Structure-Property Relationship of Blends of Ethylene-*co*-Vinyl Acetate and Epoxidized Natural Rubber

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ABSTRACT: The properties of blends of ethylene-*co*-vinyl acetate (EVA) and epoxidized natural rubber (ENR) have been studied in relation to their structures by Fourier Transform Infrared spectroscopy (FTIR) and dynamic mechanical analysis. FTIR spectra of the blends of EVA and ENR show weak dipole-dipole interactions. These blends are incompatible as determined from the dynamic mechanical analysis and further confirmed by scanning electron microscopy studies. In order to understand the influence of interaction between the polymers, the properties of blends of ENR with other reactive polymers such as ethylene-methylacrylate (EMA) and ethylene-acrylic acid copolymer (EAA), have been compared. The higher values of tensile strength and modulus of ENR/EAA are due to the higher level of interaction.

KEY WORDS: rubber-plastic blends, ethylene vinyl acetate, epoxidized natural rubber, FTIR spectroscopy, dynamic mechanical analysis.

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INTRODUCTION

BLENDING OF A rubber with a plastic yields two new classes of materials depending on the proportion of the constituent polymers—rubber modified plastics and thermoplastic elastomeric blends. Both these subjects have been reviewed extensively in the past because of their commercial importance [1–3]. Natural rubber producing countries developed various rubber-plastic blends with natural rubber (NR) as one of the components. Our earlier work focussed on the development of a series of NR-based blends [4–6]. Because of the lack of specific interaction, the properties of these blends need to be improved through phase interaction. Such blends using epoxidized natural rubber were described in earlier papers [7–9]. Enhancement of specific interaction through physical and chemical means has been discussed in the literature [10–12]. In our continuing effort to fulfil that objective, we have prepared blends of epoxidized natural rubber and ethylene vinyl acetate and investigated the interaction, the physical and dynamic mechanical properties. In order to elucidate the influence of interaction, new blends using ENR and ethylene methylacrylate copolymer and ethylene acrylic acid have been prepared. Though there is no earlier report on such blends of EVA and ENR, these are expected to have potential applications as polar oil resistant thermoplastic elastomers and rubber modified plastics.

EXPERIMENTAL

Materials

Epoxidized natural rubber (ENR50) having an epoxide content of 50 mole % and a density of 1020 $kg \cdot m^{-3}$, was supplied by the Rubber Research Institute of India.

Ethylene vinyl acetate (EVA) copolymer (Pilene EVA 1202) having a vinyl acetate content of 12%, MFI of 6.0 $dg \cdot min^{-1}$, density of 930 $kg \cdot m^{-3}$ and melting point of 81 °C, was supplied by Polyolefins Industries Limited, India.

Ethylene methylacrylate (EMA) copolymer (OPTEMA TC-120) having a methylacrylate content of 21%, density of 940 $kg \cdot m^{-3}$ and melting point of 81 °C, was supplied by Exxon Chemical Inc., U.S.A.

Ethylene acrylic acid (EAA) copolymer having an acid content of 6% (ESCOR EAA 5001) was supplied by M/s. Exxon Chemicals Eastern Inc., Bombay, India.

Blending Process

The blends of ENR and EMA/EVA/EAA were prepared over a range of compositions from 30:70 to 50:50. For comparison, the pure components were also evaluated, wherever required.

Blending of ENR and ethylene copolymers (EMA/EVA/EAA) was carried out in a Brabender Plasticorder (model PLE-330) fitted with a cam type rotor. Mixing was done at 120°C for 8 minutes at a rotor speed of 60 rpm. The plastic was first melted in the mixer for about 2 minutes and then the masticated rubber strips were added and allowed to blend for 6 minutes.

The molten blend from the mixer was passed through a laboratory mill to get a sheet of approximately 2 mm thickness.

Molding

Tensile sheets were compression molded between aluminium foils for 3 minutes at 120°C at a pressure of 10 MPa in an electrically heated hydraulic press. Moldings were cooled under compression by passing cold water through the mold. Tensile sheets were also molded at 150°C and 175°C to study the effect of molding temperature.

Physical Testing

Tensile testing was carried out as per ASTM D412 using dumb-bell shaped (type C) specimens, on a Zwick UTM (model 1445) at a cross-head speed of 500 mm/min at 25 ± 2°C. Tension set at 200% elongation was also measured as per ASTM D412. Five specimens were tested in each case and an average value was reported. The scatter was ±10% in tensile experiment.

Fourier Transform Infrared Spectroscopic (FTIR) Study

Shimadzu (model 8101M) FTIR spectrophotometer was used for the structural analysis of the blend and the pure components. Thin films (100 μm) prepared in a laboratory press at 120°C at a pressure of 10 MPa with a residence time of 3 minutes, were used for the analysis. The spectral resolution was kept at 4.0 cm^{-1} for all the samples and the scan was taken at room temperature. Forty scans were collected and the signals averaged conventionally for each sample.

Dynamic Mechanical Analysis

Dynamic mechanical measurements of the blends and the pure components were made on Dynamic Mechanical Thermal Analyser (DMTA-PL Thermal Sciences, version 1.25). The equipment which has

provisions for both automatic operation and data processing, measured dynamic moduli (G′ and G″) and damping of the specimen under oscillating load as a function of temperature. The experiment was conducted in shear mode over a temperature range of −150°C to 150°C at a frequency of 3 Hz, with a programmed heating rate of 2°C/min.

Scanning Electron Microscopy Study

Scanning electron microscope (CAM SCAN, model 2) was used for studying the cryogenically fractured surfaces of the samples. The fractured surfaces obtained by fracturing under liquid nitrogen, were carefully cut from the failed specimen without disturbing the surface. These surfaces were sputter coated with gold before SEM observations were made. The tilt angle was adjusted to zero.

Wide Angle X-Ray Scattering Studies

Wide angle X-ray diffraction studies were made for the blends of EVA and ENR50 using monochromotized CuK_α radiation. A diffractometer equipped with Philips PW1729a X-ray generator and a nickel filter was used for getting the XRD patterns of the samples. The diffraction was recorded in the angular range from 10°(2θ)) to 30°(2θ)) at a scanning speed of 3° min^{-1}.

RESULTS AND DISCUSSION

FTIR Spectroscopic Analysis

The FTIR spectra of pure EVA, ENR50 and a 50/50 wt% EVA/ENR50 blend are shown in Figure 1. The FTIR spectrum of the EVA copolymer reveals the presence of the ester groups from the strong peak at 1750 cm^{-1} and the methylene groups from the rocking vibration at 1460 cm^{-1} [Figure 1(a)]. The spectrum of ENR50 shows the epoxy ring absorption peak at 876 cm^{-1} and a peak at 839 cm^{-1} due to the C-H out-of-plane blending vibration of the cis-1,4-isoprene unit [Figure 1(b)]. But the FTIR spectrum of the 50:50 blend of EVA and ENR50 (molded at 150°C) does not exhibit any extra peak except those of EVA and ENR50 [Figure 1(c)]. This provides strong evidence for the absence of any specific chemical interaction between the two polymers. However, the epoxy ring peak at 876 cm^{-1} shows a prominent shift to 882 cm^{-1}, which may be attributed to the dipole-dipole interaction of the epoxy groups with acetate groups in the blend.

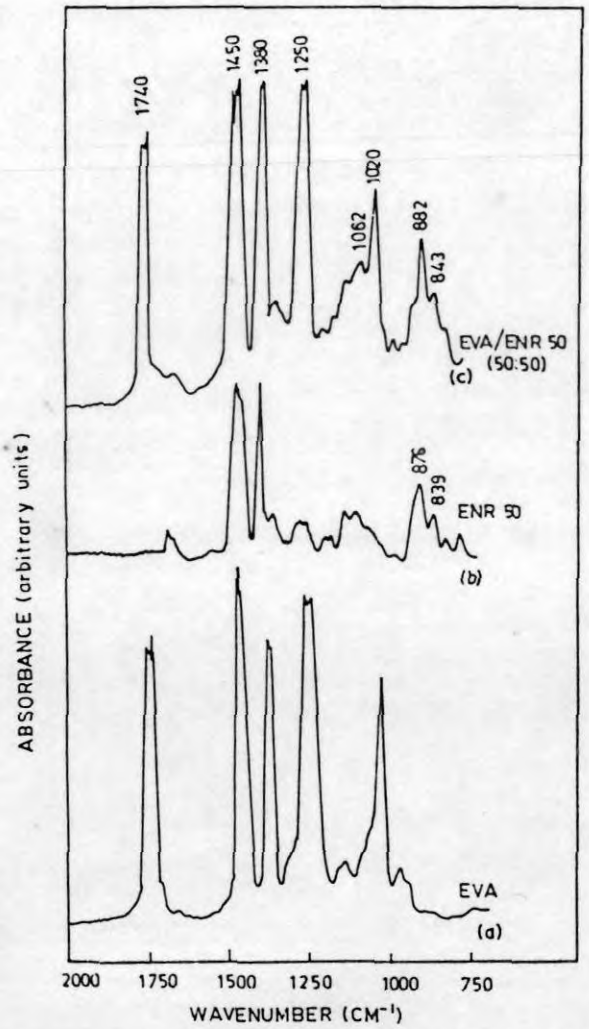


FIGURE 1. FTIR spectra of pure EVA, ENR-50 and 50:50 blend of EVA and ENR-50.

Dynamic Mechanical Analysis

Figures 2(a) and 2(b) show the temperature dependence of the dynamic mechanical properties of the EVA copolymer, ENR-50 and a 50:50 blend of EVA and ENR50. The tan δ curve shows a peak at 54°C which corresponds to the α-transition of EVA. The storage modulus shows a plateau from −110° to −20°C. However, G′ drops gradually from −20°C and falls drastically above 60°C, because of the crystalline melting of EVA. A transition at −117°C associated with local short range segmental motion of three to four methylene groups in a row is ascribed to the γ-transition temperature of the copolymer. The β-transition due to motion of the branch junctions of acetate side groups of EVA occurs at −40°C. ENR-50 shows a glass transition temperature at 10°C.

The damping curve for the blend shows two distinct peaks, which correspond to the α-transition of EVA and glass transition of ENR50 respectively. The tan δ peak at 4°C is due to the T_g of ENR50. The storage modulus decreases in three stages corresponding to the two transitions of ENR50 and EVA and the crystalline melting. The two separate T_gs of the blend suggest the incompatibility of the blend components.

Phase Morphology Study

SEM photomicrograph of the cryogenically fractured surface of 50/50 and 70/30 blends of EVA/ENR50 were taken and are shown in Figures 3(a) and 3(b) respectively. The pictures reveal the heterogeneous nature of the blends. The 50:50 blend shows the uniform distribution of the dispersed phase whose size is less than 1 μm, while the 70:30 blend shows the distribution of the aggregated domains whose size ranges from 4 to 8 μm.

Physical Properties of EVA/ENR50 Blends

The physical properties of EVA/ENR-50 blends are given in Table 1.

Pure EVA has the highest tensile strength, which decreases drastically on introduction of rubber. This is due to decrease of the crystallinity from 40% (pure EVA) to 17% for 70:30 EVA/ENR-50 blend and 14% for 50:50 EVA/ENR-50 blend (as determined from X-ray measurement). The modulus, elongation at break and tension set also decrease with increasing proportion of the rubber. Addition of rubber also imparts rubberiness to the blend as there is no yielding of EVA. The elongation at break values suggest that the morphology of the present incompatible system decides the breaking strains. Stress-strain curves of pure EVA and the blends are given in Figure 4. From the Table, it is

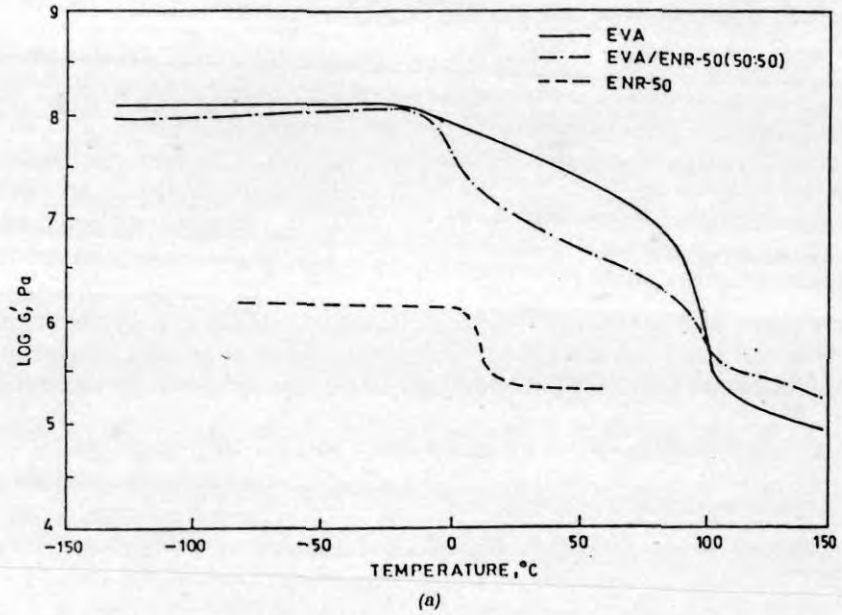
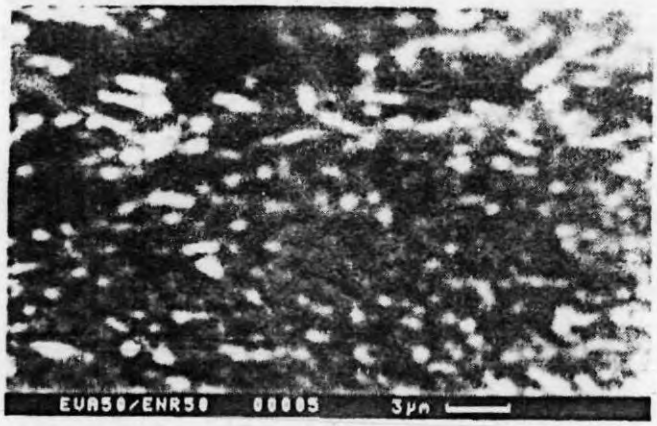
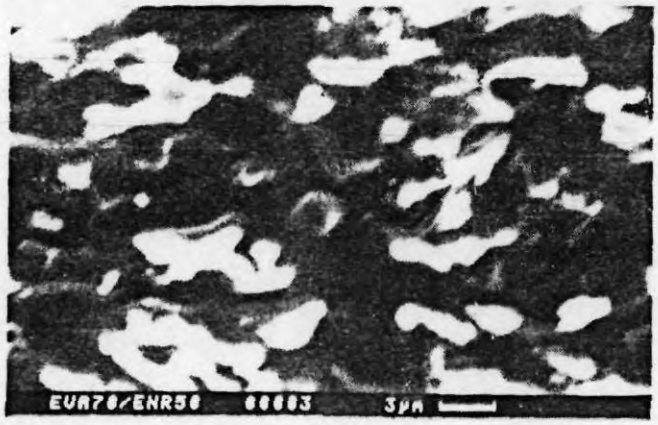


FIGURE 2. Temperature dependence of dynamic mechanical properties of EVA, ENR-50 and EVA/ENR-50 blends: (a) plot of G′ versus temperature; (b) plot of tan δ versus temperature.



(a)



(b)

FIGURE 3. SEM photomicrograph of 50:50 blend of EVA and ENR-50.

Table 1. Effect of molding temperature on physical properties.

Blend Composition	Blend Ratio	Molding Temperature °C	Physical Properties: 100% Modulus (MPa)	Tensile Strength (MPa)*	Elongation at Break (%)	Tension Set at 200°% Elongation (%)
EVA12	—	120	6.6	14.0 ± 0.4	660	118
EVA12/ENR50	70:30	120	4.76	9.7 ± 0.5	610	102
		150	4.30	8.6 ± 0.4	570	102
		175	4.10	7.7 ± 0.3	540	106
EVA12/ENR50	50:50	120	3.2	6.5 ± 0.5	540	93
		150	2.62	4.8 ± 0.3	460	91
		175	2.73	5.6 ± 0.4	520	89

*Standard deviations, σ_n, are also indicated.

also evident that there is a decreasing trend of the strength of the blends on increasing the molding temperature from 120° to 175°C, due to degradation of EVA at higher temperature and a high proportion of the same in the 70:30 blend.

Blends of ENR50 with Reactive Plastics

FTIR spectra of the blends of EVA and ENR-50 (Figure 1) show that there is weak dipole-dipole interaction between the polymers. On the contrary, IR studies of ethylene methyl acrylate (EMA)/ENR-50 blends indicate from the increase in the absorbance ratio of C-O-C stretching peak at 1113 cm^{-1} for the blend that these are interactive [9]. Furthermore, ethylene acrylic acid (EAA) and ENR-50 are interacting strongly through the formation of ester links [8].

The physical properties of the blends of ENR50 with different plastics molded at 175°C are listed in Table 2. It is evident that the blend of ENR50 with EAA copolymer has the maximum strength which is due to the stronger interaction between EAA and ENR-50. Next comes the blend of ENR50 with EMA copolymer which retains 70% of the tensile strength of pure EMA implying definite interaction between the two polymers. Finally, the blend of ENR50 with EVA copolymer, whose tensile strength is only 40% of that of pure EVA, shows the least interaction between the two polymers.

The loss tangent versus temperature plots for the ENR50/EAA, ENR50/EMA and ENR50/EVA blends are shown in Figure 5. The blends of ENR50 with EAA and EVA, show two transitions corresponding to the two phases present while the blend of ENR50 and EMA shows a single

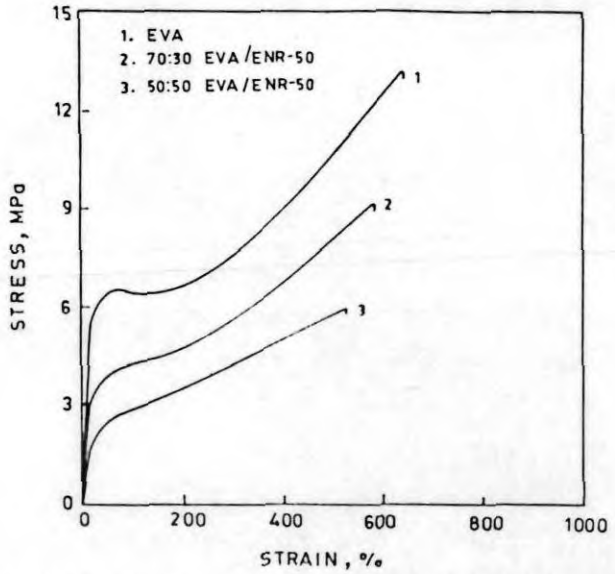


FIGURE 4. Stress-strain curves of pure EVA and the blends.

sharp transition, due to the merging of the two transitions which occur simultaneously. The damping value for the ENR peak at 4°C, in the case of blend of ENR50/EAA, is very low when compared to that of ENR50/EVA blend, implying greater amount of chemical interaction in the former blend. For the ENR50/EMA blend, the damping value for the peak at 0°C is very high, when compared to the other blends. This is due to the merging of both the transitions of EMA and ENR50 and not because of the lack of interaction between EMA and ENR50.

The storage modulus versus temperature plots for the ENR50/EAA, ENR50/EMA and ENR50/EVA blends are shown in Figure 6. The stor-

Table 2. Physical properties of ENR-50 based rubber-plastic blends (molding temperature 175°C).

Blend Composition	Blend Ratio	Physical Properties		
		100% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
EAA-6/ENR-50	50:50	4.41	6.1	210
EMA12/ENR50	50:50	1.61	4.7	740
EVA-12/ENR-50	50:50	2.73	5.6	520

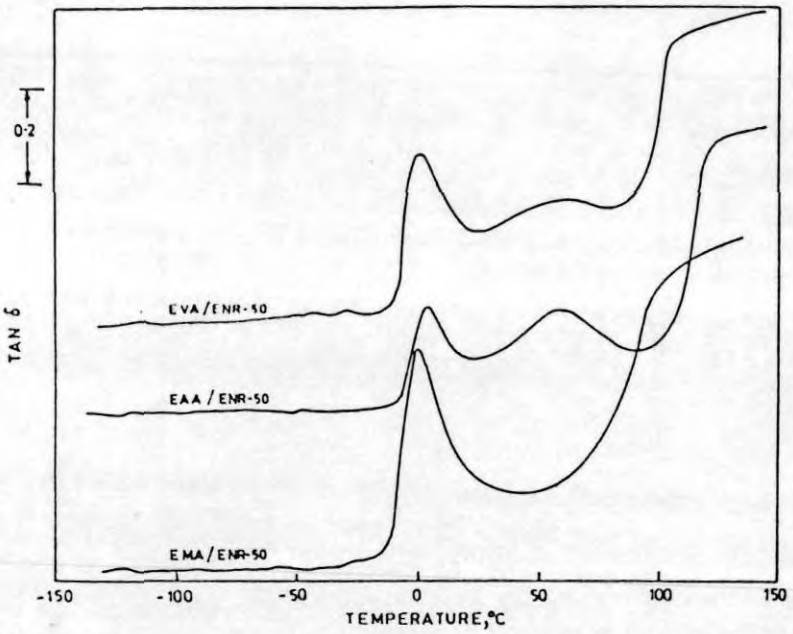


FIGURE 5. Temperature dependence of loss tangent of the blends of ENR-50 with reactive plastics (EAA, EMA and EVA).

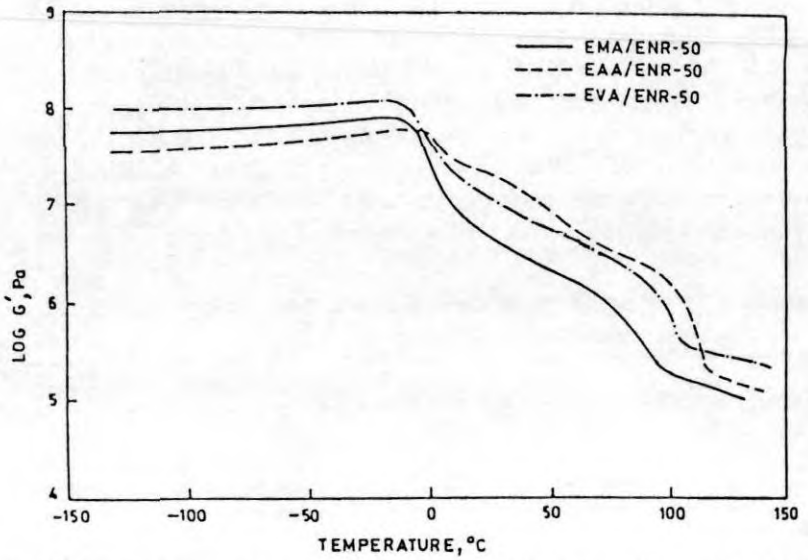


FIGURE 6. Temperature dependence of storage modulus of the blends of ENR-50 with reactive plastics (EAA, EMA and EVA).

age modulus of the blends of ENR50 with EVA and EAA show three stage reduction corresponding to the two α transitions and crystalline melting of EAA/EVA and the glass transition of ENR-50, while the G′ for the ENR50/EMA shows two stage reduction corresponding to the simultaneous α transition and glass transition of EMA and ENR respectively in the same region and the crystalline melting of EMA.

CONCLUSIONS

The following conclusions may be drawn from the present investigation:

1. FTIR spectra of the blends of EVA and ENR-50 show weak dipole-dipole interaction and there is no evidence for the presence of any chemical interaction between the two polymers, as compared to the blends of EMA/ENR-50 and EAA/ENR-50, which have been proven to be interactive from their IR spectra.
2. Blends of EVA and ENR-50 are incompatible as their dynamic mechanical spectra show two separate glass transitions. SEM photomicrographs also reveal the heterogeneous phase morphology of the blends.
3. The tensile strength, modulus and the degree of crystallinity of the EVA/ENR-50 blends decrease with increasing proportion of rubber. These properties decrease also with increasing molding temperature.
4. The tensile strength and the modulus of EVA/ENR-50, EMA/ENR-50, and EAA/ENR-50 blends show improvement in line with the level of their interaction.

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