polymer

Synergism in properties of ionomeric polyblends based on zinc salts of carboxylated nitrile rubber and poly(ethylene-co-acrylic acid)

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Abstract

Ionomeric polyblends of zinc oxide neutralized carboxylated nitrile rubber, abbreviated as Zn-XNBR and zinc oxide neutralized poly-(ethylene-co-acrylic acid), abbreviated as Zn-PEA, were prepared in the compositions ranging from 90/10 to 50/50, in parts by weight. Out of these blends, compositions of 90/10, 80/20 and 70/30, in parts by weight, behave as ionic thermoplastic elastomers. While synergism in tear strength and hardness is observed in all the three compositions, the Zn-XNBR/Zn-PEA blend ratios of 90/10 and 80/20 show synergism in tensile strength. The ionomeric polyblends show higher physical properties than the corresponding non-ionomeric polyblends. Infrared spectroscopic studies show that ionic interaction is more prominent in the blends than in the neat ionomers. Dynamic mechanical thermal analyses show the occurrence of a high temperature transition due to the relaxation of the restricted mobility region adjacent to the ionic domains. Reprocessability studies show that the ionomeric polyblends could be reprocessed without deterioration in strength. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ionomer; Zinc salt of carboxylated nitrile rubber; Zinc salt of poly(ethylene-co-acrylic acid)

1. Introduction

Polymer blending is a common and versatile technique to develop new materials with a desirable combination of properties. Most of the rubber–plastic blends are grossly incompatible because of the high interfacial tension between the polymer components. The interfacial agents or specific interactions between the polymers are believed to reduce the interfacial tension and thereby improve the interfacial adhesion for efficient transfer of stress from one phase to the other phase [1]. These specific interactions include hydrogen bonding, formation of charge transfer complexes, ion–dipole and ion–ion interactions [1,2].

Ionomers exhibit unique physical properties caused by intermolecular coulombic interactions between the ionic species [2–5]. Ionic groups pendent to the polymer chains are capable of enhancing the compatibility in the polyblends [6,7]. Blending of ionomers is believed to reduce the interfacial tension between the polymers by strong ion–ion or ion–dipole interactions. There are several reports on blends involving ion–ion or ion–dipole interactions [8–15]. Eisenberg and coworkers have studied the miscibility enhance-ment of polystyrene ionomer/poly(alkylene oxide) via ion–dipole interactions [16]. Weiss and coworkers have developed the miscible blend of polyamide6 and manganese sulphonated polystyrene by using specific ionic interactions [17]. Recently, De and coworkers have developed ionic thermoplastic elastomers from ionomeric polyblends [18–22]. The objective of the present work aims at the development of an ionic thermoplastic elastomer from ionomeric polyblends based on zinc salts of carboxylated nitrile rubber, abbreviated as Zn-XNBR and poly(ethylene-co-acrylic acid), abbreviated as Zn-PEA. The present investigation was also undertaken to elucidate the role of ion–ion interactions in the compatibilization of a rubber–plastic blends. The polymers, namely XNBR and PEA were selected because both the polymers have small amount of carboxylic acid groups on the backbone which can be neutralized with metal ions, resulting in specific ion–ion interactions between the two polymers.

2. Experimental

Details of the materials used are given in Table 1.

2.1. Preparation of ionomeric polyblends of PEA and XNBR

Formulations used for the blend preparation are given in

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Table 1
Details of the materials used

Materials	Properties	Source
Carboxylated nitrile rubber, abbreviated as XNBR	Grade X48/1; acrylonitrile content, 29%; carboxylic monomer, 1%; mooney viscosity, $ML_{(1+4)}$ 100°C, 40	Goodyear Rubber and Tyre Co., Akron, USA
Poly(ethylene-co-acrylic acid), abbreviated as PEA (trade name Polybond 1009)	Acrylic acid, 6%; M_w 97 000; melt flow rate at 190°C, 6 g/10 min	Uniroyal Chemical Co., Naugatuck USA
Zinc oxide	Rubber grade, specific gravity, 5.6	E. Merck Ltd., Mumbai, India
Stearic acid	Rubber grade, melting point, 76°C	Loba Chemicals, Mumbai, India

Table 2. Ionomeric polyblends based on PEA and XNBR were prepared in a Brabender Plasticorder, model PLE330 at 170°C and at a rotor speed of 60 rpm. First PEA was allowed to melt for 2 min. Then XNBR was added and mixed for 2 min. Finally stearic acid and zinc oxide were added and mixed for another 2 min. Preliminary studies show that 20 phr of zinc oxide was needed for almost complete neutralization of the PEA and 1 phr of stearic acid was found to increase the extent of the neutralization reaction. After mixing, the hot material was sheeted out in a two-roll mill. The mixes were then moulded at 180°C for 20 min in an electrically heated hydraulic press at a pressure of 5 MPa. After the moulding was over, the mixes were cooled to room temperature by circulation of cold water through the platens.

2.2. Measurement of physical properties

The stress–strain properties were measured with dumbbell samples according to ASTM D412 (1987) in a Zwick Universal Testing Machine (UTM), model 1445, at a cross-head speed of 500 mm/min. Tear strength was measured in the Zwick UTM, model 1445 using a 90° nick cut-crescent samples according to ASTM D624 (1986). The hardness was determined as per ASTM D2240 (1986) and expressed in Shore A. The tension set at 100% extension was determined as per ASTM D412 (1987).

2.3. Infrared spectroscopic studies

Infrared spectroscopic studies on the compression moulded thin films of the samples were carried out using Perkin–Elmer 843 spectrophotometer with a resolution of 3.2 cm^{-1}.

2.4. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analyses were carried out in a Dynamic Mechanical Thermal Analyser (DMTA No. MKII, Polymer Laboratory, UK). The testing was performed in bending mode with a frequency of 3 Hz, over a temperature range of −120 to +150°C and at a heating rate of 2°C/min.

2.5. X-ray studies

X-ray studies of the samples were performed with Philips X-ray diffractometer (type PW1840) using a nickel filtered CuKα radiation from Philips X-ray generator (type PW1729). The accelerating voltage and current were 40 kV and 20 mA, respectively.

2.6. Reprocessability studies

The reprocessability studies of the Zn-XNBR/Zn-PEA 80/20 blend (mix M2) was studied by melting the moulded sample in the Brabender Plasticorder for 6 min at 180°C and a rotor speed of 60 rpm. The sample was then remoulded in the electrically heated hydraulic press for 20 min at 180°C. The process of melting and moulding was repeated up to three cycles.

3. Results and discussion

3.1. Physical properties

The physical properties of the neat polymers and the blends measured at 25°C are summarised in Table 3. Fig. 1 shows the variation of tensile strength, tear strength and hardness with blend composition. It can be seen that the ionomeric polyblends of Zn-XNBR/Zn-PEA in compositions of 90/10 and 80/20 show synergism in tensile strength, while the synergism in the tear strength is observed in the compositions of 90/10, 80/20 and 70/30. However, the hardness shows synergism in all the compositions studied. The synergism in the physical properties is believed to be caused by the formation of a strong interfacial ionic crosslinks [23], which enhances the compatibility by decreasing the interfacial tension in the blends. It is also evident that at higher

Table 2
Formulations of the mixes

Ingredient	Mix number							
	M0	M1	M2	M3	M4	M5	M6	M7
XNBR	100	90	80	70	60	50	0	80
PEA	0	10	20	30	40	50	100	20
Zinc oxide	20	20	20	20	20	20	20	0
Stearic acid	1	1	1	1	1	1	1	0

Table 3
Physical properties at 25°C

Properties	Mix number							
	M0	M1	M2	M3	M4	M5	M6	M7
Modulus at 50% elongation, MPa	1.6	5.3	6.4	8.8	10.3	—		1.1
Modulus at 200% elongation, MPa	2.9	10.9	10.8	11.3	—	—	—	1.7
Tensile strength, MPa	13.8	35.7	26.5	13.3	12.4	12.5	16.2	1.8
Elongation at break, %	765	650	555	260	76	45	24	670
Tear strength, kNm^{-1}	50.0	88.8	101.6	88.0	70.0	45.6	65.4	24.5
Hardness, shore-A	57	70	75	85	87	90	90	44
Tension set at 100% elongation, %	10	10	20	45	—	—	—	50

PEA content (that is, beyond 30%) the blends register low elongation at break and are no longer rubbery.

In order to confirm the role of interfacial ionic bonding in the compatibility of the ionomeric polyblend, the physical properties of the 80/20 non-ionomeric polyblend (mix M7) were measured and compared with that of the corresponding ionomeric polyblend (mix M2). It is interesting to note that the ionomeric polyblend shows a higher modulus, tensile strength, tear strength and hardness, but a lower tension set and elongation at break than the corresponding non-ionomeric polyblend. The higher physical properties observed in the case of ionomeric polyblends is caused by the formation of a technologically compatible blend, wherein the intermolecular ionic interactions act as compatibilizer [7].

3.2. Infrared spectroscopic studies

Fig. 2 shows the infrared spectra of Zn-XNBR. The band observed at 1666 cm^{-1} is because of the C=C stretching mode [24]. A strong and intense band at 1591 cm^{-1} with a shoulder band at 1538 cm^{-1} is attributed to the asymmetric stretching of metal carboxylate ion [24,25]. The appearance of the doublet in this region is as a result of the occurrence of different types of zinc carboxylated coordinated structures 26]. The band at 1591 cm^{-1} is assigned to the tetrahedral structure of the zinc carboxylate ion and the band at 1538 cm^{-1} is due to the octahedral structure of zinc carboxylate ion [26,27]. The bands at 1438 and 1415 cm^{-1} are associated with various –C–H vibrations [24]. The band observed at 1415 cm^{-1} may also be ascribed to the symmetric stretching of the carboxylate group. Fig. 2 also shows the spectrum of Zn-PEA. The weak band at 1714 cm^{-1} corresponds to the hydrogen bonded carboxylic acid pairs [25]. The bands at 1590, 1562 and 1546 cm^{-1} indicate the asymmetric carboxylate stretching of zinc carboxylate ions present in Zn-PEA. The band at 1590 cm^{-1} denotes the tetrahedral structure and the doublet at 1562/1546 cm^{-1} denotes the octahedral structure of zinc carboxylate ion [26,27]. The shoulder band observed at 1620 cm^{-1} is believed to be due to the formation of acid–salt complex. The intense and strong band at 1464 cm^{-1} is ascribed to the CH$_2$ bending vibration [24]. The weak band at 1363 cm^{-1} is attributed to the –CH$_2$– wagging.

Fig. 3 shows the infrared spectra of the ionomeric polyblends. As observed in the spectrum of Zn-XNBR, all
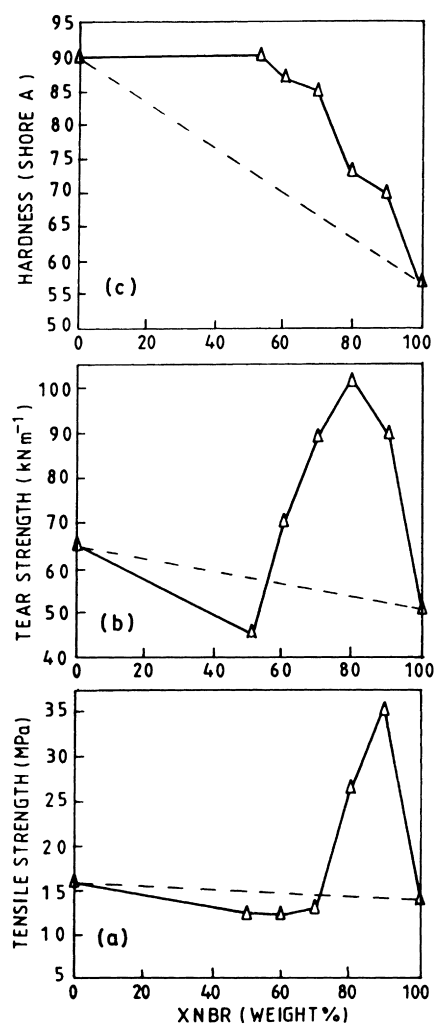
Fig. 1. Variation of (a) tensile strength; (b) tear strength and (c) hardness with blend composition, △, observed values at 25°C; – – –, additivity line.
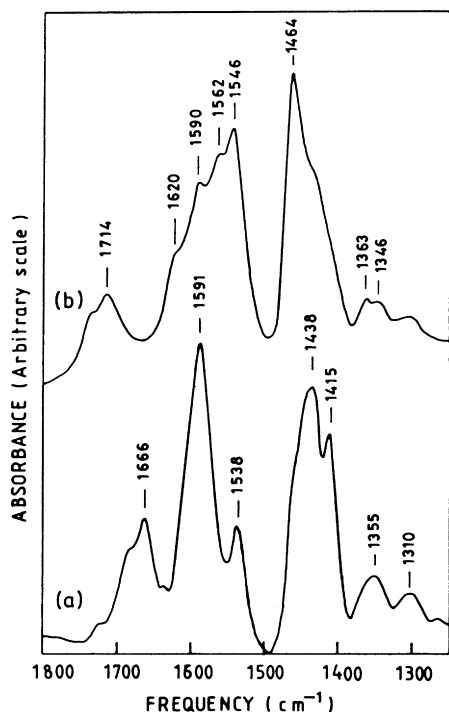
Fig. 2. Infrared spectra of (a) Zn-XNBR (mix M0) and (b) Zn-PEA (mix M6) in the range of 1800–1200 cm^{-1}.

spectra shows characteristic doublet in the asymmetric carboxylate stretching region at 1587 and 1540 cm^{-1}. The spectra of the 50/50 Zn-XNBR/Zn-PEA blend shows a weak band at 1665 cm^{-1} and a strong separate band at 1461 cm^{-1}, in contrast to the spectra of the 90/10 and 80/20 Zn-XNBR/Zn-PEA blends. The decrease in the intensity of the 1665 cm^{-1} band, which is due to C=C stretching in the spectrum of the 50/50 blend is related to the decrease in proportion of the XNBR in the blend. The appearance of a clearly resolved band at 1461 cm^{-1} is due to the –CH$_2$–bending vibration, resulting from the higher proportion of polyethylene block in the 50/50 blend. It is also noted that the intensity of the 1540 cm^{-1} decreases as compared to the band at 1587 cm^{-1} in the blends.

The interaction between the two ionomers in the blend was studied by using difference spectra. The difference spectra was obtained by subtracting the weighted addition of the spectra of the neat polymers from the experimental blend spectrum. In the case of the compatible blends there should be significant differences between the experimental infrared spectrum of the blend compared to that synthesized by weighted addition of the spectra of the pure components [28]. The difference spectra of Zn-XNBR/Zn-PEA blends in the ratios of 90/10, 80/20 and 50/50 are shown in Fig. 4. In all the cases, a positive absorption band is observed around 1586 cm^{-1}, which indicates a strong intermolecular interaction between the neat polymers in the blend and also indicates preponderance of the tetrahedral zinc carboxylate structure in the blends. The negative absorption band observed around 1544 cm^{-1}, which is due to the octahedral
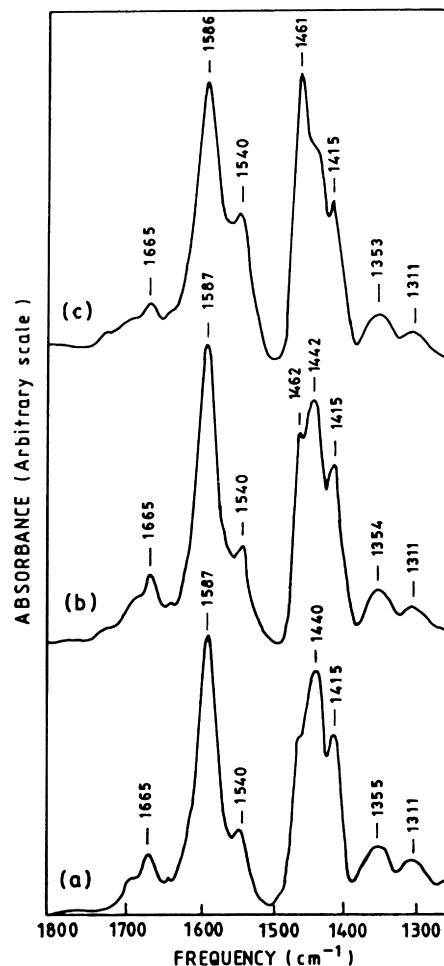
Fig. 3. Infrared spectra of (a) mix M1; (b) mix M2 and (c) mix M5 in the range of 1800–1200 cm^{-1}.

carboxylate, is also attributed to the transformation of a minor amount of hexa-coordinated zinc carboxylate into more stronger tetra-coordinated structure.

3.3. Dynamic mechanical thermal analyses

Fig. 5 shows the plots of tan δ versus temperature of neat polymers and the ionomeric polyblends. Zn-PEA shows a glass–rubber transition (T_{g1}) at $-97.5°$C, whereas Zn-XNBR shows a glass–rubber transition (T_{g2}) at 4°C. In addition to T_g's, the neat polymers also register a high temperature transition and it is more prominent in the case of Zn-XNBR than Zn-PEA. It is believed that during ionomer formation the ion pairs anchor the polymer chain to which they are attached, so that the mobility of the polymer chains in the vicinity of the ion pairs become restricted, which results in the formation of a restricted mobility region or hard phase. The transition at high temperature (T_i) is due to relaxation of the restricted mobility region [29,30]. The results are summarized in Table 4. It is also evident from the figure that the blends are immiscible. In the 90/10 Zn-XNBR/Zn-PEA blend, the T_{g1} is not observable, which is
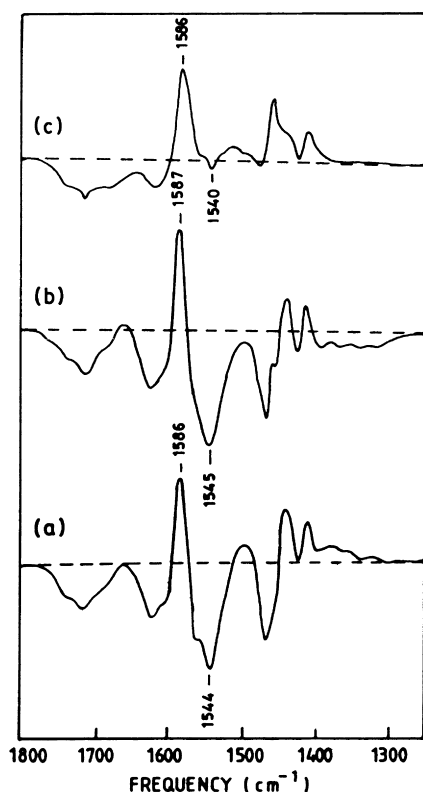
Fig. 4. Different spectra obtained by subtracting the sum of the spectra of the neat polymers from the blend spectra. (a) mix M1, (b) mix M2 and (c) mix M5 in the range of 1800–1200 cm^{-1}.

Fig. 5. Plots of tan δ vs. temperature of Zn-XNBR (– ● –); Zn-PEA (—); mix M1 (– - - –); and mix M4 (– × –).

Fig. 7 shows the variation of tan δ and log E' against the temperature of the ionomeric polyblend (mix M2) and the corresponding non-ionomeric polyblend (mix M7). It is interesting to note that mix M2 shows a distinct T_i, whereas the same is absent in the case of mix M7. The occurrence of T_i is due to the formation of an ionomer. It is also obvious that the tan δ at T_{g2} of mix M2 is much less than that of mix M7. The reduction in tan δ at T_{g2} of mix M2 is attributed to the stiffness or restriction of the free mobility amorphous portion, arising out of the strong ionic network formation. Though E' at low temperature (below T_{g2}) of the two mixes are same, mix M2 shows higher modulus at higher temperature (even beyond T_i), as compared to mix M7. The high modulus rubbery plateau of mix M2 is due to the persistence of ionic cross-links, over wide range of temperatures.

A schematic model for the formation of ionic domains by intermolecular ionic interactions in the Zn-XNBR/Zn-PEA blend is shown in Fig. 8. In this model it is proposed that the neutralization of the carboxylic acid groups present in the neat polymers by zinc oxide result in the ionic groups, which anchor the segments of the polymer chains to which they are attached. Hence the mobility of the segments of the polymer chains in the vicinity of the ionic groups

due to the low Zn-PEA content in this blend. Both T_{g1} and T_{g2} marginally increase in the blends. It has been reported that the ionic associations in ionomers act as physical cross-links and restrict the mobility of the backbone which results in an increase in T_g of the polymer [31].

The tan δ at T_{g2} decreases with increase in Zn-PEA content in the blend. This is believed to be due to increase in the stiffness arising out of the strong ionic interactions between the two polymers in the blend and also due to decrease in the amorphous Zn-XNBR phase in the blend. As observed in the case of neat polymers, the blends also exhibit additional transition at high temperature T_i. The T_i of the blends is shifted to higher temperature with increase in Zn-PEA content in the blend. The T_i's of the blends occur in between that of the neat polymers and the magnitude tan δ at T_i of the blends decreases with increase in Zn-PEA content in the blend.

The storage modulus (E') versus temperature plots of the neat polymers and the ionomeric polyblends are shown in Fig. 6. Zn-PEA shows high modulus because of its plastic nature. Zn-XNBR and the blends exhibit a rubbery plateau which is extended to the high temperature. The modulus of the rubbery plateau increases with increase in the Zn-PEA content in the blend. The existence of high modulus rubbery plateau to a wide temperature range signifies the role of multifunctional ionic network structure in resisting the flow.
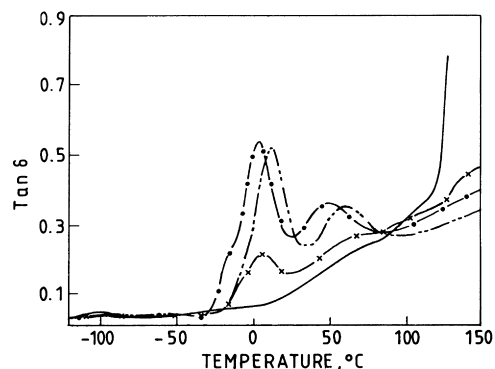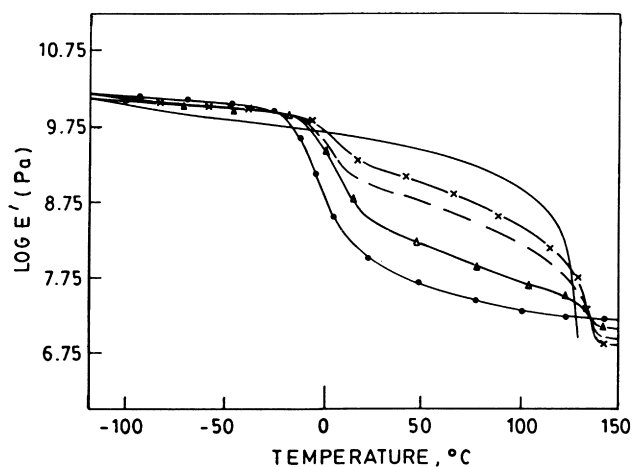

Fig. 6. Plots of log E' vs. temperature for Zn-XNBR (– ● –); Zn-PEA (—); mix M2 (– △ –); mix M3 (– – –); mix M4 (– × –).

Table 4
Results of the dynamic mechanical analysis

Mix number	Transition 1 (T_{g1}), °C	tan δ at (T_{g1})	Transition 2 (T_{g2}), °C	tan δ at (T_{g2})	Transition 3 (T_i), °C	tan δ at (T_i)
M0	—	—	4.0	0.531	50.0	0.350
M1	—	—	12.0	0.515	61.5	0.345
M2	− 95.0	0.030	12.0	0.422	63.0	0.310
M3	− 92.0	0.035	7.0	0.265	69.0	0.260
M4	− 93.5	0.035	6.5	0.212	67.5	0.262
M5	− 92.0	0.035	4.0	0.147	54.0	0.230
M6	− 97.5	0.050	—	—	68.5	0.225
M7	− 96.0	0.030	8.0	0.800	—	—

become restricted and form a separate restricted mobility region. The high temperature transition in the dynamic mechanical thermal analyses is associated with the relaxation of this restricted mobility polymer chains at the elevated temperatures.

3.4. X-ray studies

The results of X-ray studies are given in Table 5. It has been reported that formation of ionomer decreases the percent crystallinity [3]. It can be seen from the table that ionomer formation causes slight reduction in the crystallinity of the PEA. The X-ray studies also reveal that the percent crystallinity in the 80/20 Zn-XNBR/Zn-PEA ionomeric polyblend is less than the corresponding non-ionomeric polyblend. Therefore, it can be concluded that the improved physical properties of the ionomeric polyblends are not due to the crystallinity in the blend but due to the stronger ionic interaction in the blend.

3.5. Reprocessability studies

Results of reprocessability studies of the 80/20 Zn-XNBR/Zn-PEA blend (mix M2) obtained by repeated melting and moulding is given in Table 6. It is apparent that even after three cycles of melting and moulding, the modulus, tensile strength and elongation at break remain unchanged. The observation shows the thermoplastic elastomeric nature of the ionomeric polyblend. It is believed that the ionic
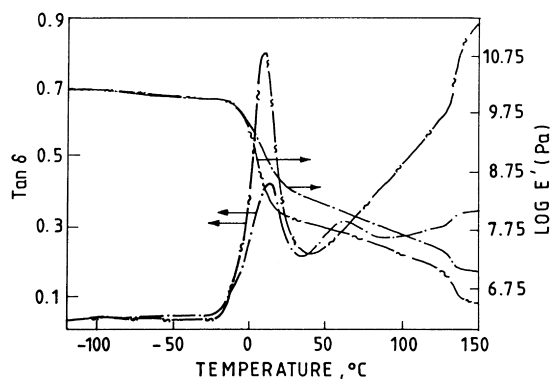
Table 5
Results of the X-ray studies

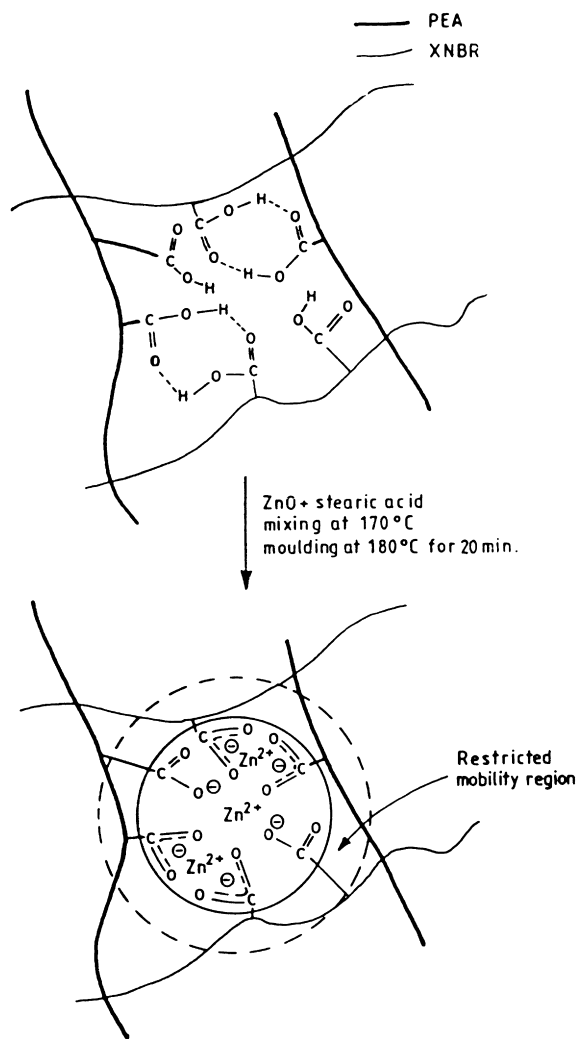| Property	Mix number					
	M1	M2	M5	M6	PEA	M7
Percent crystalinity, %	5	11	28	56	61	13

Fig. 8. Schematic model for the formation of ionic domains by intermolecular ionic interactions in the Zn-XNBR/Zn-PEA blend.

Fig. 7. Plots of tan δ and log E' vs. temperature for mix M2 (– ● –) and mix M7 (– ~ –).

Table 6
Results of reprocessability studies mix M2; moulding temperature, 180°C

Cycle number	200% modulus, MPa	Tensile strength, MPa	Elongation at break, %
1	10.8	26.5	555
2	10.5	23.5	527
3	10.7	25.5	507

domains and to some extent the crystalline domains, present in the blends act as physical cross-links, which are thermo-reversible at high temperatures.

4. Conclusions

Ionomeric polyblends of Zn-XNBR/Zn-PEA in the ratios of 90/10, 80/20 and 70/30 behave as ionic thermoplastic elastomers, which show synergism in tear strength and hardness in all the three compositions and synergism in tensile strength in the blend ratios of 90/10 and 80/20. Synergism in physical properties is believed to be due to the formation of a strong interfacial ionic cross-links, which enhance the interfacial adhesion and results in efficient stress transfer from one phase to the other phase. The results show that ion–ion interactions enhances the technological compatibility of the otherwise incompatible blend.

Dynamic mechanical thermal analyses show a high temperature transition due to the relaxation of the restricted mobility polymer chains in the ionic clusters. Reprocessability studies show that the blends could be reprocessed without deterioration in the strength, indicating the thermoplastic elastomeric nature of the blend.

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