Ionomeric Modification of a Metallocene-Based Polyolefinic Elastomer and Its Influence on the Physicomechanical Properties: Effects of the Crystallinity and Pendent Chain Length

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ABSTRACT: A new class of ionomer was developed through the grafting of acrylic acid onto a metallocene-based poly(ethylene octene) elastomer, followed by its neutralization with zinc acetate. The ionomeric product was characterized through Fourier transform infrared spectroscopy, small-angle X-ray scattering, and transmission electron microscopy studies. The effect of the crystallinity and pendent chain length on the ionomeric modification was also studied through the variation of the level and nature of comonomer, respectively. The impact of these ionomeric modifications on various physicomechanical properties was thoroughly investigated with differential scanning calorimetry and mechanical, dynamic mechanical, and thermogravimetric analysis, and the resulting properties were correlated with the structure of the modified elastomers. The ionomerization of the base elastomers caused a significant improvement in the mechanical and thermal properties compared to the corresponding pristine elastomer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3906–3914, 2009

Key words: elastomers; graft copolymers; ionomers; modification; polyolefins

INTRODUCTION

Chemical modification is a useful technique for altering the structure and physicomechanical properties of existing polymers.[1] In recent years, much attention has been given to the ionomeric modification of the polymers.[2] Polymers that contain up to about 10 mol % ionic groups randomly distributed and pendent to a hydrocarbon polymer chain are usually known as *ionomers*.[3] The introduction of a small amount of these pendent ionic groups causes a dramatic improvement in the polymer properties, including the tensile strength, modulus, abrasion resistance, tear resistance, and impact strength, through ionic interactions.[4] These features have led to an exploration of a variety of applications for ionomers, ranging through electrochemical, petrochemical, mechanical, and biotechnical venues.[5]

Recently, metallocene-based poly(ethylene octene) (POE) and poly(ethylene butene) (PBE) elastomers, developed by DuPont Dow, have received much attention because of several advantages they have over other polyolefins, which arise from their unique uniform distribution of comonomer content and narrow molecular weight distribution.[6] However, some applications are still restricted for these elastomers, mainly because of their nonpolar nature.[7] Therefore, these elastomers have been modified by polar groups through the grafting of acrylic acid (AA) for the enhancement of their oil resistance and adhesion toward polar substrates and also for better compatibility with polar polymers and fillers such as silica.[8] However, the loss of crystallinity in POE and PBE due to grafting, especially in high-crystallinity grades, displays a reduction in the overall strength and toughness of the modified elastomers.[9] Not only this, their thermal stability has not been too great, principally because of the initial weight losses from the early degradation of grafted free polar units from elastomeric macrochains. Therefore, there is a scope of enhancing the property spectrum of these functionalized elastomers by their modification as ionomers through the incorporation of ionic crosslinks via the neutralization of the carboxylic acid groups of the modified elastomers. These ionomers can have different potential applications, such as golf ball covers, membranes, food packaging materials, and adhesives.

Considering all these points, in this investigation, we examined the preparation of ionomers through the grafting of AA onto low-crystalline-grade POE, followed by its neutralization with zinc acetate. The variation of the level and nature of the comonomer (i.e., the effect of crystallinity and pendent chain

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Base elastomer matrices				Ionomer precursors		Ionomers	
Nature	Commercial grade	Crystallinity (%)/ comonomer content (wt %)	Designation	Polar modification level	Designation	Amount of ZnAc added (wt %)	Designation
POE elastomer	Engage 8150	16/39	POE_{16}	6.2 wt % AA grafting	POE_{16}–AA	9.0	POE_{16}–AA–ZnAc
	Engage 8440	27/23	POE_{27}	7.0 wt % AA grafting	POE_{27}–AA	11.0	POE_{27}–AA–ZnAc
PBE elastomer	Engage 7380	16/42	PBE_{16}	6.5 wt % AA grafting	PBE_{16}–AA	10.0	PBE_{16}–AA–ZnAc

length, respectively) on the ionomeric modification was also investigated. The detailed physicomechanical properties of all of 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 for these polymers.

EXPERIMENTAL

Materials

Different grades of polyolefin elastomers were obtained from DuPont Dow Chemical Corp. (now Dow Chemical Co., Wilmington, DE). Two different grades of lower and higher crystallinities from the POE elastomer group (POE_{16} and POE_{27}, respectively, in Table I) were taken to study the effect of crystallinity on the ionomeric modification. To study the effect of pendent chain length, one more grade with a similar crystallinity to POE_{16} was taken from the PBE elastomer group (PBE_{16}). All of the elastomers were polar-modified through the grafting of AA by a solution process. The preparation and properties of these polar-modified elastomers were discussed in our earlier communications.[8,9] These polar-modified elastomers were used as ionomer precursors for this investigation. The composition and designation of these precursors are reported in Table I. For AA grafting, AA (density = 1050 kg/m³, Aldrich, St. Louis, MO) was used after the removal of the inhibitors by vacuum distillation, and benzoyl peroxide (BPO; 98% purity, Aldrich) was used as the free-radical initiator. The solvent, laboratory-grade toluene (E. Merck, Mumbai, India), was used as received. Zinc acetate dihydrate (ZnAc; E. Merck) was used for the neutralization of the carboxylic acid groups of the ionomer precursors.

Preparation of the ionomers

Preparation of the ionomer precursors

The optimization of the reaction parameters was discussed in detail in our earlier communications.[8,9]

However, for convenience, the optimized experimental procedure for the polar modification through grafting of AA is described here also.

Grafting of AA onto the polyolefinic elastomer. POE or PBE (5 g) was placed in 100 mL of toluene and stirred for 1 h at room temperature. Once the mixture was homogenized, the solution was heated to 70°C and purged with nitrogen throughout the reaction time. Then, 10 wt % of AA was added dropwise to the reaction mixture. After AA was added, when the mixture was again homogenized, 0.3 wt % of BPO was added as an initiator to the reaction mixture, and the mixture was stirred for 6 h at that temperature. Finally, the samples were collected and dried *in vacuo* for 48 h at 40°C for complete removal of the solvent.

Grafting percentage measurements. The solution-grafted samples were taken in a filter paper and extracted in a Soxhlet apparatus for 24 h with water as the extracting medium for complete removal of unreacted AA and any homopolymer of AA formed during the reaction. After the extraction, the samples within the filter paper were vacuum-dried at 70°C to a constant weight. The extent of grafting was calculated from the weight gain of the samples with the following equation:

$$\text{Grafting } (\%) = [(W_g - W_0)/W_0] \times 100 \qquad (1)$$

where W_g is the weight of the POE or PBE after grafting and W_0 is the weight of the POE or PBE before grafting.

The optimum levels of grafting for AA-grafted POE_{16} (POE_{16}–AA), AA-grafted POE_{27} (POE_{27}–AA), and AA-grafted PBE_{16} (PBE_{16}–AA) were found to be 6.2, 7.0, and 6.5 wt % AA, respectively (Table I).

Preparation of the ionomers from the ionomer precursors (POE_{16}–AA, POE_{27}–AA, and PBE_{16}–AA)

The ionomers were prepared by the neutralization of the ionomer precursors with ZnAc through melt process. In the melt process, the ionomer precursors were mixed with ZnAc in a CSI MAX mixing extruder (model CSI-194, S/N-296, Custom Scientific

Instruments, Inc., Whippany, NJ). The mixing temperature was kept at 120°C, and that of the header was kept at 125°C. The extrudate was obtained at the aforesaid temperature with the constant addition of ZnAc to keep the output fixed at 5 g/10 min. The extrudate was pelletized and re-extruded five times under identical conditions for homogeneous neutralization by the ZnAc. Finally, the pelletized extrudates were compression-molded into a sheet about 0.5 mm thick at 125°C for 4 min in a Moore hydraulic press at a pressure of 5 MPa and subsequently cooled to room temperature with the pressure constant maintained.

For comparative study, ZnAc was used in such a way that, for all the cases, the theoretical value of the degree of neutralization (DN) was 100%, and the amount of ZnAc required for that was calculated as described later.[10]

Expression of the acid content [χ_a (equiv/kg)]. A practical unit to express χ_a for a polar (acid)-modified elastomer is equivalents of acid per weight unit of the polymer (equiv/kg). The conversion of the degree of AA grafting [DG (wt %)] to equivalent acid per weight unit of the polar modified elastomers was done as follows:

$$\chi_a = (DG/100\%) \times (1000/M_g) \qquad (2)$$

where M_g is the molecular weight of the grafted AA (72 g/mol). As per Table I, the DG values for POE_{16}–AA, POE_{27}–AA, and PBE_{16}–AA were 6.2, 7.0, and 6.5 wt % AA, respectively. Therefore, as per eq. (1), the χ_a values for the said ionomer precursors were 0.86, 0.97, and 0.90 equiv/kg, respectively.

DN. DN is defined as the fraction of acid groups that is converted into the metal carboxylate. Thus, DN is the actual amount of neutralized acid groups divided by the total amount of available acid groups for neutralization. DN was calculated as follows:

$$DN = \frac{(v \times m_{ZnAc} \times 1000)}{(M_{ZnAc} \times \chi_a \times m_{ip})} \times 100\% \qquad (3)$$

where v is the valency of the metal ion (in the case of zinc, $v = 2$), m_{ZnAc} is the mass of ZnAc required (g), M_{ZnAc} is the molecular weight of ZnAc (219.50 g/mol), and m_{ip} is the mass of the ionomer precursor (g). Therefore, as per eq. (2), for the neutralization of POE_{16}–AA, POE_{27}–AA, and PBE_{16}–AA, 9, 11, and 10 wt %, respectively, of ZnAc were added.

Characterization

Fourier transform infrared (FTIR) spectroscopic studies

FTIR studies were carried out in dispersive mode on the thin-film samples ($\sim$ 100 µm) with a PerkinElmer FTIR spectrophotometer (model spectrum RX I,

PerkinElmer, Waltham, MA), within the range 400–4400 cm^{-1} with a resolution of 4 cm^{-1}. An average of 16 scans is reported for each sample.

Small-angle X-ray scattering (SAXS) studies

SAXS was conducted with a Rigaku RU-H3R rotating-anode generator (Rijaku Corporation, Tokyo, Japan) producing Cu Kα radiation (wavelength = 0.154 nm). The data were collected with a two-dimensional GADDS/Hi-Star area detector (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. The scattering vector ($\mathbf{q}$) was calculated with eq. (4):

$$\mathbf{q} = (4\pi \sin\theta)/\lambda \qquad (4)$$

where λ is the wavelength and 2θ is the scattering angle.

Transmission electron microscopy (TEM) studies

Sample preparation included cryomicrotomy at −130°C and ambient sectioning on the sample faces. The images were acquired with a Gatan Multiscan charged coupling device on a JEOL 2000fx transmission electron microscope (JEOL Ltd., Tokyo, Japan) at 200 kV with a magnification of 320,000×.

Physicomechanical properties

Observation of the thermal transition with differential scanning calorimetry (DSC) analysis

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

Dynamic mechanical properties

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

Thermal stability

The thermal stability was studied through thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) analysis, which were carried out on a TA Instruments model Q50 at a heating rate of 10°C/min under a nitrogen atmosphere from room
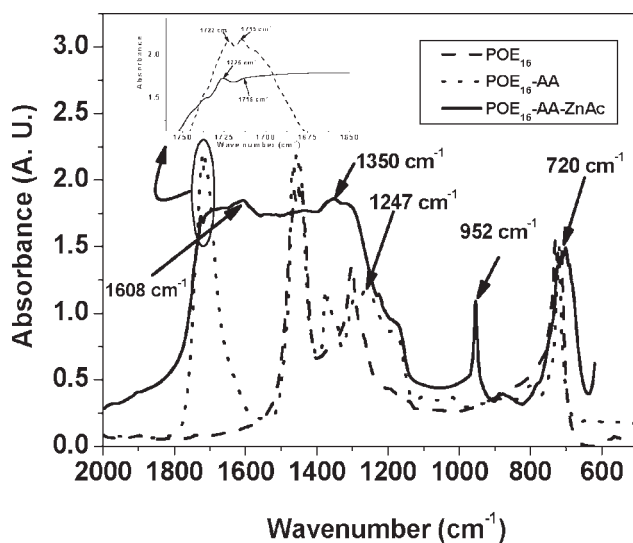
Figure 1 Comparative FTIR spectra of unmodified POE_{16}, POE_{16}–AA, and POE_{16}–AA–ZnAc samples after normalization against the peak at 720 cm^{-1}.

temperature to 600°C. Around 5 mg of the material was used for the TGA and DTG study.

Mechanical properties

The tensile stress–strain analysis and tension set at 100% extension were performed as per ASTM D 412 in a Hounsfield H10KS universal testing machine (Horsham, PA) at a crosshead speed of 500 mm/min at 25 ± 2°C. An average of three test results was reported for analysis.

RESULTS AND DISCUSSION

Characterization of the synthesized ionomers

FTIR spectroscopic studies

Figure 1 represents the FTIR spectra of the unmodified POE_{16}, POE_{16}–AA, and POE_{16}–AA–ZnAc after normalization against the characteristic peak of virgin POE_{16} at 720 cm^{-1}. In addition to all of the characteristic peaks of the virgin POE_{16}, there were two additional peaks observed at 1710 and 1247 cm^{-1} in POE_{16}–AA because of C=O and C—O stretching vibrations, respectively, for the grafted AA moieties.[8,9] These two peaks were also present after the neutralization of POE_{16}–AA with ZnAc (Fig. 1). This may have due to liberation of acetic acid in the reaction medium upon the chemical reaction between metal acetate and carboxylic acid.[11] Nevertheless, there were three more peaks in POE_{16}–AA–ZnAc after the neutralization of POE_{16}–AA with ZnAc at 1608, 1350, and 952 cm^{-1} (Fig. 1) due to asymmetric and symmetric —CO_2^- stretching vibrations of carboxylated acid salt and symmetrical

attachment of Zn^{2+} to the carboxylate ion, respectively.[12] The presence of these three additional peaks in the POE_{16}–AA–ZnAc sample confirmed the formation of ionomer after the neutralization of POE_{16}–AA with ZnAc. Similar results were found for POE_{27} and PBE_{16}.

SAXS studies

To elucidate the morphological structure of the ionomers, SAXS measurements were carried out at room temperature (25°C). The choice of room temperature probably ensured the retention of crystalline and ionic arrays in the ionomers. The representative small-angle-scattered intensity plots of POE_{16}–AA and POE_{16}–AA–ZnAc are displayed in Figure 2. All of the scattering intensities were measured as a function of the magnitude of **q**.

The ionomer precursor (POE_{16}–AA) did not exhibit any characteristic peak in the scattering profile because of its apparent homogeneous structure, whereas the carboxylated ionomer (POE_{16}–AA–ZnAc) showed a broad scattering peak at **q** = 0.07 Å^{-1}. This was probably because of microphase separation in the ionomer (POE_{16}–AA–ZnAc) caused by ionic domain formation. This scattering peak is often named the *ionic peak* in the literature.[13] Similar results have also been observed for other ionomer systems.

TEM studies

The morphological features of the representative ionomer (POE_{16}–AA–ZnAc) and its respective ionomer precursor (POE_{16}–AA) were observed via TEM. These are shown in Figure 3(a,b), respectively. The formation of ionic clusters was clearly visible in the POE_{16}–AA–ZnAc sample as spherical dark domains
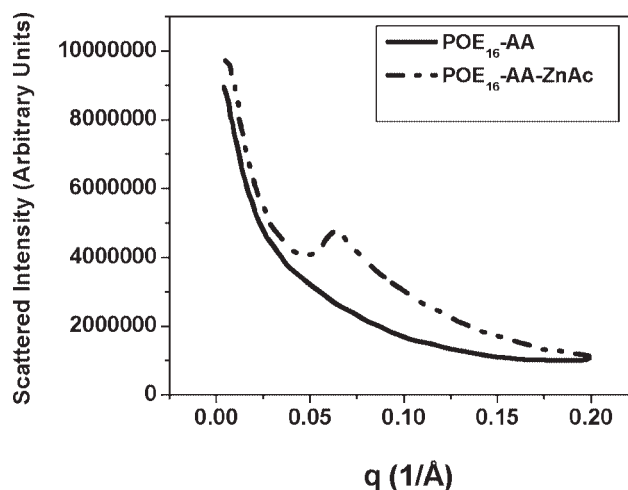

Figure 2 Comparative SAXS plots for POE_{16}–AA and POE_{16}–AA–ZnAc samples.
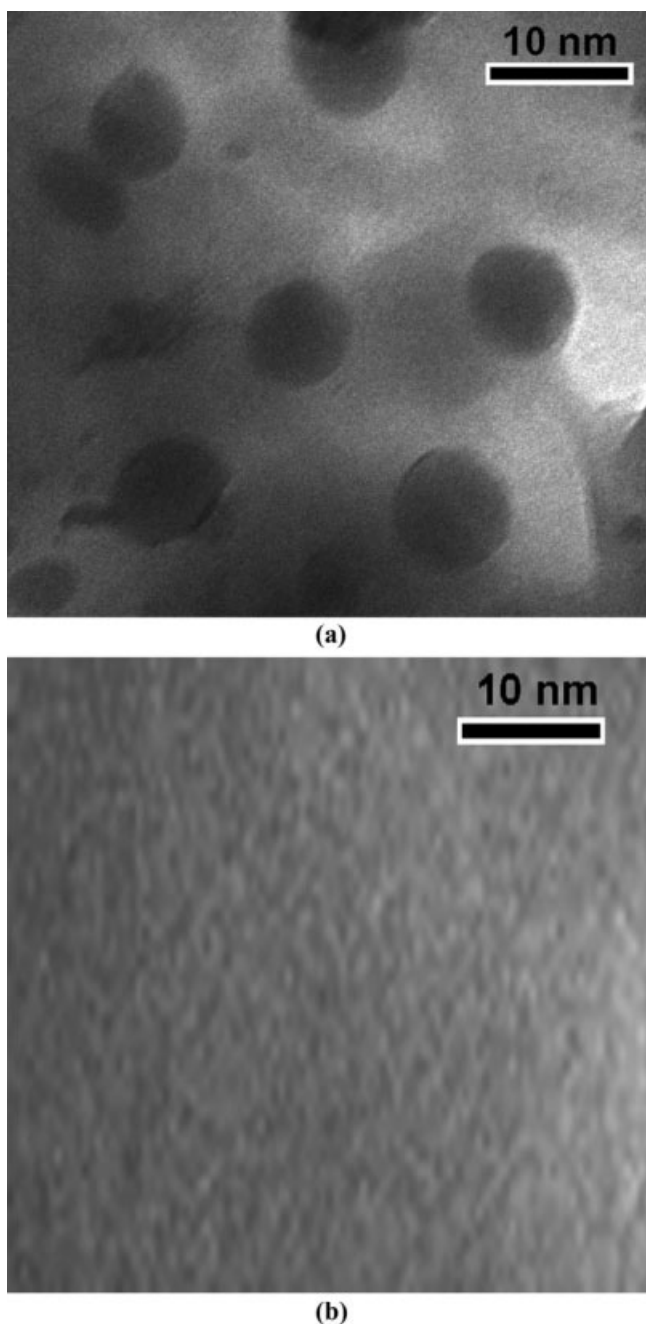
(a)

(b)

Figure 3 TEM micrographs of (a) POE$_{16}$–AA–ZnAc and (b) POE$_{16}$–AA samples.

[Fig. 3(a)]. The ionic clusters were naturally more dense than rest of the unclustered and unassociated elastomer domains and were, therefore, observed as dark features in the TEM photograph [Fig. 3(a)]. The average diameter of the domains, as calculated from this photograph, was between 4 and 8 nm. Similar observations were made for the other two ionomer systems.

The morphology of the ionic clusters as spherical dark domains in Figure 3(a) (for the POE$_{16}$–AA–ZnAc sample) may be explained with the help of Yarusso and Cooper's model[14] through Scheme 1. It

can be described by a dense core of ionic groups (region I, Scheme 1) surrounded by a layer of restricted mobility (region II, Scheme 1). This layer of restricted mobility was a result of the polymer chains attached to the ionic groups in the aggregates, as depicted in Scheme 1. The aggregates were dispersed in a matrix of polymer chains (region III, Scheme 1).

Effect of the ionomeric modifications on the physicomechanical properties of the polyolefinic elastomers

Effects on the thermal transition behavior

DSC analysis. The DSC second heating scans of the acrylated low-crystalline carboxylated ionomer system (composed of virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples) are stacked in Figure 4. The glass-transition temperature (T_g), melting temperature (T_m), and ΔH values (ΔH is the change in heat of enthalpy of the sample obtained from the DSC second heating scans) of all of the carboxylated ionomers, along with their respective ionomer precursors and virgin elastomers, are reported in Table II. The T_g increased with ionomeric modification in all cases. This was possibly explained by the fraction of elastomer domains arrested in ionic
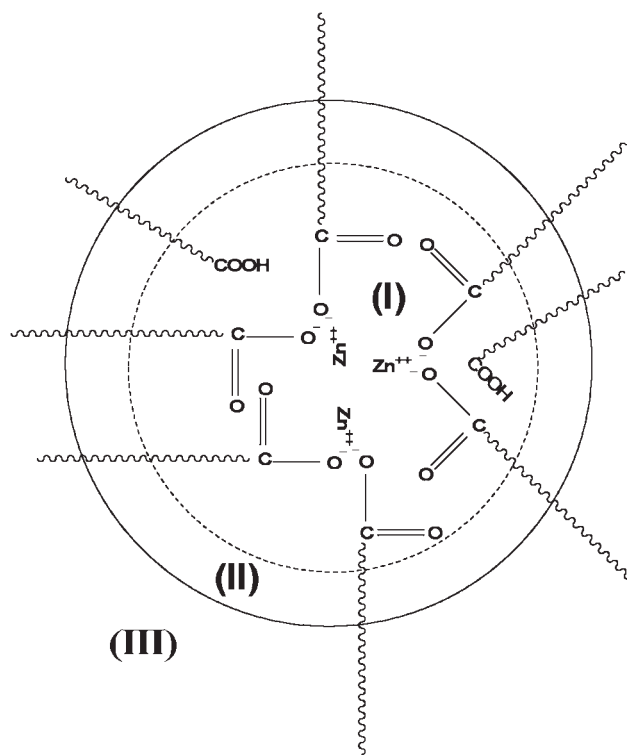
Scheme 1 Model of the ionomer morphology showing the restricted mobility layer (region II) surrounding the core (region I) of high electron density in the ionic aggregates dispersed in the polymer matrix (region III).
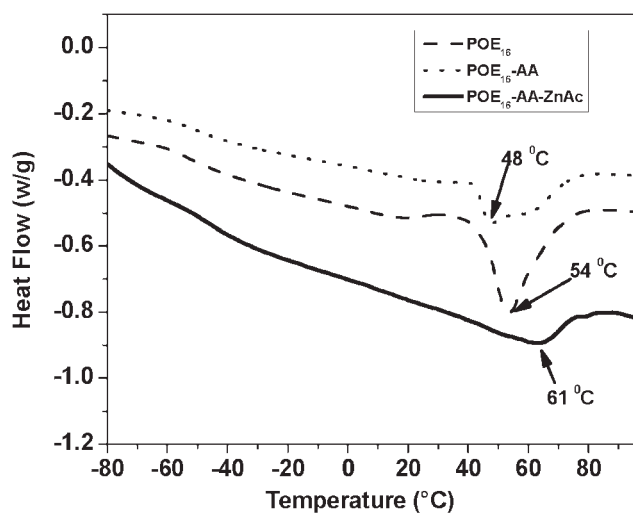
Figure 4 DSC second heating scans for virgin POE_{16}, POE_{16}–AA, and POE_{16}–AA–ZnAc samples.

clusters via strong secondary interaction (ionic cross-links); this, thereby, showed a delayed thermal response. All of the ionomers showed a shift in T_m toward the higher side because of the incorporation of metallic ions and the formation of ionic crosslinks. The metal ions acted as heat sinks, whereas the ionic crosslinks required additional energy to disintegrate, and these increased the energy intake level required for melting. ΔH decreased on ionomeric modification in all cases, which resulted in a further reduction of crystallinity. This may have been due to the introduction of ionic domains as defects within the elastomer matrices, which hindered the chain orientation during cooling, and the crystallinity was reduced further. In comparison to the respective ionomer precursors, the amount of change in T_g and T_m were greater in the cases of POE_{27}–AA–ZnAc and PBE_{16}–AA–ZnAc with respect to the POE_{16}–AA–ZnAc system because ionomeric aggregation was

stronger because of the higher grafting percentage of AA (Table I) and lower steric hindrance in comparison to the POE_{16}–AA–ZnAc system.[9] For POE_{27}–AA–ZnAc, the steric hindrance was lower because of the decreased comonomer content in POE_{27} compared to POE_{16} (Table I). The pendent side chains in PBE_{16} were of shorter length than those in POE_{16}, as shown in Scheme 2. Smaller pendent side groups in the PBE_{16}-based ionomer precursor (PBE_{16}–AA) offered less steric hindrance compared to the POE_{16}-based ionomer precursor (POE_{16}–AA), which resulted in better ionic aggregation. Not only that, because of the greater +I effect for the conjugation of a greater number of $-CH_2$ groups in the pendent chain length (Scheme 2), POE_{16}–AA⁻ (ion) was more stable than PBE_{16}–AA⁻ (ion).[9] Because of this lower stability of PBE_{16}–AA⁻ (ion), it would also be more active in the system than the POE one and, hence, offered stronger ionic aggregation than the latter.

DMTA. Figures 5 and 6 demonstrate the variation in the storage modulus (E') and loss tangent (tan δ) values against temperature, respectively, for the low-crystallinity carboxylated ionomer system (composed of the virgin POE_{16}, POE_{16}–AA, and POE_{16}–AA–ZnAc samples). Table II provides the E' [below T_g (−60°C, glassy state) and above T_g (−20°C, rubbery state)], tan δ_{max}, and Ts_g values obtained from the dynamic mode for all of the virgin elastomers, ionomer precursors, and ionomers.

Compared to the ionomer precursor, the respective ionomer in all of the systems showed a broad rubbery plateau, with a higher E' due to physical crosslinking that arose out of the ionic aggregates. Among the carboxylated ionomers, ionomers based on POE_{27} and PBE_{16} (POE_{27}–AA–ZnAc and PBE_{16}–AA–ZnAc, respectively) showed greater changes in E' (compared to their respective ionomer precursors) than the POE_{16}-based one (POE_{16}–AA–ZnAc). This was again because of the stronger ionic interactions

TABLE II
Comparison of Different Properties (DSC, DMTA, TGA, and DTG) of All of the Virgin and Modified Polyolefinic Elastomers

| | DSC | | | DMTA | | | | | TGA | DTG | |
| | | | | E' | | | | | | | |
Sample	T_g (°C)	T_m (°C)	ΔH (mJ)	−60°C (MPa)	−20°C (MPa)	T_g (°C)	Tan δ at T_g	T_{ic} (°C)	T_i (°C)	T_{max} (°C)	R_D (%/°C)
POE_{16}	−53	55	45	1125	50	−41	0.35	a	437	461	2.7
POE_{16}–AA	−49	48	34	1610	85	−39	0.33	a	442	466	2.6
POE_{16}–AA–ZnAc	−46	61	29	1850	180	−35	0.22	46	464	477	2.4
POE_{27}	−43	106	76	1210	310	−31	0.17	a	400	467	2.8
POE_{27}–AA	−39	95	62	811	308	−20	0.16	a	436	472	2.6
POE_{27}–AA–ZnAc	−34	110	56	1480	465	−14	0.07	47	460	487	2.2
PBE_{16}	−59	45	45	640	25	−33	0.28	a	422	439	3.8
PBE_{16}–AA	−49	37	33	1180	40	−31	0.25	a	426	441	3.6
PBE_{16}–AA–ZnAc	−43	57	27	1550	160	−26	0.13	46	451	457	3.2

a = no high temperature (ionic) transition.
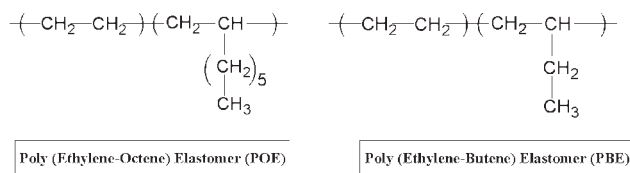
Scheme 2 Structural differences between POE and PBE.

in the case of highly crystalline and butene-based ionomer, which arose out of the higher level of AA grafting, required a higher level of zinc acetate for neutralization, and resulted in a higher crosslinking density (proportional to the modulus) and also less steric hindrance (Tables I and II).

The virgin elastomers and ionomer precursors showed one tan δ peak in the low-temperature region (Fig. 6), which was ascribed to the glass–rubber transition (T_g values obtained from the dynamic mode). In the case of all of the ionomers, the incorporation of ionic groups caused a shift in the T_g (tan δ_{max}) toward the higher side (similar to the observation made in the DSC studies) and a decrease in the low-temperature peak height (i.e., the magnitude of tan δ at T_g; Table II). This was ascribed to a restriction in the chain mobility imposed by the ionic crosslinks within these systems. Furthermore, the ionomers showed a clear high-temperature transition, also known as the *ionic transition* (T_{ic}),[15] which was 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 II).

Effects on the thermal stability

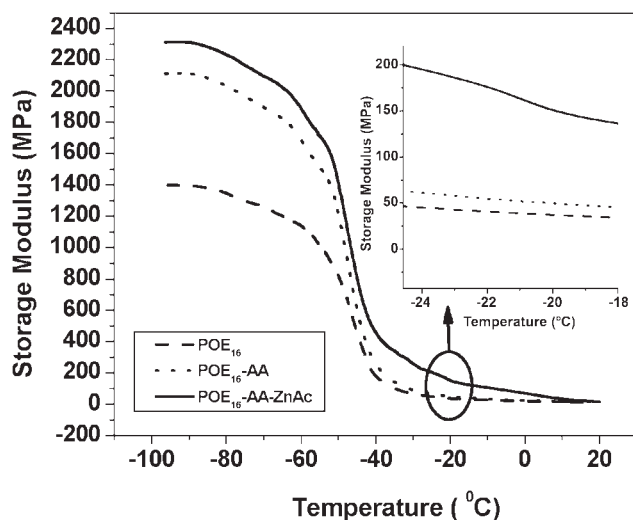Figures 7 and 8 show the representative TGA and DTG plots, respectively, for the low-crystallinity car-

Figure 6 Tan δ–temperature plots for virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples.

boxylated ionomer system (composed of the virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples). The decomposition onset temperature [i.e., the temperature corresponding to the commencement of rapid thermal degradation (T_i), which was obtained from the TGA plots], the maximum degradation temperature [i.e., the temperature corresponding to the maximum thermal degradation (T_{max}), which was obtained from the DTG plots], and the maximum rate of degradation (R_D; obtained from the DTG plots) for all of the virgin elastomers, ionomer precursors, and ionomers are summarized in Table II. The incorporation of ionic groups induced the formation of physical crosslinking and networks with a consequent improvement in T_i for all of the ionomers compared to their respective ionomer precursors. The presence of metal ions (Zn^{2+} ions in this case)
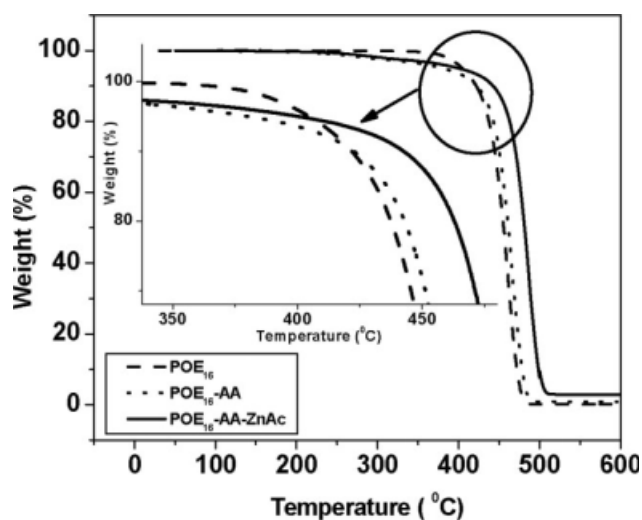

Figure 5 Plots of E' against the temperature for virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples.

Figure 7 TGA plots for virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples.
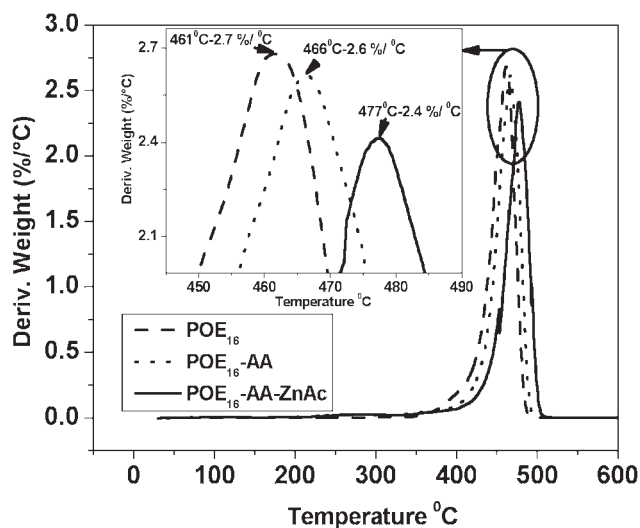
Figure 8 DTG plots for virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples.
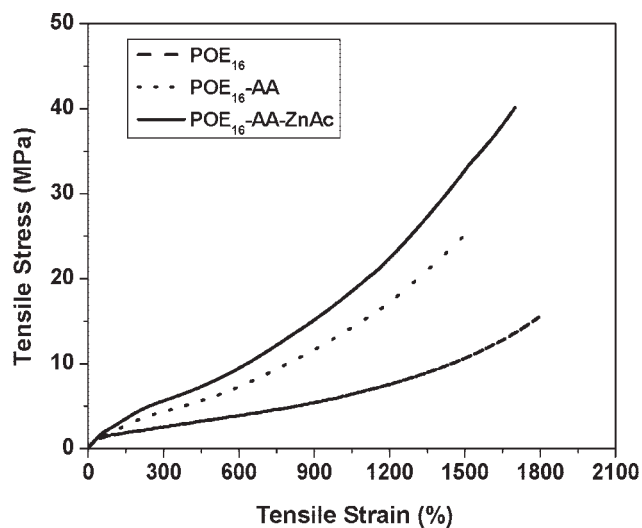
Figure 9 Comparative tensile stress–strain plots for virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples.

also helped, as it took up the good fraction of the imposed heat energy and, thereby, resisted degradation of the weak elastomer matrix.

Ionic crosslinks showed tremendous resistance against degradation and led to an improvement in the maximum degradation rate and a steady positive shift of the T_{max} for all of the ionomers from that of their respective ionomer precursors (Table II). Here also, ionomers based on POE$_{27}$ and PBE$_{16}$ showed better thermal stabilities compared to their respective ionomer precursors than the POE$_{16}$-based one because of the same reason discussed earlier (Table II).

Mechanical property studies

The stress–strain behavior of the low-crystallinity carboxylated ionomer system (composed of the virgin POE$_{16}$, POE$_{16}$–AA, and POE$_{16}$–AA–ZnAc samples) is shown in Figure 9. The mechanical prop-erty data [tensile modulus at 100, 200, and 300%, tensile strength, elongation at break (%), and tension set] for all of the virgin elastomers, ionomer precursors, and ionomers are registered in Table III. The ionomers showed higher modulus, tensile strength, and elongation at break and lower tension set values compared to their respective ionomer precursors. The enhanced mechanical properties for the ionomers were due to the formation of physical crosslinks through ionic associations, as discussed earlier. Although there was a further reduction in the crystallinity due to ionomeric modification, ionic crosslinks were formed between newly formed ionic domains. As a result, the highly crystalline carboxylated ionomer (POE$_{27}$–AA–ZnAc) not only compensated for the loss in tensile strength of its respective precursor (due to AA grafting) but also showed even better mechanical properties than its base elastomer (Table III).

TABLE III
Comparison of the Mechanical Properties of All of the Virgin and Modified Polyolefinic Elastomers

	Mechanical properties					
	Tensile modulus (MPa)					
Sample	100% elongation	200% elongation	300% elongation	Tensile strength (MPa)	Elongation at break (%)	Tension set (%)
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$_{16}$–AA	1.9 ± 0.3	3.5 ± 0.1	4.3 ± 0.3	25.7 ± 0.4	1515 ± 17	14.3 ± 0.2
POE$_{16}$–AA–ZnAc	2.5 ± 0.3	4.6 ± 0.1	5.6 ± 0.3	40.2 ± 0.4	1701 ± 19	8.9 ± 0.2
POE$_{27}$	6.0 ± 0.1	6.5 ± 0.2	7.1 ± 0.1	41.0 ± 0.3	1792 ± 14	22.3 ± 0.2
POE$_{27}$–AA	6.5 ± 0.3	7.0 ± 0.1	7.5 ± 0.3	32.3 ± 0.4	1446 ± 12	24.5 ± 0.1
POE$_{27}$–AA–ZnAc	10.5 ± 0.3	11.2 ± 0.3	12.1 ± 0.3	49.3 ± 0.3	1712 ± 21	18.7 ± 0.2
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$_{16}$–AA	2.6 ± 0.2	3.7 ± 0.2	4.7 ± 0.1	22.1 ± 0.3	930 ± 11	13.2 ± 0.2
PBE$_{16}$–AA–ZnAc	3.3 ± 0.3	4.8 ± 0.2	6.1 ± 0.1	38.1 ± 0.3	1140 ± 11	7.8 ± 0.1

CONCLUSIONS

A new class of ionomers was synthesized via the grafting of AA onto metallocene-based POEs and PBE followed by their neutralization with zinc acetate. The nanometric ionic domains (as evident from the TEM micrographs and SAXS) formed strong secondary crosslinks and resulted in a significant improvement in the mechanical and thermal properties compared to the corresponding virgin and carboxylated elastomers. For example, in the case of the high-crystalline-grade POE (POE_{27}), the tensile strength of the ionomer was 49 MPa compared to 32 and 41 MPa for the respective ionomer precursor and base elastomer. Thereby, it not only compensated for the loss in physicomechanical properties due to polar modification (AA grafting) but also imparted better thermomechanical properties compared to the pristine elastomers. In comparison to the respective ionomer precursors, the amount of change was slightly greater in the case of POE_{27}–AA–ZnAc and PBE_{16}–AA–ZnAc compared to the POE_{16}–AA–ZnAc system (e.g., the changes in tensile strength were 17, 16, and 15 MPa, respectively) because of stronger ionomeric aggregation as a result of the higher grafting percentage of AA and less steric hindrance.

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