Compatibility of Epoxidized Natural Rubber with Thermoplastic and Thermosetting Resins

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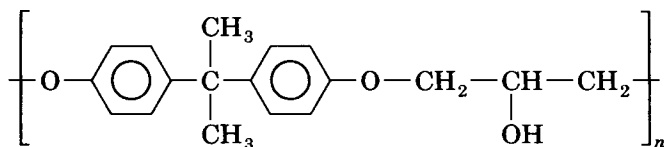
Synopsis

The compatibility behavior of epoxidized natural rubber (ENR) at two different degrees of epoxidation with hydroxyl-containing polymeric resins was investigated. These included Novolac and Resole resins, the cured epoxy of bisphenol A (CER), and phenoxy. For each system, compositions covering the complete range were studied using the dynamic mechanical (DMA), DSC and phase-contrast microscopy techniques. ENR/Novolac blends were compatible, ENR/Resole, and ENR/phenoxy semicompatible, and ENR/CER incompatible. The results were interpreted in terms of the acid character of the aromatic or aliphatic hydroxyl contained in the resin and a predictive compatibility scheme based on copolymer–copolymer miscibility theory was tested.

INTRODUCTION

In our search for compatible polymer pairs we have recently discovered[1-3] that epoxidized natural rubber (ENR) gives miscible blends with chlorinated polyolefins. Miscibility was attributed to molecular interactions, such as donor-acceptor type of a weakly acidic hydrogen, or dipole–dipole interactions. If such an interpretation is correct, ENR should be compatible with other proton-donating polymers. This led us to the choice of the polymer blend partners studied in this work; namely, polymers containing a weakly acidic hydrogen such as phenolic resins, a cured epoxy resin (CER), and the poly(hydroxy ether) of bisphenol A (phenoxy).

Though phenolics have known a significant commercial status as a commodity resin for some time,[4] the systematic study of their compatibility behavior is quite recent.[5-7] Due to the acid character of their phenolic hydroxyl, certain types are miscible[5] with electron-donating polymers, for example, polyesters, polyethers, and poly(styrene-acrylonitrile) copolymers. Epoxy resins have also found extensive applications in construction and the manufacture of composites.[8] Their range of applicability has been extended by improving their impact properties through the introduction of suitable end-reactive rubbers.[9,10] Impact property can be optimized by ensuring strong chemical or physical bonding between the matrix and the encapsulated rubbery inclusion. A related structure to the CER studied is that of the phenoxy resin,

$$\left[O\text{-}\langle\bigcirc\rangle\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}\langle\bigcirc\rangle\text{-}O\text{---}CH_2\text{---}\underset{\underset{OH}{|}}{CH}\text{---}CH_2 \right]_n$$

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This thermoplastic also shows miscibility with electron-donating polymers such as polyesters[11] and polyethers[12] due to its secondary aliphatic hydroxyl groups.

In this study the compatibility of ENR at different degrees of epoxidation, 50 mol% (ENR50) and 25 mol% (ENR25), with thermally inert (Novolac) and reactive (Resole) phenolic resins was examined. Polyblends with phenoxy and the CER of bisphenol A were also studied. The techniques used were the dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and phase-contrast microscopy.

These studies are of interest not only in order to correlate polymer structure with compatibility but also to diversify the properties of the above resins. It was expected that depending on its degree of compatibility, ENR would flexibilize the resins and/or modify their impact properties, the latter when rubbery microdomains are formed.

EXPERIMENTAL

Materials and Specimens Preparation

Epoxidized natural rubber was donated by the Malaysian Rubber Producers' Research Association Laboratory, Hertford, UK. It had been prepared by epoxidation of rubber latex using an in situ prepared peracetic acid solution.[13] Phenolic resins (Resole, Novolac) were prepared via phenole-formaldehyde condensation according to standard procedures[14] and characterized by infrared and nuclear magnetic resonance. $\overline{M}_n$ was ~ 1000 g mol^{-1}. The epoxy resin (Epikote 828) and its curing agent having the structure of a polyamide (Epilink 171), were donated by Shell, Hellas, Co. The phenoxy resin (grade PKHH) was donated by Union Carbide Co. Density was given as d = 1.175 g cm^{-3} and $\overline{M}_n$ = 2.0–2.5 × 10^4 g mol^{-1}.

Polyblends were prepared by dissolving in a common solvent; tetrahydrofuran (THF) for phenoxy and butanone-2 for the rest of them. After solvent removal, blends were dried to constant weight at 60°C in a vacuum oven. Films were obtained by compression moulding between Teflon sheets at 150–170°C (depending on composition) at 15 MPa and quenched at 0°C. In the case of epoxy resin/ENR blends, the addition of curing agent was followed by heating at various temperatures and lengths of time. Films were prepared by casting in a Teflon-coated dish. In denoting blend compositions the weight percentage of ENR in the blend will precede letter R.

Apparatus and Procedures

Differential scanning calorimetric measurements were performed with a DuPont 910 Calorimeter coupled with a 990 programmer recorder. Calibration was made with Indium standard. Sample weight was ~ 15 mg and scanning rate 10°C min^{-1}. The heating cycle applied was 25°C → 110°C (30 s) → −100°C → 100°C. Glass transition temperature (T_g) was determined during the last heat scan.

Dynamic viscoelastic data $|E^*|$ and tan δ were determined at 110 Hz using the direct reading viscoelastometer (Rheovibron Model DDV II-C, Toyo-

Baldwin) and the procedure described before.[1] Specimen dimensions were $3 \times 0.3 \times 0.08$ cm^3.

Thin films were examined under a phase-contrast microscope (Orthoplan-Leitz) with oil ($n_e^{23} = 1.518$) immersion in bright field.
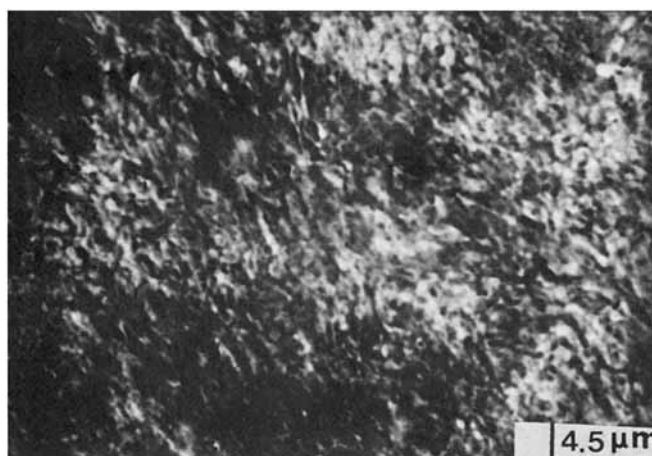
RESULTS

Morphology

In Figure 1 phase-contrast micrographs of melt-pressed films show a heterogeneous structure, especially for the ENR/phenoxy blends where distinct phase boundaries are evident. Given the refractive index of phenoxy[15] $n_D^{25} =$
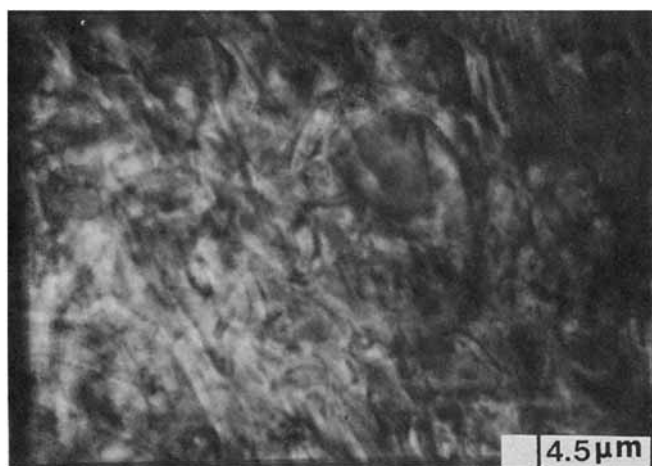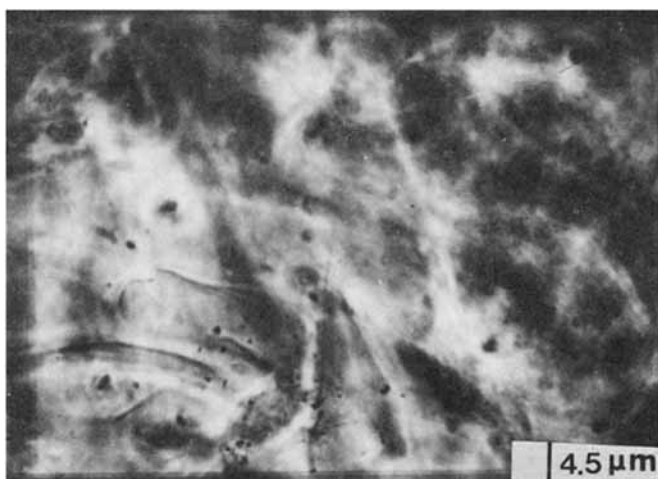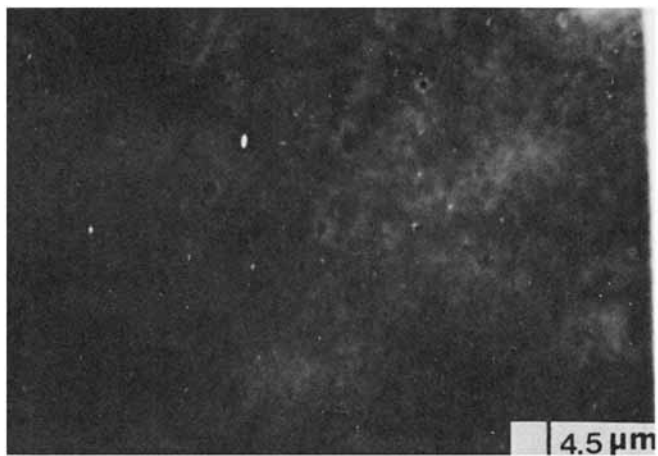

(a)

(b)

Fig. 1. Phase-contrast micrographs of ENR/Phenoxy blends: (a) 25R/75; (b) 50R/50; (c) 75R/25. ENR/Novolac blend: (d) 50R/50.

(c)

(d)

Fig. 1.   (*Continued from the previous page.*)

1.598, of ENR50[1] $n_D{}^{25}$ = 1.507, and of Novolac calculated (Vogel's equation)[16] to be n_D^{25} = 1.586, at positive phase contrast, the light areas should represent the rubbery component. More diffuse phase boundaries are shown by the compatible ENR50/Novolac blend where a finer state of dispersion is attained.

Dynamic Mechanical and Thermal Properties

ENR / Novolac. Figures 2 and 3 summarize results in terms of thermomechanical spectra and Figure 4 the T_g values obtained with the DSC. Not all compositions could be studied by the DMA since their constitution did not allow film preparation. In all cases DSC was applied to confirm and supple-
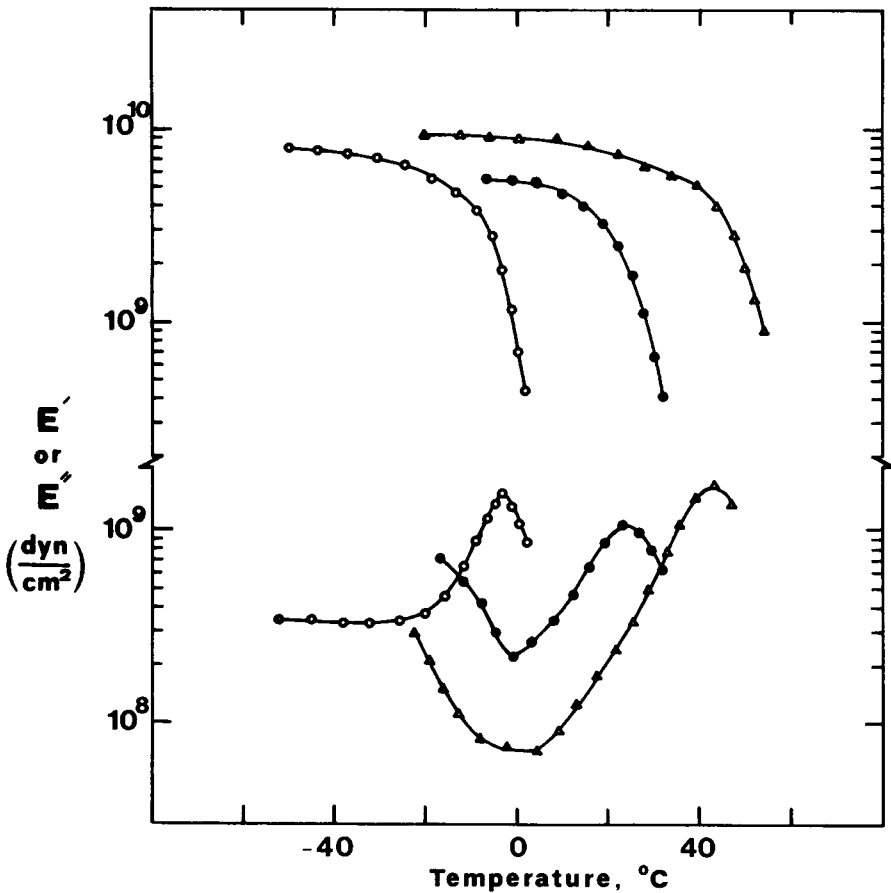
Fig. 2. Thermomechanical spectra of ENR50/Novolac blends: (○) 100R-0; (●) 75R-25; (△) 50R-50.

ment data. Using the criterion of the presence of a single T_{gb} (T_g of blend) varying regularly with composition, it is inferred that Novolac is compatible with ENR50 and ENR25 (see Figs. 2, 3, and 5). A considerable broadening is observed at the 50R/50 of the ENR25 blends. This is attributed to blend composition inhomogeneity. The T_{gb} variation for the ENR50/Novolac blends shows a significant positive deviation from the weight average line. This is usually observed when synergism is present, and is possibly the result of hydrogen-bonding interactions.[17] The characteristic S-shaped T_{gb} variation in Figure 4 seems to suggest[18] a matrix inversion when blends are slightly immiscible and one phase (of submicroscopic dimensions) is strongly attached to the continuous matrix. No such synergism was observed for the ENR25 blends. Modulus variation in Figures 2 and 3 shows the flexibilizing action of ENR when added to the stiff resin.

ENR50 / Resole. The DMA spectra in Figure 4 show two broad relaxations whose ratio and position change with composition. This is typical of a partially miscible blend. Though DSC detects a single T_{gb} (see Fig. 5), the
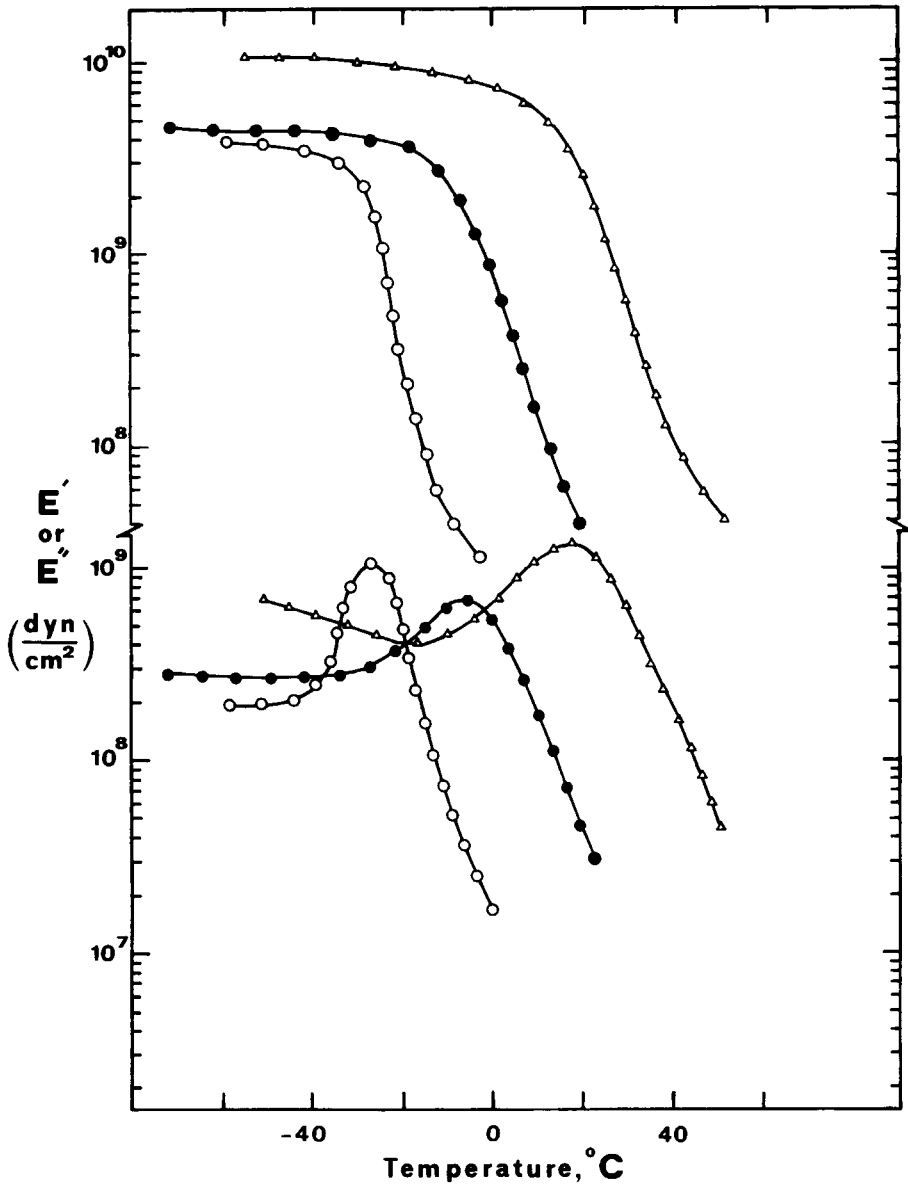
Fig. 3. Thermomechanical spectra of ENR25/Novolac blends: (○) 100R-0; (⬤) 75R-25; (△) 50R-50.

DMA technique is more sensitive in detecting close lying peaks. Partial miscibility is also reflected on the modulus variation of these blends (see intermediate step variation in Fig. 4).

ENR50 / Phenoxy. The results on this blend are summarized in Figure 6. The limited shift of the relaxation maximum at rubber-rich compositions and the existence of a single T_{gb} for 90R/10, 75R/25 blends indicates that small amounts of phenoxy are miscible in ENR50. At rubber-rich compositions the system phase-separates since two T_gs are discernible. Of these, the high
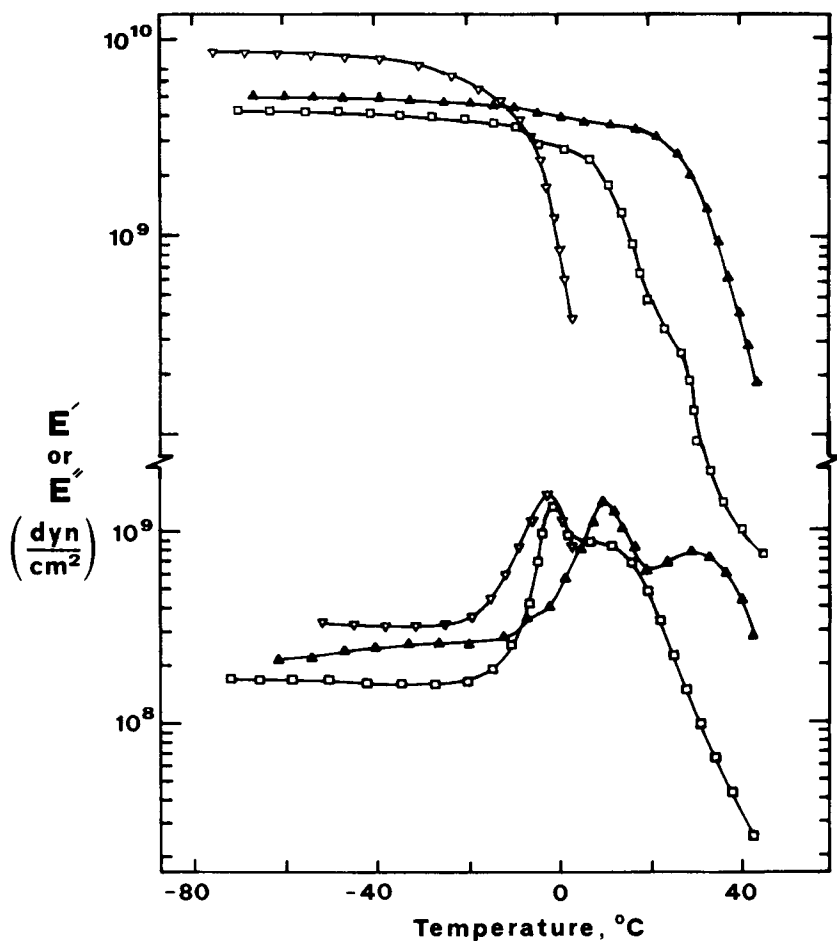
Fig. 4. Thermomechanical spectra of ENR50-Resole blends: (▽) 100R-0; (□) 75R-25; (▲) 50R-50.

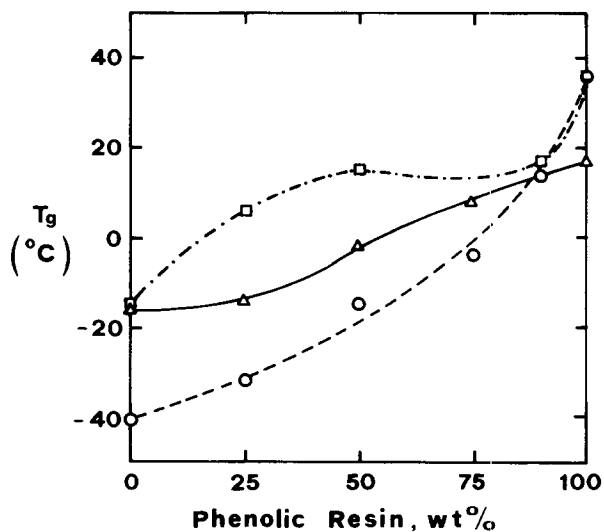Fig. 5. Composition dependence of T_{gb} of ENR/phenolic resin blends: (□) ENR50/Novolac; (○) ENR25/Novolac; (△) ENR50/Resole.
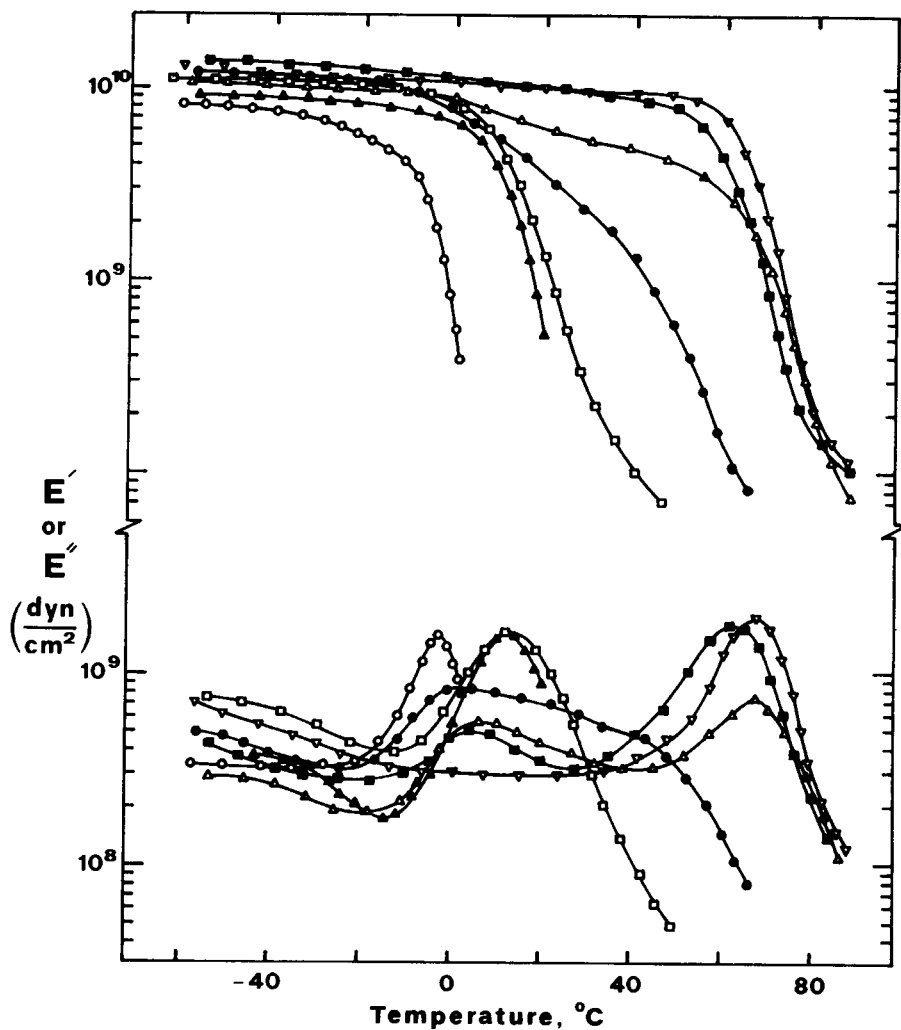
Fig. 6. Thermomechanical spectra of ENR50/phenoxy blends: (○) 100R/0; (▲) 90R/10; (□) 75R/25; (●) 50R/50; (△) 25R/75; (■) 10R/90; (▽) 0R/100.

TABLE I
Main Transitions of ENR50/CER Blends

Blend	Curing temperature (°C)	Curing time (h)	T_g (ENR50)	T_g (CER)
0R/100	80	24	—	42
50R/50	80	24	−13	42
0R/100	130	15	—	60
5R/95	130	15	−3	52
10R/90	130	15	−5	60
25R/75	130	15	−12	60
50R/50	130	15	−12	62
70R/30	130	15	−12	60
100R/0	130	15	−15	—

temperature relaxation is that of the phenoxy, the other corresponds to ENR-rich compositions.

ENR50 / CER. Table I lists T_g data of these blends cured at different conditions. As expected, the T_g of the epoxy resin changes at increased cure temperatures. Moreover, except for compositions 5R-95 and 10R-90 where the T_g, ENR shifts to higher temperatures, (possibly the result of partial miscibility), both pure component relaxations give evidence of incompatibility.

DISCUSSION

The results can be qualitatively interpreted on the basis of the acid character of the aromatic hydroxyl and to some degree by the molecular weight of the resins employed. With Novolac resins having structure (A) their compatibility with ENR is attributed to hydrogen bonding between the hydrogen of the phenolic hydroxyl and the oxygen of the oxirane ring. Such interactions between the aromatic hydroxyl and the carbonyl group of the polyesters or the ether oxygen of the polyethers have been documented in the literature.[5,6] Moreover, the degree of T_{gb} deviation from its weight average has been successfully used[6] as a measure of molecular interactions between blend partners.

(A)   (B)   (C)
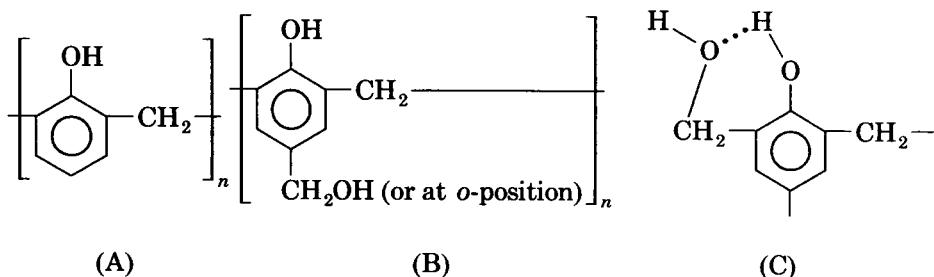
This is in line with the observation that in blends of ENR50 with Resole [see structure (B)], the interactions are weaker compared to those of the ENR50/Novolac blends (see Figs. 4 and 5). In the former blend a smaller proportion (compared to Novolac) of phenolic hydroxyls are available for hydrogen-bonding interactions, since the possibility exists for intramolecular hydrogen bonding between the aromatic hydroxyl and the o-methylol group [see structure (C)]. The significant broadening of the relaxation spectra observed in some phenolic resin blends (ENR25-Novolac and ENR50-Resole) may be accompanied by an increase in impact strength in analogy to similar blends.[19]

The limited compatibility of phenoxy compared to phenolic resins can be attributed to the weaker acid character of the aliphatic hydroxyl, and possibly to its higher molecular weight (reduced entropic factor).[20] In the case of CER it is suggested that the curing agent (of a basic polyamide structure) after epoxide ring opening, competes with ENR for the protons, giving additional inter- and intramolecular bonds. Thus ENR cannot effectively interact with CER because the latter cannot provide acidic hydrogens. In principle it is also possible for the curing agent to interact (ring opening) with ENR, "deactivat-

ing" it. It is unlikely, however, that this was realized to any significant extent, since it would alter the T_g, ENR.

An attempt was also made to correlate compatibility data using a predictive compatibility scheme tested successfully before[3] and based on copolymer–copolymer miscibility[21] and solubility[22] theories.

As explained in Ref. 21, at constant temperature a net segmental interaction parameter between the two polymers χ_b can be defined as follows,

$$f(x, y) = \chi_b - \tfrac{1}{2}\left(N_1^{-\frac{1}{2}} + N_2^{-\frac{1}{2}}\right)^2 \tag{1}$$

where N_i is the degree of polymerization for polymer i. The condition for miscibility is $f(x, y) \leq 0$ and for immiscibility $f(x, y) > 0$. χ_b can be expressed as a function of the binary segmental interaction parameters χ_{ij} and the compositions in volume fraction, x, y of the two copolymers $(A_xB_{1-x})_n$ and $(C_yD_{1-y})_n$

$$\chi_b = xy\chi_{AC} + (1 - x)y\chi_{BC} + x(1 - y)\chi_{AD} + (1 - x)(1 - y)\chi_{BD} -$$
$$-x(1 - x)\chi_{AB} - y(1 - y)\chi_{CD} \tag{2}$$

Since χ_{ij} parameters are not, as a rule, available, they can be calculated as suggested by Krause[22] using relations

$$\chi_{ij} = V_r\left(\delta_i - \delta_j\right)^2/RT \tag{3}$$

and

$$\delta = \rho\Sigma F_i/M \tag{4}$$

where F_i are molar constants obtained using literature data,[22] (Hoy's data in this work), V_r is a reference volume (close to the molar volume of the smallest repeat unit), δ_i is the solubility parameter of homopolymer having density ρ and consisting of units i each of molar mass M. In the case of "unknown" homopolymers, density was obtained using the scheme proposed by Askadskii.[23]

Use of pertinent data in Eq. (2) defines a miscibility map in a composition-composition plot in which the axes represent copolymer compositions and the condition for miscibility is defined by the loci where $f(x, y) \leq 0$. Accordingly, each copolymer pair in such a plot is represented by a point, and the pair is miscible or immiscible depending on whether it lies inside or outside the miscibility region.

For the ENR/Novolac blends, ENR is assumed to be a random copolymer $(A_xB_{1-x})_n$ consisting of epoxidized and unaltered isoprene units, A and B, respectively. Novolac and Resole is equivalent to $(C_yD_{1-y})_n$ with C identified as a substituted phenol and D a methylene group. For ENR/phenoxy blends,
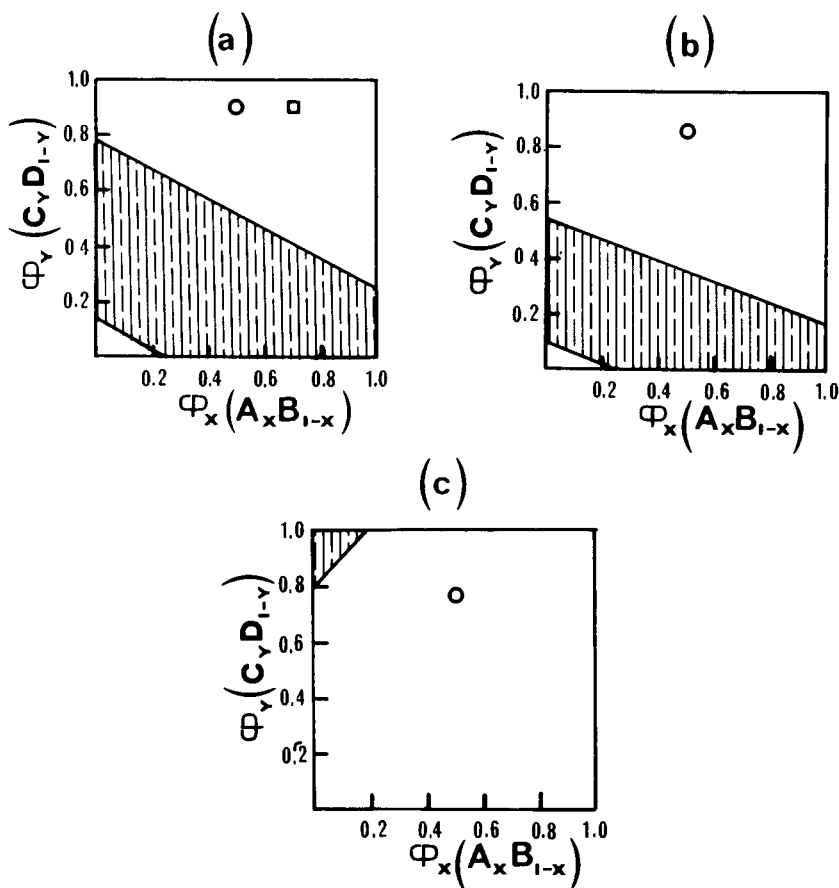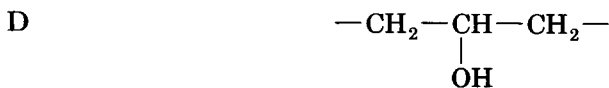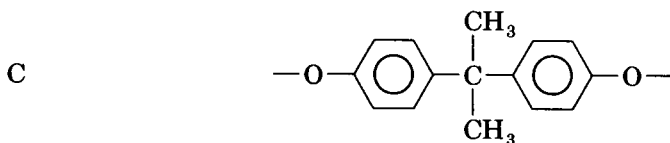
Fig. 7. Miscibility maps of blends. (a) ENR/Novolac: (O) ENR25/Novolac, (□) ENR50/Novolac. (b) ENR/Resole: (O) ENR50/Resole. (c) ENR/phenoxy: (O) ENR50/phenoxy.

C and D are identified, respectively, as:

C

D

The results of testing the above scheme are shown in Figure 7. All of the above pairs are predicted immiscible.

Though the scheme is not theoretically rigorous in that it assumes all χ_{ij} to be positive, it is not surprising that its incompatibility prediction on the

ENR/Novolac blend is at variance with the experimental results using the DMA technique. There may be two reasons for this discrepancy. Thus as shown by experimental results and documented in the literature,[5,6] hydrogen bonding is prevalent in these blends while solubility theory applied to derive χ_{ij} interaction parameters assumes that no specific forces are acting. Also, Eq. (2) is derived on the assumption that a real homogeneous mixture is formed. Phase-contrast micrographs and to a lesser extent, the DMA technique revealed however, that ENR/Novolac blends are not homogeneous at the molecular scale.

CONCLUSIONS

1. The compatibility of some of the polymer blends studied can be explained by hydrogen-bonding interactions.
2. ENR with a sufficiently high degree of epoxidation is compatible, but probably not miscible at the molecular level, with Novolac resins. The degree of compatibility is reduced when methylol groups are also present (Resole).
3. CER is incompatible with ENR because acidic hydrogens are not available due to the competing action of the curing agent. Phenoxy with a similar structure is partially miscible since no curing agent is present.

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