with DM16D stays relatively independent of temperature from 80 to 160 °C for 5 min in a Brabender mixer and of amine concentrations from 0.05 to 0.2 mol equiv. [28]. By assuming that most amines added have sufficiently quaternized BrPMS in BIMS to about the same extent, differences in viscosity and in torque between BIMS quaternized with difference amines reflect, mostly, the strength of ionic associations.

3.2. Molecular weight amplification and gelation

The $\tan \delta$ master curves for BIMS and for BIMS with 0.5 mol equiv. DMCD after time-temperature superposition are shown in Fig. 1. Depression of the $\tan \delta_m$ in DMCD-quaternized BIMS is clearly indicated. The peak observed for both samples at high frequency, above 10^4 rad/s, at the normalized 25 °C temperature corresponds to the unique above- T_g relaxation of isobutylene-based polymers associated with the sub-Rouse mode [29,30]. The high $\tan \delta$ at lower frequency for BIMS is the result of BIMS flowing. However, $\tan \delta$ is constant and independent of frequency at frequencies below $\tan \delta_m$ for the 0.5 mol equiv. DMCD quaternized BIMS. This indicates solid behavior, suggesting that this DMCD-quaternized BIMS is a gel. However, this

Table 3
BrPMS conversion in BIMS quaternized with 0.1 mol equiv. of amine

Amine	DMCD	DM16D	DMHTD	M2C	M2HT
Conversion (%)	100	95	95	96	94

gel is only a physical association rather than a chemical crosslink. While this quaternized BIMS cannot flow at 100 °C, it does flow at 150 °C. This means that ionic associations in this polymer could be displaced, at higher temperatures, through the postulated ion-hopping mechanism. A dimethyl alkyl amine quaternized BIMS ionomer is designated as a ‘gel’ in Table 4 if its $\tan \delta$ was found to be independent of frequency at low frequencies. Measured $\tan \delta_m$ values and corresponding amplifications of molecular weight, calculated based on M_c of 19,682 g/mol, for quaternized BIMS ionomers evaluated in this study are also listed in Table 4. This M_c value, determined from the $\tan \delta_m$ value for BIMS, is in fair agreement with the published value of 15,200 g/mol for polyisobutylene [31].

The solution quaternized BIMS with a molar equivalent of DMCD shows an amplification factor of 2.0 which is in line with expected value based on the values shown in Table 4 for solid-state quaternized BIMS. The amplification factors of BIMS-dimethyl alkyl amine ionomer are plotted versus amine content in Fig. 2. It is interesting to note that these ionomers become gels when their amplification factors are greater than 1.5. This 1.5 molecular weight amplification factor may provide an estimate of ionic pairing extent in ionic multiplets of these ionomers. However, due to the softening of the storage modulus in BIMS quaternized with dialkyl methyl amines, resulting

Table 4
Values of $\tan \delta_m$ and molecular weight amplification in BIMS quaternized with dimethyl alkyl amines

Amine	$\tan \delta_m$	Amplification ^a	Gel
No amine	0.157	1.0	No
DMCD (0.1 ^b)	0.149	1.07	No
DMCD (0.25)	0.121	1.39	No
DMCD (0.5)	0.105	1.65	Yes
DMCD (0.75)	0.095	1.87	Yes
DM16D (0.1)	0.142	1.13	No
DM16D (0.25)	0.140	1.15	No
DM16D (0.5)	0.099	1.77	Yes
DM16D (0.75)	0.092	1.94	Yes
DMHTD (0.1)	0.153	1.03	No
DMHTD (0.25)	0.111	1.54	No
DMHTD (0.5)	0.111	1.54	Yes
DMHTD (0.75)	0.084	2.18	Yes

^a Molecular weight amplification factor.

^b Molar bromine equivalent of amine added.

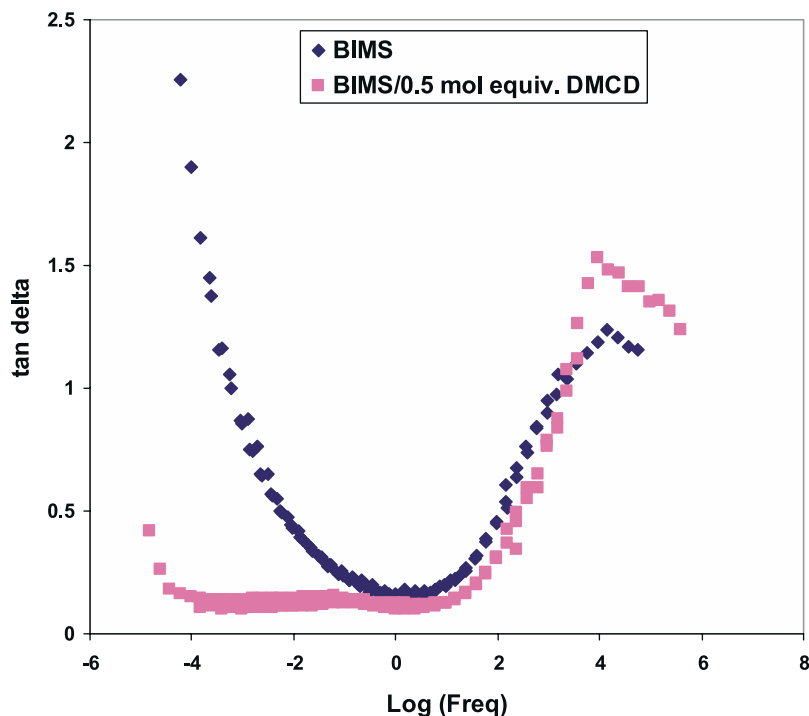


Fig. 1. $\tan \delta$ master curves of BIMS and BIMS quaternized with 0.5 bromine molar equivalent of DMCD.

from the plasticization effects, $\tan \delta_m$ cannot be applied to determine their molecular weight amplifications.

3.3. Ionic association strength and capillary viscosity

MPT capillary viscosity values of BIIR and BIMS melt quaternized with DMCD at 130 °C are tabulated in Table 5 for four shear rates and at two measurement temperatures. These viscosity values are expressed as viscosity ratios normalized by that of unmodified BIIR and BIMS, respectively. Due to the degradation of BIIR in the mixer,

the viscosity values applied for unmodified BIIR are those measured from blank BIIR sheared in a Brabender mixer at 130 °C for 5 min. There are no significant differences in viscosity values for BIMS before and after mixing. As indicated in Table 5, it appears that DMCD addition does not raise BIIR viscosity at concentrations of less than 0.5 mol equiv. and could only slightly enhance BIIR viscosity at 100 °C but not at 150 °C, at 0.5 mol equiv. or higher concentrations. In comparison, DMCD significantly raises the BIMS viscosity, by more than 2 times, at all concentrations. Viscosity values of DMCD quaternized BIMS at 100 °C are so high at 0.5 mol equiv. or higher amine concentration that they could not be measured. This strong contrast between DMCD modified BIIR and BIMS reflects the reactivity of the benzylic bromine in BIMS as

Table 5

Capillary viscosity ratios of modified BIIR and BIMS to unmodified BIIR and BIMS, respectively, at four shear rates and at two temperatures

	at 30 1/s	at 100 1/s	at 300 1/s	At 1000 1/s
BIIR/DMCD-0.1 ^a	1.0/1.0 ^b	1.0/1.0	1.0/1.0	1.0/1.0
BIIR/DMCD-0.25	1.0/1.0	1.0/1.0	1.0/1.0	1.0/1.0
BIIR/DMCD-0.5	1.1/1.0	1.1/1.0	1.2/1.0	1.1/1.0
BIIR/DMCD-0.75	1.2/1.0	1.4/1.0	1.6/1.0	1.5/1.0
BIMS/DMCD-0.1	2.0/2.7	1.9/1.8	2.0/1.6	2.0/1.6
BIMS/DMCD-0.25	3.5/3.7	3.6/2.5	3.7/2.3	3.4/2.3
BIMS/DMCD-0.5	gel ^c /5.4	gel/4.0	gel/3.9	gel/3.7
BIMS/DMCD-0.75	gel/6.6	gel/4.7	gel/5.0	gel/4.6

^a Molar bromine equivalent of amine added.

^b 100 °C/150 °C.

^c Could not be measured. Polymer exited the capillary die in crumbs and pieces, exhibiting solid displacement rather than liquid flow—gel.

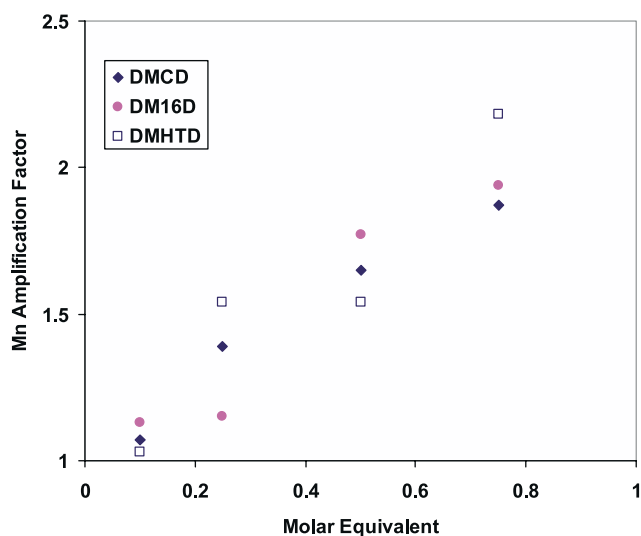


Fig. 2. Molecular weight amplification by ionic associations in BIMS ionomers.

compared with that of the allylic bromine in BIIR. Considering that most rubber compounding operations are done in less than 5 min, melt quaternization of BIMS, in reference to that of BIIR, is easily applicable and can provide maximum viscosification with minimal amine addition.

As shown in Table 5, although viscosity values of quaternized BIMS ionomers with 0.5 and 0.75 mol equiv. DMCD cannot be determined at 100 °C, viscosity values of these ionomers can be measured at 150 °C. Additionally, the shear thinning exponents of these ionomers at 150 °C are about the same as that of unmodified BIMS (see Figs. 3–5). This indicates that the flow of these ionomers is a thermally activated process. Viscosity ratios of BIMS ionomers, quaternized with either of the five dimethyl alkyl amines or with the two dialkyl methyl amines, are listed in Table 6 for ionomers with only 0.1 bromine molar equivalent of amine. The viscosity curves, as a function of shear rate, of these ionomers with 0.25, 0.5, and 0.75 mol equiv. of amine measured at 150 °C are also shown in Figs. 3–5, respectively. All quaternized BIMS ionomers that were designated as a gel according to $\tan \delta$ measurement (see Table 4) cannot flow at 100 °C in MPT rheometer. The viscosity values of 0.75-molar-equivalent DMHTD quaternized BIMS are so high that they could not be measured even at 150 °C. As shown in Figs. 3–5, viscosity enhancement, or ionic association strength, in tertiary amine quaternized BIMS follows DMHTD \sim DMCD > DM16D \sim DMHED > DMHR > M2C \sim M2HT. However, the viscosity differences among various dimethyl alkyl amine quaternized BIMS and among those quater-

nized by two dialkyl methyl amines are not large. Instead, the viscosity difference between the group of dimethyl alkyl amines and that of dialkyl methyl amine is more significant and increases with increasing amine concentration. Weaker associations in dialkyl methyl amine quaternized BIMS could be attributed to the steric hindrance of the dialkyl groups on ionic multiplet pairing. However, the reason for the maximal enhancement in viscosity in DMHTD-quaternized BIMS is not clearly known at the present time and may be related to the optimal alkyl length of the DMHTD to provide best combination of better dispersion and stronger ionic associations in BIMS.

3.4. Mixing with thermoplastics

As indicated by the viscosity master curves for PP4262 and BIMS-A shown in Fig. 6, PP4262 has slightly higher viscosity at 220 °C than that of BIMS-A at low shear rates. At higher shear rates, PP4292 becomes more viscous than BIMS-A. This increase in viscosity differences with shear rates is a result of different shear thinning behavior between PP and BIMS. The shear thinning exponent for PP is 0.7 whereas the value for BIMS is 0.9. According to the Taylor drop breakup theory [32,33], matching mixing component viscosity could provide smaller dispersion sizes. However, during Brabender mixing of PP and BIMS, there are varying shear rates depending on whether polymers are in the areas of small clearance (high shear rates or even extensional flow) or high clearance (low shear rates). It has been suggested [34] that the drop breakup occurs in areas of small clearance and droplet coalescence by shear-induced

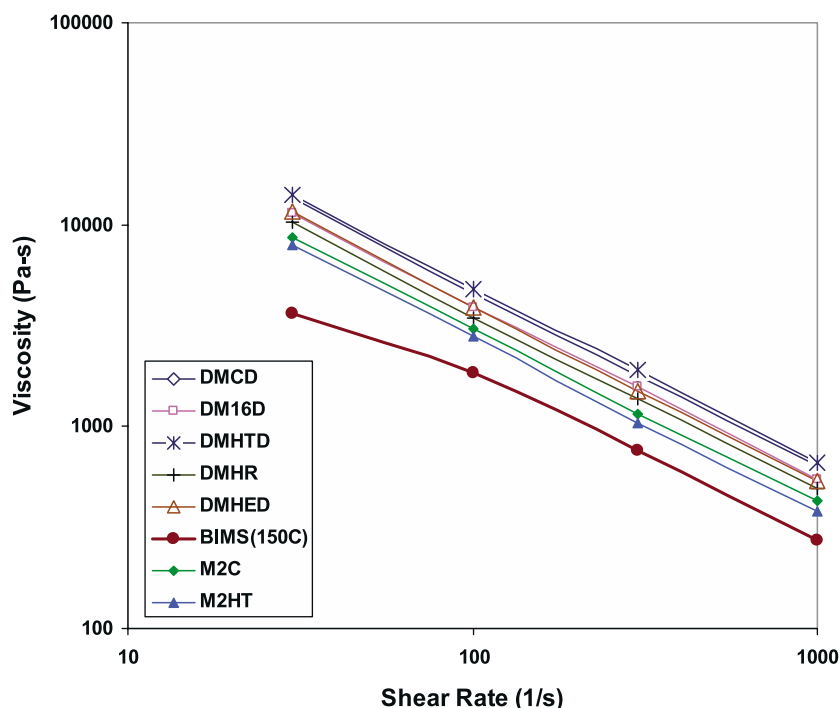


Fig. 3. Capillary viscosity values of 0.25-molar-equivalent amine quaternized BIMS at 150 °C measured by MPT.

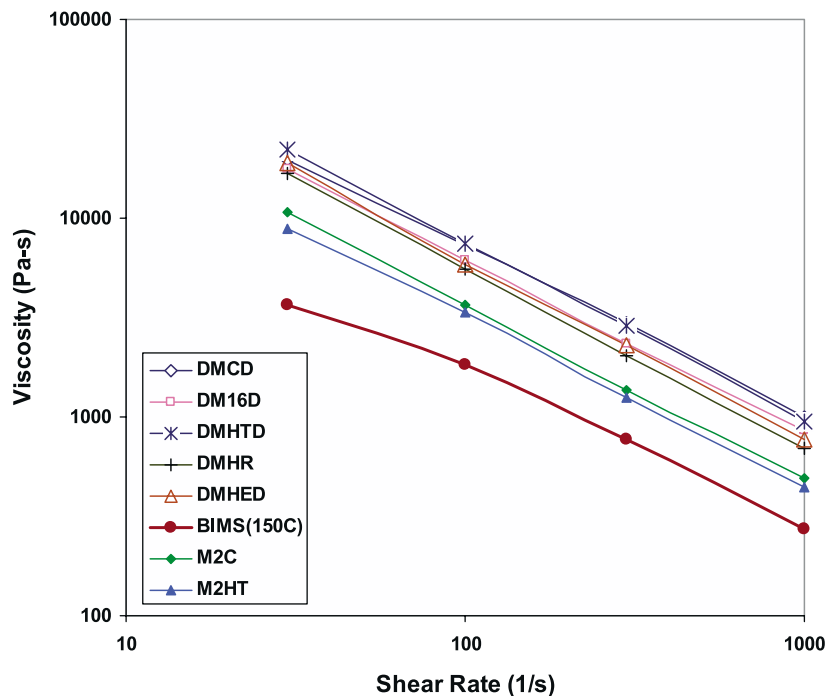


Fig. 4. Capillary viscosity values of 0.5-molar-equivalent amine quaternized BIMS at 150 °C measured by MPT.

collision is present in areas of large clearance. By raising the BIMS-A viscosity, using 0.5 bromine molar equivalent of DM16D in this case, viscosity values of this BIMS ionomer at high shear rates can be matched to those of PP, which could assist the breakup at areas of low clearance leading to smaller dispersions. At the same time, viscosity values of this BIMS ionomers at low shear rates are higher than those of PP at areas of large clearance, which could slow down the

coalescence. As shown in Table 7, finer quaternized BIMS-A dispersions in PP are obtained.

3.5. BIIR green strength enhancement

Properties of model innerliner compounds are listed in Table 8.

As previously reported [35], BIIR green compounds have

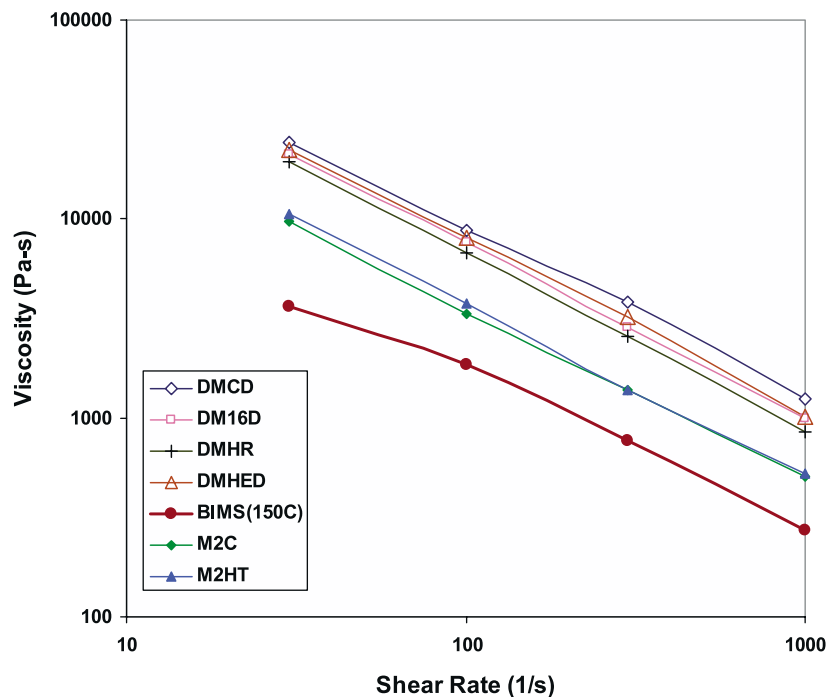


Fig. 5. Capillary viscosity values of 0.75-molar-equivalent amine quaternized BIMS at 150 °C measured by MPT.

Table 6

Viscosity ratios of modified BIMS, with 0.1 molar bromine equivalent of amine, to unmodified BIMS at two shear rates and at two temperatures

	100 °C 100 1/s	100 °C 1000 1/s	150 °C 100 1/s	150 °C 1000 1/s
DMCD	1.92	2.02	1.76	1.58
DM16D	1.77	1.77	1.59	1.41
DMHTD	2.02	2.00	1.65	1.47
DMHR	1.84	1.81	1.50	1.38
DMHED	1.84	1.98	1.60	1.44
M2C	1.58	1.57	1.31	1.18
M2HT	1.66	1.50	1.25	1.07

Table 7

Number average BIMS dispersion sizes in PP

Blends	Dispersion size (micron)
PP/BIMS-A	2.08
PP/BIMS-A (quaternized by DM16D)	1.42

adequate green strength at room temperature for rubber processing and tire building but are defensive at higher temperatures. Hence, green strengths of these compounds were all measured at 40 °C instead of room temperature. Green strength, expressed as 100% modulus, of the BIIR compound containing 1 phr of DM16D, compound #2, is slightly better than that of the BIIR compound, compound #1. This similar small enhancement in green strength can also be obtained in compound #3 with the addition of 20 phr of BIMS-B. Using 20 phr DM16D-quaternized BIMS-B in compound #4, green strength of this compound and its elongation to break are significantly better than those of compound #1. The cured properties of compound #4 are similar to those of the reference compound but with much better aging resistance. It should be also noted that the BIIR cured compound aging resistance could also be improved with the simple addition of DM16D (see aging property comparison between compounds #1 and #2).

Table 8

Properties of model innerliner compounds

Compound	1	2	3	4
Description	BIIR	BIIR/ DM16D	BIIR/ BIMS	BIIR/BIMS/ DM16D
40 °C Green strength				
100% Modulus (Mpa)	0.188	0.212	0.211	0.292
Elongation (%)	317	341	326	643
Cured tensile strength, unaged, test temperature 25 °C				
100% Modulus (Mpa)	1.2	1.21	1.27	1.23
% Strain at break	688	685	723	748
Cured tensile strength, aged 48 h at 120 °C, test temperature 25 °C				
100% Modulus (Mpa)	1.94	1.51	1.83	1.49
% Strain at break	564	644	596	698
Cured tensile strength, aged 48 h at 140 °C, test temperature 25 °C				
100% Modulus (Mpa)	1.79	1.48	1.88	1.48
% Strain at break	562	640	586	697
Shore A hardness (cured)				
Unaged	47.1	51.1	54.3	51.9
Aged (48 h at 120 °C)	58.1	53.1	58.2	54.1
Aged (48 h at 140 °C)	60.7	54.5	57.1	54.1

4. Conclusions

Melt quaternization of BIMS using tertiary amines could be readily accomplished in an internal mixer at 130 °C for

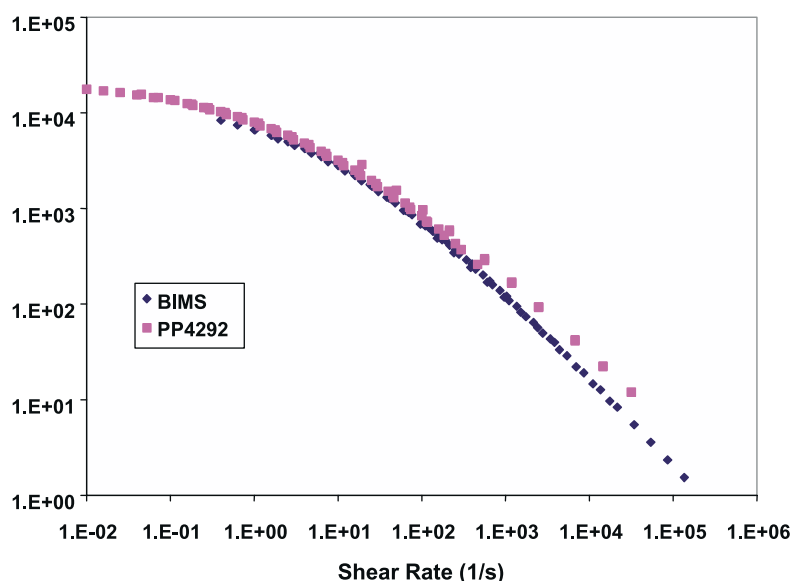


Fig. 6. Viscosity curves of BIMS-A and PP4292 at 220 °C.

5 min. The conversion is around 95% for both dimethyl alkyl and dialkyl methyl amines. During mixing, torque increased in less than 30 s after amine addition for dimethyl alkyl amines. The relative fast functionization and subsequent ionic associations in melt quaternized BIMS may have contributed to the formation of micro-gels in these ionomers. The onset time for torque rise was found to increase with increasing alkyl length of the dimethyl alkyl amine. No changes in torque could be detected in BIIR after tertiary amine addition. The $\tan \delta_m$ suppression values measured in dimethyl alkyl amine melt quaternized BIMS indicate that molecular weight amplifications as a result of ionic association in these ionomers are in line with that obtained from solution quaternized BIMS. These melt quaternized BIMS ionomers become gels when their molecular weight amplification factor is above 1.5. This 1.5 molecular weight amplification factor may provide an estimate of ionic multiplet pairing extent in these ionomers.

Using capillary viscosification in these ionomers as a measure of their ionic association strengths, it was found that the addition of tertiary amine in BIIR at 130 °C for 5 min has little effect on BIIR viscosity. Considering the relatively slower reactivity of the allylic bromine in BIIR as compared with that of the benzylic bromine in BIMS, quaternization of BIIR requires much longer time, longer than the 5 min shown in this study, as demonstrated previously [16,17]. Although some of these quaternized BIMS ionomers cannot flow at 100 °C in a MPT capillary rheometer, they did exhibit flow at 150 °C. In addition, the shear thinning exponents of these ionomers at 150 °C are about the same as those of unmodified BIMS. This indicates that the flow of these ionomers is a thermally activated process. The viscosity difference between the dimethyl-alkyl-amine quaternized BIMS and that quaternized by dialkyl methyl amines is significant and becomes wider with increasing amine concentration. The apparent weaker ionic associations in dialkyl methyl amine quaternized BIMS may be attributed to the steric hindrance of the dialkyl groups on ionic multiplet pairing.

Viscosity of BIMS can be raised significantly through quaternization to facilitate its mixing with thermoplastics. Finer BIMS dispersions were obtained in a PP/BIMS blend where BIMS was quaternized with a tertiary amine as compared with that in a pure PP/BIMS blend. BIMS ionomers can also be added into BIIR innerliner compounds to enhance their green strengths. Although green strength of a BIMS innerliner compound can be significantly increased with tertiary amine addition, the corresponding rises in compound viscosity and elasticity might compromise its processability. Instead, blending in a small amount of a quaternized BIMS ionomer, less than 30 phr, into a BIIR innerliner compound was demonstrated to increase its green strength significantly without damaging processability. Additionally, the aging resistance of this BIMS ionomer containing BIIR compound was found to improve substantially.

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