

Synergism in Properties of Ionomeric Polyblends Based on Zinc Salts of Maleated High-Density Polyethylene and Carboxylated Nitrile Rubber

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ABSTRACT: An ionic thermoplastic elastomer (ITPE) was prepared by melt blending zinc salts of carboxylated nitrile rubber (Zn–XNBR) and maleated high-density polyethylene (Zn–mHDPE). The synergism in physical properties of the ITPE is due to the formation of strong intermolecular ionic crosslinks, which act as a compatibilizer. Infrared studies revealed that ionic interactions are stronger in the ionomeric polyblends as compared to the neat ionomers. The ionomeric polyblend of Zn–XNBR/Zn–mHDPE shows higher physical properties than those of the corresponding nonionomeric polyblend of XNBR/mHDPE. Dynamic mechanical thermal analyses showed the occurrence of a high-temperature transition in the neat ionomers and the ionomeric polyblend, due to the relaxation of the restricted mobility region in the ionic cluster region, but it is absent in the nonionomeric polyblend. Reprocessability studies and measurements of physical properties show the thermoplastic elastomeric nature of the ionomeric polyblend. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 483–492, 1998

Key words: zinc salt of carboxylated nitrile rubber; zinc salt of maleated HDPE; ionomeric polyblend; synergism in properties; reprocessability; thermoplastic elastomer

INTRODUCTION

Ionomers are ion-containing polymers in which the ionic portion is small.^{1–4} The ionic aggregates present in an ionomer act as physical crosslinks and drastically change the polymer properties.^{5,6} The ionic crosslinks are capable of enhancing the compatibility in the ionomeric polyblends.^{7–9} The compatibility of the blend of two dissimilar polymers can be achieved by either adding a third component as a compatibilizing agent or by creating a specific interaction between the polymers.¹⁰ These interactions include hydrogen bonding, formation of charge-transfer complexes,

and ion–dipole and ion–ion interactions.^{11,12} The blending of two ionomers enhances the compatibility via ion–ion interactions. Coran and Patel developed a thermoplastic elastomer from nitrile rubber and polypropylene using different compatibilizing agents.¹³ The compatibilizing agent reduces the interfacial tension between the two polymers.¹⁰ The compatibilization of the polymer blends by specific ion–dipole and ion–ion interactions has recently received wide attention.^{14–26} Lu and Weiss developed miscible blends of bisphenol A polycarbonate and lightly sulfonated polystyrene ionomers.²⁷ Kurian et al. studied the ionomeric blend of zinc salt of sulfonated EPDM and zinc salt of poly(ethylene-co-methacrylic acid).²⁸ This article reports the results of studies on the ionomeric polyblend of zinc oxide-neutralized XNBR, abbreviated Zn–XNBR, and zinc ox-

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Table III Physical Properties at 25°C

Properties	Mix No.							
	M0	M1	M2	M3	M4	M5	M6	M7
Modulus at 200% elongation (MPa)	2.6	7.3	8.5	10.9	13.0	13.0	—	2.9
Modulus at 300% elongation (MPa)	3.3	8.4	11.1	13.5	15.1	14.9	—	3.0
Tensile strength (MPa)	23.1	24.4	23.8	23.4	22.1	21.3	15.3	3.0
Elongation at break (%)	961	695	630	550	517	471	38.0	301
Tear strength (kNm ⁻¹)	37.2	67.5	81.0	82.7	93.9	99.2	126.5	37.3
Hardness (Shore A)	55	60	69	79	82	86	91	62
Tension set at 100% elongation (%)	8	10	18	25	40	65	—	72

Infrared Spectroscopic Studies

The FTIR-ATR spectra of the samples were taken in Shimadzu FTIR spectrophotometer, Model 8101, using a 45° KRS5 prism at a resolution of 4 cm⁻¹.

X-ray Studies

X-ray studies of the samples were performed with a Philips X-ray diffractometer (type 1840) using nickel-filtered CuK α radiation from a Philips X-ray generator (type PW1729). The accelerating voltage and current were 40 KV and 20 mA, respectively.

RESULTS AND DISCUSSION

Physical Properties

The physical properties of the neat polymers and the blends are summarized in Table III. It is seen from the table that the modulus of the blends increases with increase in mHDPE content. The variation of tensile strength with blend composition is shown in Figure 1. It is interesting to note that the blends show synergism in tensile strength, in the sense that the observed values are higher than the calculated values. The synergism in tensile strength of the blends indicates enhanced compatibility in the blends, resulting from the interfacial ionic crosslinks.^{25,28}

Figure 1 also shows the variation of tear strength with blend composition. As observed in the case of tensile strength, blends show synergism in tear strength as well. The ionic domains and crystallites present in the blends act as physical crosslinks,⁸ which may act as tear deviators. In contrast to the tensile strength, the tear

strength decreases with increase in the rubbery phase in the blend. Figure 1 also shows the variation of hardness with blend composition. The blends register higher hardness than the calculated values and the behavior is similar to that observed with the tear strength. The tension set increases with increase in the Zn-mHDPE content, due to increase in the plastic content.

The stress-strain properties of mixes M3 and M7 are shown in Figure 2. It is also evident from Figure 2 and Table III that the ionomeric polyblend of 70/30 Zn-XNBR/Zn-HDPE (mix M3) exhibits higher physical properties than those of the corresponding nonionomeric polyblend of 70/30 XNBR/mHDPE (mix M7), indicating that strong intermolecular ionic interactions are responsible for the enhanced compatibility and higher physical properties in the ionomeric polyblend.

Dynamic Mechanical Thermal Analyses

Figure 3 shows representative plots of the neat ionomers and their blends. Results of the dynamic mechanical thermal analyses of the neat ionomers and their blends are summarized in Table IV. Zn-mHDPE shows a weak low-temperature transition at -99.5°C, which is ascribed to the glass-rubber transition temperature (T_{g1}) of the polymer. Zn-XNBR shows a glass-rubber transition at 0°C (T_{g2}). Both the neat polymers show an additional transition at a higher temperature (T_i), which is related to the relaxation of the restricted mobility region in the vicinity of the ionic aggregates.²⁹⁻³¹ The higher $\tan \delta$ at T_i for Zn-XNBR as compared to that for Zn-mHDPE is due to the presence of a higher concentration of zinc carboxylate ions in Zn-XNBR (7 wt %) than in Zn-mHDPE (1 wt %). $\tan \delta$ at T_i for Zn-mHDPE

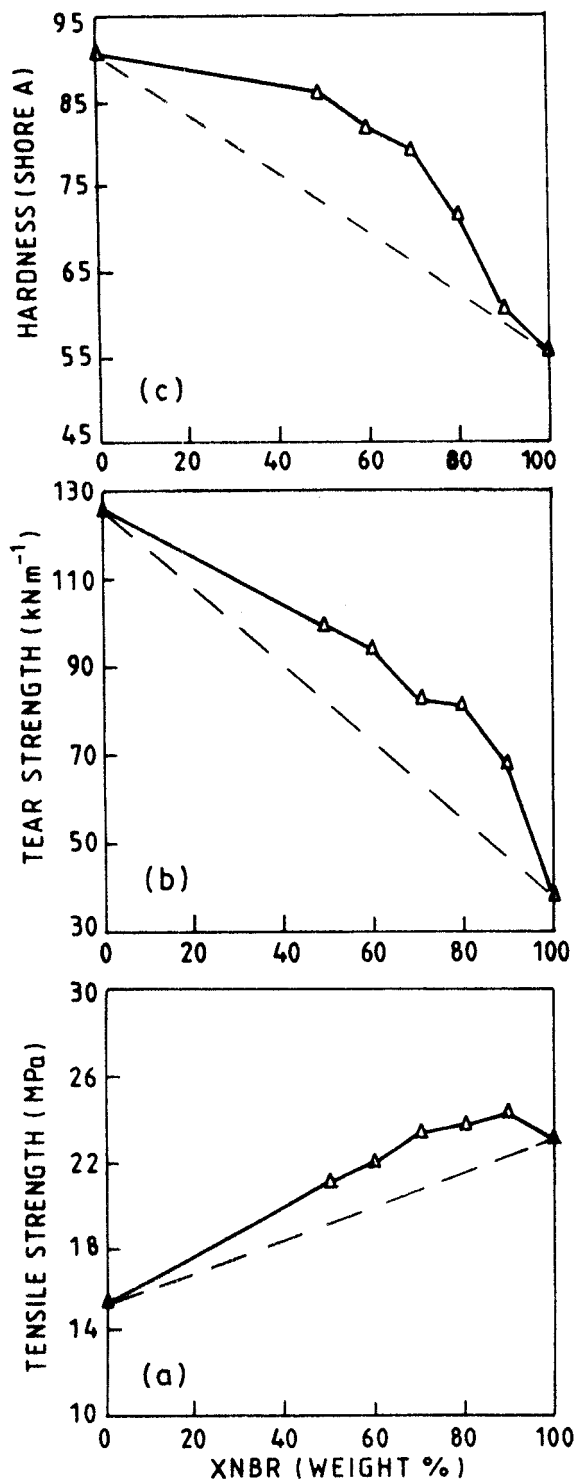


Figure 1 Variation of (a) tensile strength, (b) tear strength, and (c) hardness with blend composition: (Δ) observed values at 25°C; (---) additivity line.

is less pronounced because of its masking by the gradual increase of $\tan \delta$ due to the melting of crystallites.

The immiscible nature of the polyblends is evident from the occurrence of two T_g 's corresponding to the neat polymers. The absence of T_{g1} in mix M1 may be due to a very low proportion of Zn-mHDPE in the blend. It is also interesting to note that the T_g 's of both Zn-mHDPE and Zn-XNBR are slightly shifted to the high-temperature side in the blends except for mix M1. The slight increase in T_g values is believed to be due to the strong intermolecular ionic crosslinks between the two polymers. As is observed in the case of neat polymers, the blends also show a T_i due to the relaxation of the restricted mobility region. It has been reported that the magnitude of $\tan \delta$ at T_i depends on the ion content in the polymer as well as the thickness of the restricted mobility layer in the ionic cluster region.^{29,31} Therefore, it is assumed that the reduction in $\tan \delta$ at T_i with increase in Zn-mHDPE is due to the decrease in the carboxylate ion content in the blends.

Figure 4 shows the variation of the storage modulus (E') and loss tangent ($\tan \delta$) with tem-

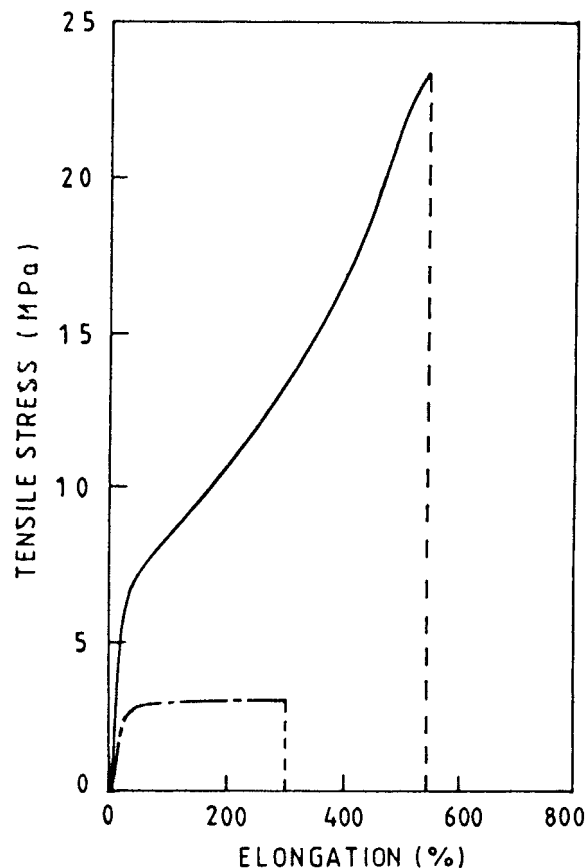


Figure 2 Stress-strain plots of (—) mix M3 and (---) mix M7.

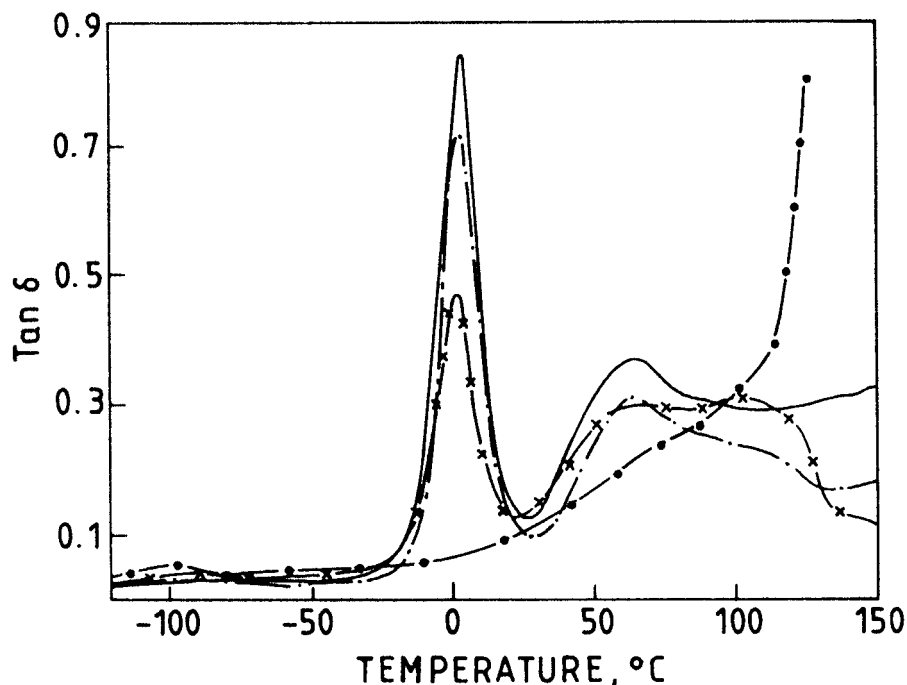


Figure 3 Plots of $\tan \delta$ versus temperature of (—) Zn-XNBR, (—●—) Zn-mHDPE, and Zn-XNBR/Zn-mHDPE blends: (—·—) mix M2 and (—×—) mix M4.

perature for the ionomeric polyblend (mix M3) and the corresponding nonionomeric polyblend (mix M7). It is interesting to note that mix M7 shows no high-temperature transition, while the corresponding ionomeric polyblend (mix M3) shows the high-temperature transition at 65°C. This confirms that the high-temperature transition is due to the occurrence of the rigid phase in the vicinity of the ionic clusters in mix M3. It is also evident that mix M3 exhibits a higher modulus at high temperature than that of mix M7, which is attributed to the effect of ionic crosslinks.

Infrared Spectroscopic Studies

The infrared spectra of Zn-mHDPE and Zn-XNBR in the range of 1750–1250 cm^{-1} are shown in Figure 5. The absence of the band corresponding to the hydrogen-bonded carboxylic acid pairs (1700–1720 cm^{-1}) indicate almost complete neutralization in both the polymers. The spectrum of Zn-XNBR shows a weak band at 1665 cm^{-1} , which is ascribed to the $-\text{C}=\text{C}-$ stretching mode³² and the asymmetric carboxylate stretching region shows a doublet at 1587 and 1541 cm^{-1} . These bands are strong and intense compared to the

Table IV Results of Dynamic Mechanical Analyses

Mix No.	Transition 1 (T_{g1}) (°C)	Tan δ at (T_{g1}) (°C)	Transition 2 (T_{g2}) (°C)	Tan δ at (T_{g2}) (°C)	Transition 3 (T_i) (°C)	Tan δ at (T_i) (°C)
M0	—	—	0.0	0.885	63.0	0.370
M1	—	—	-4.0	0.870	56.0 ^a	0.330
M2	-98.5	0.030	2.0	0.603	61.5 ^a	0.316
M3	-93.0	0.040	1.0	0.560	65.0 ^a	0.325
M4	-91.5	0.042	2.5	0.460	62.5 ^a	0.305
M5	-95.0	0.042	0.5	0.365	62.0 ^a	0.257
M6	-99.5	0.054	—	—	72.0 ^a	0.223
M7	-96.0	0.038	1.0	0.635	—	—

^a Peak broadens on addition of mHDPE.

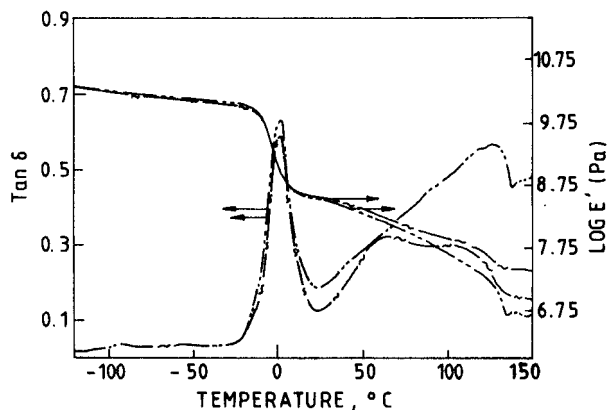


Figure 4 Plots of $\tan \delta$ and $\log E'$ versus temperature of (— ~ —) mix M3 and (— · — · —) mix M7.

spectrum of Zn-mHDPE, which shows the doublet at 1596 and 1552 cm^{-1} . The stronger asymmetric carboxylate stretching band observed in

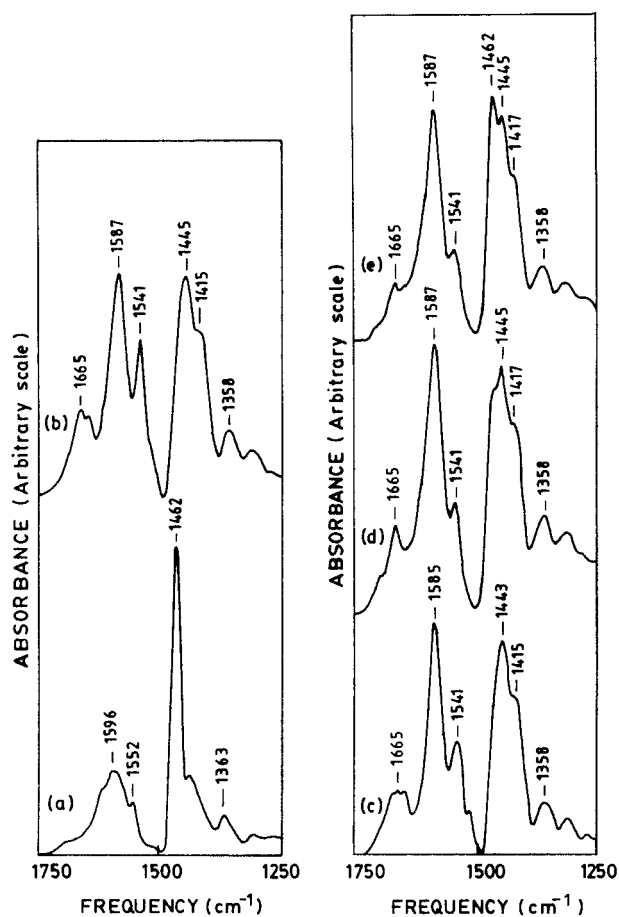


Figure 5 Infrared spectra of (a) Zn-mHDPE, (b) Zn-XNBR, (c) mix M1, (d) mix M3, and (e) mix M5 in the range of 1750 – 1250 cm^{-1} .

the case of Zn-XNBR is due to the presence of a higher proportion of carboxylate ions in Zn-XNBR than in Zn-mHDPE. The splitting of the asymmetric carboxylate stretching band into a doublet is assigned to the different coordinated structures of the zinc cation. The band, strong and intense, at 1462 cm^{-1} is due to a $-\text{CH}_2-$ bending vibration of Zn-mHDPE.^{32,33} The bands observed at 1445 and 1415 cm^{-1} in the case of Zn-XNBR indicate different $-\text{C}-\text{H}$ vibrations. The band at 1415 cm^{-1} may also have a contribution from the symmetric carboxylate stretching.³⁴ A weak band at 1358 cm^{-1} accounts for the $-\text{CH}_2-$ wagging.

Infrared spectra of ionomeric polyblends (mixes M1, M3, and M5) in the range of 1750 –

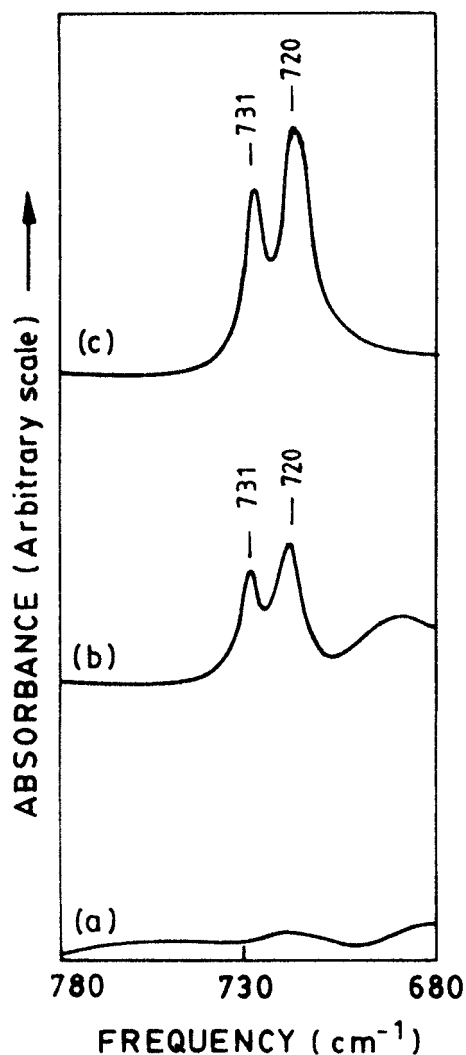


Figure 6 Infrared spectra of (a) Zn-XNBR; (b) mix M3, and (c) Zn-mHDPE in the range of 780 to 680 cm^{-1} .

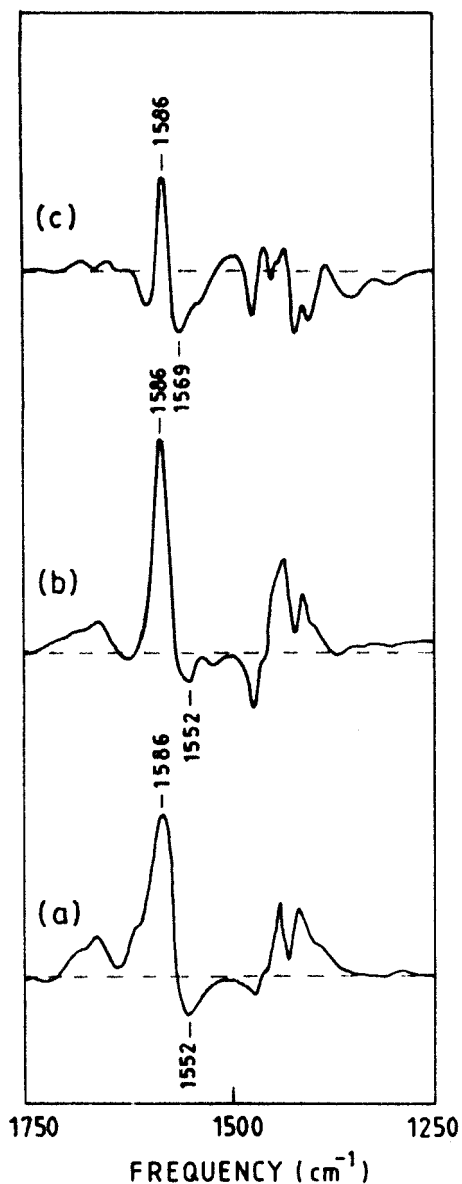


Figure 7 Difference spectra obtained by subtracting the sum of the spectra of the neat polymers from the blend spectra: (a) mix M1; (b) mix M3; (c) mix M5.

1250 cm^{-1} are also shown in Figure 5. These spectra show a strong and intense doublet at 1587 and 1541 cm^{-1} in the asymmetric carboxylate stretching region. The band at 1587 cm^{-1} is assigned to the tetrahedral structure of zinc carboxylate and the 1541 cm^{-1} band accounts for the octahedral structure of the zinc carboxylate ion.^{34,35} It is also interesting to note that as the amount of the Zn-mHDPE content in the blend increases the intensity of the 1541 cm^{-1} band decreases as compared to the 1587 cm^{-1}

band. The intensity of the -C=C- stretching band at 1665 cm^{-1} is also found to decrease with increase in the Zn-mHDPE content in the blend. The spectrum of mix M5 shows a clearly resolved band at 1462 cm^{-1} , indicating a $\text{-CH}_2\text{-}$ bending vibration.

Figure 6 shows the infrared spectra of the neat polymers and mix M3 in the range of $780\text{--}680\text{ cm}^{-1}$. In contrast to the spectrum of Zn-XNBR, the spectrum of Zn-mHDPE shows a distinct doublet at 720 and 731 cm^{-1} , due to a -CH_2 rocking vibration. The formation of a doublet is assigned to the presence of a polyethylene crystalline block. The band at 731 cm^{-1} has a contribution from the crystalline phase, whereas the band at 720 cm^{-1} represents the contributions from both crystalline and amorphous phases.³⁶ The spectrum of mix M3 also shows a doublet, indicating the development of crystallinity in the blend.

The intermolecular ionic interactions in the blends were studied with the help of difference spectra and the results are shown in Figure 7. The difference spectra were obtained by subtracting the weighted addition spectra of the neat polymers from the observed spectra of the corresponding blends. It has been reported that in the case of incompatible blends the spectrum

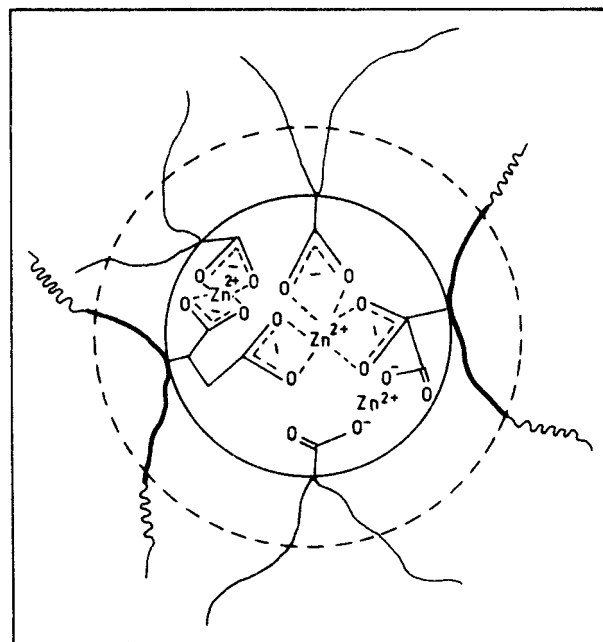


Figure 8 Schematic model for the formation of cluster region in the ionomeric polyblend: (—) Zn-XNBR; (~~~~) Zn-mHDPE.

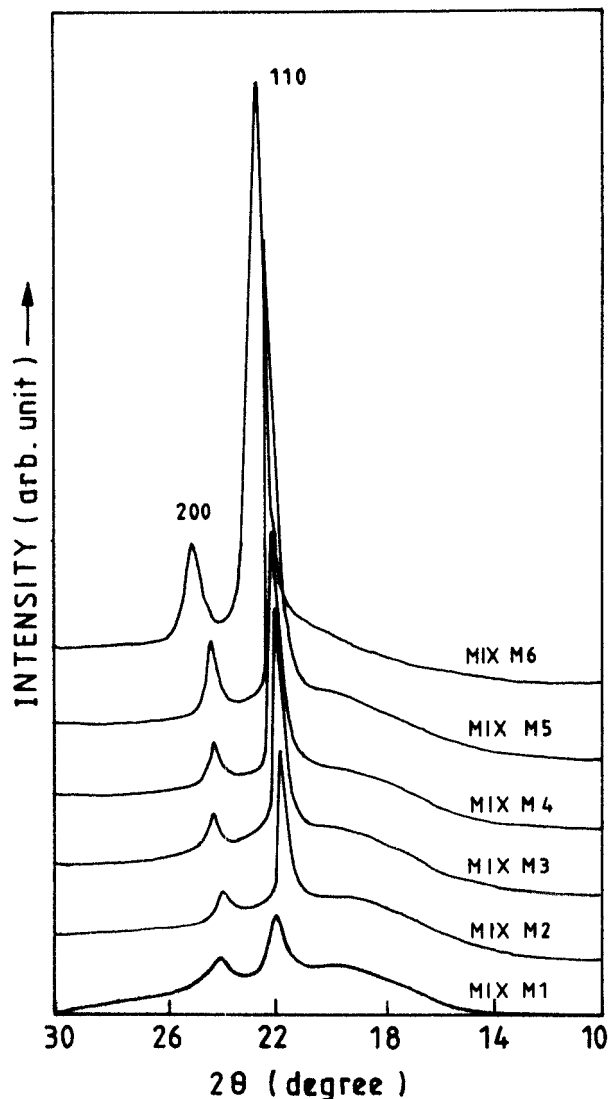


Figure 9 X-ray diffraction diagrams of Zn-mHDPE and its blends.

of the blend should be similar to that obtained by the summation spectra of the neat polymers.³⁷ But the compatible blends show marked changes in the spectra. It is evident from the difference spectra that ionic interactions are

stronger in the blends than are those in the neat polymers. This is supported by the positive absorption band at 1586 cm^{-1} , which is due to the tetrahedral asymmetric COO^- stretching band in the difference spectra. It is also noted that the 1552 cm^{-1} band intensity in the case of mixes M1 and M3 and the 1569 cm^{-1} band intensity in the case of mix M5 decrease in the blend. This also indicates a change in spectral features in the blends, due to the mutual interaction between the ionic groups present in the ionomers. Figure 8 shows the schematic representation of the formation of ionic aggregates involving both Zn-XNBR and Zn-mHDPE in the polyblend, along with the restricted mobility region.

X-ray Studies

Figure 9 shows the X-ray diffraction diagrams of Zn-mHDPE and the blends. Zn-mHDPE and the blends show two distinct crystalline peaks at $2\theta \cong 22^\circ$ and $2\theta \cong 24^\circ$, due to reflections from 110 and 200 crystal planes. The intensity of these peaks in the blends increases with increase in the Zn-mHDPE content.

Table V shows the results of X-ray studies on Zn-mHDPE and its blends. It is evident that the percent crystallinity in Zn-mHDPE is less than that in mHDPE. Also, the degree of crystallinity in the ionomeric polyblend (mix M3) is less than that in the corresponding nonionomeric polyblend (mix M7). This is in agreement with the observations made earlier in the sense that formation of an ionomer decreases the extent of crystallinity in the polymer.²

Recyclability Studies

Results of recyclability studies of mix M3 made at 170°C are summarized in Table VI. Even after three cycles of molding, the blend shows no change in properties, indicating the thermoplastic nature of the blend. The recyclability of the

Table V Results of X-ray Studies

Property	Mix No.							mHDPE
	M1	M2	M3	M4	M5	M6	M7	
Percent crystallinity (%)	4	12	18	24	30	52	21	60

Table VI Results of Reprocessability Studies by Repeated Moldings of Mix M3 at 170°C

Cycle No.	Modulus at 200% (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1	10.9	23.4	550
2	11.4	24.2	563
3	11.2	23.9	543

blend is due to the thermoreversible nature of both crystalline and ionic domains.

CONCLUSIONS

1. Ionomeric polyblends based on XNBR and mHDPE in the composition range of 90/10 to 60/40 behave as an ionic thermoplastic elastomer (ITPE).
2. The synergism in tensile strength, tear strength, and hardness is due to the formation of intermolecular ionic crosslinks, which act as a compatibilizer. Modulus, elongation at break, hardness, and tension set increase with increase in mHDPE content.
3. The ionomeric polyblend (mix M3) shows higher physical properties than those of the corresponding nonionomeric polyblend (mix M7).
4. Dynamic mechanical thermal analyses show a high-temperature transition in the neat ionomers and the ionomeric polyblends, due to the relaxation of the restricted mobility region in the vicinity of the ionic cluster region. The high-temperature relaxation is absent in the nonionomeric polyblend.
5. Infrared studies reveal that the ionic interactions are stronger in the blends than are the neat ionomers.

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