J Mater Sci (2009) 44:3125–3134
DOI 10.1007/s10853-009-3415-x

Ionomeric modification of metallocene-based polyolefinic elastomers with varied pendant chain length and its influence on physico-mechanical properties

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Received: 15 September 2008 / Accepted: 17 March 2009 / Published online: 2 April 2009

Abstract A new class of ionomer was developed through sulfonation of the metallocene-based poly(ethylene–octene) elastomer, followed by its neutralization with zinc acetate. Ionomeric products were characterized through Fourier transform infrared (FT-IR) spectroscopy, small angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) studies. The effect of pendant chain length on the ionomeric modification was also studied through the variation of the comonomer. The impact of these ionomeric modifications on various physico-mechanical properties was thoroughly investigated by using differential scanning calorimetry, mechanical, dynamic mechanical, and thermogravimetric analysis. The resultant properties were correlated with structures of the modified elastomers. Ionomerisation of the base elastomers causes a significant improvement in the stress–strain, as well as the thermal properties compared to the corresponding pristine elastomer.

Introduction

Chemical modification is an effective method for altering structure and physico-mechanical properties of existing polymers [1]. In current years, much attention has been paid to ionomeric modification of polymers [2]. Polymers containing up to about 10 mol% ionic groups randomly distributed and pendant to a hydrocarbon polymer chain are usually termed as ionomers [3]. Presence of this small amount of pendant ionic groups imparts dramatic improvement in polymer properties like tensile strength, modulus, abrasion resistance, tear resistance, and impact strength through ionic interactions [4]. Because of these characteristics, the ionomers have established their applications in electrochemical, petrochemical, mechanical, and bio-technical fields [5].

Recently, the metallocene-based ‘polyethylene–octene’ and ‘polyethylene–butene’ elastomers, described as POE and PBE, respectively, developed by DuPont Dow, have received much attention due to their unique uniform distribution of comonomer content and narrow molecular weight distribution [6]. However, because of their hydrophobic nature and lack of polar sites, some applications are still restricted for these elastomers [7]. Therefore, these elastomers have been modified by polar groups through sulfonation for enhancement of their oil resistance, adhesion toward polar substrate and also for better compatibility with polar polymers, as well as fillers like silica [8]. However, loss of crystallinity plays an important role for decrease of overall strength and toughness of the sulfonated elastomers. Also thermal stability has not been too great, principally due to initial weight losses from early degradation of grafted free polar units from elastomeric macrochains [8]. Therefore, there is a scope of enhancing the property spectrum of these functionalized elastomers by modifying them as ‘ionomer’ through incorporation of ionic crosslinks via neutralization of the sulfonic acid groups of the modified elastomers. These ionomers can be excellent prospective materials for golf ball covers, membranes, food packaging, and adhesives.

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Considering all these points, in this investigation, we have described the preparation of ionomers through sulfonation of POE, followed by its neutralization with zinc acetate. The effect of pendant chain length on the ionomeric modification has also been investigated through the variation of the comonomer. Detailed physico-mechanical properties of all these zinc-ionomers are also reported in this article and correlated with the microstructure. To the best of our knowledge, this kind of extensive study has not been reported so far on these polymers.

Experimental section

Materials

Different grades of polyolefinic elastomers were obtained from DuPont Dow Chemical Corporation, Wilmington, DE. Two different grades of similar crystallinity, from poly(ethylene–octene) and poly(ethylene–butene) elastomer groups (POE_{16} and PBE_{16}, respectively in Table 1) were taken to study the effect of pendant chain length on ionomeric modification. All the elastomers were polar modified through sulfonation by solution process. Preparation and properties of these polar modified elastomers were discussed in our earlier communication [8]. These polar modified elastomers were used as "ionomer precursor" for the present investigation. The composition and designation of these precursors are reported in Table 1.

For sulfonation reaction, sulfuric acid (E. Merck, Mumbai, India) and acetic anhydride (E. Merck, Mumbai, India) were used to produce the acetyl sulfate (AS) solution (sulfonating agent) and ice and $CaCl_2 \cdot 6H_2O$ (E. Merck, Mumbai, India) were used to prepare the ice-bath. The solvents, chloroform (E. Merck, Mumbai, India) and methanol (E. Merck, Mumbai, India), all of laboratory grade, were used as received.

Zinc-acetate dihydrate (ZnAc, E. Merck, Mumbai, India) was used for neutralization of the sulfonic acid groups of the ionomer precursors.

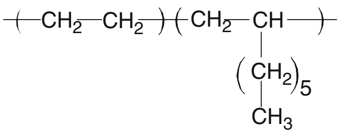
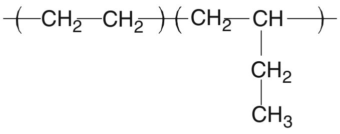
Preparation of ionomer precursor through sulfonation of polyolefinic elastomer

Optimization of reaction parameters were discussed in detail in our earlier communication [8]. However, for convenience, the optimized experimental procedure for the polar modification (sulfonation) has been described here also.

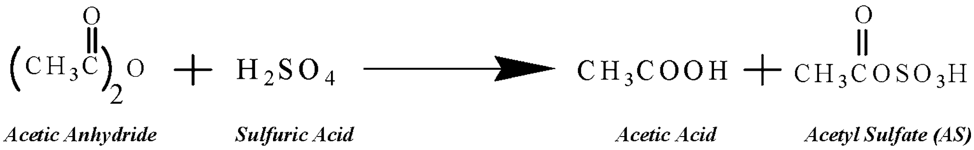
Sulfonation of polyolefinic elastomer

Five gram of 'POE_{16} or PBE_{16}' was taken in 100 mL of chloroform. After complete dissolution, the solution was heated to 50 °C and purged with nitrogen throughout the reaction time. Then 2 mL of acetyl sulfate (prepared by the reaction of concentrated H_2SO_4 and acetic anhydride in 1:4 volumetric ratio as per Scheme 1) was added and stirred for 2 h at that temperature for sulfonation reaction (as per Scheme 2). Afterward 30 mL of methanol was added to arrest the sulfonation reaction. The product was then steam stripped, washed with boiling water for 2 h, and dried

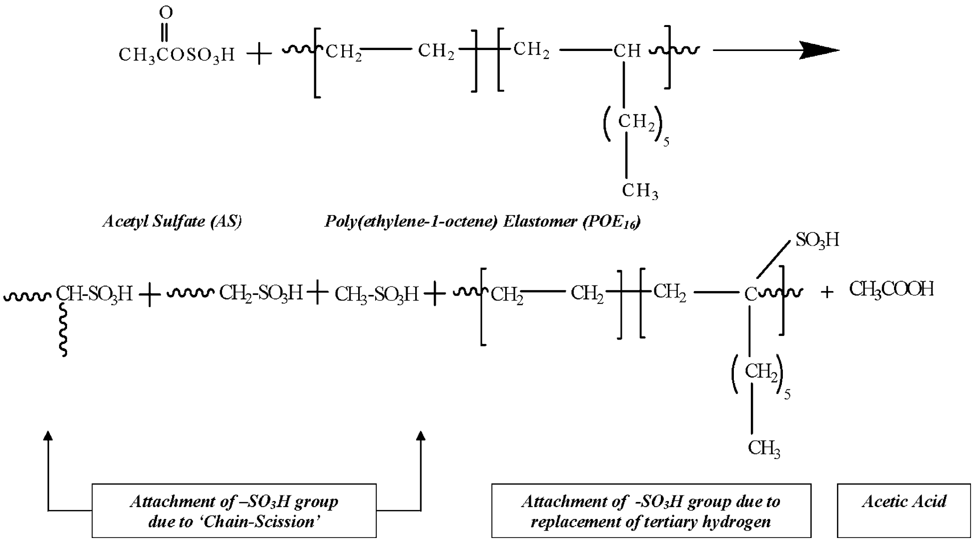
Table 1 Composition and designation of 'base elastomers', 'ionomer precursors' and 'ionomers'

Base elastomer matrices				Ionomer precursors		Ionomer	
Nature	Commercial grade	Crystallinity (%) and comonomer content (wt%)	Designation	Polar modification level	Designation	Amount of ZnAc added (wt%)	Designation of 'ionomers'
Poly(ethylene–octene) elastomer  $-(CH_2-CH_2)-(CH_2-CH(-(CH_2)_5-CH_3))-$	ENGAGE 8150	16 and 39	POE_{16}	6.50 wt% of sulfonic acid group ($-SO_3H$)	POE_{16}-S	09	POE_{16}-S–ZnAc
Poly(ethylene–butene) elastomer  $-(CH_2-CH_2)-(CH_2-CH(-CH_2-CH_3))-$	ENGAGE 7380	16 and 42	PBE_{16}	7.0 wt% of sulfonic acid group ($-SO_3H$)	PBE_{16}-S	10	PBE_{16}-S–ZnAc

Scheme 1 Preparation of acetyl sulfate (AS) solution



Scheme 2 Sulfonation reaction on POE_{16} moiety



under vacuum at 70 °C till constant weight was achieved. All the sulfonated elastomers were stored in a desiccator containing $CaCl_2$, due to their extremely hygroscopic nature.

Preparation of ionomer from the ionomer precursor

Ionomers were prepared by neutralization of the 'ionomer precursors' with ZnAc through melt process. In the melt process, 'ionomer precursors' were mixed with ZnAc in a 'CSI MAX Mixing Extruder' (Model CSI-194, S/N-296 by Custom Scientific Instruments Inc., NJ, USA). The mixing temperature was kept at 120 °C and that of the header at 125 °C. The extrudate was obtained at the aforesaid temperature with the constant addition of ZnAc for keeping the output fixed at 5 gm/10 min. The extrudate was pelletized and re-extruded for 5 times under identical condition for homogeneous neutralisation by the ZnAc. Finally, the pelletized extrudates were compression molded into a ~0.5 mm thin sheet at 125 °C for 4 min in a Moore hydraulic press at a pressure of 5 MPa and subsequently cooled down to room temperature maintaining the pressure constant.

For comparative study, ZnAc was used in such a way that for all the cases theoretical value of 'degree of neutralization (DN)' was 100% and amount of ZnAc required for that was calculated as described below [9].

Expression of acid content

A practical unit to express the acid content for polar (sulfonic acid) modified elastomer is 'equivalent acid per unit weight of polymer (eq. kg^{-1})'. Conversion of the 'degree of sulfonation' to 'equivalent acid per unit weight' of the polar modified elastomers was done as per Eq. 1

$$\chi_a = (\mathrm{DG}/100\%) \cdot \left(1000/M_g\right) \qquad (1)$$

where:

χ_a acid content (eq. kg^{-1});
DG degree of sulfonation in weight percentage (wt%)
M_g molecular weight of sulfonic acid group (81 gm mol^{-1})

As per Table 1, 'degree of sulfonation' for POE_{16}-S and PBE_{16}-S were 6.5 and 7.0 wt% of sulfonic acid group ($–SO_3H$), respectively. Therefore, as per Eq. 1, acid content (χ_a) for the said ionomer precursors were 0.8 and 0.9 eq. kg^{-1}, respectively.

Degree of neutralisation (DN)

The degree of neutralization (DN) is defined as the fraction of the acid groups that is converted into the metal sulfonate. Thus, the degree of neutralization is the actual amount of neutralized sulfonic acid groups divided by the total amount of available sulfonic acid groups for neutralization. The degree of neutralization (DN) was calculated using Eq. 2

$$DN = \left[(v \cdot m_{ZnAc} \cdot 1000)/\left(M_{ZnAc} \cdot \chi_a \cdot m_{ip}\right)\right] \cdot 100\% \quad (2)$$

where:

DN degree of neutralization (%);
V valency of metal ion (in the case of zinc, v equals to 2);
m_{ZnAc} mass of zinc-acetate dihydrate required (gm);
M_{ZnAc} molecular weight of zinc-acetate dihydrate (219.50 gm·mol^{-1});
χ_{a} acid content (eq. kg^{-1});
m_{ip} mass of ionomer precursor used (gm);

Therefore, as per Eq. 2, for 100% degree of neutralization (DN) of POE$_{16}$-S and PBE$_{16}$-S, 9 and 10 wt% of ZnAc were added, respectively.

Characterization

Fourier transform infrared (FT-IR) spectroscopic studies

FT-IR studies were carried out in dispersive mode on thin film samples (~100 μm) using Perkin Elmer FT-IR spectrophotometer (model spectrum RX I), within a range of 400–4400 cm^{-1} using a resolution of 4 cm^{-1}. An average of 16 scans has been reported for each sample.

Small angle X-ray scattering (SAXS) studies

SAXS was conducted using Rigaku RU-H3R rotating anode generator producing CuK$_{\alpha}$ radiation. ($\lambda = 0.154$ nm). The data were collected using a two dimensional GADDS/HI-STAR area detector manufactured by Siemens, consisting of an array of 512 × 512 wires. All experiments were conducted at 25 °C in an evacuated flight path at a sample to detector distance of 63.8 cm. 'q' has been calculated using Eq. 3, where 2θ is the scattering angle and q is the scattering vector.

$$q = (4\pi \ \mathrm{Sin}\theta)/\lambda \quad (3)$$

Transmission electron microscopy (TEM) studies

Sample preparation included cryo-microtomy at −130 °C, and ambient sectioning on the sample faces. The images were acquired with the Gatan Multiscan CCD on the JEOL 2000fx TEM at 200 kV at a magnification of 320,000×.

Differential scanning calorimetric (DSC) analysis

DSC studies were carried out on a TA instrument (model Q100 V 8.1), at a heating rate of 10 °C/min under nitrogen atmosphere in the temperature range of –100 to 100 °C. The second heating scans of all the samples were reported to nullify the thermal history.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical spectra of the samples were obtained by using a DMTA machine [TA instruments (model 2980 V1.7B)] in the temperature range of –100 to +100 °C. The specimens were analyzed in tension mode at a constant frequency of 1 Hz, using 0.01% strain at a heating rate of 2 °C/min.

Studies on mechanical properties

Tensile stress–strain analysis and tension set at 100% extension were performed as per the ASTM D 412 method in a Universal Testing Machine (Hounsfield-H10KS) at a crosshead speed of 500 mm/min at 25 ± 2 °C. An average of three test results was reported for analysis.

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analysis

The TGA analysis were carried out on a TA instruments (model Q50), at a heating rate of 10 °C/min under nitrogen atmosphere from room temperature to 600 °C. Around 5 mg of the material was used for the TGA study.

Results and discussion

Characterization of the synthesised 'ionomers'

Characterization results of sulfonated ionomer (POE$_{16}$-S–ZnAc) based on POE$_{16}$ have been discussed in this part for comprehensive representation of the whole findings.

FT-IR spectroscopic studies

Figure 1 represents the FT-IR spectra of virgin POE$_{16}$, POE$_{16}$-S, and POE$_{16}$-S–ZnAc, after normalizing against the characteristic peak of virgin POE at 720 cm^{-1}. In this case, beside all the characteristic peaks of virgin POE$_{16}$, four additional peaks are observed at 1350, 1200, 1050, and 630–570 cm^{-1} in the POE$_{16}$-S; these are owing to asymmetric SO$_2$ and symmetric SO$_2$ stretching, S–O stretching vibrations of the alkyl sulfonic acid, as well as stretching vibration of the C–SO$_3$H bond, respectively [10]. After neutralization of POE$_{16}$-S with ZnAc, three additional peaks at 1725, 952, and 731 cm^{-1}, respectively in the POE$_{16}$-S–ZnAc are observed. These are due to liberation of acetic acid upon reaction of the metal acetate with the

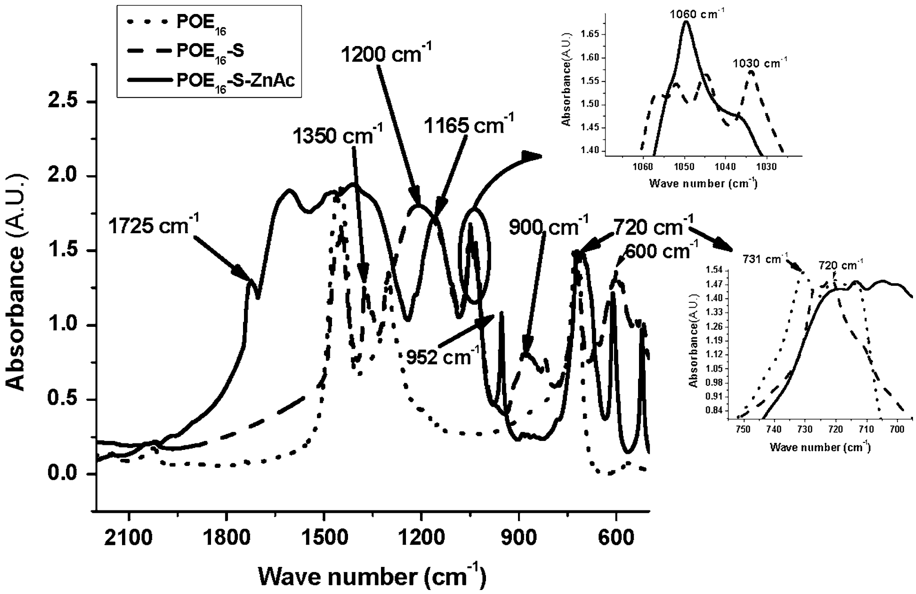


Fig. 1 Comparative FT-IR spectra of unmodified POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples after normalizing against the peak at 720 cm^{-1}

sulfonic acid group, symmetrical attachment of Zn^{2+} to the sulfonate ion and ionic aggregation due to the sulfonate cation, respectively [11]. Moreover, shifting of 1350 and 1200 cm^{-1} peaks of POE_{16}-S to 1165 and 1030 cm^{-1}, respectively in POE_{16}-S–ZnAc sample, further indicates interconversion of asymmetric and symmetric SO_2 stretching vibrations of the alkyl sulfonic acid moieties in POE_{16}-S into asymmetric and symmetric SO_3 stretching vibration of the sulfonic acid salt ($\mathrm{SO}_3^{-}\ \mathrm{M}^{+}$) in POE_{16}-S–ZnAc [12]. These additional informations in respect of shifting, as well as generation of new peaks in POE_{16}-S–ZnAc confirm the formation of sulfonated ionomer of POE_{16}. Similar results have been found for PBE_{16} also. Reaction yields, measured from the amount of conversion of alkyl sulfonic acid moieties (–$\mathrm{SO}_3\mathrm{H}$ group) into sulfonic acid salt (–$\mathrm{SO}_3\mathrm{M}$ group) and calculated from the ratio of normalized peak area at 1165 cm^{-1} by normalized peak area at 1350 cm^{-1} are found 86.1 and 87.2 for POE_{16} and PBE_{16}, respectively.

SAXS studies

In order to elucidate the morphological structure of the ionomers, SAXS measurements have been carried out at room temperature (25 °C). Choice of room temperature probably ensures retainment of crystalline, as well as ionic arrays in the ionomers. The representative small angle scattered intensity plots of POE_{16}-S and POE_{16}-S–ZnAc are displayed in Fig. 2. All the scattering intensities have been measured as a function of the magnitude of the scattering vector (q). The ionomer precursor (POE_{16}-S) does not exhibit any characteristic peak in the scattering profile due to apparent homogeneous structure, whereas the sulfonated ionomer (POE_{16}-S–ZnAc) has shown broad scattering peak at $q = 0.07\ \mathring{A}^{-1}$. This is probably due to microphase separation in the ionomer (POE_{16}-S–ZnAc) caused by ionic domain formation. This scattering peak is often named as 'ionic peak' in the literatures [13].

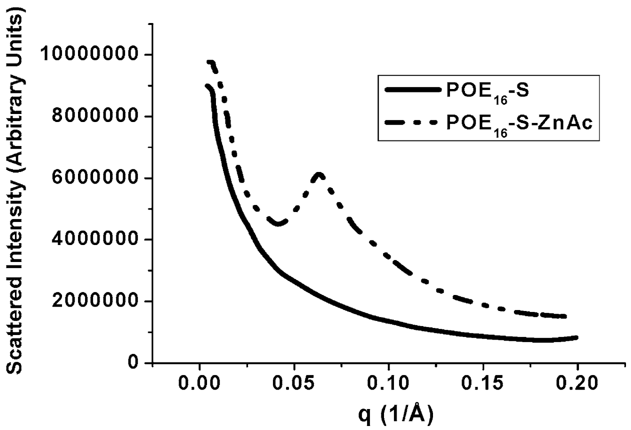


Fig. 2 Comparative SAXS plots for POE_{16}-S and POE_{16}-S–ZnAc samples

TEM studies

Morphological features of representative ionomer (POE_{16}-S–ZnAc) and its respective ionomer precursor (POE_{16}-S) are observed via transmission electron micrograph and shown in Fig. 3a and b, respectively. Formation of ionic clusters is clearly visible in POE_{16}-S–ZnAc sample as spherical dark domains (Fig. 3a), which is absent in case of POE_{16}-S (Fig. 3b). Ionic clusters are naturally more dense than rest of the unclustered and unassociated elastomer domains and are therefore as dark features in the TEM photograph (Fig. 3a). The average diameter of the domains as calculated from this photograph lies between of 4–8 nm.

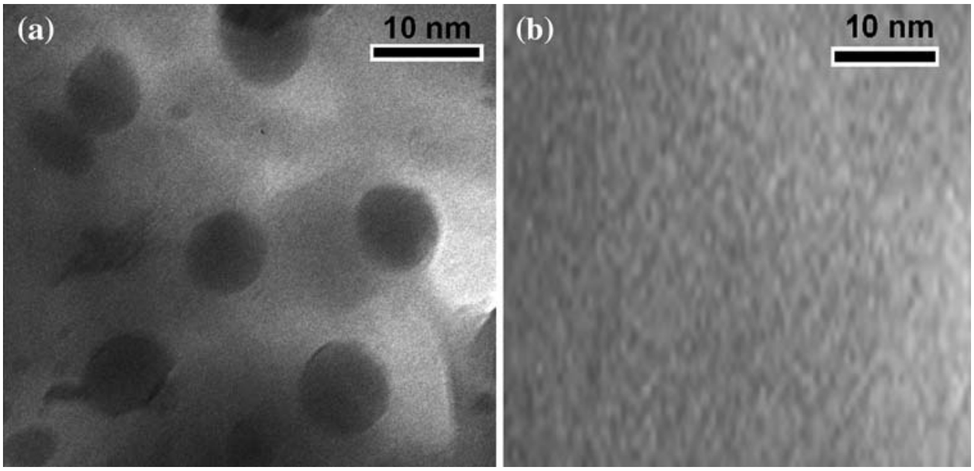
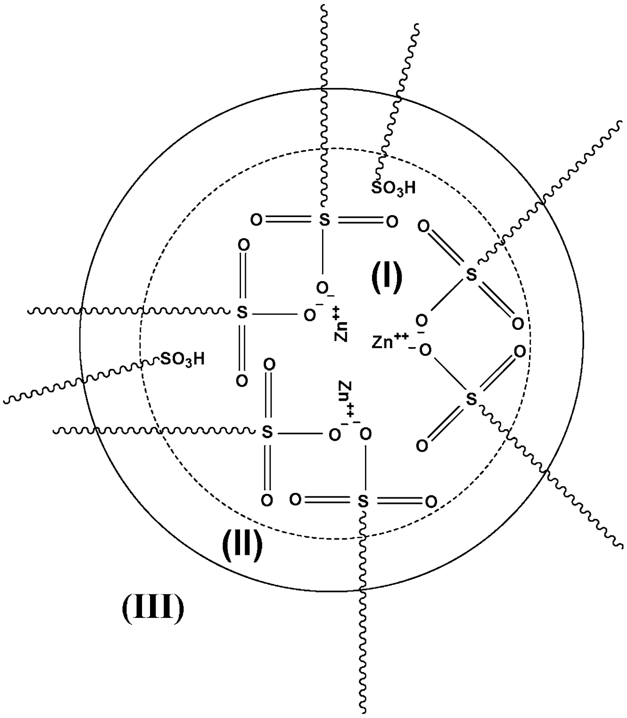


Fig. 3 **a** TEM micrograph of POE_{16}-S–ZnAc sample. **b** TEM micrograph of POE_{16}-S sample

The morphology of ionic clusters as spherical dark domains in Fig. 3a (for POE_{16}-S–ZnAc sample) may be explained with the help of Yarusso and Cooper's model [14] through Scheme 3. It can be described by a dense core of ionic groups (region I, in Scheme 3) surrounded by a layer of restricted mobility (region II, in Scheme 3). This layer of restricted mobility is a result of the polymer chains attached to the ionic groups in the aggregates as depicted in Scheme 3. The aggregates are dispersed in a matrix of polymer chains (region III, in Scheme 3).



Scheme 3 Model of ionomer morphology, showing the restricted mobility layer (region II) surrounding the core (region I) of high electron density in the ionic aggregates dispersed in the polymer matrix (region III)

Effect of ionomeric modifications on physico-mechanical properties of the polyolefinic elastomers

Physico-mechanical properties of the sulfonated ionomers are discussed in this section of the paper. Results on sulfonated ionomer system based on POE_{16} (comprising of virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples) are all plotted and displayed in this section, whereas data on other ionomer system (based on PBE_{16}) are compiled and reproduced in a tabular form for convenience.

Effects on thermal transition behavior

DSC analysis DSC second heating scans of sulfonated ionomer system based on POE_{16} (comprising of virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples) are stacked in Fig. 4. T_g, T_m, and ΔH values (obtained from the DSC second heating scans) of all sulfonated ionomers along

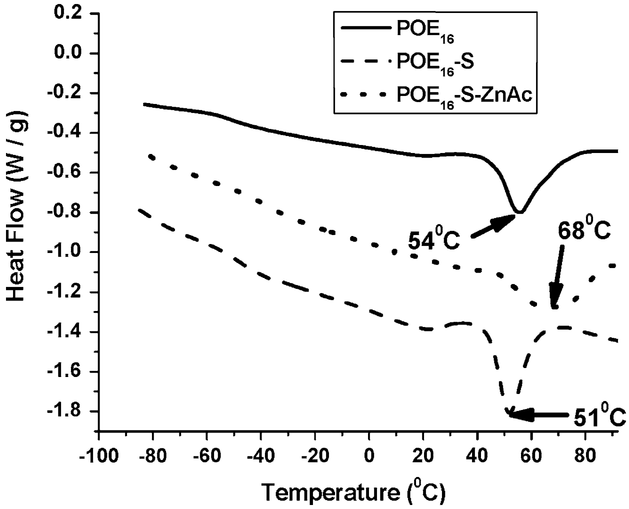


Fig. 4 DSC second heating scans for the virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples

Table 2 Comparison in different properties (DSC, DMTA, TGA, and DTG) of virgin and modified polyolefinic elastomers

Samples	DSC			DMTA					TGA	DTG	
	T_g (°C)	T_m (°C)	ΔH (mJ)	Storage modulus E' at −60 °C (MPa)	Storage modulus E' at −20 °C (MPa)	T_g (°C)	tanδ at T_g	T_{ic} (°C)	T_i (°C)	T_{max} (°C)	R_D (%/°C)
POE_{16}	−53	54	45	1300	50	−41	.35	a	437	461	2.7
POE_{16}-S	−48	51	31	310	25	−32	.37	a	426	481	2.4
POE_{16}-S–ZnAc	−42	68	28	1700	95	−29	.34	46	449	494	2.1
PBE_{16}	−59	45	45	640	25	−33	.28	a	422	439	3.8
PBE_{16}-S	−49	37	30	180	18	−21	.29	a	406	461	3.5
PBE_{16}-S–ZnAc	−41	57	26	1550	60	−16	.13	46	451	497	3.1

T_g glass transition temperature, T_m melting temperature, ΔH heat of fusion, E' storage modulus, *tanδ* loss tangent, T_{ic} ionic transition temperature, T_i temperature corresponding to commencement of rapid thermal degradation, T_{max} temperature corresponding to maximum thermal degradation, R_D rate of degradation

with their respective ionomer precursors and virgin elastomers are reported in Table 2. All the ionomers show shift in the T_g toward higher side. This is possibly explained considering fraction of elastomer domains arrested in ionic clusters via strong secondary interaction (ionic crosslinks), thereby showing delayed thermal response. T_m increases on ionomeric modification in all the cases toward higher temperature side due to formation of ionic crosslinks. The metal ions act as heat sinks, whereas the ionic crosslinks require additional energy to disintegrate and these increase the energy intake level required for melting. The ΔH decreases on ionomeric modification in all the cases resulting in further reduction of crystallinity. This may be due to introduction of ionic domains as defects within the elastomer matrices, hindering the chain orientation during cooling and the crystallinity is reduced further. In comparison to the respective ionomer precursors, the amount of change in T_g and T_m are more in the case of PBE_{16}-S–ZnAc with respect to the POE_{16}-S–ZnAc system, because ionomeric aggregation is stronger due to the higher level of sulfonation (Table 1) and less steric hindrance in comparison to the POE_{16}-S–ZnAc system. The pendent side chains in PBE_{16} are of shorter length than that in POE_{16} as shown in Table 1. Smaller pendant side groups in PBE_{16}-based ionomer precursor (PBE_{16}-S) offer less steric hindrance compared to POE_{16}-based ionomer precursor (POE_{16}-S), resulting better ionic aggregation.

DMTA Figures 5 and 6 demonstrate the variation in storage modulus (E') and loss tangent (tanδ) values against temperature, respectively for the sulfonated ionomer system based on POE_{16} (comprising of virgin POE_{16}, POE_{16}-S, and

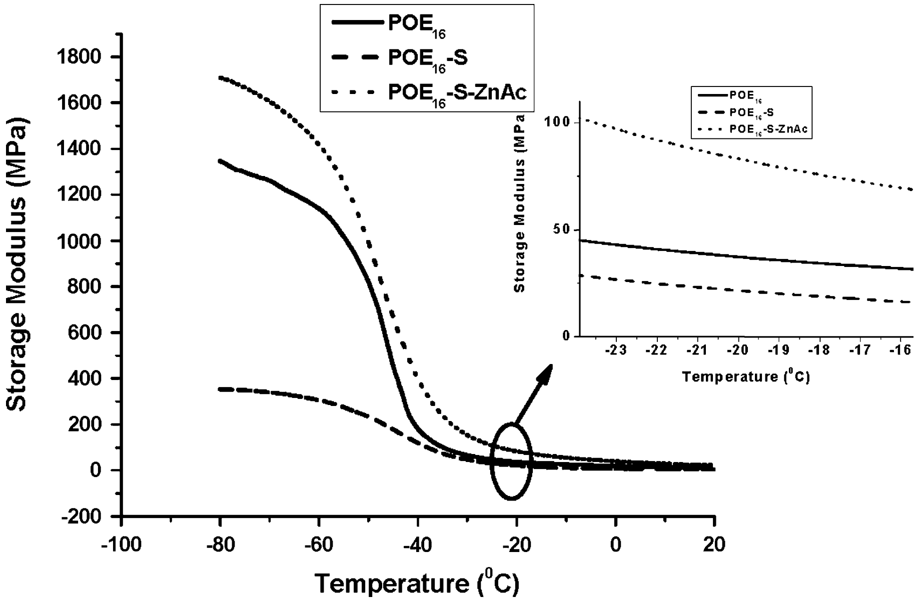


Fig. 5 Plots of dynamic storage modulus against temperature for the virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples

POE_{16}-S–ZnAc samples). Table 2 provides the dynamic modulus (E') [below T_g (−60 °C, glassy state) and above T_g (−20 °C, rubbery state)], Tanδ_{max} and T_g values obtained from dynamic mode for all the virgin elastomers, ionomer precursors, and ionomers.

As compared to ionomer precursor, the respective ionomer in all the systems shows a broad rubbery plateau, with higher storage modulus due to physical crosslinking arising out of the ionic aggregates. Among the sulfonated ionomers, ionomers based on PBE_{16} (PBE_{16}-S–ZnAc, respectively) show greater change in storage modulus compared to their respective ionomer precursor than the POE_{16} based one (POE_{16}-S–ZnAc). This is again due to the stronger ionic interactions in the case of butene based ionomer, arising out of the higher level of sulfonation requiring higher level of zinc acetate for neutralization, which results in higher crosslinking density (proportional to modulus) and also less steric hindrance (Tables 1 and 2).

The virgin elastomers and ionomer precursors show one loss tangent peak in the low temperature region (Fig. 6), which is ascribed to the glass–rubber transition (T_g values obtained from the dynamic mode). In the case of all the ionomers, formation of ionic crosslinks result in shifting of the T_g (tanδ_{max}) toward higher side (similar to the observation made in DSC studies) and a decrease in the low temperature peak height (that is magnitude of tanδ at T_g) (Table 2). This is ascribed to restriction in chain mobility imposed by the ionic crosslinks within these systems. Furthermore, the ionomers show a 'clear' high temperature transition, also known as 'ionic transition' (T_{ic}) [15] which is attributed to the presence of a second phase arising out of the immobile segments or the restricted mobility regions adjacent to the ionic domains (Fig. 6 and Table 2).

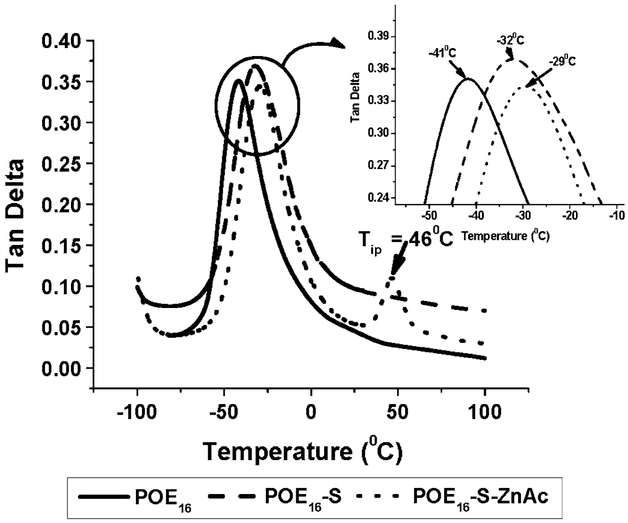


Fig. 6 Tanδ versus temperature plots for the virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples

Effects on thermal stability—TGA and DTG analysis

Figures 7 and 8 show the representative TGA and DTG plots for the sulfonated ionomer system based on POE_{16} (comprising of virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples). The on-set temperature (i.e., temperature corresponding to commencement of rapid thermal degradation, Ti obtained from TGA plots), the maximum

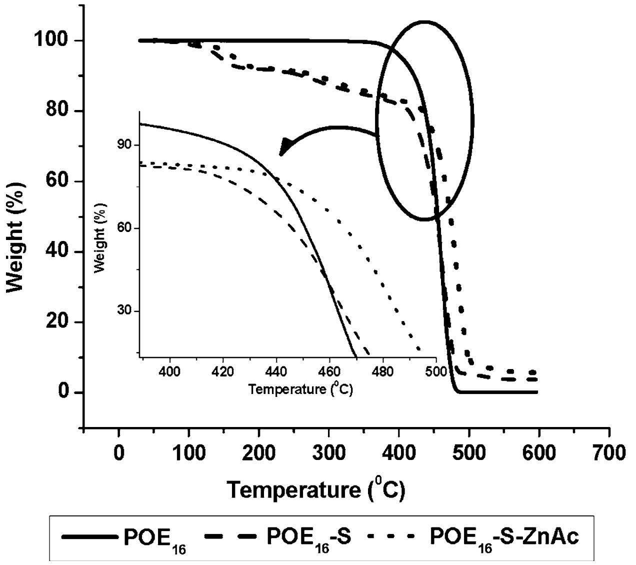


Fig. 7 TGA plots of the virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples

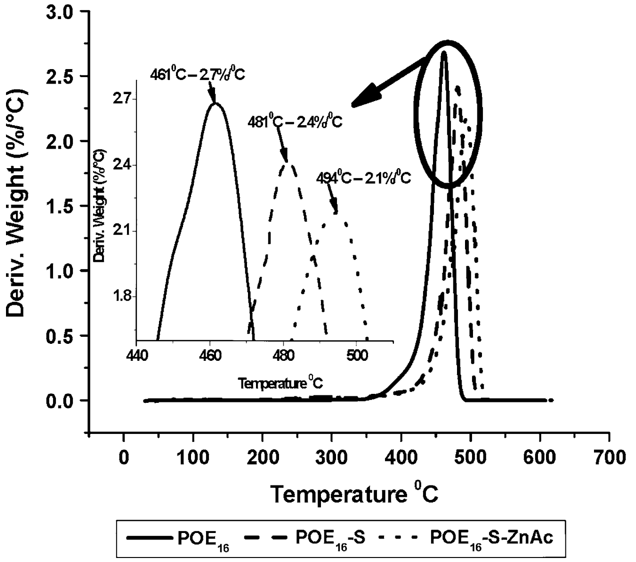


Fig. 8 DTG plots of the virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples

degradation temperature (i.e., temperature corresponding to maximum thermal degradation, T_{max} obtained from the DTG plots) and maximum rate of degradation (R_D, obtained from the DTG plots)) for all the virgin elastomers, ionomer precursors and ionomers are summarized in Table 2. Incorporation of metallic ions induces formation of physical crosslinking and networks with consequent improvement in T_i for all the 'ionomers' as compared to their respective 'ionomer precursor'. Presence of metal ions (Zn^{++} ions in this case) also helps as it takes up the good fraction of the imposed heat energy and thereby resists degradation of the weak, elastomer matrix.

Since metal ions act as heat sinks and ionic crosslinks require additional energy to disintegrate, ionomers show tremendous resistance against degradation which finally leads to the improvement in 'degradation rate' as well as steady positive shift of the T_{max} for all the 'ionomers' over respective 'ionomer precursor' (Table 2). Not only that, amount of non-degraded material (residue) is also more in the case of 'ionomers' from that of their respective 'ionomer precursor' (Fig. 7). Here also, ionomers based on PBE_{16} show better thermal stability compared to their respective 'ionomer precursor' than the POE_{16} based one due to the same reason as discussed earlier (Table 2).

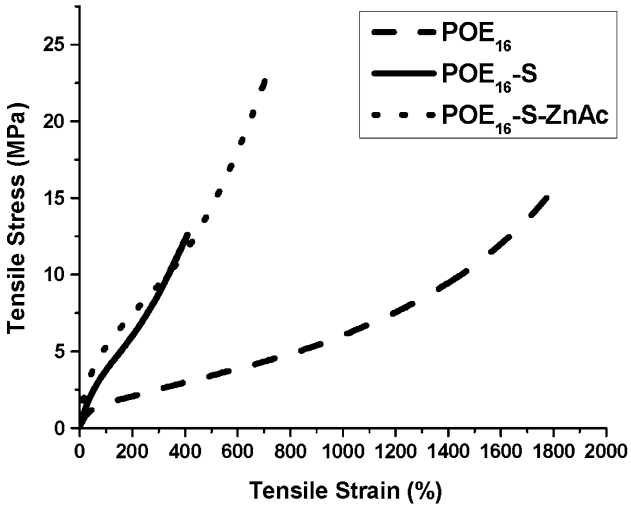


Fig. 9 Comparative tensile stress–strain plots of the virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples

Studies on mechanical properties

The stress–strain behavior of the POE_{16} based sulfonated ionomer system (comprising of virgin POE_{16}, POE_{16}-S, and POE_{16}-S–ZnAc samples) is shown in Fig. 9. Mechanical properties (tensile modulus at 100, 200, and 300%, tensile strength, elongation at break (%), and tension set) for all the virgin elastomers, ionomer precursors, and ionomers are registered in Table 3. The ionomers show higher modulus, tensile strength, elongation at break, and lower tension set as compared to their respective ionomer precursor. The enhanced mechanical properties for the ionomers are due to the formation of physical crosslinks through ionic associations as discussed earlier. Although there is further reduction in crystallinity due to ionomeric modification, ionic crosslinks between newly formed ionic domains in ionomers compensate the loss in tensile strength of their respective precursor (due to sulfonation) and also show even better mechanical properties than its base elastomer (Table 3).

Conclusions

A new class of ionomers has been synthesized via sulfonation onto the metallocene-based POE, as well as PBE followed by their neutralization with zinc acetate. The nanometric ionic domains form strong secondary crosslinks and result in a significant improvement in mechanical, as well as thermal properties compared to the corresponding virgin, as well as sulfonated elastomers. Ionomer based on PBE_{16} shows better thermo-mechanical properties compared to their respective ionomer precursor and the POE_{16} based one.

Table 3 Comparison of mechanical properties of virgin and modified polyolefinic elastomers

Samples	Mechanical properties					
	Tensile modulus (MPa) at elongation of			Tensile strength (MPa)	Elongation at break %	Tension set %
	100%	200%	300%			
POE_{16}	1.6 ± 0.1	2.0 ± 0.2	2.5 ± 0.1	15.5 ± 0.3	1796 ± 16	13.7 ± 0.1
POE_{16}-S	3.8 ± 0.3	6.0 ± 0.1	8.8 ± 0.3	12.6 ± 0.4	410 ± 08	15.6 ± 0.3
POE_{16}-S–ZnAc	5.3 ± 0.2	7.4 ± 0.2	9.3 ± 0.1	23.3 ± 0.3	718 ± 11	09.3 ± 0.1
PBE_{16}	2.2 ± 0.4	3.0 ± 0.3	3.8 ± 0.2	17.0 ± 0.4	972 ± 13	12.9 ± 0.1
PBE_{16}-S	4.6 ± 0.2	7.7 ± 0.2	9.7 ± 0.1	14.1 ± 0.3	230 ± 11	15.2 ± 0.2
PBE_{16}-S–ZnAc	7.3 ± 0.3	9.8 ± 0.2	11.1 ± 0.1	28.1 ± 0.3	540 ± 11	06.8 ± 0.1

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