

Miscibility of Blends of Epoxidized Natural Rubber and Poly(ethylene-co-acrylic acid)

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SYNOPSIS

The blends of epoxidized natural rubber (50 mol %) (ENR) and poly(ethylene-co-acrylic acid) (PEA) (6 wt %) are demonstrated to be partially miscible up to 50% by weight of PEA and completely miscible beyond this proportion. The miscibility has been confirmed by a DSC study which exhibits a single second-order transition (T_g) for the 30 : 70 and 50 : 50 (ENR : PEA) blends. For the 70 : 30 (ENR : PEA) blend, the T_g 's shift toward an intermediate value but do not merge to form a single T_g , making the blend partially miscible. The miscibility has been assigned to the esterification reaction between —OH groups formed *in situ* during melt blending of ENR and —COOH groups of PEA. The occurrence of such reactions have been confirmed by UV and IR spectroscopic studies. The existence of a single phase of the blends beyond 50 wt % of PEA has been shown by SEM studies.

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INTRODUCTION

Recently, polymer blends have generated a great deal of research interest in academic and industrial laboratories throughout the world because of the ease with which polymer properties can be modified to achieve a desired set of characteristic properties that cannot be achieved by simple copolymerization. Thus, the production of reactive polymer alloys/blends has become a frontier area of research and development activity in polymer technology in the past two decades. One can expect the synergistic/additive properties of the components to occur.

However, miscible polymer blends are generally characterized by the occurrence of a negative free energy of mixing which is rare in the case of high molecular weight polymers. The negative free energy of mixing in the case of high polymers is generally caused either by specific interaction or by chemical reactions between the constituents. In the case of thermoplastic blends, miscibility may also be attained by cocrystallization in the polymer segments. The specific interactions responsible for a negative

free-energy change during mixing with high polymers may be categorized as under the following:

1. Hydrogen bonding—Miscibility of polymer blends may occur through hydrogen bond formation between the polymer constituents. Margaritis et al.¹ showed that poly(vinyl chloride) (PVC) and epoxidized styrene butadiene copolymer at different levels of epoxidation are miscible due to hydrogen bonding. Thermoplastic polyurethane and the ethylene methyl acrylate copolymer are miscible via hydrogen bond formation.²
2. Dipole-dipole interaction—This also leads to miscibility. Varughese et al.³ showed that the blends of epoxidized natural rubber (ENR) and PVC are miscible due to the dipole-dipole interactions.
3. Ion-dipole interaction—Eisenberg and Hara⁴ demonstrated that ion-dipole interaction enhances considerably the miscibility among the blends of polystyrene ionomers and poly(alkylene oxides).
4. Ion-ion interaction—Miscibility by ionic interactions in polytetrafluoroethylene (PTFE) and poly(ethylene acrylate) blends has been assigned to ion-ion interaction.⁵

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5. Intramolecular repulsive interaction—Poly(methyl methacrylate) (PMMA) with the copolymers of styrene and acrylonitrile within a restricted range of copolymer composition also leads to miscibility.⁶
6. Cococrystallization—Although a rare phenomenon, isomorphous polymer blends are miscible in both molten and crystalline states. Poly(vinyl fluoride) and poly(vinylidene fluoride),⁷ poly(isopropyl vinyl ether) and poly(*sec*-butyl vinyl ether),⁸ and ultrahigh molecular weight polyethylene (UHMWPE) with HDPE or LDPE⁹ are miscible.
7. Chemical reactions—Chemical reaction between the blend constituents either via an esterification reaction or by the formation of direct covalent bonds leads to miscibility.

Suzuki et al.¹⁰ demonstrated that blends of bisphenol A, polycarbonate (PC), and poly(ethylene terephthalate) (PET) above the melting temperature of PET are miscible via a transesterification reaction. Robeson¹¹ reported the ester exchange reaction between blends of polyacrylate and PET to yield a homogeneous material. Santra et al.^{12,13} demonstrated that blends of ethylene methylacrylate copolymer and polydimethyl siloxane rubber (PDMS) rubber are miscible throughout the composition range via chemical reaction between α -H of the ester group of the EMA copolymer and the vinyl silicone group of the PDMS rubber. Jo and Lee¹⁴ studied the miscibility of blends of poly(ethylene oxide) and poly(styrene-*co*-acrylic acid) (SAA) as a function of the comonomer content of the copolymer. The miscibility has been assigned to the specific interaction between ethylene oxide and acrylic acid segments and intermolecular repulsive force in SAA copolymer. Vazquez-Torres et al.¹⁵ reported the miscibility between poly(vinyl acetate) (PVA) and poly(acrylic acid) (PAA) blends through a transesterification reaction by DSC, TGA, and IR spectroscopy. With the help of ¹³C-NMR spectroscopy, the transesterification reaction between poly(ethylene ether carbonate) and polyols has been proved by Harries.¹⁶ Porter and Wang¹⁷ have established the miscibility via a transesterification reaction between blends like PC and poly(butylene terephthalate) (PBT), PC, and PET by spectral and thermal analysis. However, growth in this area has been limited, possibly due to the fact that a relatively small number of reactive polymeric blends have been revealed.

Poly(ethylene-*co*-acrylic acid) (PEA) containing 6 wt % of acrylic acid possesses high tensile strength, excellent adhesion to metals, and very good flow

properties because of its thermoplastic nature. On the other hand, ENR has very good flexibility, high abrasion resistance, excellent solvent resistance, and low gas permeability, but it has very low tensile strength (about 100 times less than that of PEA) and very poor processability.

It is expected that blending of ENR with PEA shall improve the strength properties of ENR as well as its processing characteristics, on the one hand, whereas flexibility and the impact resistance property of PEA shall be improved, on the other hand. Recently, Roy et al.¹⁸ demonstrated that the processibility of ENR could be improved by incorporating a small proportion of PEA (10 wt %) into it during melt blending. They showed that an esterification reaction takes place during the melt blending of ENR with PEA.

The present article deals with the study of the miscibility of the blends of ENR and PEA through an esterification reaction. The chemical reactions between the blend constituents were established by IR and UV spectroscopic studies and the miscibility was established by differential scanning calorimetric studies. To assert a single-phase formation, scanning electron microscopy studies of the blends were carried out.

EXPERIMENTAL

Materials

Epoxidized natural rubber (ENR) containing 50 mol % of epoxy groups (EPOXYPRENE-50) was supplied by Guthrie, Malaysia, with the following specifications: specific gravity of 1.03 and Mooney viscosity varying from 70 to 100. Poly(ethylene-*co*-acrylic acid) (PEA) (ESCOR-5001) was supplied by EXXON Chemicals, Belgium, with the following specifications: acrylic acid content of 6 wt %, melt index of 2, and density of 0.93.

Preparation of the Blends

Blending of the components was carried out in a Brabender plasticorder (Model PLE-330) at 150°C

Table I Composition of Blends

Blend Code	Wt % of ENR	Wt % of PEA
N100	100	0
N70	70	30
N50	50	50
N30	30	70
N0	0	100

for 10 min and at 80 rpm rotor speed. PEA was first melt-sheared for 2 min in the plasticorder, then ENR was added and blended for a further 8 min until stable torque was obtained. The blend composition was varied from 100 parts by weight of ENR-50 (N100) to 100 parts by weight of PEA (NO), as shown in Table I.

UV Spectroscopic Study

Thin films of the blends as well as pure components were prepared in a compression-molding press at 150°C under a pressure of 10 MPa with a residence time of 2 min. The films were analyzed by a Shimadzu (UV-3100) UV-vis-NIR spectrophotometer at room temperature in the range from 190 to 400 nm. The UV spectra of ENR, one of the pure components, and the blends were taken with respect to PEA as the reference sample.

IR Spectrophotometric Study

Thin films of equal thickness (<0.5 mm) prepared for the UV study were also used for the IR spectroscopic study. The films were analyzed in a Perkin-Elmer (Model 843) IR spectrophotometer fitted with a computer data analyzer at room temperature, in the range from 4000 to 400 cm^{-1} .

Differential Scanning Calorimetric (DSC) Study

A DSC study of the pure components as well as of the blends were carried out in a Stanton Redcroft thermal analyzer (Model STA-625) equipped with a computer data analyzer version C4-20 in the temperature range varying from -150 to +50°C at a heating rate of 10°C/min in the presence of a ni-

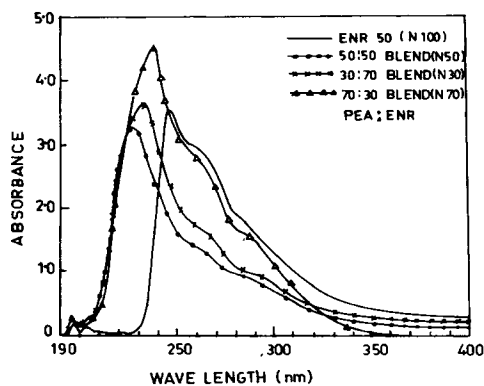


Figure 1 UV spectra of ENR and blends of ENR and PEA in the range from 190 to 400 nm.

Table II Peak Positions of the Blends and ENR from UV Study

Blend Code	Peak I (nm)	Peak II (nm)	Peak III (nm)
N100	247.5	201	196
N70	235	202	196
N50	226	202	196
N30	232	202.9	196
N0	a	a	a

^a Reference sample.

trogen atmosphere. Approximately 10 mg of each sample was taken for the study.

SEM Study

Pellets of the blends, punched out of the molded sheets, were etched in tetrahydrofuran solvent for 48 h at room temperature for removing the unreacted ENR-50, if any. The samples were dried at 70°C for 12 h in an air oven and cooled in a desiccator. The phase morphology of the etched surfaces of the blends were studied in a scanning electron microscope (Model Cam Scan Series-II) after sputter-coating the surfaces with gold at a 0° tilt angle in order to observe phase separation, if any.

RESULTS AND DISCUSSION

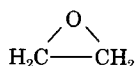
UV Spectroscopy

Figure 1 shows the UV spectra of ENR and its blends with PEA in the range from 190 to 350 nm, which gives the peaks corresponding to the promotion of electrons from one electronic level to the other.

Since PEA is one of the blend constituents chosen as the reference sample, the peaks due to acid groups are suppressed along the abscissa in Figure 1. This is also true for the unreacted acid groups present in the blends. However, Table II shows the wavelengths of the peaks for the blends of ENR-50 and PEA. ENR shows a major peak at 247.5 nm, which may be assigned to the $n-\sigma^*$ transition of the $-\text{O}-\text{C}-$ group of the secondary alcohol that is formed during melt mixing of ENR. Theoretically, the ethylenic ($\text{CH}_2 = \text{C} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$) radical should show an absorption in the range of 170–190 nm,^{19–21} but due to the presence of an $-\text{OH}$ group at the α -position and 2-ring residues,¹⁹ the absorption shows a “bathochromic” shift of $(30 + 10) = 40$ nm toward the higher range. Thus, the absorption peak appears in

the range of 210–235 nm. However, in a macromolecular system like ENR because of the molecular entanglements, the absorption spectrum in the UV range is further shifted toward a higher value by 10–15 nm, i.e., to 247.5 nm.

The peak at 201–202 nm may be assigned as to the $n-\sigma^*$ transition of the tetrahydrofuran rings present in ENR, but, theoretically, this absorption peak should have appeared at 180–200 nm.^{19,22,23} The small peak appearing at 195–196 nm may be assigned to the presence of epoxy rings in ENR after processing. Actually, the ethylene oxide



monomer shows a peak at 158 nm,¹⁹ but as ENR consists of epoxy groups as well as of *cis*-1,4-isoprene units placed intermittently in the polymer, a shift in the absorption band from 158 to 195 nm was observed.

In the case of blends of ENR and PEA, the major peak of ENR at 247.5 nm shows a shift toward the lower wavenumber which has been assigned to the ester link formed due to interaction via a chemical reaction between the blend constituents. This type of shift is known as a “hypsochromic shift.” But the minor peaks appearing at 202 and 196 nm do not show any significant change in their positions, implying that there is no remarkable change in the furanyl ring and epoxide ring structures. This is quite reasonable, as ENR has been subjected to identical conditions of processing in all the blends. Since PEA has been taken as the reference sample, no separate peaks should appear for the unreacted acids present in the blends in the UV spectra. However, the significant shift in the major peak of ENR in the blends as reported above has been assigned to the chemical reaction between the secondary alcoholic group of ENR generated during melt mixing and the carboxylic acid group present in PEA leading to the esterification reaction. Therefore, the absorption peak of ENR (247.5 nm) shows a hypsochromic shift toward lower values in the blends, i.e., 235 nm for N70 blend, 226 nm for N50 blend, and 232 nm for the N30 blend. These values almost coincide with the theoretically calculated values for β : β unsaturated esters.^{19,23} (Base value = 217 nm + 2-ring residues of 10 nm = 227 nm). But in the case of the N70 blend, the absorption peak appearing at 235 nm is broad as compared to that of ENR, due possibly to the presence of excess ENR and due to intermolecular entanglements at the interface between the two-component polymers. In case of the N50 blend, the major absorption peak is further

shifted to a much lower value of 226 nm without changing the magnitude of the minor peaks. This may be due to an extensive esterification reaction between the blend constituents. For the N30 blend, the major peak is observed at 232 nm without disturbing the minor peaks. This type of shift in the ester peak of the blends is called the hypsochromic shift or the “blue shift” and has been assigned as to the lesser electron-donating nature of the resulting ester groups. This can be explained as follows:

In the case of a free secondary alcoholic group $\begin{array}{c} \diagdown \\ \text{C} \text{---} \text{O} \text{---} \text{H} \end{array}$, the lone pairs of electrons are readily available on the oxygen atom, increasing its electron density. Thus, it is more electron-donating in nature. In case of the ester ---C---O---C group, the electron density on alcoholic oxygen is delocalized because of the presence of carbonyl carbon adjacent to it, reducing its density and, therefore, its capability of electron donation. On the other hand, the oxygen in ---C---O---C--- is more acidic than is the oxygen in $\begin{array}{c} \diagdown \\ \text{C} \text{---} \text{O} \text{---} \text{H} \end{array}$; hence, the absorption should be at a lower wavelength for the ester group than that for the alcoholic ---OH group, i.e., $\begin{array}{c} \diagdown \\ \text{C} \text{---} \\ \text{O} \text{---} \text{H} \end{array}$, $n-\sigma^*$ transition.^{19,21,23}

IR Spectroscopy

Figures 2 and 3 show the IR spectra of the pure components ENR and PEA in the range from 4000 to 400 cm^{-1} . Table III shows the assignment of absorption bands corresponding to different functional groups for ENR and PEA.

Figure 2 shows the IR spectrum of ENR-50 after mastication for 10 min at 150°C. At this temperature, the epoxy rings break down to different functional groups such as secondary alcohol, furan ring structures, aliphatic ethers, and carbonyl groups.^{24,25} The small peak at 1031 cm^{-1} may be assigned to the asymmetric stretching (---C---O str) of the secondary alcohol group. This has been further supported by the appearance of a peak at 3489 cm^{-1} (R---O---H) for intermolecular hydrogen bonding. Formation of the furanized ring structures and ether links have been evidenced by the occurrence of peaks at 1065 and 1110 cm^{-1} , respectively, in the spectrum.²⁴ Figure 3 shows the IR spectrum of PEA. The peak at 1704 cm^{-1} corresponds to the presence of the $\begin{array}{c} \diagdown \\ \text{C} \text{=} \text{O} \end{array}$ stretching vibration of the carboxylic acid group present, which has been further supported by the occurrence of an absorption band at 3636 cm^{-1} assigned to the self-associated hydrogen bond-

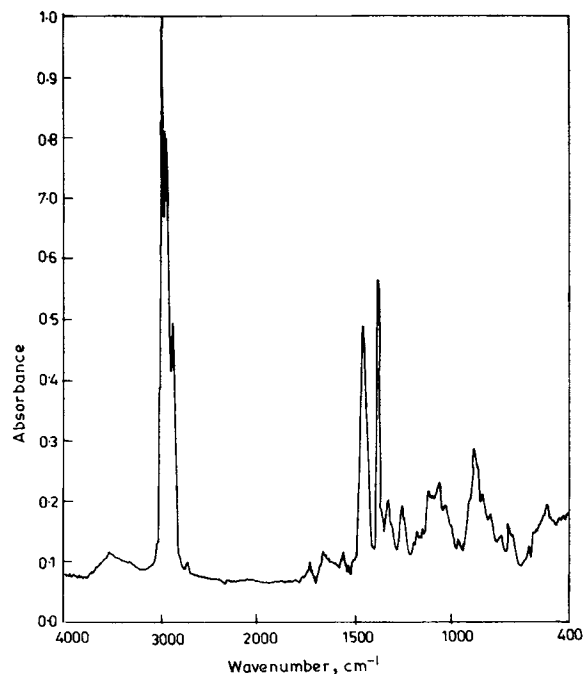
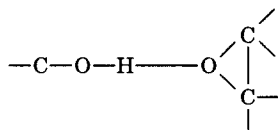


Figure 2 IR absorption spectra of pure ENR in the wavenumber region from 4000 to 400 cm^{-1} .

ing between the two adjacent acid groups in the copolymer.²⁵

Figure 4(a) shows the characteristic peaks of the N50 blend (ENR : PEA = 50 : 50) in the region 2000–400 cm^{-1} . For a better comparison, the spectrum of the artificial blend is also given in the same scale in Figure 4(b). Figure 5 shows the difference spectra of the N50 blend and the artificial blend (mechanical mixture of N0 and N100). The difference spectra clearly show the ester peak at 1735 cm^{-1} due to the >C=O stretching vibration of ester formed during melt blending at 150°C for 10 min. The blend also shows a broad and small peak at 3539 cm^{-1} in between the hydrogen-bonding region of PEA (3636 cm^{-1}) and ENR (3489 cm^{-1}), which is attributed to the intermolecular hydrogen bonding, formed either between the alcoholic —OH group of ENR and the carbonyl group of PEA, i.e., $\text{R-OH} \cdots \text{O}=\text{C}$, or between —C—OH of the residual acid with the undisturbed epoxy group, i.e.,



of ENR or both. The presence of a secondary alcoholic group has already been detected by IR, which gives an absorption band at 1031 cm^{-1} .²⁵ Therefore,

we infer that the secondary alcohol generated during melt processing of ENR is mostly utilized in the reactions with the carboxylic acid present in the system to form ester bridges and the rest is utilized in the formation of hydrogen bonds as described above. In the spectra of the blend [Fig. 3(a)], the ester peak is not distinctly observable at the 1735 cm^{-1} region as it is overshadowed by the acid peak at 1704 cm^{-1} , having a broad base from 1800 to 1600 cm^{-1} . The difference spectra of the artificial blend and the N50 blend, i.e., (N50–N0–N100), shows a prominent ester >C=O stretching peak at 1735 cm^{-1} with a broad base starting from 1720 to 1750 cm^{-1} (Fig. 5), indicative of a considerable esterification reaction.

Figure 6(a)–(c) shows the difference spectra of N30, N50, and N70 blends after subtracting the intensity of the artificial blend in the region 1800–1700 cm^{-1} . The ester peak which appears in the region 1720–1750 cm^{-1} confirms the occurrence of an esterification reaction between the blend constituents.²⁵ The areas of these peaks are given in Table IV. These values depict a clearer picture of the extent of the reaction (keeping the film thickness constant). Table IV shows that in the N30 blend the extent of

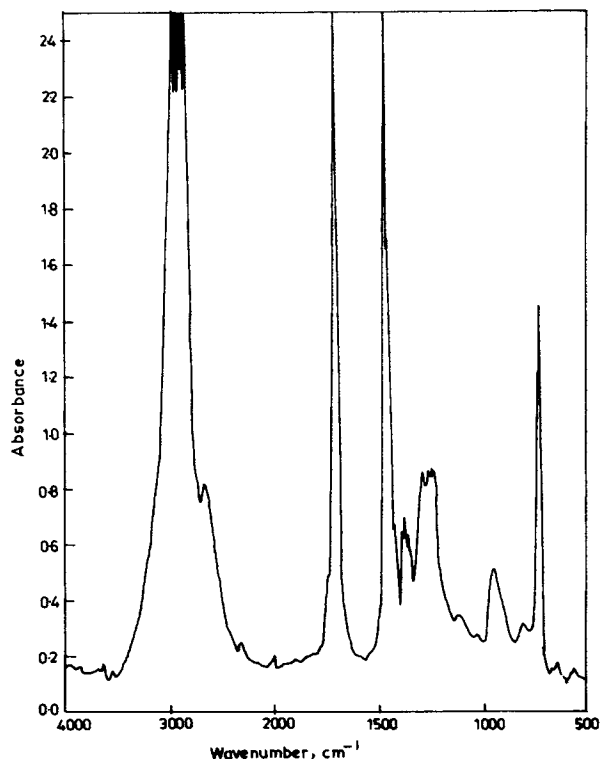


Figure 3 IR absorption spectra in pure PEA in the wavenumber region from 4000 to 400 cm^{-1} .

Table III IR Data of ENR and PEA

Theoretical Wavenumber (cm^{-1})	Experimentally Observed Bands (cm^{-1})	Functional Groups	Assignment of Bands	Reference
Peaks of ENR-50				
3550–3230	3489	Alcoholic —OH	Intermolecular Hydrogen bonding $\text{R}-\text{O}\cdots\text{H}$ $\text{H}\cdots\text{O}-\text{R}$	20, 23, 25
1140–1110	1110	Aliphatic ether	Assym. C—O st.	23, 25
1070–1065	1065	Tetrahydrofuran rings	Ring vib.	23, 25
1035–1030	1031	Secondary alcohol	Assym. C—O st.	23, 25
880–785	870	<i>cis</i> -Epoxide ring	Ring vib.	23
Peaks of PEA				
3650–3200	3636	Acidic —OH	Intermolecular self-associated hydrogen bonding	22
1725–1700	1704	Acidic $\text{C}=\text{O}$	$\text{C}=\text{O}$ st.	20, 22

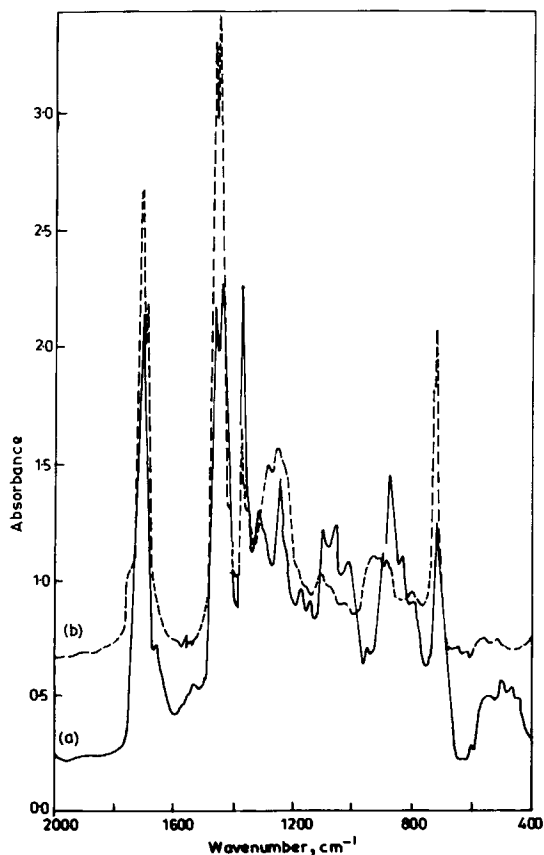


Figure 4 (a) IR absorption spectra of N50 blend. (b) IR absorption spectra of artificial blend.

esterification reaction is more than that in the N50 blend, which is more than that in the N70 blend.

Figure 7 shows the IR spectra of the N30 blend processed at five different temperatures, i.e., at 120, 130, 140, 150, and 160°C, in the region 1720–1800 cm^{-1} to study the extent of the reaction at different temperatures. The areas of the various peaks are given in Table V. It shows that the area of the acid peak at 1704 cm^{-1} and the alcohol peak at 1031 cm^{-1} (Ref. 25) gradually decreases as the temperature of melt processing is increased from 120 to 160°C. Beyond 150°C of melt mixing, the areas do not show any significant change and the area under the ester peak increases marginally; hence, melt processing

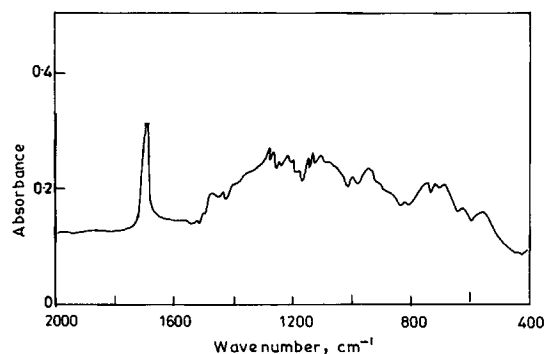


Figure 5 Difference spectra (N50–N0–N100) in the wavenumber region from 2000 to 400 cm^{-1} .

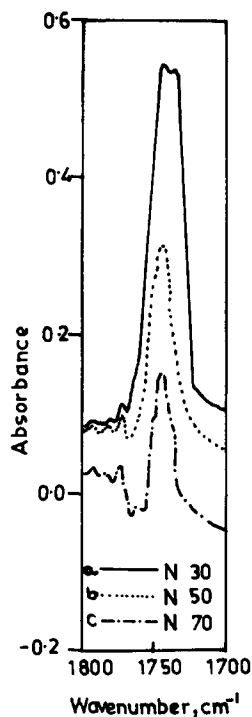


Figure 6 (a) Difference spectra of N30 minus artificial blend. (b) Difference spectra of N50 minus artificial blend. (c) Difference spectra of N70 minus artificial blend in the region 1800–1700 cm^{-1} .

at 150°C was taken as the optimum. This has been confirmed from the peak areas of both the epoxy ring (at 870 cm^{-1}) and furan ring structures (at 1066 cm^{-1}), which decreases from 39.9 and 35.3 to 28.3 and 30, respectively, as the temperature is increased from 120 to 150°C. At 160°C, the area of the epoxy peak is reduced further to 27.5 from 39.9 at 120°C and the furan peak area is increased marginally to 31.1, as expected. On the other hand, the ester peak area at 160°C almost remains at par with that observed at 150°C. As per Table V, the ester peak area at 150°C of melt mixing is the highest, confirming an extensive esterification reaction at this temperature. These observations show that the optimum temperature for reactive blending of ENR with PEA should be 150°C. A plausible mechanism for the es-

Table IV Peak Areas of the Ester Formed in N30, N50, and N70 Blends

Blend	Area
N30	5.8
N50	3.2
N70	1.4

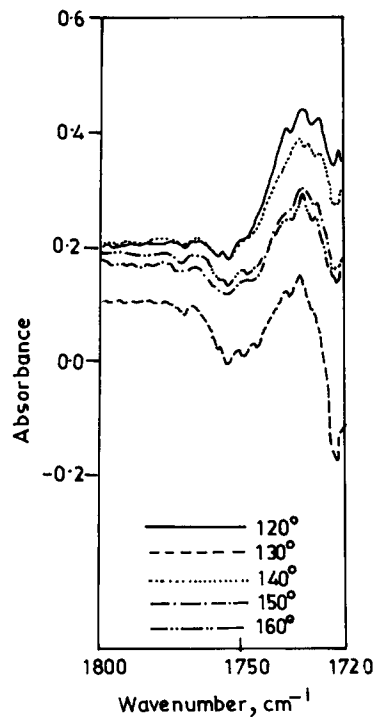


Figure 7 Infrared absorption spectra of N30 blend at five different temperatures (from 120 to 160°C) in the region 1800–1700 cm^{-1} .

terification reaction between ENR and PEA is suggested in Scheme I.

Differential Scanning Calorimeter (DSC) Study

For understanding the miscibility between the blend constituents, differential scanning calorimetric studies of the pure components ENR and PEA and those of the blends have been carried out in the temperature range from -150 to 50°C , as shown in Figure 8(a) and (b). A DSC thermogram of pure PEA (N0) shows a sharp second-order transition at -126°C , which has been assigned to the glass transition temperature (T_g) of PEA. This is the temperature at which short-range, small segmental motions of three to four methylene groups in a row, like that in polyethylene ceases vibrating²⁶ [Fig. 8(a)]. A DSC thermogram of ENR-50 [Fig. 8(a)] shows a sharp transition at -18°C , which is considered to be the glass transition temperature (T_g) of ENR-50. This is due to the segmental motion of the main chain in the elastomer. Figure 8(b) also shows the DSC traces of the blends of ENR and PEA in various proportions (N30, N50, and N70). Table VI compiles the data of the glass transition tempera-

Table V Peak Areas of N30 Blend in the Temperature Range of 120–160°C

Temperature (°C)	Acid	Epoxy	Alcoholic	Tetrahydrofuran	Ester
120	66.22	39.94	30.05	35.30	4.83
130	58.11	34.58	27.24	31.30	5.76
140	51.80	34.90	26.52	30.85	5.80
150	49.10	28.30	22.28	30.00	6.80
160	48.80	27.50	21.83	31.1	6.85

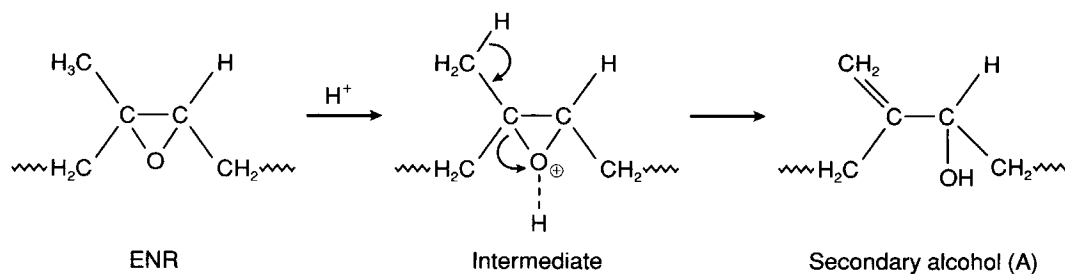
tures of the blends obtained from DSC thermograms and that calculated by using the Fox equation²⁷:

$$\frac{W}{T_{gb}} = \frac{W1}{T_{g1}} + \frac{W2}{T_{g2}} \quad (1)$$

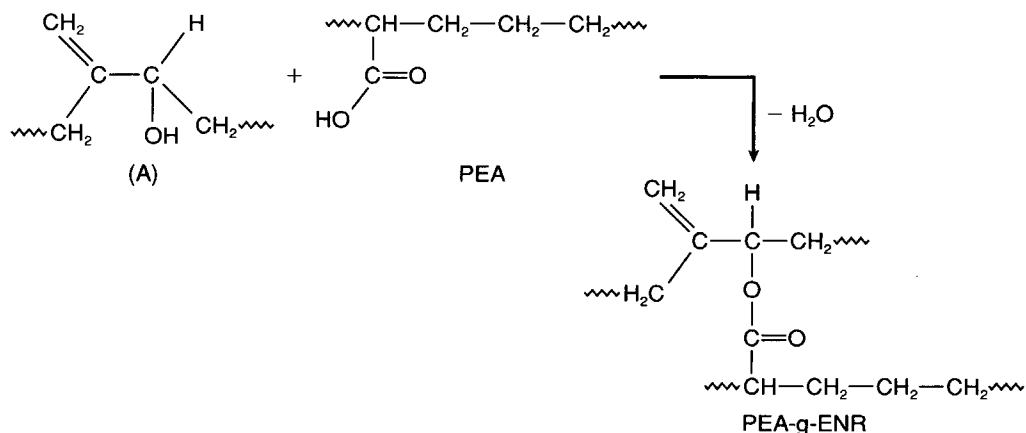
where $W1$ and $W2$ are the weight fractions of the pure components (1) and (2) and T_{g1} and T_{g2} are the glass transition temperatures of (1) and (2). W and T_{gb} are the weight fraction and the glass transition temperatures of the blends, respectively.

Interestingly, the N70 blend shows a broad second-order transition (T_g) with two distinct humps corresponding to two T_g 's at -26 and -20°C , respectively. These values are not the same as those of the pure components, but are intermediate between them and are very close to each other. This is characteristic of presence of microinhomogeneity in the blend. Thus, the N70 blend can be categorized as a partially miscible blend. This has been explained on the basis of the lower extent of the esterification reaction between PEA and ENR, as PEA contains

step-1



step-2



Scheme 1

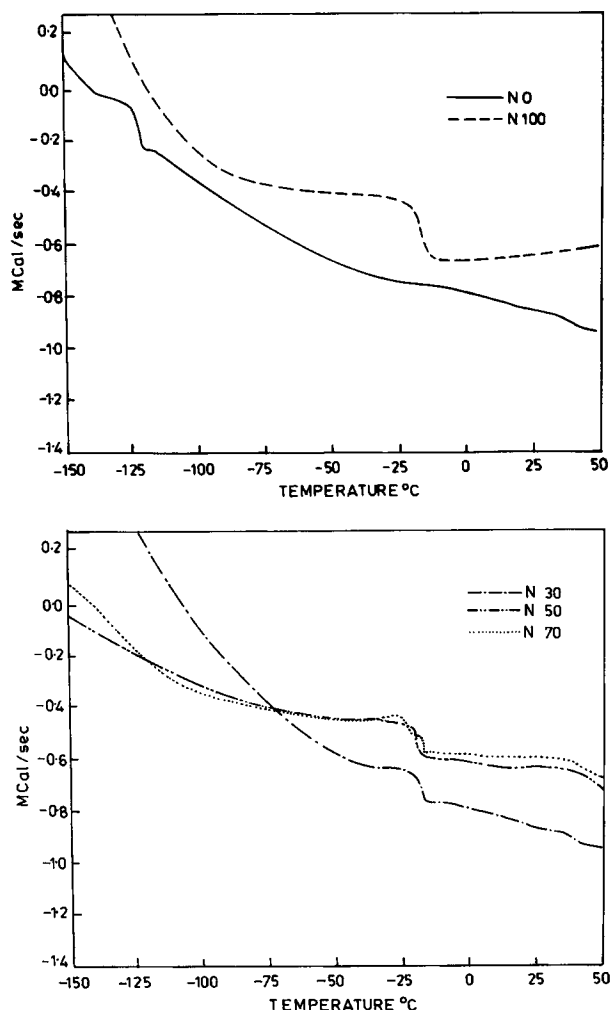


Figure 8 (a) DSC thermograms of pure PEA (N0) and ENR (N100) in the temperature range -150°C to $+50^{\circ}\text{C}$. (b) DSC thermograms of N70, N50, and N30 blends in the temperature range of -150 to $+50^{\circ}\text{C}$.

only 6 wt % of the acid, i.e., 2.4 mol % and its proportion in the blend is only 30 wt %. In a macromolecular system, some of the reactive sites quite often are caged in due to molecular entanglements of the chains, thereby hindering intermolecular interactions. This has been confirmed further from the phase morphology studies which show a microphase separation in the matrix [Fig. 9(b)] as compared to the unetched surface [Fig. 9(a)]. As per the Fox eq. (1), a miscible blend of ENR and PEA in the proportion 70 : 30 should have shown a single transition at -24.23°C , but, instead, it showed two transitions very close to each other, indicating the presence of microinhomogeneity in the blend. Hence, the blend may be termed partially miscible. As the proportion of PEA in the blend is increased

to 50% by weight (N50), it exhibits a single and sharp second-order transition at -21°C , as shown in Figure 8(b). But according to the Fox equation, this value should have been shown at -31.5°C . Thus, there is a positive deviation of the glass transition temperature of the blend by 10.5°C from that calculated by using the Fox equation, indicative of the interaction via a chemical reaction between the blend constituents. This chemical reaction has been assigned to the esterification reaction between the $-\text{OH}$ groups of ENR generated *in situ* and $-\text{COOH}$ groups of PEA during the reactive processing restricting the mobility of the main chain. Therefore, the T_g is raised. The SEM study of the blend does not show any phase separation [Fig. 10(a) for the unetched and Fig. 10(b) for the etched surface].

As the proportion of PEA is further increased to 70% by weight in the blend (i.e., N30), the interaction via a chemical reaction is remarkably enhanced due to the availability of more and more acid groups in the system. Thus, a single and sharp glass transition temperature at -24°C is observed for the blend as shown in the DSC thermogram, confirming the phase homogeneity between the blend constituents. As per the Fox equation, the T_g should have appeared at -45°C , but the experimental T_g occurs at -24°C , showing a positive deviation of 21°C above that calculated theoretically. Thus, the blend N30 is considered to be completely miscible to the molecular level. Similar observations have been made earlier by Brinke and Karasz.²⁸ This may be explained as follows: In a system where 50 mol % of the epoxy groups are present in the ENR, a part of the epoxide groups are converted into the allylic alcohol groups during melt-blending. Since 70 wt % of PEA contains more acid groups in the system, there is greater interaction with the hydroxyl groups of ENR generated *in situ*, forming ester links leading to a grafted polymer PEA-*g*-ENR. Therefore, a single and sharp glass transition temperature at -24°C ,

Table VI Second-order Transition Temperatures from DSC Study

Blends	Theoretical T_g ($^{\circ}\text{C}$)	Experimental T_g ($^{\circ}\text{C}$)
N100	—	-18
N70	-24.23	-26 and -20
N50	-31.5	-21
N30	-45.0	-24
N0	—	-126

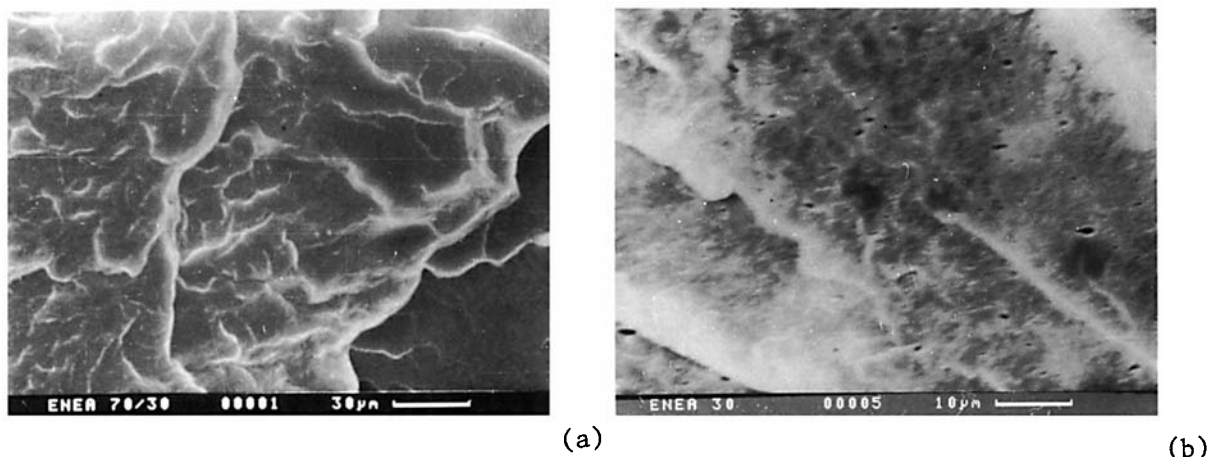


Figure 9 (a) SEM photomicrograph of unetched, cryogenically fractured N70 blend. (b) SEM photomicrographs of cryogenically fractured N70 blend after 48 h of etching in THF.

which is much above that calculated by using the Fox equation (-45.0°C), is observed. This positive deviation of the glass transition temperature is indicative of greater chemical interaction via the esterification reaction between PEA and ENR, which has been further supported by the occurrence of a single homogeneous phase in the system after solvent-etching, as shown by Figure 11(b) as compared to that before etching shown in Figure 11(a). The SEM photomicrograph of the N30 blend does not show any phase-separation. A similar observation was reported by Santra et al.¹² for blends of the EMA copolymer and PDMS rubber, which exhibit miscibility throughout the composition range due to a chemical reaction forming EMA-*g*-PDMS rubber.

CONCLUSIONS

The following conclusions have been drawn from the present study:

- (i) The UV study indicates the occurrence of a chemical reaction between the blend constituents at all the compositions by exhibiting a hypsochromic shift (blue shift) of the $n-\sigma^*$ transition in the blend.
- (ii) The IR study confirms the reaction between the $-\text{OH}$ groups of ENR and $-\text{CO OH}$ groups of PEA through the ester links. The presence of the ester peak at 1735 cm^{-1} in all the blend compositions has been established.
- (iii) The DSC study shows the occurrence of a single glass transition temperature of the blends at and above 50 wt % of PEA, which confirms their miscibility.
- (iv) Blends of ENR and PEA are completely miscible beyond 50 wt % of PEA and are partially miscible below 50 wt % of PEA due to chemical interaction via an esteri-

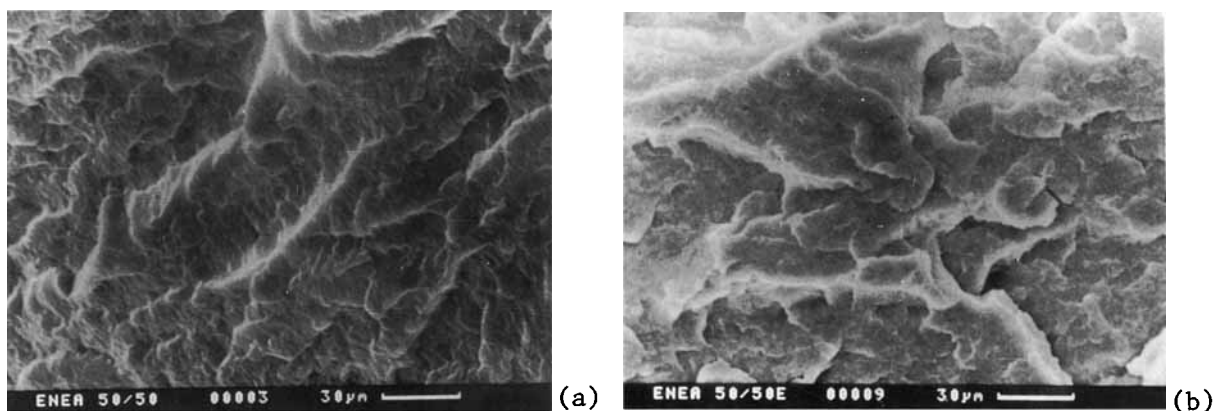


Figure 10 (a) SEM photomicrograph of unetched, cryogenically fractured N50 blend. (b) SEM photomicrographs of cryogenically fractured N50 blend after 48 h of etching in THF.

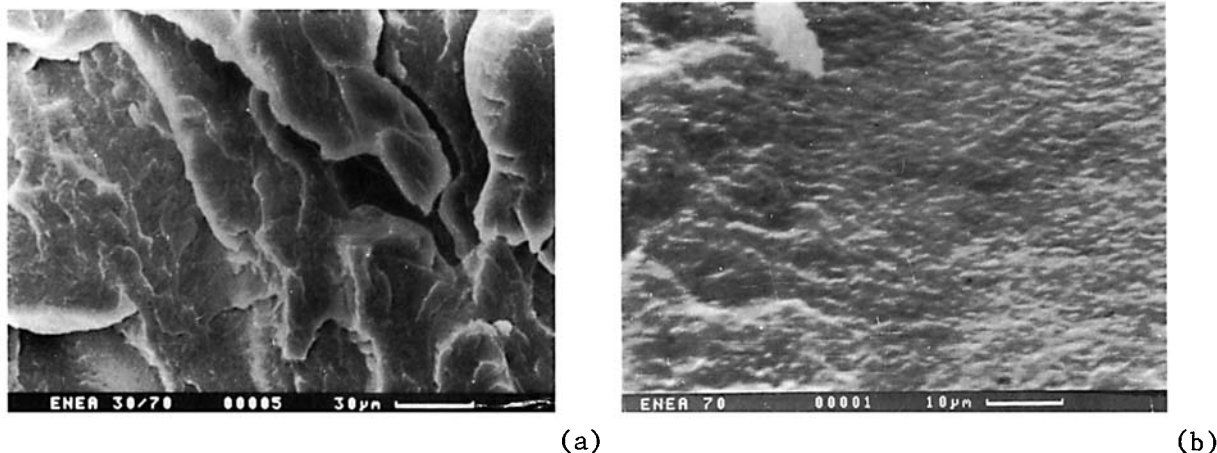


Figure 11 (a) SEM photomicrograph of unetched, cryogenically fractured N30 blend. (b) SEM photomicrographs of cryogenically fractured N30 blend after 48 h of etching in THF.

fication reaction during melt blending in a Brabender plasticorder, leading to PEA-*g*-ENR.

- (v) The SEM study of etched surfaces confirms phase homogeneity, i.e., the existence of a single phase in N50 and N30 blends and microphase inhomogeneity in the N70 blend.

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