Ionic Elastomer Blends of Zinc Salts of Maleated EPDM Rubber and Carboxylated Nitrile Rubber

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ABSTRACT: Blends of zinc salts of maleic anhydride-grafted EPDM rubber and carboxylated nitrile rubber behave as ionic elastomers. Measurement of physical properties suggest that the blend is compatible. It is proposed that the compatibility arises presumably due to formation of interfacial ionic aggregates. Dynamic mechanical and infrared spectroscopic studies reveal that the ionic aggregates can be solvated by ammonia. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 153–160, 1998

Key words: ionomeric polyblend; Zn–salt of maleated EPDM rubber; Zn–salt of carboxylated nitrile rubber; ionic elastomer; compatible blends.

INTRODUCTION

Both carboxylated nitrile rubber (known as XNBR) and maleated EPDM rubber (known as m-EPDM) are known to form ionic elastomers on neutralization with a suitable base like zinc oxide (ZnO).[1–5] Both the ionic elastomers can be processed like thermoplastics in the presence of zinc stearate.[4,6]

The present article aims at the development of an ozone-resistant and oil-resistant ionic thermoplastic elastomer based on the blend of XNBR and m-EPDM. One important consideration in making such a blend of two chemically dissimilar polymers is the lack of their compatibility. Very often, such systems are grossly incompatible, and interfacial agents are required to obtain compatible blends.[7,8]

Although blends of ionomers with other polymers have been studied,[9–12] studies on the rubbery ionomers have received little attention. The present article reports the results of studies on the binary blend of zinc oxide neutralized m-EPDM and XNBR. Studies include measurement of physical properties, dynamic mechanical properties, and infrared spectroscopic studies.

EXPERIMENTAL

m-EPDM was supplied by Uniroyal Chemical Co., (Naugatuck, CT). Its weight average molecular weight (M_w) was 3.99×10^5, and its number average molecular weight (M_n) was 1.16×10^5. The maleic acid/anhydride content was 1%. Mooney viscosity, ML_{1+4} at 100°C, was 60.

XNBR was supplied by Goodyear Rubber and Tire Co. (Akron, OH). Its carboxyl content was 1 mol %. Mooney viscosity, ML_{1+4} at 100°C, was 48.

ZnO was laboratory-grade reagent and was obtained from BDH Chemicals (Calcutta, India).

Composition of the blends is shown in Table I. Blends were prepared in a two-roll mixing mill at room temperature at a nip gap of 2 mm. First, XNBR was premasticated for about 1 min so that it can form a smooth band. Next, ZnO was mixed separately with m-EPDM for about 2 min. Finally, the ZnO–m-EPDM rubber masterbatch was blended thoroughly with XNBR for about 3 min.

The blends were molded for 1 h at 170°C. Molding was done in an electrically heated press at a

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Table I Physical Properties[a]

Property	Formulation,[b] XNBR/m-EPDM (in parts by weight)				
	100/0	80/20	50/50	20/80	0/100
100% Modulus (MPa)	2.11	1.93	1.52	1.28	1.12
	(0.76)		(1.10)		(1.03)
300% Modulus (MPa)	4.25	4.14	3.08	2.15	1.84
	(0.81)		(1.30)		(1.43)
Tensile strength (MPa)	17.84	14.12	11.20	8.32	4.40
	(2.02)		(2.87)		(3.82)
Elongation at break (%)	944	850	863	1010	850
	(900)		(650)		(600)
Tear strength (N/cm)	441	419	373	349	332
Tension set at 100% extension (%)	17	22	22	13	13

[a] Values in parentheses are the results of measurements of ammonia-treated samples.
[b] Each formulation contains 10 parts of ZnO.

pressure of 10 MPa. After molding, the mixes were cooled to room temperature by circulation of cold water through the platens.

Physical properties were determined in a Zwick UTM 1445 at a crosshead speed of 500 mm min^{-1}. Tensile stress–strain and tension set tests were done using dumbbell specimens cut according to ASTM D412 specification. Tension set was measured at 100% extension. Tear strength was determined with 90° nick-cut crescent tear samples cut according to ASTM-624 die C specification.

Dynamic mechanical studies were made under tension mode, using a viscoelastometer, namely Rheovibron (DDV-III-EP) of M/s (Orientec Corp., Tokyo, Japan). Sample size was 3.5 cm × 6.5 mm × 2 mm. Testing was conducted at a frequency of 3.5 Hz over a temperature range of $-100°C$ to $+200°C$ at a heating rate of 1°C min^{-1}.

Infrared spectra were taken in a Perkin-Elmer dispersive infrared spectrophotometer, model 843, attached with a computer for data processing. The spectrophotometer was equipped with a coated deuterated triglycine sulfate pyroelectric type detector, and protected by a cesium iodide window and interchangeable dispersion gratings. Spectra were taken at a resolution of 3.2 cm^{-1} with an in-built noise level of 0.3% transmittance. The inherent frequency accuracy was ±4 cm^{-1} in the range of 4000 to 2000 cm^{-1} and ±2 cm^{-1} in 2000 to 200 cm^{-1}. A set of 16 scans were signal-averaged.

Ammonia treatments were done by keeping the samples in a desiccator over ammonia vapor for 48 h.

RESULTS AND DISCUSSION

Physical Properties

The representative stress–strain plots for different mixes are shown in Figure 1. Results of measurement of the physical properties are summa-
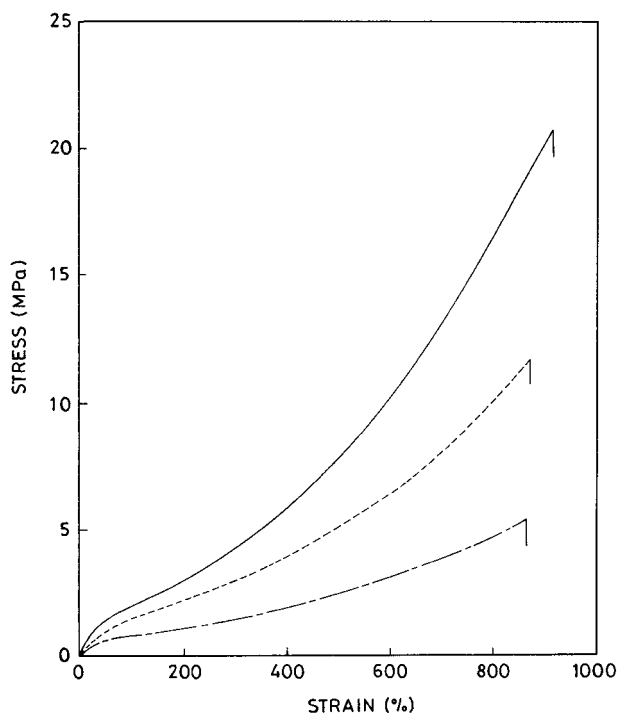
Figure 1 Representative stress–strain plots for m-EPDM/XNBR/ZnO systems. —·—, 100/0/10; ---, 50/50/10; and ——, 0/100/10.
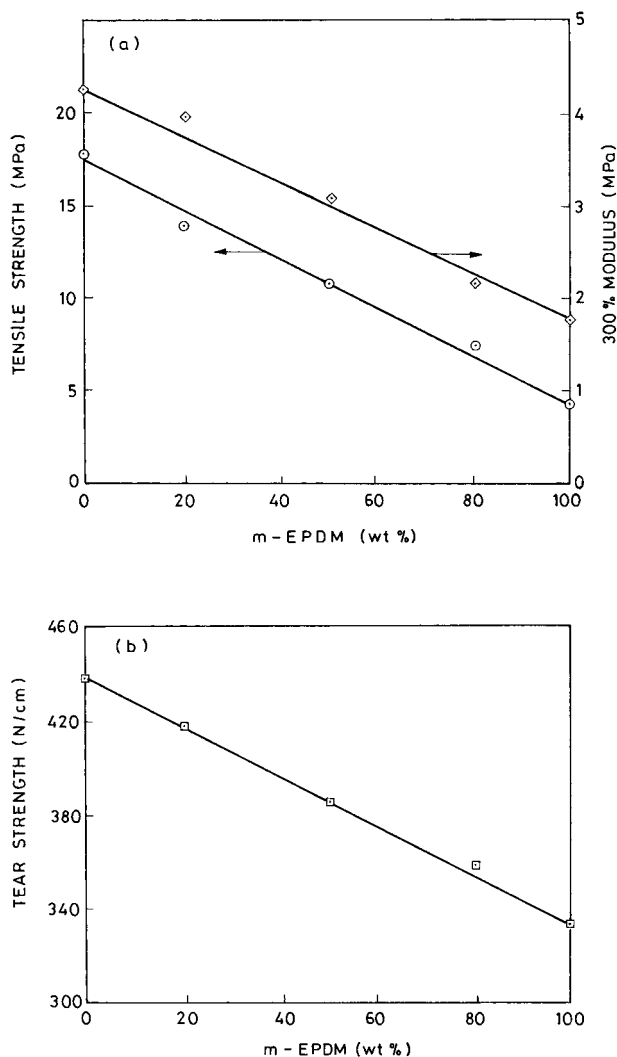
Figure 2 Variation of physical properties with blend ratio in m-EPDM/XNBR/ZnO systems. (a) Tensile strength and 300% modulus. (b) Hysteresis loss and tear strength. Solid lines indicate the calculated average values. Experimental results are shown by the points on the lines.

Results of dynamic mechanical properties are summarized in Table II. The results show that the ZnO-neutralized XNBR shows two peaks in the tan δ curve. The most intense peak occurs around 0.7°C. This low temperature tan δ peak is accompanied by a pronounced fall of storage modulus from the glassy state to the rubbery state. This transition is believed to be due to main chain glass-rubber transition, and the corresponding temperature is abbreviated as Tg_2. The second peak occurs at a higher temperature around 60°C, which is in the same temperature range reported earlier in the case of XNBR–ZnO system.[6] In ionic polymers, the high temperature peak is reported to be due to relaxation of immobile chains present in the ion-rich domains, which constitute the second phase. The ionic forces of interaction leads to formation of ionic aggregates called multiplets and clusters that greatly restrict the mobility of the adjacent chains and becomes responsible for the formation of the biphasic structure.[13–15] The high temperature relaxation is labeled as Ti.

The m-EPDM–ZnO ionic elastomer shows the main glass-rubber transition around −41.8°C (known as Tg_1) and a weak high temperature transition around +40°C. That the weak transition is not due to melting of any crystallites is substantiated by the fact that m-EPDM contains 50% of ethylene units and the material is essen-
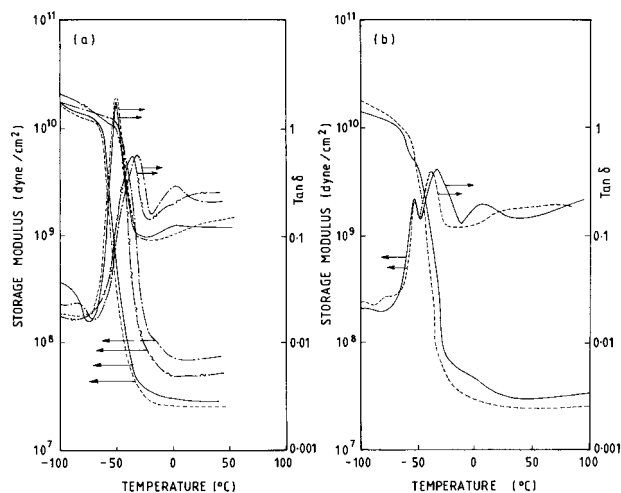
rized in Table I. From Figure 1 and Table I, it is evident that the XNBR–ZnO system shows maximum tensile strength, modulus, and tear resistance, whereas the m-EPDM–ZnO system shows the lowest values. For a compatible blend of two polymers, the physical properties should lie in between the two component polymers and follow the additivity rule.[8] From Figure 2, it is evident that the physical properties follow the additivity line.

Dynamic Mechanical Properties

In Figure 3 is shown typical plots of storage modulus and loss tangent (tan δ) against temperature.

Figure 3 Representative plots of storage modulus and tan δ against temperature. (a) —, 100/0 m-EPDM/ZnO; -----, 100/0 m-EPDM/ZnO after ammonia treatment; − · −, 100/0 XNBR/ZnO; ≂ −, 100/0 XNBR/ZnO after ammonia treatment. (b) —, 50/50/10 m-EPDM/XNBR/ZnO system; -----, 50/50/10 m-EPDM/XNBR/ZnO system after ammonia treatment.

Table II   Results of Dynamic Mechanical Analyses[a]

Formulation, XNBR/m-EPDM/ZnO (Parts by Weight)	Tg_1[b] (°C)	Tan δ at Tg_1	Tg_2[c] (°C)	Tan δ at Tg_2	Ti (°C)	Tan δ at Ti
100/0/10	—	—	+0.7 (−5.3)	0.586 (0.535)	51.3 [d]	0.297 [d]
80/20/10	−39.7	0.069	+0.7	0.485	50.8	0.238
50/50/10	−38.6 (−34.8)	0.197 (0.216)	−2.2 (−10.5)	0.398 (0.400)	42.3 [d]	0.180 [d]
20/80/10	−36.2	0.604	−9.3	0.189	40.4	0.130
0/100/10	−41.8	1.192	— (−40.0)	— (1.199)	38.0 [d]	0.094 [d]

[a] Values in parentheses are the results of measurements of ammonia-treated samples.
[b] Tg_1 refers to the m-EPDM phase.
[c] Tg_2 refers to the XNBR phase.
[d] Transition absent.

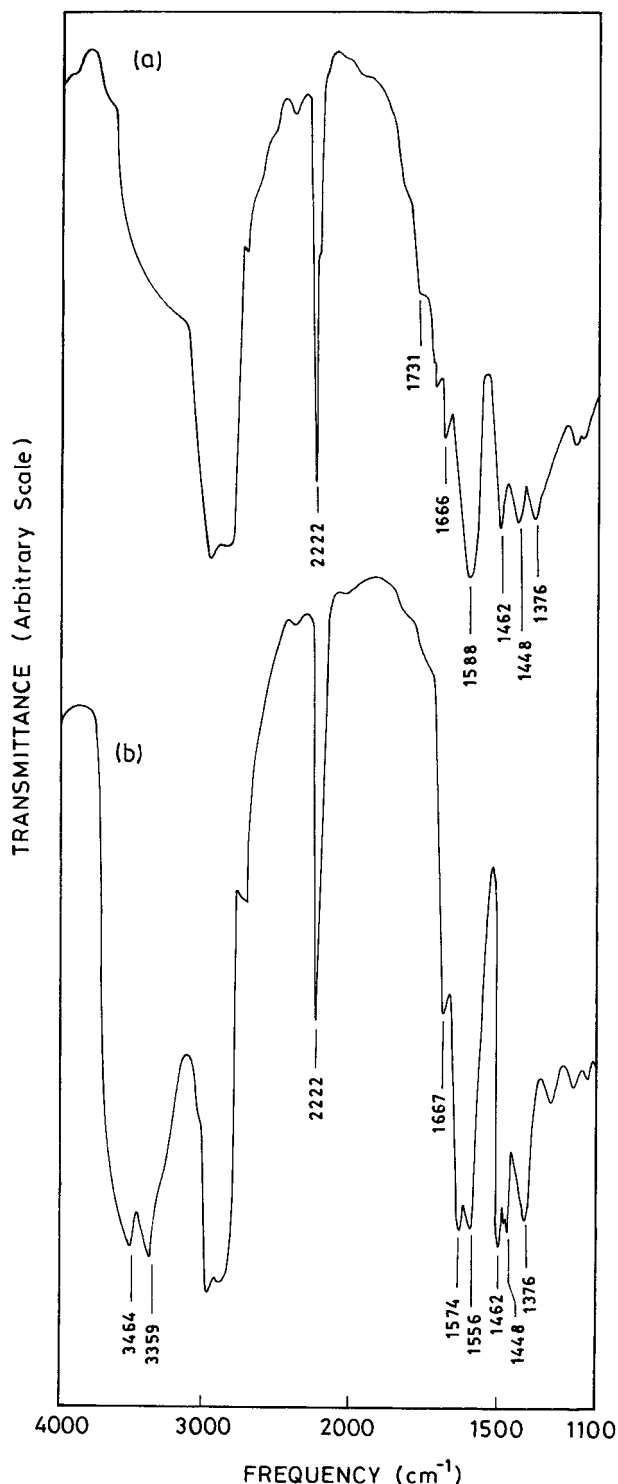tially a random copolymer, which is essentially devoid of any degree of crystallinity.[16]

Solvation

Previously, it has been reported that dimethyl sulfoxide solvates the ionic aggregates and causes disappearance of the high temperature peak.[4,17] It has also been reported that glycols, water, and amines are good solvating agents for ionic aggregates in ionomers.[18,19] Solvation occurs due to either complex formation with the cation or formation of hydrogen bonds with the anion. In the present case, the blend and the component polymers were solvated by keeping the samples in ammonia-saturated atmosphere for 48 h. This results in a drastic fall in physical properties like tensile strength and modulus (Table I). Because XNBR is more polar than m-EPDM, diffusion of ammonia is greater in XNBR-rich blends, and the fall is more prominent in the blends with high XNBR content.

Effect of ammonia treatment on the plots of tan δ and storage modulus *vs.* temperature is shown in Figure 3, and the results of the dynamic mechanical studies are shown in Table II. It is evident that ammonia causes minor reduction in the glass-rubber transition temperature and lowers down the storage modulus at the rubbery region apparently due to some plasticization of the main chain. However, ammonia treatment causes disappearance of the high temperature ionic transition. It is believed that the ionic aggregates are solvated by ammonia, thus suppressing the formation of the rigid phase due to immobility of

chains adjacent to the ionic domains. Disruption of the ionic domains results in loss of physical properties, as discussed previously.

That ammonia causes destruction of the ionic aggregates by solvation is substantiated by the results of infrared spectroscopic studies. Ammonia is reported to have a broad infrared absorption band around 3414 cm^{-1}, and another band at 3337 cm^{-1} due to N—H stretching vibration.[20] The infrared spectra of ammonia-treated 50/50 XNBR–m-EPDM blend is shown in Figure 4 and compared with the spectra of the untreated blend. On ammonia treatment, there occurs a broad band with two peaks around 3460 cm^{-1} and 3360 cm^{-1}. Considering the 3414 cm^{-1} band as the main band for ammonia, the low frequency shift of N—H stretching peak (i.e., from 3414 cm^{-1} to 3360 cm^{-1}) can be assigned due to interaction of ammonia with the ionomer by hydrogen bonding, ion-dipole forces, and complexation.[21–25] Lu and Weiss[21] have reported that the spectrum of polyamide-6 is characterized by a broad band with absorbance maxima around 3300 cm^{-1},[21] which was attributed to composite absorption of N—H groups present in different phases. They have shown that, on complexation with manganese-sulfonated polystyrene, the band was broadened and the peak maximum was shifted to a lower frequency region. It was also observed that a higher frequency band of free N—H stretching (3447 cm^{-1}) was shifted to a lower frequency region. Effects were attributed to complexation of Mn^{+2} by amino groups and formation of H—bonds between N—H groups with sulfonate anions. On the other hand, a new peak in the blend appeared

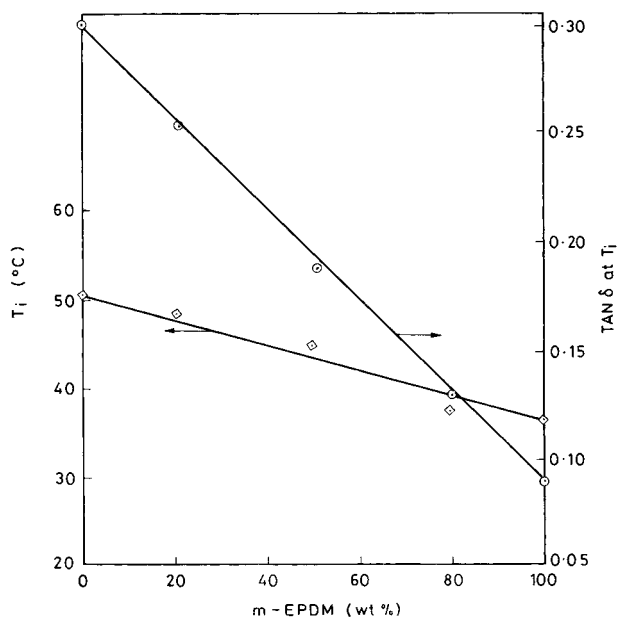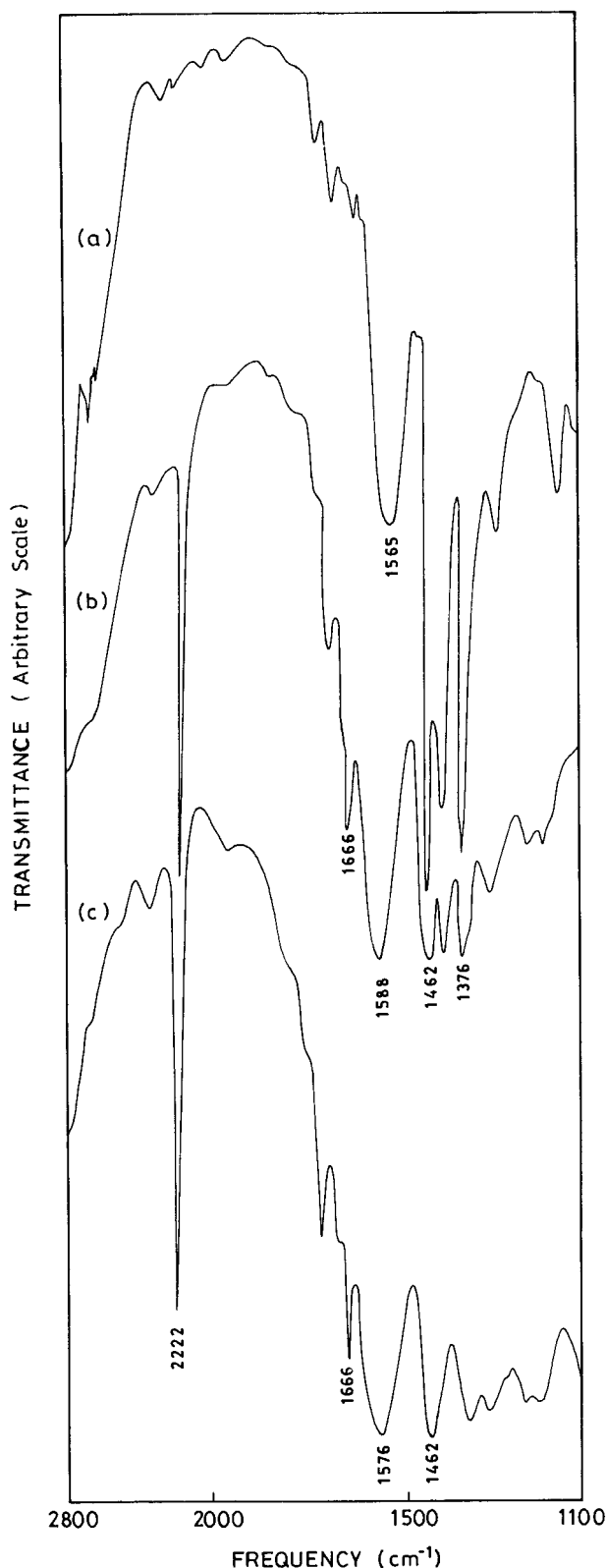been reported in the case of polyamide-zinc sulfonated polystyrene blend.[22] Similar reasoning may be ascribed to the occurrence of the higher frequency band at 3460 cm^{-1} in the present case.

It has been stated earlier that any group that forms complex with the cationic part, as well as forms hydrogen bonds with the anionic part, should result in a shift to a lower frequency of the ionic peak (due to anionic stretching).[21-23] In the present case (e.g., for the 50/50 XNBR–m-EPDM blend), the —COO$^-$ asymmetric stretching frequency peak that occurs around 1588 cm^{-1} (refs. 27–29) before ammonia treatment is shifted to a lower frequency region and forms a doublet at 1574 and 1556 cm^{-1} after ammonia treatment. For XNBR–ZnO and m-EPDM–ZnO systems also (spectra not shown), similar observation was made. The downfield shift of the —COO$^-$ asymmetric stretching frequency band is thus explained by considering its hydrogen bonding with N—H groups resulting in weakening of the ionic associates. Appearance of the doublet is believed to be due to the changes in the geometrical arrangement of the —COO$^-$ groups surrounding the central metal ion[24] as a result of complexation of the metal ion by ammonia and hydrogen bonding of the —COO$^-$ groups with N—H groups. Similar low frequency shift was observed in the hydrated Nafion system.[25]

It is thus apparent that the high temperature transition in XNBR–ZnO and m-EPDM—ZnO

Figure 4 Infrared spectra of 50/50/10 m-EPDM/ XNBR/ZnO system. (a) Before ammonia treatment. (b) After ammonia treatment.

at 3520 cm^{-1}. This peak was attributed to delocalization of a lone pair of electrons as a result of complexation.[21] Similar observations have also

Figure 5 Dependence of Ti and tan δ at Ti on blend composition of m-EPDM/XNBR/ZnO system.

Figure 6 Infrared spectra of different systems (a) 100/10 m-EPDM/ZnO, (b) 100/10 XNBR/ZnO, and (c) 50/50/10 m-EPDM/XNBR/ZnO.

systems and their blends is due to the rigid phase arising out of the ionic aggregates, which, however, gets complexed and masked by ammonia, suppressing the formation of the biphasic structure in the constituent polymers and their blend.

Compatibilization

It is apparent from Table II and Figure 3 that there occurs two thermal events in the blends that are ascribed to two glass transitions and the corresponding temperatures are Tg_1 and Tg_2. The glass-transition temperature of the two components shows no appreciable change on blending. Hence, we can conclude that the blend is essentially immiscible. This is not unexpected in view of the difference in polarity of the two polymers.[7]

The high temperature transition corresponding to Ti in the blends shows the existence of single transition, which occurs inbetween the Ti's of the two polymers (Fig. 5, Table II). Tan δ values at Ti indicate that, for XNBR—ZnO system, tan δ is much greater than that for the m-EPDM–ZnO system. This is believed to be due to a higher extent of cluster formation in the XNBR—ZnO system, which in turn depends on the higher extent of carboxylate salt formation. It has been reported that higher ion content in an ionic polymer facilitates phase separated ionic cluster formation.[25]

Dependence of the tan δ at Ti on blend composition is shown in Figure 5. The experimental values are very close to the calculated averages. Accordingly, it is proposed that the ionic domains arising out of the constituent polymers merge together and form a hard phase at the interface of the two polymers. It is believed that the ionic aggregates serve as interfacial crosslinking sites
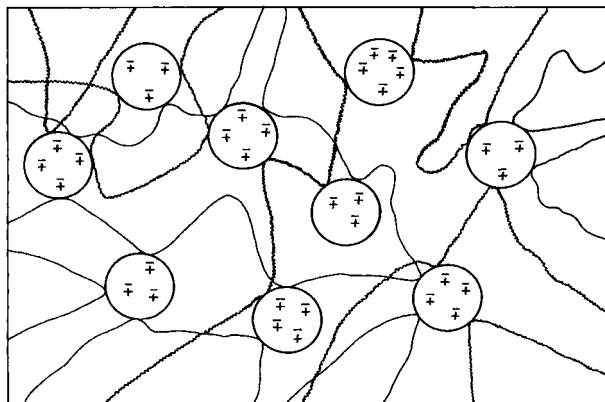
Figure 7 Schematic representation of interfacial ionic aggregates. ∿∿, XNBR; ∿∿, m-EPDM.

Table III   Results of Recycling by Repeated Moldings of the Blend Composition XNBR/m-EPDM/ZnO (50/50/10)

Cycle No.	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1	3.08	11.20	863
2	3.10	11.11	854
3	3.23	11.20	850
4	3.28	11.06	841

and compatibilize the two otherwise incompatible polymers in the blend.

In Figure 6 is shown the infrared spectra of XNBR–ZnO, m-EPDM–ZnO, and their 50/50 blend. The XNBR—ZnO system shows a sharp band at 1576 cm^{-1} and m-EPDM–ZnO shows a band at 1565 cm^{-1}. The band in this region is believed to be due to asymmetric stretching of carboxylate ions, which stands for bridging type of metal carboxylates.[27–30] In the 50/50 XNBR–m-EPDM blend, a sharp single band occurs at 1588 cm^{-1}. In the blend system in absence of any interaction, the blend spectrum should reveal the spectral features associated with both the components.[31] In reality, however, the carboxylate stretching peak for the blend is shifted at a higher frequency region. The high-frequency shift of the ionic peak is believed to be due to the formation of stronger ionic associates.[22] In the blend system, if the ionic aggregates are formed at the two phase interfaces, the polarity surrounding it is reduced due to the presence of nonpolar EPDM phase. Ionic cluster phase formation is believed to be more prominent in a medium of low polarity.[26] Thus, results of infrared spectroscopic studies substantiates the theory of interfacial ionic bridge formation. On the basis of dynamic mechanical analyses and infrared studies, a schematic model of the ionic polymeric blend is proposed and shown in Figure 7.

Results of reprocessability studies of a representative blend system are shown in Table III. The composition is reprocessable and physical properties after repeated moldings up to three cycles remained almost unchanged.

CONCLUSIONS

1. Blends of zinc salts of m-EPDM rubber and carboxylated nitrile rubber act as ionic thermoplastic elastomers.

2. In the presence of ammonia, the high temperature relaxation due to ionic groups in the polymer disappears due to solvation of the ionic species by ammonia.
3. Results of reprocessability studies reveal that the blend is reprocessable at least up to three cycles of molding.

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