

Blends of Ionomers

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SYNOPSIS

Blends of zinc oxide-neutralized maleated EPDM terpolymer, (m-EPDM) and zinc salt of an ethylene-methacrylic acid copolymer, (Zn-EMA), wherein Zn-EMA does not exceed 50% by weight, behave as an ionic thermoplastic elastomer. A typical 60/40 m-EPDM/Zn-EMA blend has the following properties: 100% modulus, 5.53 MPa; tensile strength, 12.10 MPa; elongation at break, 220%; and tension set at 100% elongation, 29%. Properties of the blends are greater than those predicted by the additivity rule. Dynamic mechanical and infrared spectroscopic studies revealed that the ionic bonds are formed at the interfaces of m-EPDM and Zn-EMA, which facilitates formation of the technologically compatible blend. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Neutralization of maleated EPDM rubber (m-EPDM) by metal oxide is known to form an ionic elastomer.¹ Zinc salt of an ethylene-methacrylic acid copolymer (Zn-EMA) is one of the earliest thermoplastic ionomers.²

The present investigation aimed at the development of an ionic thermoplastic elastomer by blending zinc oxide neutralized m-EPDM and Zn-EMA. It is well known that thermoplastic elastomers can be prepared by blending a rubber with a thermoplastic in the right proportions.³⁻⁶ One important consideration in making such a rubber-plastic blend is the compatibility of the two components. Very often, the components are grossly incompatible⁷ and interfacial agents or compatibilizers are needed to obtain technologically compatible blends. A number of interfacial agents and compatibilization methods have been developed.^{8,9} However, blends based on ionomers have not received wide attention. Lu and Weiss reported that the miscibility of polycaprolactone with a styrenic block copolymer was improved by ionomer formation in the latter.¹⁰ Ionomers based on sulfonated polystyrene have been found to show improved miscibility with polyamides.^{11,12} Eisenberg and co-workers developed a series of blends based

on an acid-functionalized polymer and an amino-type basic component.¹³⁻¹⁵ The blends show limited miscibility due to acid-base interaction or salt formation and processing of the materials is difficult.¹⁶ A mixture of zinc-sulfonated EPDM and zinc salt of sulfonated polystyrene was reported to compatibilize the blend of EPDM and polystyrene.¹⁷ Blends based on polyurethane ionomers with polyacrylonitrile were studied recently.¹⁸ Fitzgerald and Weiss reviewed blends of ionomers.¹⁹

The present article reports the results of studies on the binary blends of zinc oxide-neutralized m-EPDM and Zn-EMA. Studies include measurement of physical properties, dynamic mechanical properties, reprocessibility behavior, and infrared spectroscopic studies.

EXPERIMENTAL

m-EPDM was supplied by Uniroyal Chemical Co., U.S.A. Its weight-average molecular weight (M_w) was 3.99×10^5 , and its number-average molecular weight (M_n), 1.16×10^5 . Its maleic acid/anhydride content was 1%, and ethylene content, 55%, and the Mooney viscosity, $ML_{(1+4)}$, 100°C, was 60. The zinc oxide used was a laboratory-grade reagent and was obtained from Bayer Chemicals, Calcutta, India.

Zn-EMA was supplied by E. I. DuPont de Nemours & Co., USA. It has a carboxylate content of 10.7 meg/100 g polymer. The material was partially

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Table I Formulations of the Mixes

Ingredient	Mix No.									
	E	Z0	Z0D	Z1	Z2	Z3	Z4	Z5	Z5D	Z10
m-EPDM	100	100	100	90	80	70	60	50	50	0
Zn-EMA	0	0	0	10	20	30	40	50	50	100
ZnO	0	10	10	10	10	10	10	10	10	10
DCP	2.0	—	—	—	—	—	—	—	—	—
DMSO	—	—	10	—	—	—	—	—	10	—

neutralized. Solution neutralization indicated that about 4 g of ZnO was required for the neutralization of 100 g rubber. Since solid-phase neutralization of a carboxylated polymer needs an excess of ZnO (about 2–2.5 times the amount required in solution neutralization),²⁰ 10 g ZnO per 100 g of polymer was taken to ensure complete neutralization. Compositions of the blends are given in Table I. Preliminary results of measurements of physical and dynamic mechanical properties of the 50/50 m-EPDM/Zn-EMA blend neutralized with different ZnO loadings revealed that there was no change in properties at a ZnO level higher than 10 phr.

Blends were prepared in a Brabender Plasticorder, Model PLE-330, at 170°C and at a rotor speed of 60 rpm. First, Zn-EMA was charged and allowed to melt. Then, m-EPDM was added and allowed to mix for 2 min. Finally, zinc oxide was added and mixed for another 2 min. Next, the material was dumped and sheeted out in a two-roll mill at room temperature. For ensuring proper mixing, the sheeted-out material was again mixed in the Brabender for an additional 2 min and then finally sheeted out. The mixes were then molded at 170°C for 20 min at a pressure of 10 MPa. The molding time was selected on the basis of results of preliminary experiments. After molding, the mixes were cooled to room temperature by circulation of cold water through the platens. The hardness was determined as per ASTM D 2240 (1986) and expressed in Shore A and D.

Tensile stress-strain, hysteresis, and tension set were tested with dumbbell samples cut according to the ASTM D 412 specification using a Zwick UTM, Model 1445, at a crosshead speed of 500 mm/min. Hysteresis was studied by stretching the samples up to an elongation of 200%. Tension set was measured at 100% extension. Tear strength was measured with nick-cut 90°-crescent tear samples cut according to ASTM 624-86 die C.

Dynamic mechanical properties were measured under a tension mode using a viscoelastomer,

namely, a Rheovibron (DDV-III-EP) of Orientec Corp., Tokyo, Japan. Sample size was 3.5 × 6.5 × 2 mm. Testing was carried out at a frequency of 3.5 Hz over a temperature range of -100 to +200°C and the heating rate was 1°C/min.

Infrared spectra were measured with melt-cast films in a Perkin-Elmer dispersive infrared spectrophotometer, Model 843. The spectrophotometer was equipped with silver iodide dispersion gratings and a pyroelectric detector. The spectra were taken at a resolution of 3.2 cm⁻¹ with an in-built noise level of 0.5% transmittance. A total of 16 scans were averaged. The spectral data were processed using a dedicated computer.

RESULTS AND DISCUSSION

Figure 1 shows the stress-strain plots of the polymers and their blends. At a very high Zn-EMA level

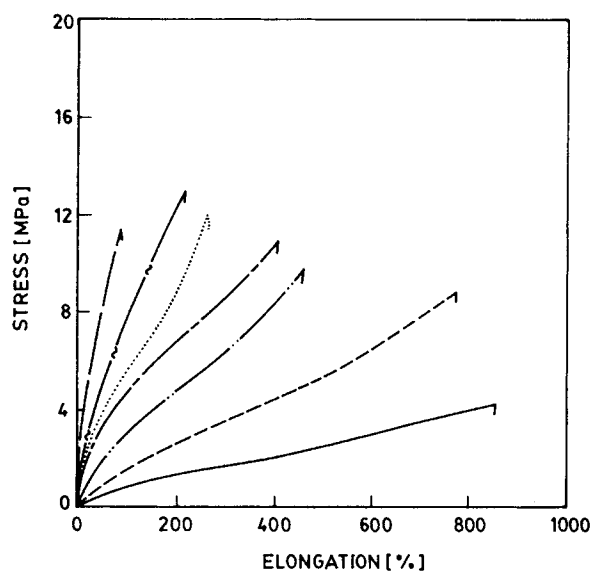


Figure 1 Stress-strain plots for neat polymers and different blend compositions: (—) Z0; (---) Z1; (- · - ·) Z2; (- - -) Z3; (· · · ·) Z4; (- ~ -) Z5; (- - -) Z10.

(i.e., > 50 wt %), the blend compositions showed thermoplastic characteristics (i.e., low elongation at break and high tension set), the results not shown in Figure 1. Accordingly, the m-EPDM/Zn-EMA blend ratios chosen were 90/10, 80/20, 70/30, 60/40, and 50/50, the figures being expressed in parts by weight. The results of measurements of physical properties are summarized in Table II. It is evident that Zn-EMA containing 10 phr of zinc oxide behaves as a rigid plastic, while the ZnO neutralized m-EPDM behaves as a rubber. As the plastic content in the blend increases, there is an increase in tensile strength, modulus, tear resistance, and hysteresis, while the elongation at break falls. The tension set is low in the compositions studied. In general, the set increases with increase in plastic content, and the maximum set of 31% was obtained in the case of 50/50 blend of m-EPDM/Zn-EMA. This is within the acceptance limit of set values for thermoplastic elastomers.²¹

Figure 2 shows the variation of experimental tensile strength and tear resistance of the blends at 25 and 70°C. The figure also shows the calculated strength on the basis of weighted averages. It is seen

that at room temperature the observed strength is greater than that predicted. However, at 70°C, the observed and the predicted values are similar. This indicates the existence of a thermoreversible interaction between the component polymers, leading to property enhancement or a synergistic effect in the property under ambient conditions. A synergistic effect in the property was observed in the case of compatible blends.²² It is apparent that the blend of zinc salt of m-EPDM and Zn-EMA forms a technologically compatible blend and, presumably, the ionic bonds acting as physical crosslinks formed at the interfaces participate in the compatibilization mechanism. A higher test temperature causes disruption of the ionic bonds and drop in physical properties.

Figure 3 shows typical plots of $\tan \delta$ against temperature. Results of dynamic mechanical studies are summarized in Table III. The values of T_g , $\tan \delta$ at T_g , T_i , and $\tan \delta$ at T_i were collected from the data stored in the computer attached to the instrument. Zinc oxide-neutralized m-EPDM shows two transitions, one at -41.8°C , which is due to the glass-rubber transition and abbreviated $T_g(A)$, and a weak

Table II Results of Measurements of Physical Properties at 25°C^a

Properties	Mix No.						
	Z0	Z1	Z2	Z3	Z4	Z5	Z10
Hardness (Shore A/Shore D)	47 Shore A	13 Shore D	17 Shore D	20 Shore D	22 Shore D	25 Shore D	44 Shore D
Modulus 100% (MPa)	1.10 (0.53)	1.84 (1.20)	3.26 (1.60)	4.85 (1.84)	5.53 (2.02)	6.38 (2.38)	^b ^b
Modulus 200% (MPa)	1.48 (0.89)	2.92 (1.75)	5.03 (2.56)	7.64 (2.65)	8.99 (2.87)	^b (3.01)	^b ^b
Tensile strength (MPa)	4.40 (2.20)	8.90 (2.29)	9.80 (3.00)	11.24 (3.64)	12.10 (4.22)	13.40 (4.40)	11.54 (5.12)
Elongation at break (%)	850 (310)	760 (281)	458 (264)	382 (274)	220 (260)	175 (238)	76 (89)
Tear strength (N/cm)	332.0 (130.0)	380.6 (242.0)	461.2 (260.0)	476.2 (310.9)	530.9 (330.7)	580.9 (382.0)	670.4 (605.2)
Hysteresis (J/m ²) × 10 ²	3.3	7.4	22.0	28.3	74.0	^b	^b
Tensile set at 100% extension (%)	13	13	17	22	29	31	^b

^a Figures in parentheses are the results of measurements at 70°C.

^b Could not be determined, because of the low elongation at break.

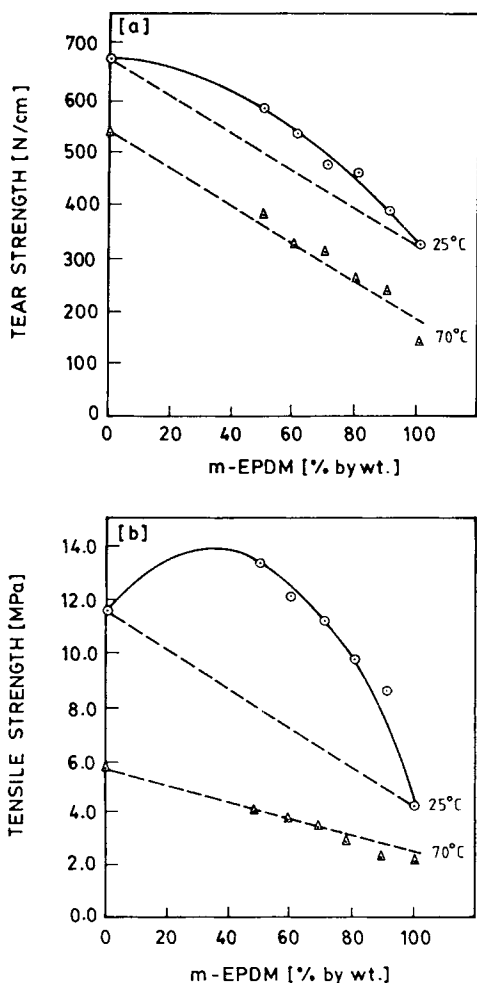


Figure 2 (a) Variation of tear strength with blend composition: (○) Observed values at room temperature; (△) observed values at 70°C; (-----) additive line. (b) Variation of tensile strength with blend composition: (○) Observed values at room temperature; (△) observed values at 70°C; (-----) additive line.

transition at +38°C, which is presumably due to the occurrence of a rigid phase arising out of the ionic aggregates. That the high temperature relaxation is due to ionic clusters and not to any other transition of the base polymer is confirmed by the absence of the peak in the m-EPDM-DCP system (mix E) and in the dimethyl sulfoxide (DMSO)-treated m-EPDM-ZnO system (mix ZOD). DMSO is known to exert a profound solvation effect on the ionic clusters, which counteracts the formation of restricted mobility zone.²³ Similarly, DMSO treatment of mix Z5 causes lowering of T_i and $\tan \delta$ at T_i (Fig. 3 and Table III). Zinc oxide-filled Zn-EMA shows three transitions: (a) one at -4.0°C, which is due to the glass-rubber transition²⁴ and abbreviated $T_g(B)$, (b) the second transition occurring at

+64.3°C, which is presumably due to the rigid phase arising out of the ionic aggregates called multiplets and clusters,^{25,26} and (c) the third transition around +90°C, which is possibly due to the melting of the crystalline polyethylene blocks. It has been reported earlier that in the case of crystalline ionomers transition due to ionic aggregates occurs at a lower temperature than the crystalline melting temperature.^{27,28} In the case of rubbery ionomers, transitions due to ionic groups have been reported to occur in the same temperature range as observed in the present case.²⁹ The transition around 64.3°C is called

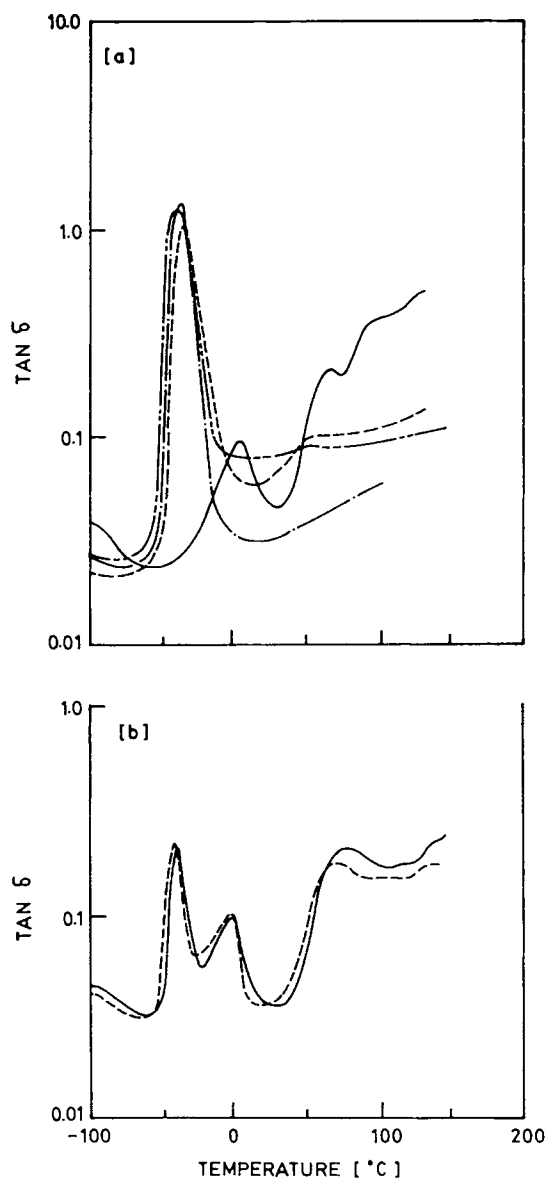


Figure 3 Typical plots of $\tan \delta$ against temperature: (a) (-----) Z0; (—) Z10; (- · -) E; (· · ·) ZOD. (b) (—) Z5; (-----) Z5D.

the ionic transition. The temperature corresponding to the ionic transition is abbreviated T_i . Table III shows that the blends register different transitions corresponding to T_g (A), T_g (B), and T_i . The low-temperature transition corresponding to T_g (A) shifts to slightly higher temperature in the blend, while that corresponding to T_g (B) remains almost unchanged. The high-temperature transition, corresponding to T_i , in the blends occurs in between the T_i 's of the constituent polymers, except in the case of mix Z5 where the T_i is even higher than that of the Zn-EMA-ZnO system. It is also seen that the $\tan \delta$ at T_i for mix Z10 is much greater than mix Z0, indicating that the phase separation due to the ionic aggregates is more prominent in the case of Zn-EMA, as compared to the m-EPDM system. This is due to a higher extent of carboxylate salt formation in Zn-EMA. It has been reported that higher ion content in an ionic polymer facilitates phase-separated ionic cluster formation.³⁰

Dependence of $\tan \delta$ at T_i on the blend composition is shown in Figure 4. The experimental values are higher than are the weighted averages. This means that the rigid phase in the blends is stronger than that predicted by the additivity rule. Accordingly, it is proposed that besides ionic crosslinks occurring in between the two chain segments of the same polymer ionic crosslinks can also occur between the chain segments of m-EPDM and Zn-EMA. The ion-pair interaction first forms multiplets, resulting in considerable restriction in the chain mobility. At a sufficiently high level of multiplet formation, the tightly held chains coalesce to form clusters, causing severe restriction in chain mobility and forming a separate phase, which is called the ionic phase or ionic cluster phase.²⁶ The multiplet-cluster model is shown in Figure 5. In this

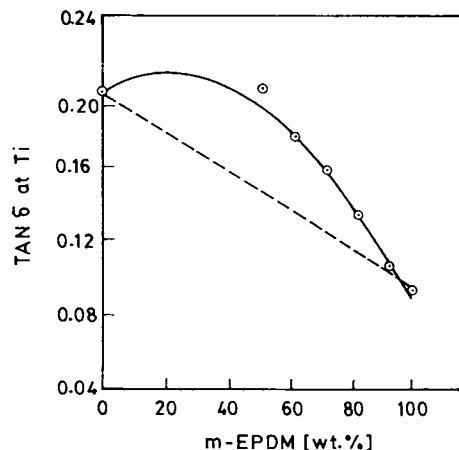


Figure 4 Variation of $\tan \delta$ at T_i with blend composition: (O) observed values; (· · · · ·) additive line.

model, it is proposed that both m-EPDM and Zn-EMA chains participate in cluster formation.

IR spectra of m-EPDM-ZnO and Zn-EMA-ZnO systems are shown in Figure 6. The m-EPDM-ZnO system shows a broad diffused band at 1565 cm^{-1} , which is believed to be due to asymmetric stretching of carboxylate groups.³¹⁻³⁴ It has been reported that metal carboxylates in ionic polymers containing a bridging type of carboxylate group shows a band in the vicinity of 1570 cm^{-1} .³⁵ Accordingly, the peak at 1565 cm^{-1} is believed to represent the bridging type of carboxylate groups. The low intensity of the peak suggests a low degree of salt formation. The Zn-EMA-ZnO system, on the other hand, shows a high intensity band at 1588 cm^{-1} , indicating a high extent of metal carboxylate salt formation. A similar observation was made earlier and the peak is believed to be due to carboxylate anionic stretching in a well-defined ionic aggregate.³⁶ The carboxylate

Table III Results of Dynamic Mechanical Studies

Mix No.	T_g (A) (°C)	Tan δ at T_g (A)	T_g (B) (°C)	Tan δ at T_g (B)	T_i (°C)	Tan δ at T_i
Z0	-41.8	1.192	—	—	38.0	0.094
E	-44.0	1.273	—	—	—	—
Z0D	-42.7	1.208	—	—	a	a
Z1	-33.2	0.977	-2.1	0.096	51.9	0.105
Z2	-33.1	0.589	-6.1	0.072	52.1	0.130
Z3	-35.4	0.469	-1.7	0.062	58.0	0.157
Z4	-36.4	0.382	-1.7	0.085	60.2	0.170
Z5	-40.0	0.192	-6.2	0.094	73.3	0.211
Z5D	-40.0	0.225	-7.1	0.101	55.3	0.175
Z10	—	—	-4.0	0.092	64.3	0.197

a Absent.

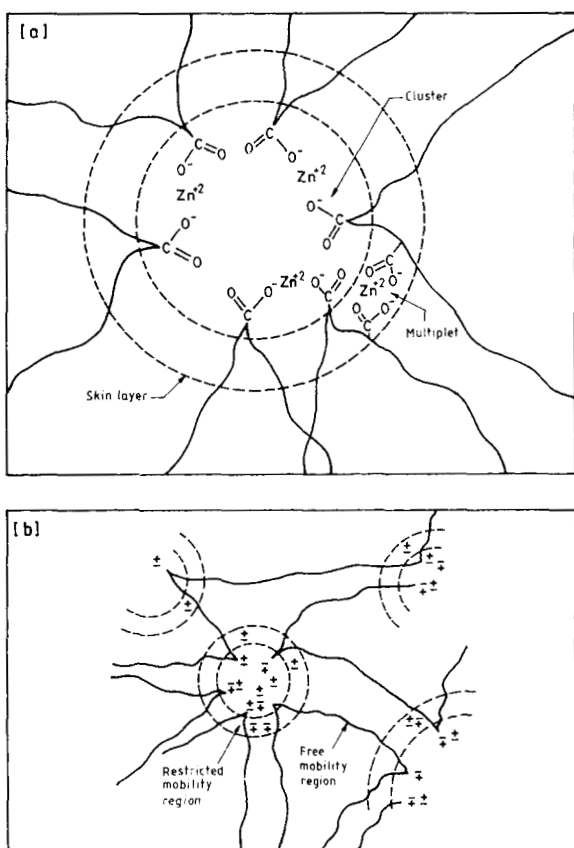


Figure 5 Multiplet cluster model showing formation of biphasic structure in the blend.

asymmetric stretching peak in the case of mix Z10 occurs at a higher frequency than that in mix Z0. This is believed to be due to the occurrence of stronger ionic aggregates or clusters in mix Z10. It was reported earlier that in ionic polymers, in the absence of effects like H-bonding, strengthening of the ionic cluster phase is accompanied by a shift of carboxylate stretching band to a higher-frequency region.³⁷ The summation spectrum of the two samples (after normalization of the spectra of the constituent polymers) is also shown in Figure 6(c). It is reported that in the absence of any interaction the spectrum of a blend is likely to be equivalent to the summation spectrum of the constituent polymers.³⁸

However, in the present case, interaction between the ionic aggregates of the two polymers and formation of an interfacial ionic cluster phase are likely to influence the spectral features associated to the carboxylate asymmetric stretching band. The summation spectrum of mixes Z0 and Z10 is shown in Figure 7. This indicates the existence of a broad band with absorption maxima around 1588 cm^{-1} along with a shoulder at 1565 cm^{-1} , which are the

peak positions for mixes Z10 and Z0, respectively. Application of a polynomial program for resolving this broad diffused band³⁹ gives a profile, also shown in the Figure 7, wherein the two peaks are resolved. The summation spectra suggests that in the absence of any interaction the ionic aggregates associated to the component polymers are likely to maintain their own identity in the blend. The blend corresponding to mix Z5, however, shows only a sharp peak at 1586 cm^{-1} . The existence of the single spectral band indicates that the metal carboxylates associated to two polymers in the blend are present in the same environment. It is expected that if the two ionic peaks combine the intermediate band position should be

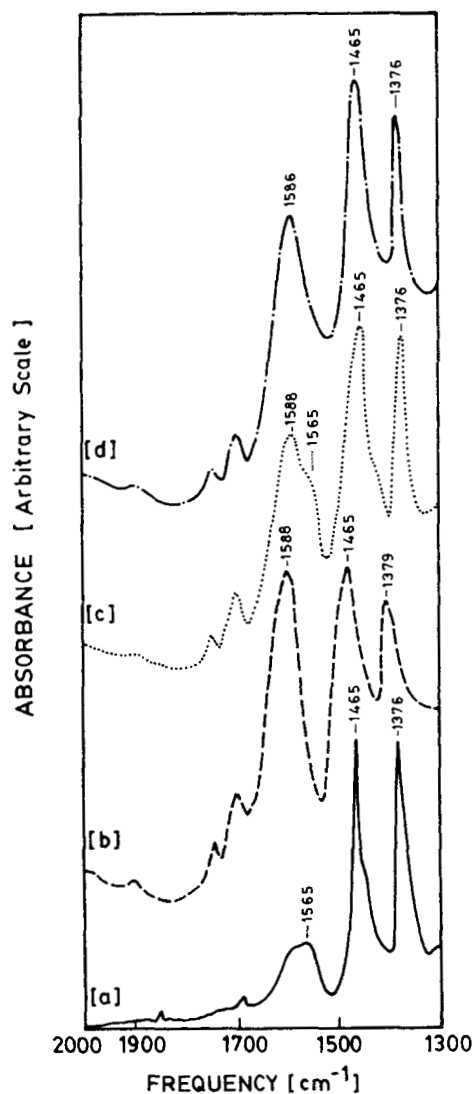


Figure 6 Infrared spectra of (a) Z0, (b) Z10, (c) summation averaged spectrum of Z0 and Z10, and (d) blend Z5.

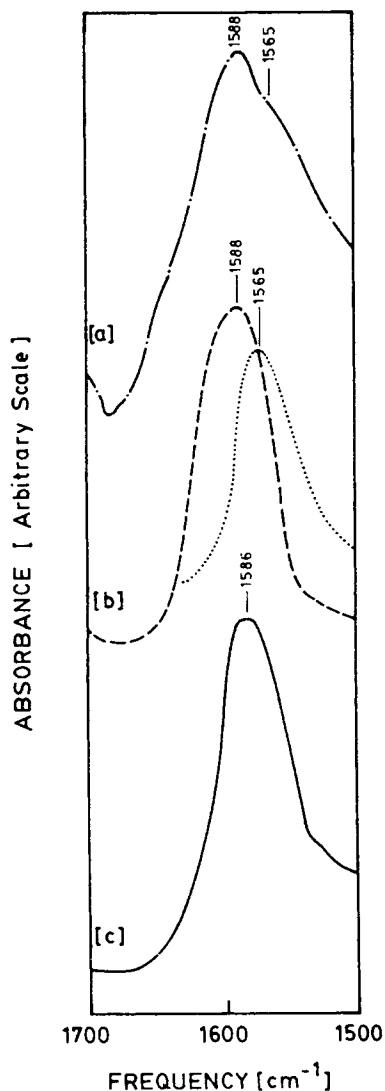


Figure 7 (a) Same as Figure 6(c), with the frequency scale expanded. (b) Resolved spectra of (a). (c) Same as Figure 6(d), with the frequency scale expanded.

around 1574 cm^{-1} . In reality, however, the band is shifted to the higher frequency side by 12 cm^{-1} .

The frequency shift of the infrared spectral band may be due to the following reasons: first, there may be a refractive index dispersion effect i.e., a change

in the refractive index when the IR beam passes through two phases having unequal refractive indices. Such refractive index dispersion alters the band shape and shows a change in frequency.⁴⁰ If the refractive index dispersion is operative, the sharp bands common to both the systems are likely to change position. In practice, however, the 1465 cm^{-1} band which is due to combined effect of C—H asymmetric bending vibration of $-\text{CH}_2-$ and $-\text{CH}_3$ groups and C—C stretching vibration occurs in the same position in the blend. The sharp peak associated to C—H bending of $-\text{CH}_3$ groups are present in 1376 cm^{-1} in mixes Z10, Z0, and Z5 (Fig. 6). Therefore, we can conclude that the refractive index dispersion effect is not the cause for the frequency shift of the spectral band.

The second possibility is intermolecular interaction. The high-frequency shift is reported to be a result of ionic cluster strengthening.³⁷ IR spectroscopic studies, therefore, suggest that phase separation due to ionic cluster formation is more than expected. Due to incorporation of m-EPDM-ZnO system in the blend, the polarity across the interface is reduced because the ethylene-methacrylic acid with a 10% carboxyl group is more polar than is m-EPDM. It was reported that phase separation due to cluster formation becomes more prominent in a medium of lower polarity.³⁰

Since the ionic bonds are heat fugitive, the blends show thermoplastic behavior. Table IV shows the effect of repeated moldings on the physical properties of the blend. It is apparent that even after three cycles of molding there is no change in modulus, tensile strength, and elongation at break. This shows that the blends behave as a thermoplastic elastomer.

CONCLUSIONS

m-EPDM/Zn-EMA blends in the compositions of 90/10, 80/20, 70/30, 60/40, and 50/50 in the presence of ZnO show thermoplastic elastomeric characteristics. An increase in Zn-EMA content in the

Table IV Results of Recyclability Studies by Repeated Moldings; Blend, Mix Z5; Molding Conditions: Temperature, 200°C ; Pressure, 10 MPa; Time, 20 Min

Cycle No.	100% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
1	6.38	13.40	175
2	6.43	13.27	161
3	6.34	13.52	184

blend increases the modulus, tensile strength, tear resistance, hysteresis, and tension set, but decreases the elongation at break. The 50/50 blend composition has the following properties: 100% modulus, 6.38 MPa; tensile strength, 13.40 MPa; elongation at break, 175%; tear resistance, 580 N/cm; and tension set at 100% extension, 31%. Properties of the blends are greater than those predicted by the additivity rule. On the basis of dynamic mechanical analysis and IR spectroscopic studies, it is believed that the ionic bonds are formed at the interfaces of m-EPDM and Zn-EMA chain segments, which are heat-fugitive and responsible for inducing compatibilization in the blend components under ambient conditions.

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