

Ionic Elastomer Blends of Zinc Salts of Maleated Natural Rubber and Carboxylated Nitrile Rubber: Effect of Grafted Maleic Anhydride

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ABSTRACT: Zinc neutralized maleated natural rubbers (Zn-MNR) were prepared by solution grafting and neutralization with zinc acetate in one-step. It was later used for blending with carboxylated nitrile rubber (XNBR) in the composition of 50/50 parts by weight. The effect of grafted anhydride content (1.2, 1.6, 2.0, and 2.5% wt of NR) on the tensile properties of ionic rubber blends (Zn-MNR/XNBR) was investigated. The tensile strength of the ionic blends was found to be greater than those of pure rubbers. The modulus, tensile, and tear strength of the blends dramatically increased with increasing levels of grafted anhydride. The ionic rubber blends also possessed superior physical properties compared to those of the corresponding non-ionic rubber blends (MNR/XNBR). Dynamic mechanical

thermal analysis and scanning electron microscopic studies were performed to verify the process of mixing. Fourier transform infrared spectroscopic studies were carried out to characterize the nature of specific intermolecular interactions between Zn-MNR and XNBR chain segments. The results indicated that the ion-ion (Zn^{2+} - COO^-) interactions between Zn-MNR and XNBR are formed at the interface, which provides the mean of compatibilization in the ionic rubber blends. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1444–1455, 2007

Key words: zinc neutralized maleated natural rubber; carboxylated nitrile rubber; ionic rubber blend; dynamic mechanical thermal analyzes; mechanical properties

INTRODUCTION

The incorporation of small quantities (<10%) of ionic functional groups (e.g., COO^- , SO_3^{2-}) into elastomeric backbone, so called elastomeric ionomer or ionic elastomer, can exert a major influence on their properties. These highly polar ionic groups, distributed along the low dielectric constant of the host elastomer, tend to interact to form at least two types of ionic aggregates that basically determine the molecular structure and deeply modify the physical properties.^{1–4} Small ionic aggregates interspersed in the polymeric matrix, identified as multiplets, act as transient crosslinks. Larger ionic clusters, containing ionic material and appreciable amounts of nonionic polymeric material, provide a material phase-separated characteristics.⁵ This principle has been applied to develop a useful type of ionic elastomer based on carboxylate rubbers via copolymerization or graft polymerization of acrylic acid monomer, such as acrylic acid and metha-

crylic acid, and subsequent neutralization by metal oxides to form ionic crosslinks that produces rubbers with high tensile strength and elongation at break.^{6–7} In addition, it is conceivable that the use of ionic elastomers to produce specific interfacial interactions between components in polymer blends could promote the adhesion between rubber phases or compatibility of the blend, especially for those of chemically dissimilar polymers. Such interactions involve hydrogen bonding, ion–ion interaction, ion–dipole interaction, acid–base interaction or transition metal complexation.^{8–10} Lu and Weiss⁹ successfully developed miscible blends of nylon 6 and zinc sulfonated polystyrene ionomer. They have concluded that miscibility was caused by the formation of transition metal complexation between the zinc sulfonate and the amide groups of nylon 6. Kurian et al.¹⁰ have reported that interaction of ionic groups in a thermoplastic ionomer (zinc salt of ethylene-methacrylic acid copolymer, Zn-EMA) with one another in an ionic elastomer (zinc salt of sulfonated ethylene–propylene–diene monomer rubber, Zn-SEPDM) could dramatically improve the physical properties and compatibility of the blends.

Natural rubber (NR) has excellent mechanical characteristics, but it has rather poor resistance to chemicals. It is known that carboxylated nitrile rubber

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(XNBR) is similar to nitrile rubber, a copolymer of acrylonitrile-butadiene rubber, with one primary difference: the polymer backbone is chemically modified with a carboxylic acid containing group resulting in outstanding abrasion resistance and superior chemical resistance. Theoretically, blending of NR and XNBR could result in the materials combining the superior mechanical properties of NR and the oil resistant properties of XNBR. But, the degree of mixing at the interface in the blend will be limited because of these two rubbers having substantially different solubility parameters. Therefore, the properties of the rubber blends may be inferior to those of the individual components. It is well established that maleic anhydride (MA) functional groups are useful for reactive compatibilization in heterogeneous nonpolar rubber/polar thermoplastic blends i.e., NR/nylon 6,¹¹ NR/cassava starch¹² and ethylene-propylene rubber/nylon 6 blends.¹³ Generally, the MA groups can be introduced to polymers by grafting^{14–16} or copolymerization¹⁷ of MA, end capping¹⁸ and other schemes.¹⁹ Among these schemes, the grafting of MA onto the polymer backbone in the presence of organic peroxide has been the relatively simple route to obtain a maleated polymer. For maleated rubbers, it has been reported that the grafted MA units could be treated by zinc oxide to form small numbers of ionic groups.^{20–21} Several authors have claimed that the ionic functional groups present in zinc salts of maleated EDPM rubbers (Zn-MEPDM) could substantially enhance interfacial activity when combined with XNBR,²² a zinc salt of ethylene-methacrylic acid copolymer (Zn-EMA)²³ and ethylene-acrylic acid copolymer.²⁴ However, no previous study has been made to investigate the use of metal salt of maleated natural rubber (MNR) as a reactive component in polymer blending.

Currently, the grafting of MA onto NR is usually carried out in solution^{25–26} or in melt.^{11–12} From these studies it is clear that the melt modification yields a comparatively lower percent of grafting (about 1% by wt of NR) than the solution approach does because of low solubility and diffusion of the molten MA in the NR and also because of the high volatility of MA at elevated temperatures. A high degree of crosslinking reaction is often obtained during melt grafting. However, a considerable amount of solvent is used to graft MA in a polymer solution. Therefore, in this study, a reduced amount of solution prepared in a one step process was used to produce the zinc neutralized maleated natural rubber (Zn-MNR) to avoid the purification step to remove the solvent. The solution blending of Zn-MNR and XNBR was studied. The effect of the level of grafted anhydride content, corresponding to ion content in NR, on the mechanical properties of the blend was examined. Dynamic mechanical thermal analysis (DMTA), fourier transform infrared spectroscopic (FTIR), and scanning electron

microscopic (SEM) studies of the blends were also conducted.

EXPERIMENTAL

Materials

Air dried sheet NR (Thavorn Rubber Industry, Ltd., Songkla, Thailand) was used for preparation of the MNR. XNBR (trade name, Krynac X7.40, Bayer, Germany) was used. Its carboxylic acid content was 7 wt % and its mooney viscosity, ML1 + 4 at 100°C was 40. All chemicals and reagents used were AR-grade. MA (Fluka Chemika, Switzerland) was used to the graft modification. Benzoyl peroxide (BPO) (Fluka Chemika, Switzerland) was used as a free radical initiator. Zinc acetate (ZnAc) (Fluka Chemika, Switzerland) was used as neutralizing agent. Toluene, acetone, and methanol (Lab Scan, Ireland) were used as solvents.

Preparation of the zinc salts of maleated natural rubber (Zn-MNR) and carboxylated nitrile rubber (Zn-XNBR)

NR (150 g) was masticated on a two-roll mill (150 × 300 mm²) at room temperature to reach Mooney viscosity (ML1 + 4 at 100°C) of ~40. The copolymers of MA and NR (MNR) were synthesized by solution free radical polymerization using BPO as the initiator. The reactor and associated equipments used for preparation the MNR is shown diagrammatically in Figure 1. Dried NR dissolved in toluene (5% w/v) was added into glass reactor. The NR solution was continuously stirred under N₂ for 1 h at 60°C. MA (9 wt % of NR) and BPO (1 wt % of NR) were added into the reactor. The reaction was then carried out at 80°C with stirring for 2 h. The amounts of BPO used were varied from 1,

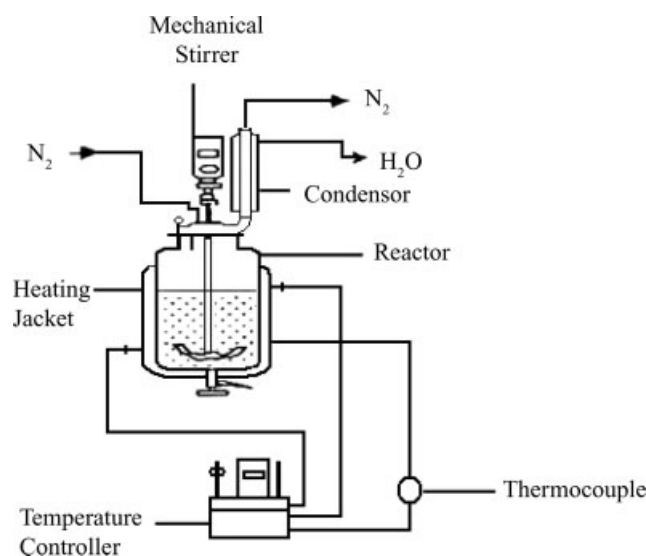


Figure 1 Diagrammatic representation of reactor and associated equipment used for the preparation of MNR.

2, 3, and 4 wt % of NR. This is to provide the functionalization of NR within a range of degrees of MA grafting from 1.2, 1.6, 2.0 to 2.5% by wt of NR, as determined by titration method.²⁵ Next, the zinc acetate was added to the freshly prepared grafting reaction medium to neutralize the grafted MA precursor. Because the neutralization step was carried out in the grafting reaction medium, all unreacted MA has to be taken into account. For this purpose, the weight (g) of MA used for preparation of the graft copolymer is converted to an acid equivalent weight per 100 g of NR. The excess quantity of ZnAc (1.5-fold of acid equivalent/100 g NR) in methanol was added to a stirred grafting mixture solution to neutralize the acid function. The mixtures were then stirred thoroughly at 30°C for 1 h. The ionic rubbers were then cast into films and dried in a hot-air oven and a vacuum oven at 40°C for 24 and 16 h, respectively, to remove any trace of residual solvent, then kept in a desiccator. The zinc neutralized MNR is denoted as Zn-XMNR, where X refers to number of grafted MA groups in wt % of NR. For the preparation of zinc carboxylated nitrile rubber (Zn-XNBR), the carboxylic acid groups of the rubber containing 7 wt % of ions were neutralized by the addition of zinc acetate of the same quantities as used for neutralization of MNR to a 5% (w/v) solution of the rubber in toluene. The cast film Zn-XNBR was dried in a hot-air oven at 40°C for 24 h and dried under vacuum at 40°C for 16 h.

Blending of zinc neutralized MNR and XNBR (Zn-MNR/XNBR)

Binary blends of Zn-MNR and XNBR were prepared by solution mixing. The freshly prepared Zn-MNR solution was added to a stirred XNBR solution, which was weighed separately and dissolved in toluene, to obtain a blend of 50/50 (wt %/wt). The blend solution was stirred for 1 h at ambient temperature and the solution was cast into films. The sample films were dried in an oven at 40°C for 24 h and in vacuum at 40°C for 16 h. The analogous samples prepared from blending MNR and XNBR were also studied.

Fourier transform infrared spectroscopy

The FTIR spectra of the Zn-MNR, Zn-MNR/XNBR, and MNR/XNBR were recorded on an Omnic ESP Magna-IR 560 in the ranges of 4000–400 cm⁻¹ with resolution of 2 cm⁻¹. The rubber spectra were obtained by using casting films on KBr discs. The solvent (toluene) was evaporated in a hot air oven at 40°C for 1 h and in a vacuum oven at 40°C for 3 h.

Measurement of mechanical properties

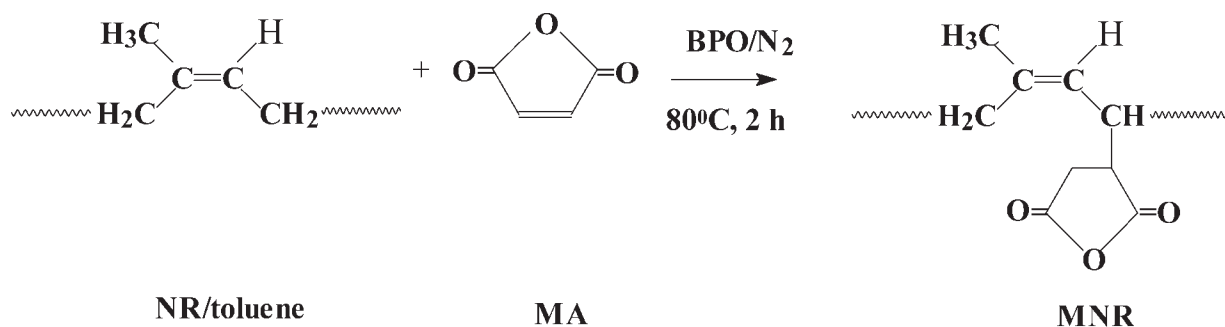
The films of the rubber samples, about 0.8 mm in thickness, were cut into dumbbell-shaped and

TABLE I
Mechanical Properties of Zn-MNR, Zn-XNBR, and Zn-MNR/XNBR Blends

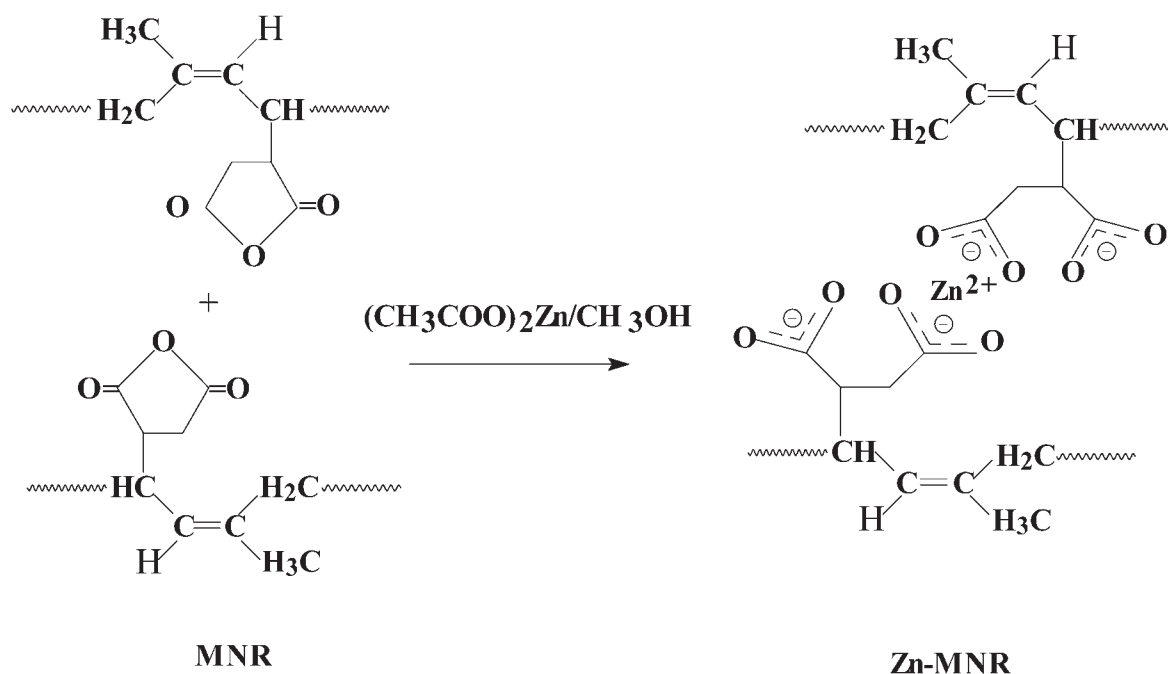
Properties	Zn-MNR ^a					Zn-MNR/XNBR (50/50 wt %/wt) ^a					Zn-XNBR
	1.2	1.6	2.0	2.5		1.2	1.6	2.0	2.5		
100% Modulus (MPa)	0.23 ± 0.02	0.23 ± 0.02	0.46 ± 0.03	0.54 ± 0.03		0.94 ± 0.04 (0.40 ± 0.05)	1.15 ± 0.09 (0.57 ± 0.02)	1.28 ± 0.16 (0.64 ± 0.03)	1.57 ± 0.09 (0.82 ± 0.06)		1.83 ± 0.20
300% Modulus (MPa)	0.35 ± 0.03	0.48 ± 0.01	1.01 ± 0.06	1.17 ± 0.07		1.36 ± 0.15 (0.47 ± 0.02)	2.12 ± 0.19 (0.62 ± 0.03)	2.58 ± 0.23 (0.88 ± 0.05)	3.31 ± 0.40 (1.37 ± 0.14)		2.50 ± 0.24
Tensile strength (MPa)	1.90 ± 0.59	5.19 ± 0.71	10.58 ± 0.60	14.13 ± 0.37		6.94 ± 0.47 (2.70 ± 0.42)	10.57 ± 0.97 (3.79 ± 1.12)	12.08 ± 0.97 (6.15 ± 0.95)	16.02 ± 1.56 (12.17 ± 0.85)		2.54 ± 0.22
Elongation at break (%)	925 ± 25	917 ± 38	865 ± 29	833 ± 21		758 ± 104 (1220 ± 135)	650 ± 54 (1050 ± 56)	565 ± 32 (870 ± 48)	468 ± 58 (733 ± 18)		315 ± 12
Tear strength (N/mm)	5.63 ± 0.55	8.33 ± 0.44	12.94 ± 1.08	19.11 ± 0.63		13.75 ± 0.30 (7.36 ± 1.12)	21.32 ± 0.96 (8.37 ± 0.57)	26.09 ± 0.77 (9.48 ± 1.05)	31.04 ± 0.32 (12.75 ± 0.94)		19.96 ± 1.15

Values in parentheses are the data for nonionic rubber blends (MNR/XNBR).

^a Concentration of grafted MA (wt %).



Scheme I



Scheme II

Figure 2 Proposed reaction product of maleic anhydride and natural rubber (scheme I) and ionic crosslinking reaction during the neutralization of MNR with zinc acetate in methanol (scheme II).

unnicked 90° angle test-pieces for tensile and tear tests, respectively. The tensile and tear properties were examined according to ASTM D412-98a and ASTM D D624-98. The testing was performed on Tensometer, Hounsfield H10KS, UK at room temperature with an extension rate of 500 mm/min.

Dynamic mechanical thermal analyses

Dynamic mechanical thermal analyses were carried out in Dynamic Mechanical Thermal analyser (DMTA 7). Sample dimension was 10 × 25 × 0.3 mm³. The testing was conducted in tension mode with a frequency of 2.5 Hz over a temperature range of -100°C to 100°C, and at a heating rate of 5°C/min.

Scanning electron microscopy

Scanning electron micrographs of fractured blends were taken with SEM model LEO145 VP. The blend samples were immersed in liquid N₂ for 15 min and then fractured. The SEM analysis was operated by using accelerating voltage of 15 kV and magnification of 1000×.

RESULTS AND DISCUSSION

Mechanical properties

The comparison of the mechanical properties of neat ionomeric rubbers, Zn-MNR containing different percentage of grafted MA contents (1.20, 1.60, 2.0, and

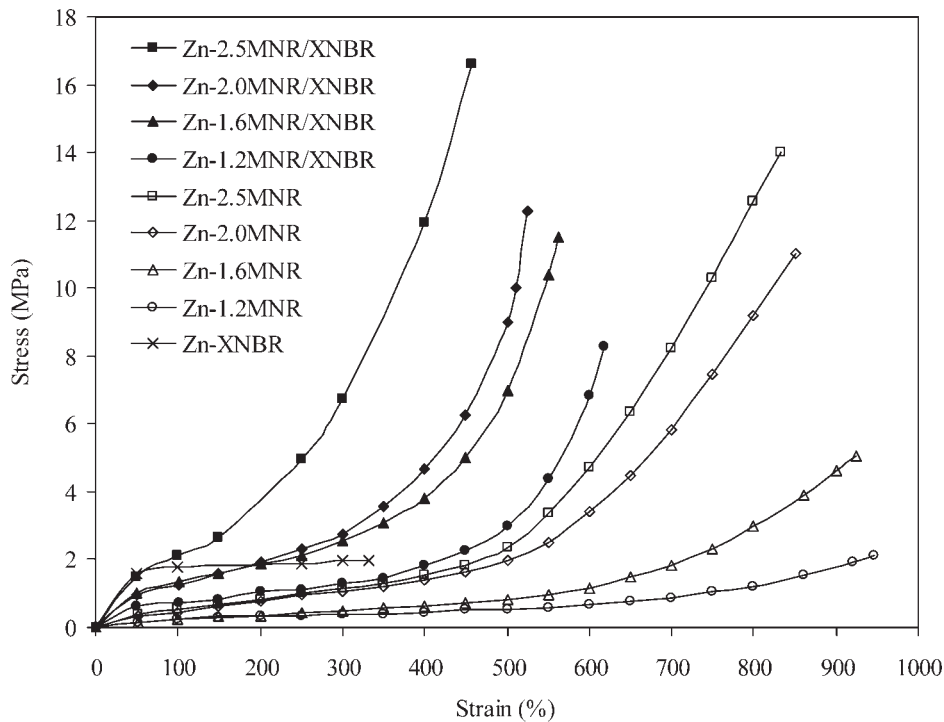


Figure 3 Comparison of stress-strain plots for the ionic rubbers and ionic rubber blends of different degrees of grafted MA concentrations.

2.50 wt %), and zinc salts of carboxylated nitrile rubber (Zn-XNBR), binary ionic rubber blends (Zn-MNR/XNBR) and corresponding nonionic rubber blends (MNR/XNBR) are given in Table I. It can be seen that the Zn-MNR samples possess higher tensile strength and elongation at break than those of Zn-XNBR, except in the case of the tensile strength of Zn-MNR with 1.2 wt % grafting. But the modulus and tear strength of Zn-MNR were lower relative to those of Zn-XNBR. When the percentage of grafting increases, the modulus, tensile and tear strength of zinc salts of MNRs also increase, coupled with a decrease in the elongation at break. This is probably attributed to the increase in zinc carboxylate ($\text{Zn}^{2+}\text{-COO}^-$) groups in the ionic NR. It has been previously addressed that the zinc carboxylate groups in an ionic rubber are capable of ionically reacting to form physical crosslinks, which resulted in significant improvement in physical properties.¹⁻⁴ In the grafting modification of NR using BPO as an initiator, the attachment of MA group to NR molecule resulting in MNR may be presented by reaction in scheme I in Figure 2. Upon reaction with zinc acetate dissolved in methanol, the reactive grafted anhydride ring of the MNR was opened, and subsequently ionized with zinc to form intermolecular ionic crosslinking between MNR as proposed in the scheme II in Figure 2. Typical stress-strain profiles for the ionic rubber blends compared with the neat ionic rubbers are illustrated in Figure 3. It is obvious that the ionic rubber blends

show much greater tensile stress at break than does either of the single components. This resulted from the ionic association between the constituent rubbers leading to strong interfacial ionic crosslinking and thus resulting in better stress transfer across the rubber phases. The plots of tensile strength, elongation at break, and tear strength of the zinc neutralized and unneutralized rubber blends as a function of concen-

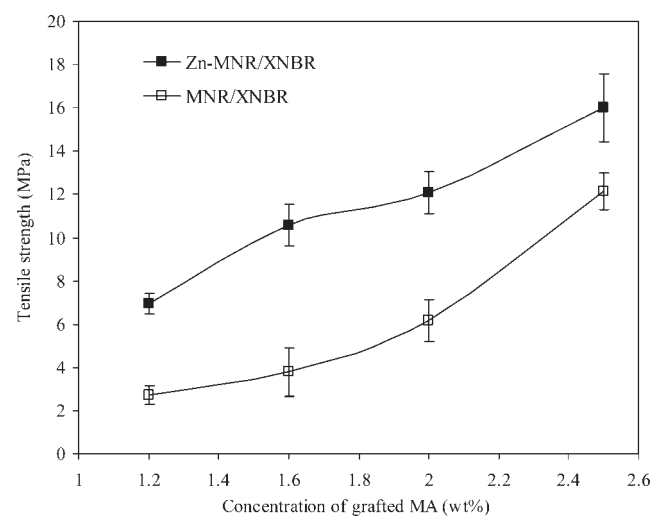


Figure 4 Variation of tensile strength with different degrees of grafted MA concentration for ionic rubber blend (Zn-MNR/XNBR) compared with corresponding nonionic rubber blend (MNR/XNBR).

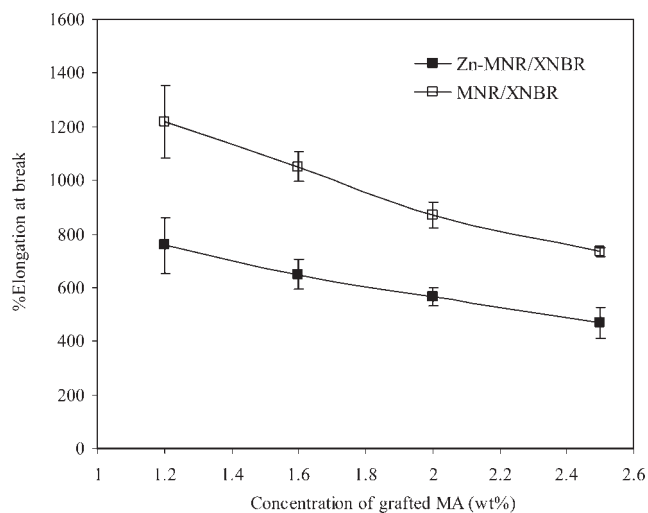


Figure 5 Variation of elongation at break with different degrees of grafted MA concentration for ionic rubber blend (Zn-MNR/XNBR) compared with corresponding nonionic rubber blend (MNR/XNBR).

tration of grafted MA are shown in Figures 4–6. It can be seen that the tensile strength increases as the grafting percentage of MA is increased. These increasing trends could be explained by a greater degree of specific interactions, i.e., ionic bonding and hydrogen bonding present in the Zn-MNR/XNBR and MNR/XNBR blends, respectively. The formation of interfacial ionic crosslinks in the Zn-MNR/XNBR blend and hydrogen bonding in the MNR/XNBR blend are schematically presented as shown in Figure 7(a,b) respectively. It is also noted that the tensile strength of ionic rubber blends is much higher than those of the corresponding nonionic blends indicating the strong molecular ionic association. However, the elongation at break in the case of the ionic blends is lower than that of the nonionic blend, and decreases with an increasing level of grafted MA as shown in Figure 5. This results from a reduced mobility or flexibility of the backbone chains caused by ionic aggregates in the ionic rubber blend. The effect of the grafting content on the tear strength is shown in Figure 6. It is clearly seen that the tear strength of Zn-MNR/XNBR blends increases with increases in ionic content and with much greater magnitude when compared with the MNR/XNBR blends. The ionic aggregates in the blends could act as physical crosslinks, and hence result in increasing tear properties.

Dynamic mechanical thermal analysis

The miscibility of an elastomer blend can usually be estimated by the measurement of the glass transition temperature, T_g .²⁷ Typically, profiles of $\tan \delta$ plotted against temperature show a damping ($\tan \delta$) peak corresponding to a transition from glass to rubber.

The temperature at which the peak occurs reflects the glass transition temperature, T_g . In miscible blends, a single peak occurs at a T_g intermediate to the T_g 's of the pure components; whereas, in the case of immiscible or partially miscible blends multiple peaks are observed at the T_g 's of the respective components.²⁸

The representative curves of $\tan \delta$ and $\log E'$ versus temperature for the neat ionomers: Zn-2.5MNR and Zn-XNBR and the two ionic rubber blends: Zn-2.5MNR/XNBR and Zn-1.6MNR/XNBR are shown in Figures 8 and 9, respectively. The summary results of dynamic mechanical thermal properties are given in Table II. As can be seen from Figure 8 the Zn-2.5MNR shows the glass transition temperature at -72.5°C (T_{g1}). For Zn-XNBR, the damping peak at -10.5°C corresponds to the glass to rubber relaxation of the Zn-XNBR (T_{g2}). It is interesting to note that the zinc salt of carboxylated nitrile rubber exhibits a two-step decrease in storage modulus as the temperature is increased, reflecting two different transitions, as shown in Figure 9. A lower temperature transition is in accordance with T_g of Zn-XNBR, and a higher temperature transition in the range of 40 – 50°C is caused by the relaxation of immobile chains in the ion-rich domains or ionic cluster.^{2–3,5} The high-temperature transition is labeled as T_i . The data of T_i determined from the storage modulus curve is also incorporated in Table II. A similar observation has been reported earlier in the case of an XNBR-ZnO system.²⁹ However, the cluster peak for Zn-XNBR is not prominent in the plot of $\tan \delta$ curve (Fig. 8) because of the influence of rubber flow.^{30–31} In the case of Zn-2.5MNR, the high-temperature transition of the clustering above the T_g is not observed (Fig. 9). It has been reported that there is a limiting ion concentration below which the cluster formation does not occur.⁵

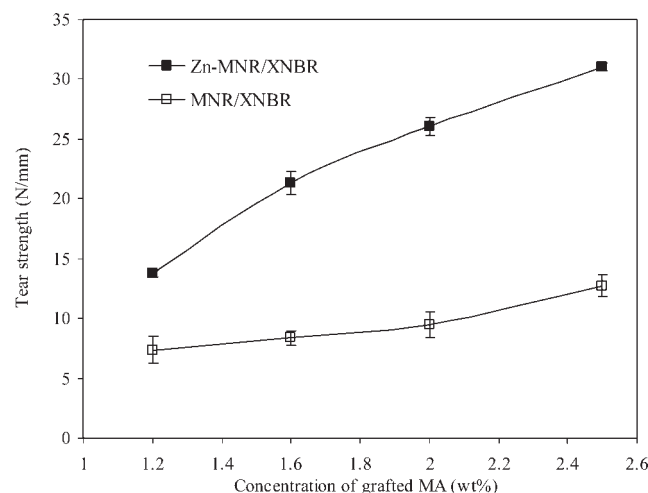
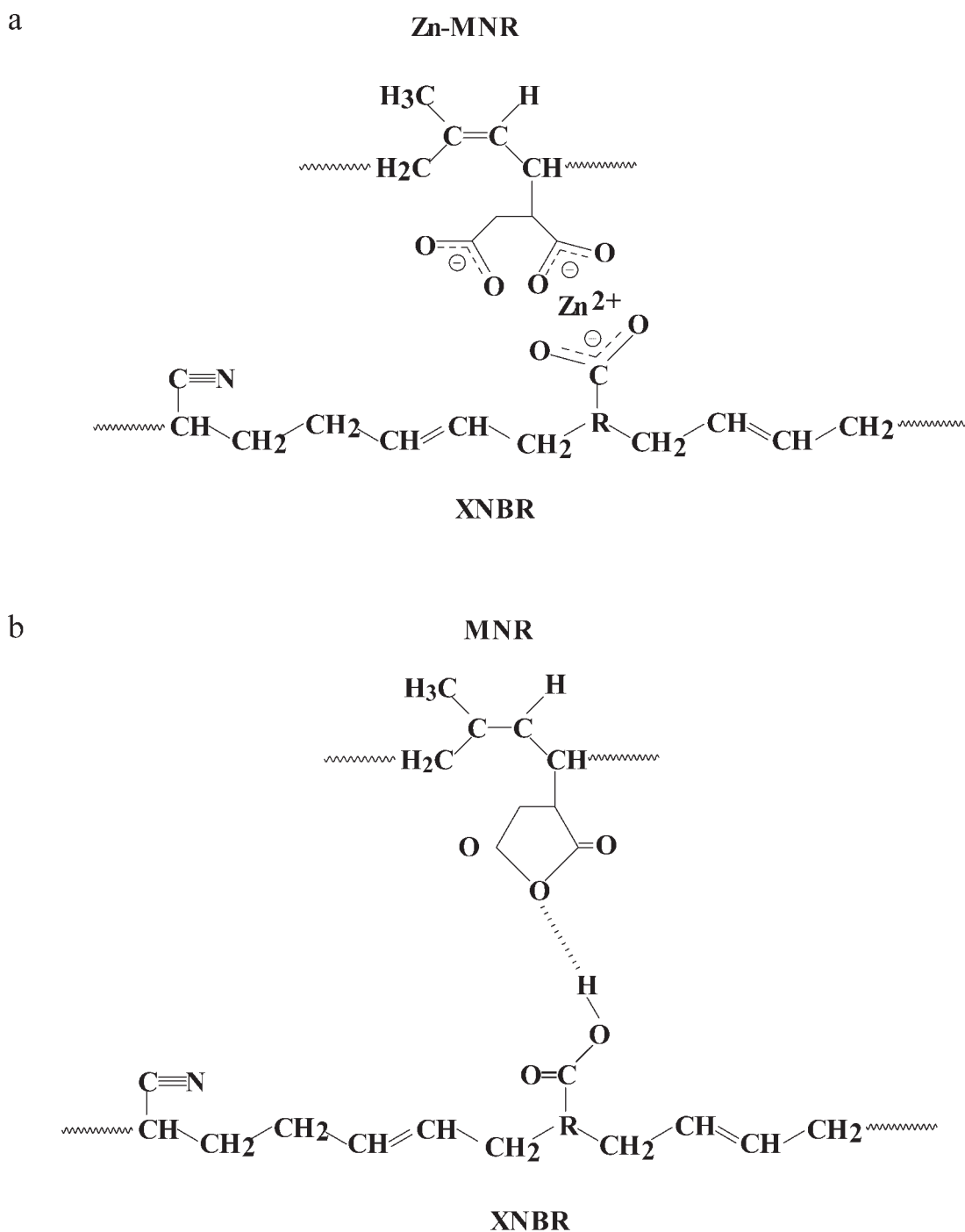


Figure 6 Variation of tear strength with different degrees of grafted MA concentration for ionic rubber blend (Zn-MNR/XNBR) compared with corresponding nonionic rubber blend (MNR/XNBR).



R is a chain segment containing carboxylic acid groups

Figure 7 Probable schematic representation of (a) interfacial ionic crosslinks for the Zn-MNR/XNBR blend and (b) interfacial hydrogen bonding for MNR/XNBR blend.

Thus, we believe that the numbers of carboxylate groups are below this limit and no cluster is formed in the Zn-2.5MNR. The ionic blend, Zn-2.5MNR/XNBR, shows the $\tan \delta$ peaks at -72.1 and -7.9°C associated with the T_g 's of neat ionic rubbers, suggesting the presence of multiphases in the blend. The \tan

δ curve for the ionic rubber blend containing relatively lower percentage MA grafting in NR phase (Zn-1.6MNR/XNBR) is also compared in Figure 8. The blend exhibits T_{g1} and T_{g2} at -70.8 and -5.0°C , corresponding to glass transition of NR and XNBR, respectively. The observation of storage modulus

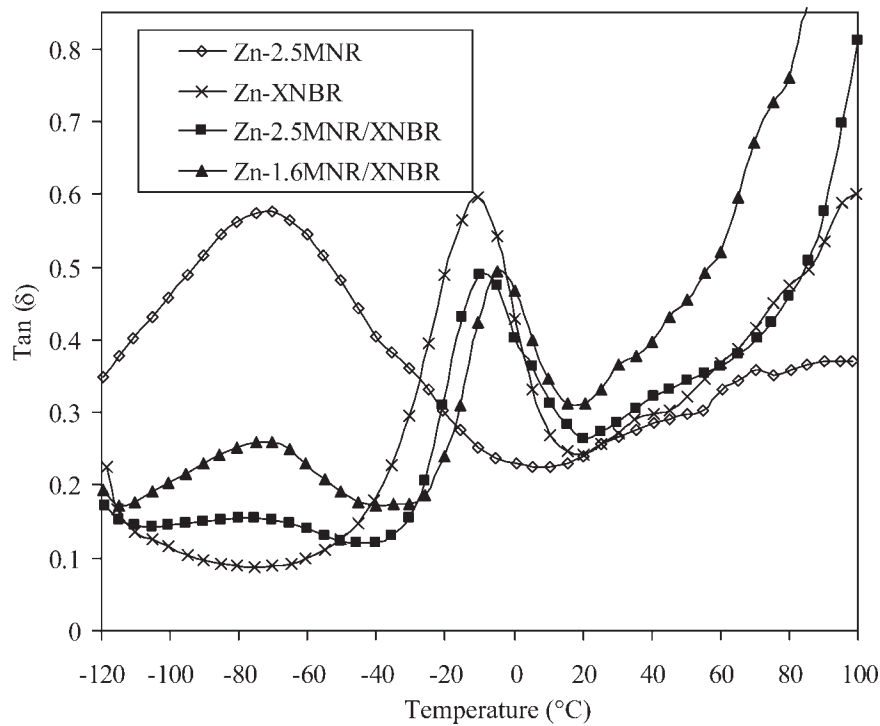


Figure 8 Variation of $\tan \delta$ with temperature for Zn-2.5MNR, Zn-XNBR, Zn-2.5MNR/XNBR and Zn-1.6MNR/XNBR.

curve of Zn-2.5MNR/XNBR shown in Figure 9 indicates that the ionic transition is in the temperature range of 80–100°C. It has been reported earlier that the transition due to ionic groups in rubbery ionom-

ers has been found to occur in a similar temperature range.^{32–33}

The variation of $\tan \delta$ and $\text{Log } E'$ with temperatures of the ionomeric blend (Zn-2.5MNR/XNBR) and the

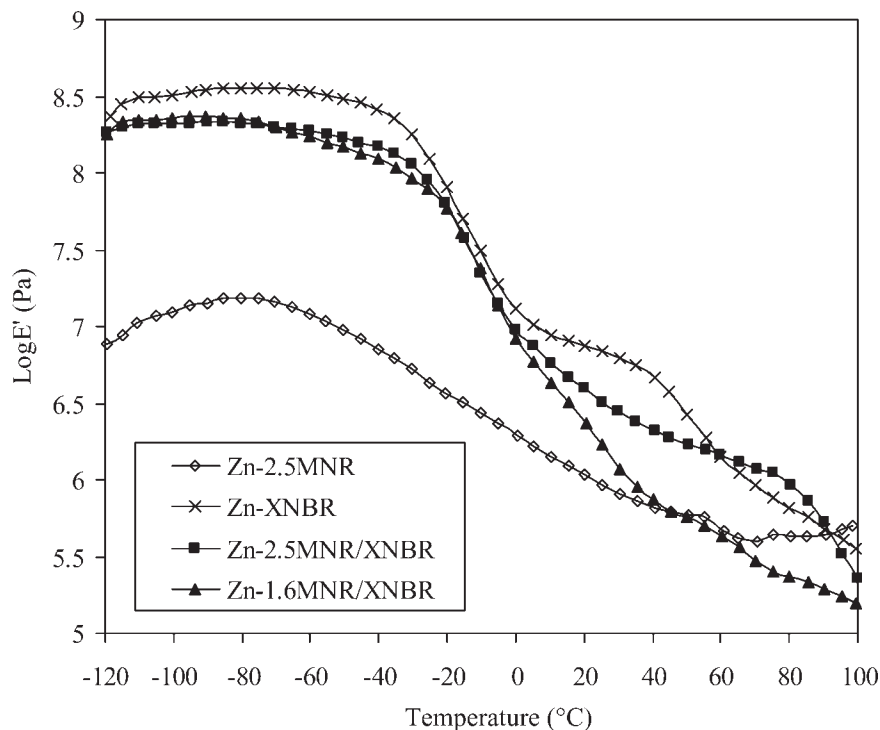


Figure 9 Variation of storage modulus ($\text{Log } E'$) with temperature for Zn-2.5MNR, Zn-XNBR, Zn-2.5MNR/XNBR and Zn-1.6MNR/XNBR.

TABLE II
Results of Dynamic Mechanical Thermal Analysis for Zn-2.5MNR, Zn-XNBR, Zn-2.5MNR/XNBR, Zn-1.6MNR/XNBR, and 2.5MNR/XNBR

Sample	Transition 1 (T_{g1})	Transition 2 (T_{g2})	Transition 3 (T_i)
Zn-2.5MNR	-72.5	-	-
Zn-XNBR	-	-10.5	40–50
Zn-2.5MNR/XNBR	-70.5	-10.2	80–100
Zn-1.6MNR/XNBR	-70.2	-5.0	-
2.5MNR/XNBR	-40.5	-10.5	-

corresponding nonionic rubber blend (2.5MNR/XNBR) is shown in Figure 10. It is apparent that both blends have damping peaks associated with the glass transition of individual rubbers. In the present study, we have observed that pure MNR, containing 2.5% grafted MA, showed a single damping peak at temperature about 45°C which is in the same order with the T_g of the MNR in nonionomeric blend (40°C) (Fig. 10). By comparing the storage modulus curve of the blends with and without zinc neutralization, it can be seen that a high-temperature transition is not observed in the case of nonionic rubber blend. It is also obvious that the modulus curve of the ionic rubber blend is higher than that of nonionic rubber blend because of the stiffening of chains resulting from a strong ionic network. Hence, these results emphasize the influence of ionic interaction between the two rub-

bers on the dynamic mechanical behavior of Zn-2.5MNR/XNBR.

Fourier transform infrared spectroscopy

It has been shown by a number of studies that FTIR spectroscopy is potentially an effective method for investigation the structure of carboxylated ionomers.^{34–36}

The infrared bands in the 1650–1500 cm^{-1} region of frequency are generally assigned to the antisymmetric vibration of carboxylate anion (COO^-) of ionomers.^{37–38} Infrared spectra of Zn-MNR, XNBR, Zn-XNBR, Zn-MNR/XNBR, and MNR/XNBR in the frequency range between 2300–600 cm^{-1} are shown in Figure 11. The MA(%) grafting of 1.6 was chosen for comparison. Designations of the different peaks in the FTIR spectrum are given in Table III. The spectra of zinc neutralized MNR shows a slightly broad and intense band in the region of around 1600–1565 cm^{-1} and another band appears at 1421 cm^{-1} as shoulder to 1446 cm^{-1} . The former is believed to result from associated carboxylate groups in ionic clusters or multiplets, suggesting the presence of neutralized carboxylic acid groups, and the latter is due to antisymmetric stretching in the carboxylate group of unassociated carboxylate in a nonionic matrix.³⁹ Earlier observations have been similarly reported in zinc neutralization of maleated EPDM rubber.^{22–24} The band at 1785 cm^{-1} is

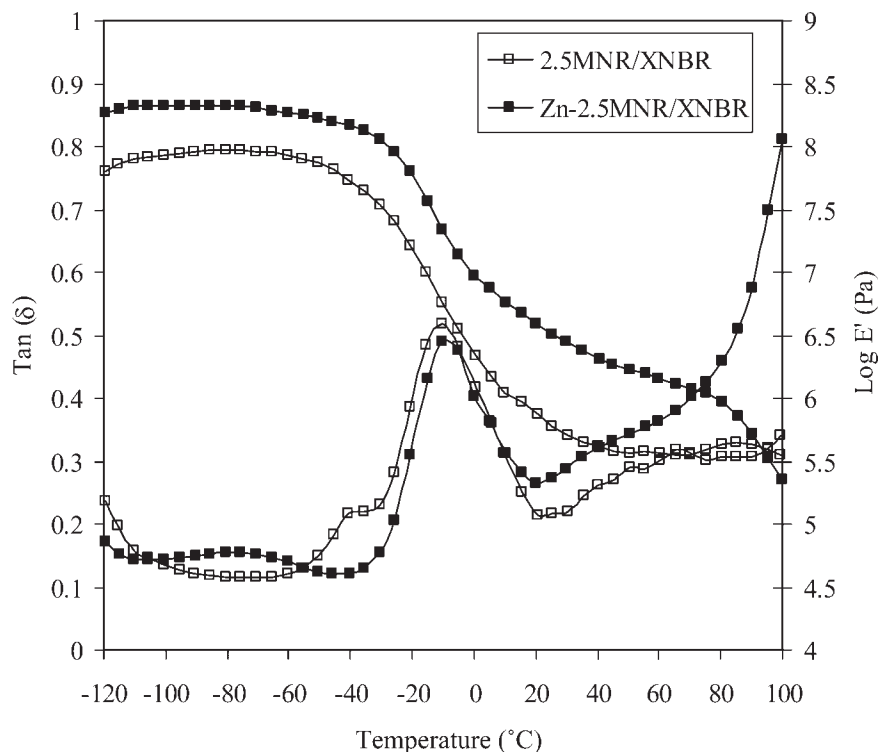


Figure 10 Variation of $\tan \delta$ and storage modulus ($\text{Log } E'$) with temperature for ionic rubber blend (Zn-2.5MNR/XNBR) compared with corresponding nonionic rubber blend (2.5MNR/XNBR).

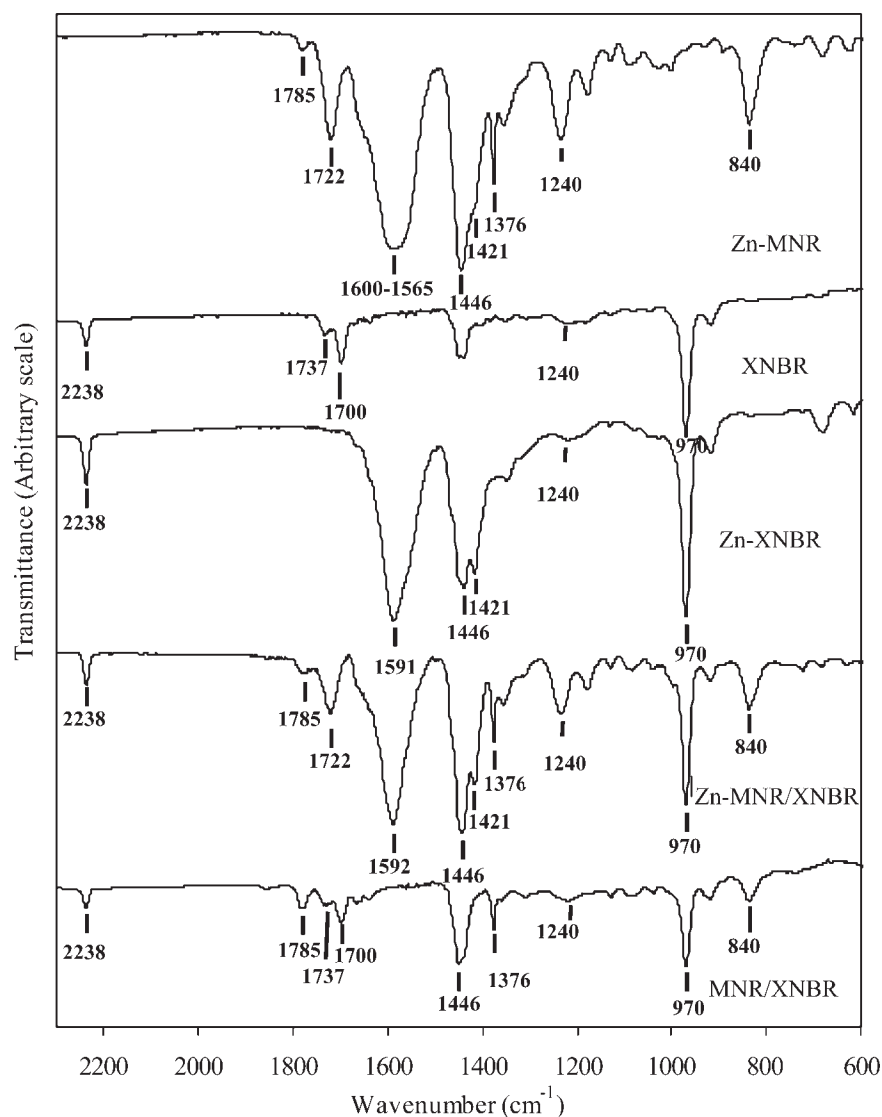


Figure 11 FTIR spectra for (a) Zn-1.6MNR, (b) Zn-XNBR and (c) Zn-1.6MNR/XNBR and (d) 1.6MNR/XNBR.

ascribed to vibration of carbonyl (C=O) in the grafted cyclic five membered-ring of anhydride,^{40–41} indicating that the neutralization was limited in the MNR. The absorption band of the unneutralized grafted MA

groups was observed in all of the ionic NRs of different MA (%) content. A vibration of the carbonyl group representing the existence of carboxylic acid (1720 cm⁻¹) was also observed. This resulted from the

TABLE III
Peak Assignments of FTIR Spectra for Zn-MNR, Zn-XNBR, Zn-MNR/XNBR, and MNR/XNBR in the Frequency Region of 2300–600 cm⁻¹

Frequency (cm ⁻¹)	Assignment
2238	–C=N stretching vibration of –CN group in XNBR
1792–1780	symmetric –C=O stretching vibration of cyclic anhydride
1737	–C=O stretching vibration of free –COOH group in XNBR
1720–1700	–C=O stretching vibration of H-bonded –COOH group
1650–1500	asymmetric C=O stretching vibration of zinc carboxylate group
1420	asymmetric C=O stretching vibration of carboxylate group
1490–1450	–CH bending of –CH ₃ group in NR chains
1376	–CH bending of –CH ₃ group in NR chains
1240	–C–O wagging of –COOH group
970	–CH out of plane bending on <i>trans</i> –CH=CH– in XNBR chain
840	–CH out of plane bending on C=C in <i>cis</i> 1,4-polyisoprene

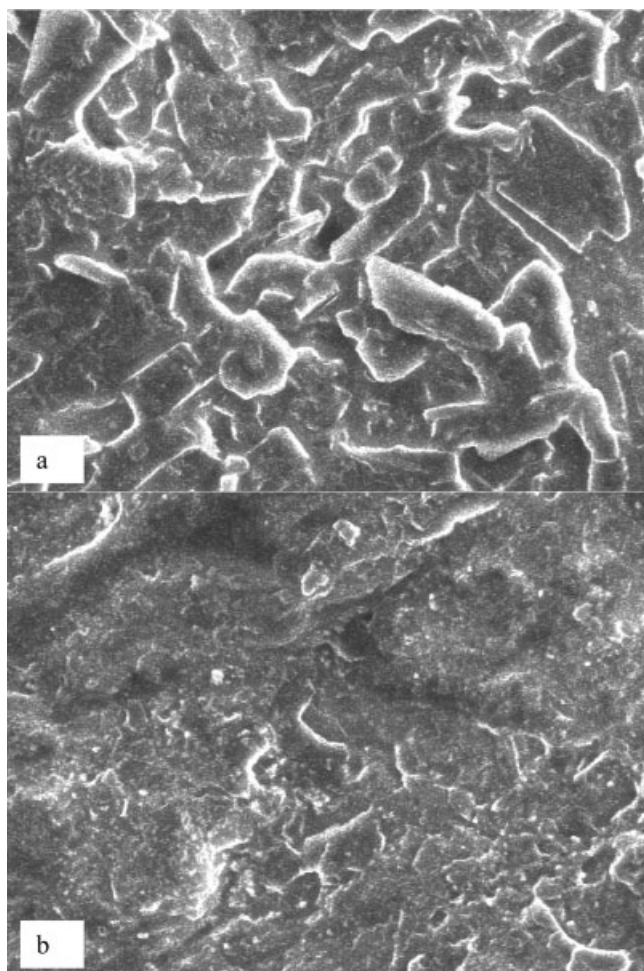


Figure 12 SEM photomicrographs of (a) 2.5MNR/XNBR and (b) Zn-2.5MNR/XNBR.

ring opening of anhydride by the addition of hydrogen donor molecules, methanol, during neutralization.²⁶ For Zn-XNBR, the absorbance band in the region of $1700\text{--}1720\text{ cm}^{-1}$, which is usually assigned to the H-bonded -COOH in the XNBR, is absent because of the complete neutralization. This is accompanied with the emerging of a sharp and intense band at 1591 cm^{-1} corresponding to zinc carboxylate salts.^{34,42} The infrared spectrum of ionic rubber blend (Zn-MNR/XNBR) shows a single sharp peak at 1592 cm^{-1} which is clearly not seen in the spectra of corresponding nonionic rubber blend (MNR/XNBR). The carbonyl absorption band of XNBR (at 1700 cm^{-1}) disappears after mixing. It has been shown that in the absence of any interaction the ionic aggregates associated to the component ionic rubbers are prone to retain their characteristic features in the blend.^{22–23} Thus, the single and sharp spectral band (at 1592 cm^{-1}) of the ionic rubber blend reveals that the zinc carboxylates, which are associated to the two rubbers in the blend, have the same local environment. These results further substantiate the formation

of salt junctions that will tie the NR and XNBR phases.

Scanning electron microscopic studies

The fracture surfaces taken from the specimens of both ionic and nonionic rubber blend were examined to study the compatibility in the blend. The SEM photomicrographs of 2.5MNR/XNBR and Zn-2.5MNR/XNBR are shown in Figure 12(a,b), respectively. It can be seen that the ionic rubber blend [Fig. 12(b)] shows finer surface and much smaller domain size when compared with the nonionic rubber blend [Fig. 12(a)]. This would be an implication of enhanced compatibility resulting from an increase in the adhesion between rubber phases which was attributable to the formation of strong interfacial ionic interaction. Similar observations have been reported earlier by Antony and De.²⁴ This investigation is again consistent with the data obtained from the measurement of mechanical properties.

CONCLUSIONS

The blends of zinc MNR and carboxylated nitrile rubber (Zn-MNR/XNBR) exhibit considerable improvement in the tensile strength over those of the neat rubbery ionomers. This improvement is due to the formation of strong interfacial ionic crosslinks which enhance the compatibility in the blends. The modulus, tensile strength and tear strength of the ionic blends increased, but the elongation at break decreases with the increase in levels of grafted MA. The physical properties of the ionic rubber blends are also much greater than those of the corresponding nonionic rubber blends (MNR/XNBR). Dynamic mechanical thermal analyses show that the ionic rubber blends exhibited multiphase structures. FTIR studies indicate the presence of ionic intermolecular interactions between the zinc carboxylate groups attracted to the Zn-MNR and XNBR chain segments in the ionic blend. SEM studies demonstrated the enhanced compatibility in the ionic rubber blend. From the above studies, it is expected that the zinc salts of MNR may be used as a reactive blend component in developing useful materials, i.e., thermoplastic elastomer materials based on the Zn-MNR and high performance engineering plastics

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