Miscibility of chlorinated polymers with epoxidized natural rubber: 3. Blends with chlorinated polyethylenes

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(Received 19 January 1987; revised 5 May 1987; accepted 8 May 1987)

The miscibility of epoxidized natural rubber (ENR) at two levels of epoxidation (25 and 50 mol%) with chlorinated polyethylene containing 25 and 48 wt% chlorine was investigated over the complete composition range. The techniques used were dynamic mechanical analysis, differential scanning calorimetry, phase-contrast microscopy and stress–strain properties. Miscibility can be traced to specific interactions involving the chlorine atom and the oxirane group, in analogy to low-molecular-weight compounds. The results are in line with previous work on the miscibility of ENR with other chlorinated polymers. All the above ENR/chlorinated polymer compatibility data were used to test a compatibility prediction scheme based on the copolymer–copolymer miscibility theory.

(Keywords: miscibility of blends; epoxidized natural rubber; chlorinated polyethylene; blend miscibility prediction; copolymer–copolymer miscibility theory)

INTRODUCTION

It is generally recognized[1,2] that miscibility in polymer blends can be attained through the interplay of various intermolecular forces, e.g. donor–acceptor[3], dipole–dipole[4], ion–dipole[5]. These arise from various groups residing in the constituent monomers and in this connection the concept of the principle of 'complementary dissimilarity' proved useful[6]. This principle has been invoked to explain the miscibility of poly(vinyl chloride) (PVC) with poly(ε-caprolactone)[6] and with polyesters[7], the interaction being of the donor–acceptor type. Recently, a more generalized approach has been applied[8-10] to include all possible interactions between blend partners as well as intramolecular forces acting between homopolymer and copolymer units.

Lately, we discovered[11,12] that epoxidized poly(hydrocarbons), e.g. epoxidized natural rubber (ENR) can give miscible blends when mixed with chlorine-containing polymers, the oxirane group serving as a proton acceptor and/or participating in polar interactions.

We were led to these systems by considering the fact that cyclic ethers (e.g. tetrahydrofuran, THF) have strong solvating power for PVC and other chlorinated hydrocarbons[13]. It is also known[14] that epoxidized oils (mainly esters) are used as PVC plasticizers. Thus in our previous studies, ENR containing 50 mol% oxirane groups (ENR50) was shown[11] to be miscible with PVC at the segmental level, throughout the composition range.

It was also found that a smaller amount (25 mol%) (ENR25) of oxirane units was insufficient to attain miscibility in all blend compositions. In a related work[12], it was demonstrated that for miscibility to take place the acidic α-hydrogen of the halogenated polymer is not required. Thus ENR50 was found to be miscible with chlorinated polypropylene (CPP) and a poly(vinylidene chloride–alkyl acrylate) copolymer containing ~90 mol% vinylidene chloride units. In both these cases miscibility can be attributed to donor–acceptor interactions due to β-hydrogens and/or dipole–dipole interactions[15], in analogy to miscible PVC–polyester blends[4].

Aside from theoretical interest related to the molecular origin of miscibility, this line of research could be of practical value since PVC modification[16] or plasticization by polymeric plasticizers[17] is of lasting technological interest. Also, since epoxidation is a relatively straightforward polymer modification reaction[18], it could provide a new route for preparing miscible polymer systems with other polar and/or proton-donating polymers.

In this work the miscibility behaviour of ENR (with different levels of epoxidation) was examined with chlorinated polyethylene (CPE) at two degrees of chlorination. This choice of blend components would give information on the lower composition range of active groups (chlorine and oxirane) required for miscibility to be attained.

Since the CPE with the lower chlorine content had a residual crystallinity, it was also of interest to examine whether miscibility affects this parameter as in other miscible semicrystalline blends[19] and, if so, to attempt to determine the interaction parameter χ_{12} using available theory[20,21] associated with the T_m depression of the crystalline component in the blend.

Blends were studied in the complete composition range using microscopic, dynamic mechanical (d.m.a.) and d.s.c. techniques. Tensile testing was also applied for certain blends to assess their mechanical behaviour at high elongation and possible synergistic reinforcement. Once miscibility was established, the data could provide

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0032-3861/87/122122-08$03.00

the basis for testing relationships proposed to quantify T_g and modulus dependence on composition. An attempt is also made to rationalize available compatibility data[11,12] of ENR with halogen-containing polymers, using recent theory[9] developed to explain miscibility of homopolymer–copolymer and copolymer–copolymer blends.

EXPERIMENTAL

ENR was donated by the Malaysian Rubber Products Research Association Laboratory, Hertford, UK. It was prepared by epoxidation of rubber latex using an *in situ* prepared peracetic acid solution[22]. It was reported[23] that epoxidation proceeds in a random manner and the *cis* configuration is maintained. G.p.c. measurements of ENR50 in THF gave $\bar{M}_n = 5.5 \times 10^4\,\mathrm{g\,mol^{-1}}$ and a polydispersity index $I = 4.7$.

CPE in powder form was obtained from Aldrich-Europe, Belgium. Two samples containing 25 wt% (CPE25) and 48 wt% (CPE48) chlorine were used. The product was prepared by a slurry-phase chlorination of high-density PE. (The small percentage of talc present was removed by centrifuging solutions in chloroform.) D.s.c. measurements showed that CPE48 was amorphous while CPE25 had ~20% bulk crystallinity. Specific gravity was given as 1.25 and 1.08, respectively and g.p.c. measurements of CPE48 in THF gave $\bar{M}_n = 6.1 \times 10^4\,\mathrm{g\,mol^{-1}}$ and $I = 2.5$.

Blends were prepared by combining stock solutions of the two components in $CHCl_3$ (common solvent), followed by fast evaporation in a rotary evaporator. The residual mass was dried in a high vacuum at 50°C for 4 days. Films were prepared by hot pressing between Teflon sheets at ~140–160°C depending on composition and quenching at 0°C.

Blends were studied over the complete composition range for the systems ENR50/CPE48, ENR25/CPE48, ENR50/CPE25 and ENR25/CPE25. In the designation to be used, the weight percentage of each constituent is enclosed in parentheses. Thus (10)ENR25/(90)CPE48 denotes a blend with 10 wt% ENR25 and 90 wt% CPE48.

Thin films prepared by melt pressing and quenching were examined under a phase-contrast microscope with oil ($n_D^{23} = 1.518$) immersion in bright field. D.s.c. measurements were carried out using a 910 calorimeter system coupled with a 990 programmer–recorder. Calibration was made with an indium standard. Sample weight was ~15 mg and heating rate was $10°\mathrm{C\,min^{-1}}$. The first heating cycle to 150°C was followed by quenching to 0°C and heating to determine T_g and T_m. Dynamic viscoelastic data, loss tangent $\tan\delta$ and complex modulus $|E^*|$ were obtained at 110 Hz using a direct-reading viscoelastometer (Rheovibron, model DDV II-C, Toyo-Baldwin). Specimen dimensions were $3 \times 0.3 \times 0.08\,\mathrm{cm^3}$. Near-equilibrium stress–strain measurements were made at 30°C using the procedure applied before[24]. Duplicate runs made showed good repeatability.

RESULTS

Morphology

Figure 1 shows phase-contrast micrographs of some compositions. Pure CPE48 and CPE25 show inhomogeneity—the result of non-uniform chlorination[25]. Given the higher polarizability of the chlorine atom, at positive phase-contrast, dark areas should represent the chlorine-containing regions in the solid. Because of this, phase-contrast microscopy is not very discriminating. However, as *Figures 1f* and *1g* show, blends of ENR50/CPE25 display distinct phase boundaries, in addition to the light–dark pattern characteristic of CPE. This contrasts them from ENR50/CPE48 (*Figure 1b*) and ENR25/CPE48 blends (*Figure 1d*) shown to be miscible or partially so (see below).

Dynamic mechanical properties

CPE48 blends. The dynamic mechanical analysis (d.m.a.) results for ENR50/CPE48 blends are given in *Figure 2* in terms of storage modulus E' and loss modulus E''. Pure component data for the main β relaxation at about −5°C (ENR50) and at 22°C (CPE48) are in agreement with previous work[11,26]. The gradual T_{gb} (E''_{max}) shift with composition and the shape (no broadening) of the relaxation indicate miscibility at the segmental level at all compositions. The T_{gb} variation is given in *Figure 3*, where relevant functional relationships proposed by Fox[27] and Gordon and Taylor[28] are also drawn. The latter with $k = 0.48$ fits well, provided that the 50/50 composition is ignored. A similar value ($k = 0.45$) was determined for the ENR50/CPP studied before[12]. Modulus variation with composition does not suggest any antiplasticization effects observed[29] with polar plasticizers.

Figure 4 gives the d.m.a. spectra for the ENR25/CPE48 blends. The results indicate miscibility at low and high ENR25 levels (a single T_{gb} is observed) and partial miscibility at the intermediate composition where the two main relaxations persist, though converging to each other. In both *Figures 2* and *4* the shoulder at about −50°C for blends with high ENR content is attributed to a low-temperature (local-mode) relaxation originally observed[11] for pure ENR50 at about −80°C and shifted to higher temperature by antiplasticization.

CPE25 blends. In the case of the ENR50/CPE25 blends, the proximity of the T_g values of the components makes it impossible to use the usual criterion for identifying compatibility. D.s.c. gave a T_g for both components at about −15°C and d.m.a.[11,26] at about −5°C. Thus to assess compatibility, morphology and tensile data had to be relied on. Both indicated that the blends are incompatible at all compositions. The thermomechanical spectra of ENR25/CPE25 are given in *Figure 5*. As the amount of CPE25 increases the T_{gb} shifts upwards but remains close to the main ENR25 relaxation at −26°C. The spectra indicate miscibility within a limited composition range. Overall, the d.m.a. behaviour is unusual in that, though a single peak (broadened at higher CPE levels) is observed, its position is not shifted beyond −22°C and the CPE25 peak is not detected even at low ENR levels.

Thermal properties

D.s.c. measurements were made to supplement T_g data and to determine the effect of ENR on T_m and on the degree of CPE25 crystallinity. The T_m reduction at ~123°C was minimal (1.0°C). The effect on crystallinity is

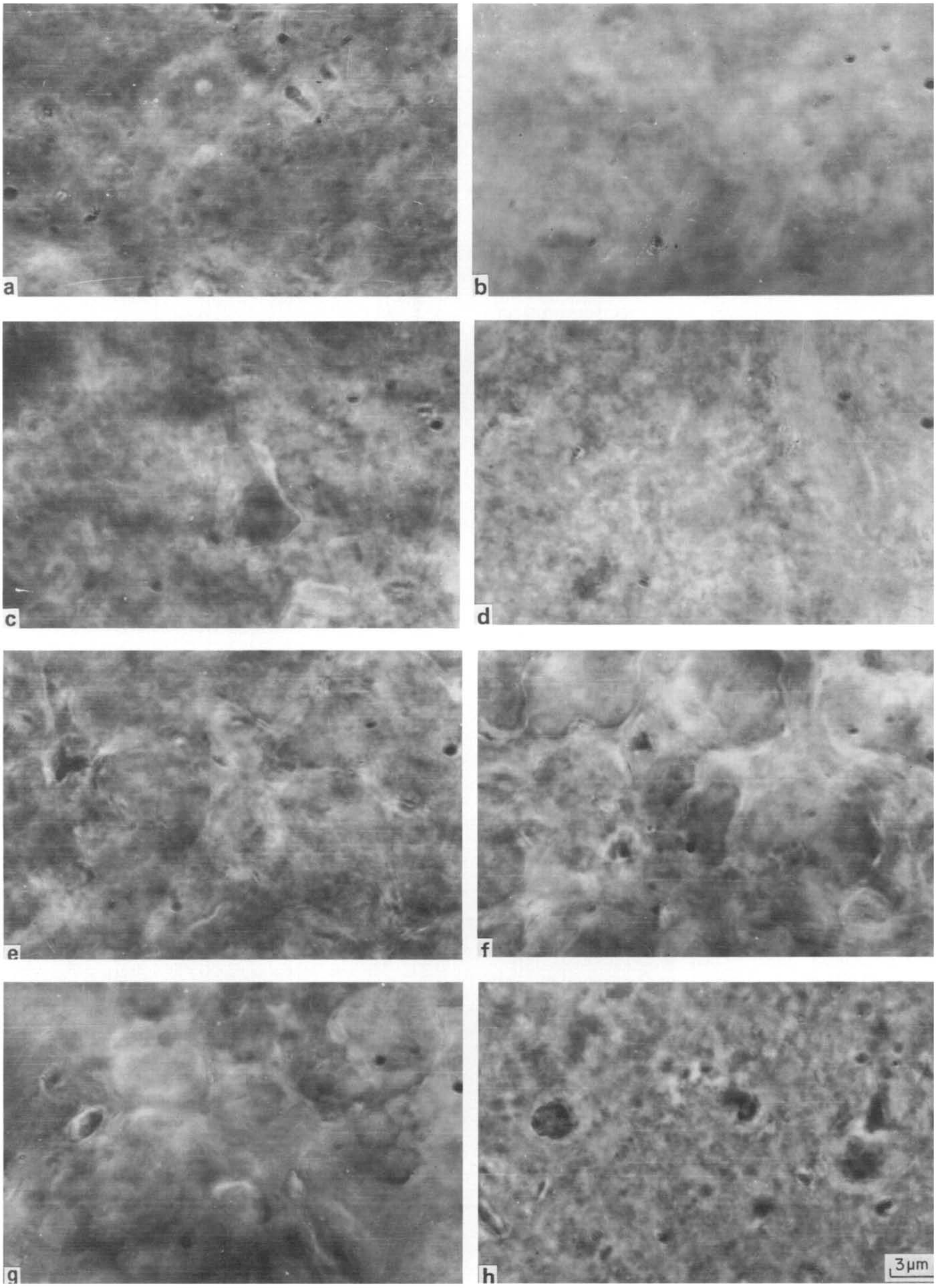

Figure 1 Phase-contrast micrographs of blends: (a) CPE48; (b) (50)ENR50/(50)CPE48; (c) (25)ENR25/(75)CPE48; (d) (50)ENR25/(50)CPE48; (e) (75)ENR50/(25)CPE25; (f) (50)ENR50/(50)CPE25; (g) (25)ENR50/(75)CPE25; (h) CPE25

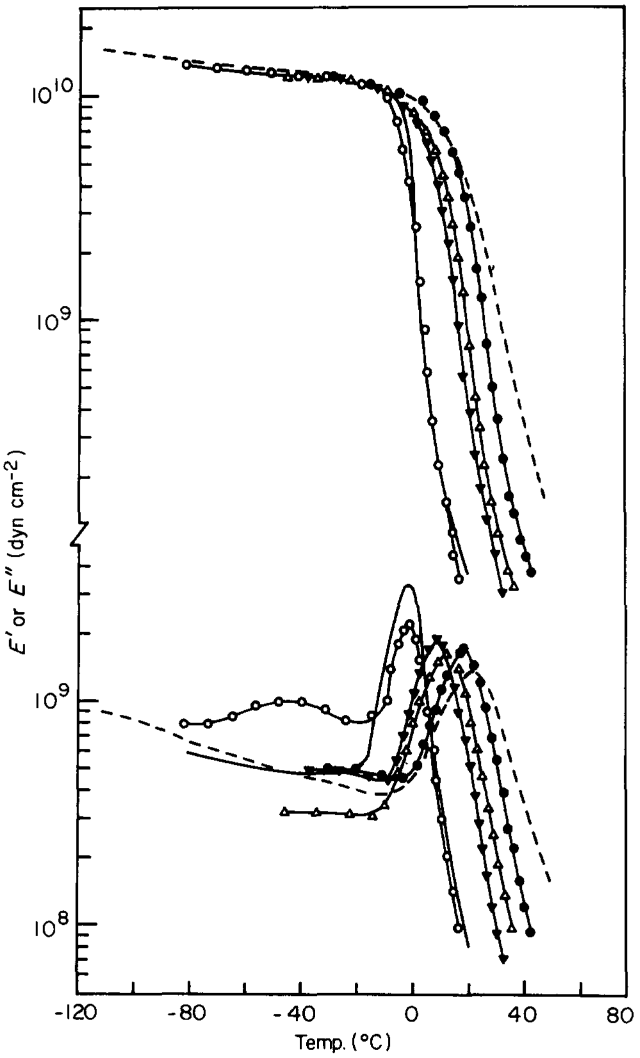

Figure 2 Thermomechanical spectra of ENR50/CPE48 blends: ——, (100)/(0); ○, (80)/(20); ▼, (50)/(50); △, (25)/(75); ●, (10)/(90); ---, (0)/(100)

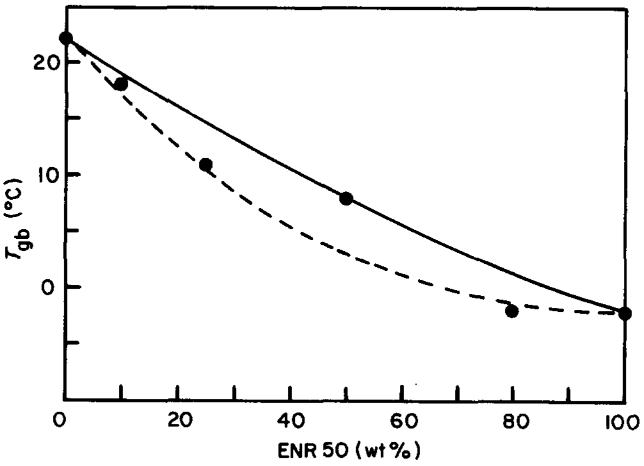

Figure 3 Composition dependence of T_{gb} of ENR50/CPE48 blends: ——, Fox relationship[27], $1/T_{gb} = W_1/T_{g1} + W_2/T_{g2}$; ---, Gordon–Taylor relationship[28], $T_{gb} = T_{g1} + k(W_2/W_1)(T_{g2} - T_{g1})$

shown in *Figure 6*. Crystallinity referred to total blend mass decreases linearly with ENR (simple dilution effect). CPE25 crystallinity increases slightly in the presence of ENR. This could be the result of a decrease of blend melt viscosity[31], facilitating diffusional processes, or of an increased nucleation rate as in the case of iPP crystallizing in the presence of ethylene-propylene rubber[32]. The above data indicate that crystalline domains in CPE25 are little affected by miscibility interactions between the amorphous constituents in the blend. Analogous findings were reported[26] for acrylic rubber–CPE25 blends.

Stress–strain properties

In previous work[11,12] dealing with ENR/PVC and ENR/CPP it was found that relatively large amounts (50 wt%) were required to plasticize the high-modulus thermoplastic. For these systems it was proposed that the low 'plasticizing' efficiency of ENR may be traced to the effective crosslinking of the solid due to polar forces caused by the oxirane group. In the present system, owing to the lower modulus of CPE, the influence of intermolecular forces originating from ENR can be discerned already at low rubber levels. In *Figure 7* it is seen that indeed modulus and ultimate elongation are increased with the addition of ENR50 compared to pure CPE48. (Further increase of ENR reverses the trend, causing the solid to flow.) The same figure shows the poor ultimate properties of the (50)ENR25/(50)CPE48, shown to be partly miscible by d.m.a. Preliminary tests with ENR50/CPE25 blends indicated very poor tensile behaviour.

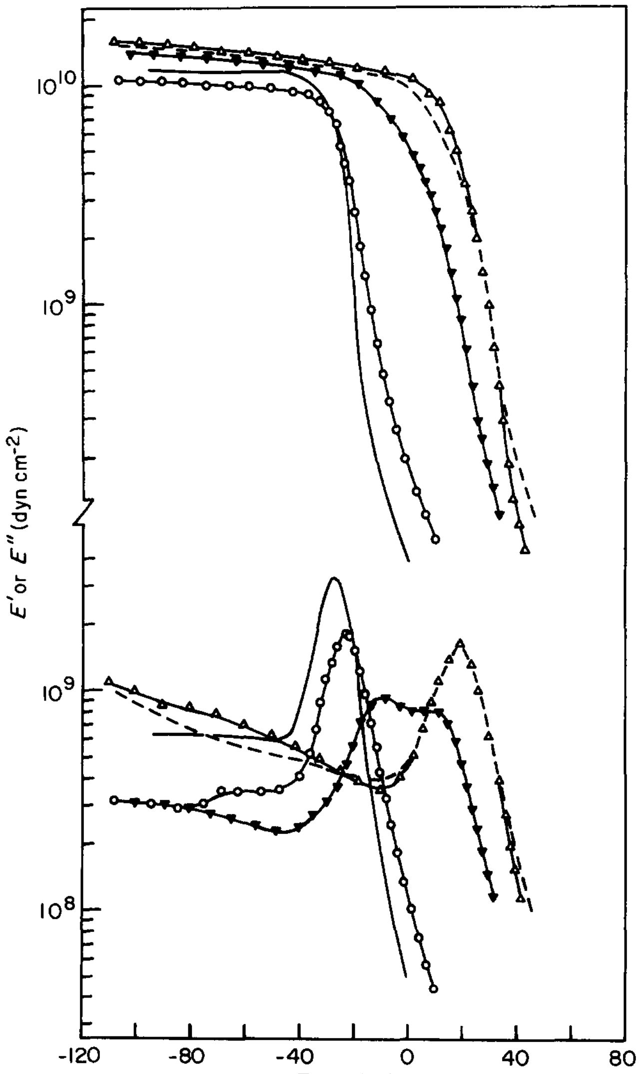

Figure 4 Thermomechanical spectra of ENR25/CPE48 blends: ——, (100)/(0); ○, (75)/(25); ▼, (50)/(50); △, (25)/(75); ---, (0)/(100)

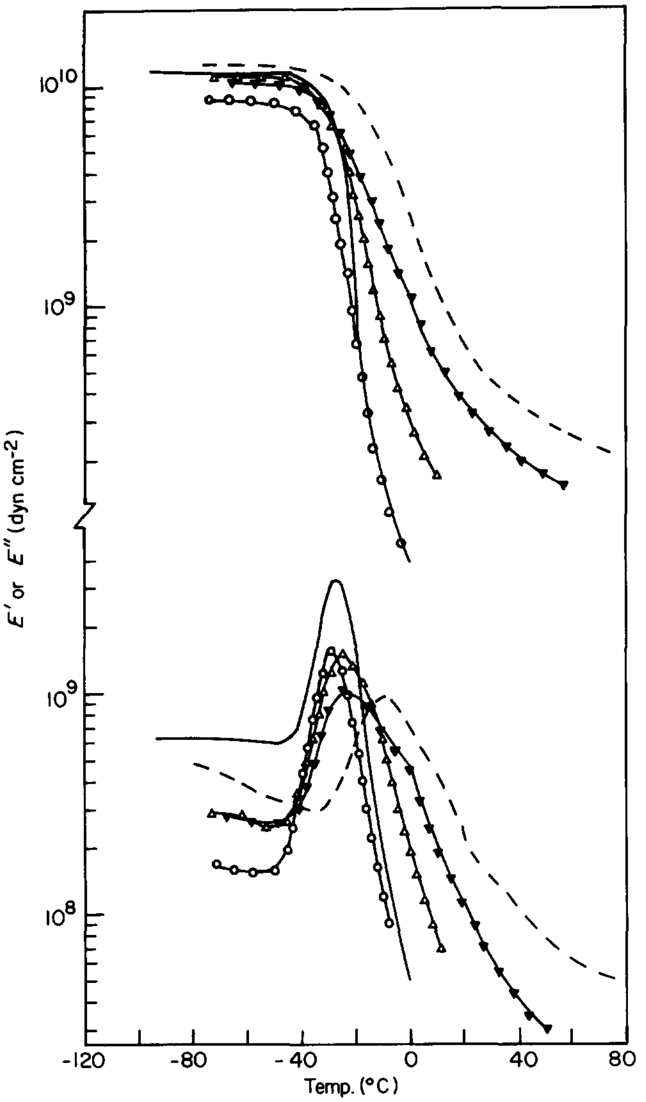

Figure 5 Thermomechanical spectra of ENR25/CPE25 blends: ———, (100)/(0); ○, (75)/(25); △, (50)/(50); ▼, (25)/(75); – – –, (0)/(100)

DISCUSSION

Among the four blends covered in this study, experimental evidence suggests that only ENR50/CPE25 blends are incompatible. The rest are miscible (ENR50/CPE48) or miscible at certain compositions.

Since small-deformation mechanical properties (e.g. modulus) are influenced by molecular relaxations, hence by the molecular environment of the polymeric chains, it was of interest to test various mixing rules that might be applicable to miscible systems. The fundamental difficulty in such blends lies in the fact that pure components lose their identity because of segment–segment interaction. Therefore, predicting blend modulus from pure component data has not always been successful.

When interactions align different chains in parallel, use of the parallel model may be justifiable[33], i.e.

$$E_b = E_1\Phi_1 + E_2\Phi_2 \qquad (1)$$

Another possibility for nearly miscible systems would be the interpenetrating model[34]:

$$\log E_b = \Phi_1 \log E_1 + \Phi_2 \log E_2 \qquad (2)$$

where E_b and E_i are the modulus of the blend and the modulus of component i at volume fraction Φ_i. Another relationship that was used[26] with some success in an analogous system takes into account the reduction of the modulus E_2 of the thermoplastic due to plasticization by component 1. This is assumed to be proportional to the change of T_{g2} relative to the overall T_g difference of the two constituents. Thus equation (1) is modified to read:

$$E_b = E_1\Phi_1 + E_2[1-(T_{g2}-T_{gb})/(T_{g2}-T_{g1})]\Phi_2 \qquad (3)$$

The test of the above relationships is given in *Figure 8* for the ENR50/CPE48 blends. Though none of the models is completely satisfactory when tested over an extended temperature range, the results suggest alignment of chains in parallel.

A problem of great importance in the area of polyblend research has been to develop a scheme capable of

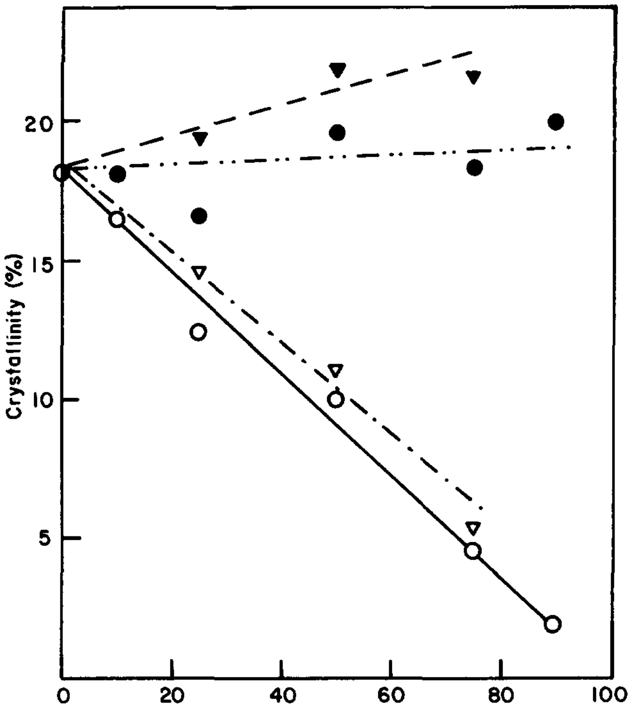

Figure 6 Composition dependence of blend crystallinity: ○, ENR50/CPE25; ▽, ENR25/CPE25. Filled symbols denote crystallinity of CPE25. $\Delta H_{f,PE} = 293\ J\ g^{-1}$ (ref. 30)

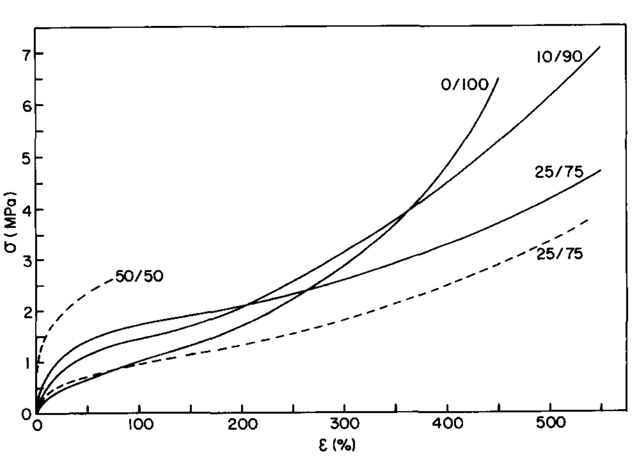

Figure 7 Stress–strain properties of some CPE48 blends: ———, with ENR50; – – –, with ENR25. First numeral denotes wt% of ENR

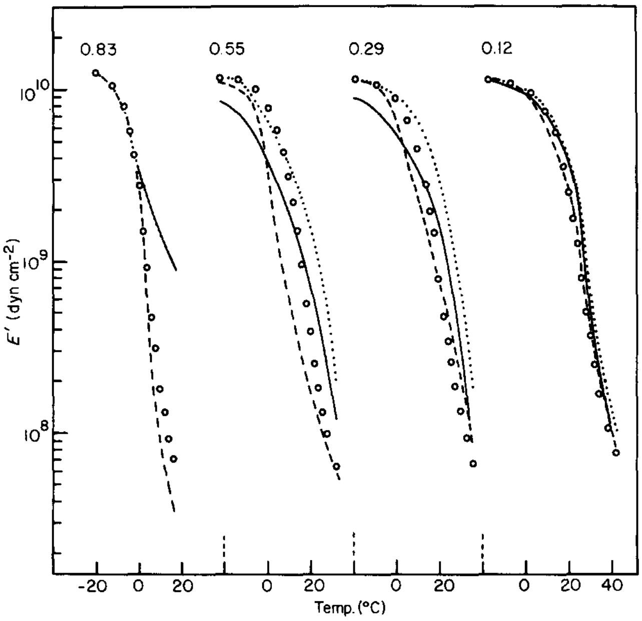

Figure 8 Comparison of experimental and calculated E' (blend) values: ○, experimental values; ·····, equation (1); - - - - -, equation (2); ———, equation (3). Numbers above curves denote ENR volume fraction in CPE 48 blends

predicting miscibility. Several such schemes of varying degree of complexity have been recently proposed[1,8-10,35]. Since this study concludes that ENR is compatible with various halogenated polymers[11,12], an attempt was made to correlate data using available theory[9] applicable to miscible copolymer–copolymer blends[9,36]. The relevant theory[9] predicts that for a homogeneous blend of two statistical copolymers consisting of A,B and C,D structural units, an interaction parameter χ_b is introduced as follows:

$$f(x,y) \equiv xy\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} - \chi_b^{cr} \equiv \chi_b - \chi_b^{cr} \quad (4)$$

where x and y denote the compositions in volume fraction of the two copolymers $(A_xB_{1-x})_n$ and $(C_yD_{1-y})_n$ and

$$\chi_b^{cr} = \tfrac{1}{2}(N_1^{-1/2} + N_2^{-1/2})^2$$

N_i being the degree of polymerization of copolymer i. For high-molar-mass polymers the above quantity is near zero and can be ignored. The condition for miscibility is defined by $\chi_b \leq 0$ and for immiscibility by $\chi_b > 0$.

As noted by Kambour[10], relationship (4) predicts miscibility even if all χ_{ij} are positive provided χ_{AB} and χ_{CD} are sufficiently large (intramolecular forces). In addition to assumptions stated in ref. 9, it was assumed that homopolymers can be considered as copolymers and following Paul and Barlow[8] the sequence of the basic units in the chain was not taken into account. This is plausible since recent calculations have shown[36] that in dealing with alternating copolymers (identifiable as our homopolymers, e.g. PVC, PVDC, CPP), the extra interactional energy $\chi_{\text{distribution}}$ to be added to χ_b in equation (4) vanishes. The next step is to calculate the segmental interaction parameters χ_{ij} of the classical Flory–Huggins theory with the relationship[35]:

$$\chi_{ij} = (V_r/RT)(\delta_i - \delta_j)^2 \quad (5)$$

where V_r is a reference volume taken to be close to the molar volume of the smallest repeat unit and δ_i and δ_j are the solubility parameters of the homopolymers (real or fictitious) made up of structural units i and j, respectively. The δ values can be calculated using group molar attraction constants[35,37] and the relationship:

$$\delta = \rho \sum_i (F_i/M) \quad (6)$$

where ρ is the density of the polymer, M the molar mass of the repeat group and F_i the molar attraction constant of the chemical group i in the repeat unit. In our calculations V_r is taken to be 50 cm^3 mol^{-1}, temperature is 25°C and density values were obtained from the literature[38,39]. In cases of unknown polymers, e.g. $\text{+CCl}_2\text{+}_n$, $\text{+CCl(CH}_3\text{)+}_n$ and +CHCl+_n, the density was calculated using the scheme proposed by Askadskii[39], the particular values being 1.76, 1.43 and 1.50 g cm^{-3}, respectively.

For the blends studied, the basic units making up the copolymers were the isoprene unit (NRu) ≡ A, the epoxidized isoprene unit (ENRu) ≡ B, the methylene (Me) ≡ C and the chloromethylene group –CHCl– (CMe) ≡ D. These units are involved in the ENR/CPE blends covered in this study and the ENR/PVC blends studied before[11]. Units $\text{–CCl}_2\text{–}$ and $\text{–C(CH}_3\text{)Cl–}$ are coded as (DCMe) ≡ D and (CMMe) ≡ D, respectively. These, in combination with methylene units, form the PVDC and CPP polymers $(C_yD_{1-y})_n$, respectively, whose miscibility with ENR was also reported[12].

Table 1 lists the segmental interaction parameters χ_{ij} (calculated using equation (5)), associated with the various basic units of the polymers composing the blends listed in columns 1–3. Use of these interaction parameters in equation (4) yields, at constant temperature, a zone of compatibility in a composition–composition plot. Polymer pairs within this shaded zone and on its border ($\chi_b \leq 0$) are miscible, outside it ($\chi_b > 0$) immiscible.

Figure 9a summarizes the results for ENR/CPE and ENR/PVC[11] blends. The scheme correctly predicts ENR50/CPE48 and ENR50/PVC to be miscible, ENR50/CPE25 and ENR25/PVC to be immiscible, and ENR25/CPE48 and ENR25/CPE25 to be nearly so. In the same figure it is seen that the exact value of the reference volume V_r does not greatly influence the miscibility region. *Figures 9b* and *9c*, correspondingly, correctly predict ENR/CPP and ENR/PVDC to be miscible[12]. Equation (5) stipulates that segmental interactions are positive or zero. This is the result of applying the solubility theory concepts. Another

Table 1 Segmental interaction parameters χ_{ij} of blends at 25°C

ENR/PVC ENR/CPE		ENR/PVDC		ENR/CPP	
NRu/ENRu	0.078	NRu/ENRu	0.078	NRu/ENRu	0.078
NRu/Me	0.006	NRu/Me	0.006	NRu/Me	0.006
NRu/CMe	0.071	NRu/DCMe	0.047	NRu/CMMe	0.035
ENRu/Me	0.126	ENRu/Me	0.126	ENRu/Me	0.126
ENRu/CMe	0.000	ENRu/DCMe	0.004	ENRu/CMMe	0.009
Me/CMe	0.118	Me/DCMe	0.086	Me/CMMe	0.008

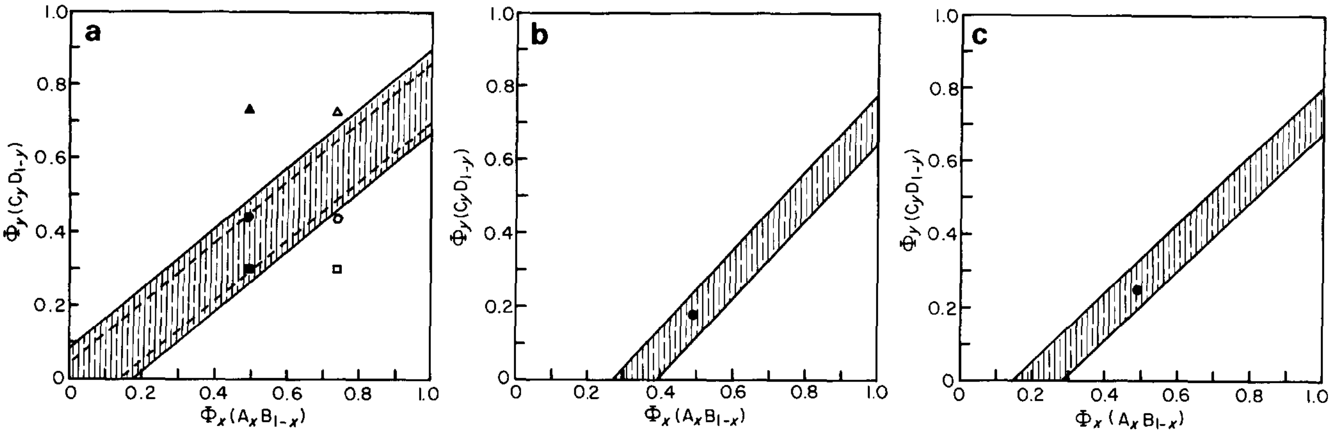

Figure 9 Miscibility maps of ENR/chlorinated polymer blends at 25°C: (a) ■, ENR50/PVC; ●, ENR50/CPE48; ▲, ENR50/CPE25. Open symbols denote corresponding blends with ENR25. (b) ENR/CPP blends. (c) ENR/PVDC blends. (Broken lines in (a) define miscibility map calculated with $V_r = 100\,\mathrm{cm^3\,mol^{-1}}$)

limitation in the present scheme is the necessity of knowing the density fairly accurately since it significantly affects the location of the miscibility region. For unknown polymers the Askadskii scheme[39] can be used. In the case of $\left(\mathrm{CCl_2}\right)_n$ and $\left(\mathrm{CHCl}\right)_n$ polymers it was found that agreement with experiment was obtained with the Askadskii constant $k = 0.600$ (the minimum proposed for semicrystalline polymers). For polyethylene $\rho = 0.850\,\mathrm{g\,cm^{-3}}$ (amorphous). On the same issue the question raised by Krause[35] on the polymer density being affected by miscibility *per se* still remains.

Recent findings[40] indicate that chlorinated polymers are compatible with other epoxidized poly(hydrocarbons) as well, e.g. poly(*cis*-1,4-butadiene).

CONCLUSIONS

Epoxidized polymers, specifically poly(hydrocarbons), are miscible with chlorinated polymers, possibly the result of specific interactions, in analogy with low-molecular-weight compounds. In general, increasing the degree of chlorination improves compatibility.

With certain assumptions and combining concepts from the Flory–Huggins theory for mixtures with recent theory proposed on copolymer–copolymer miscibility, it is possible to formulate a compatibility prediction scheme which predicts satisfactorily compatibility data related to the above blends.

NOTE

Shortly before this manuscript was to be submitted, it came to our attention that, on the basis of recent work by Cantow[41], the scheme proposed by Balazs *et al.*[36] on the effect of sequence distribution needs amendment. This does not invalidate the scheme used here.

ACKNOWLEDGEMENT

This work was supported in part by the Ministry of Industry, Energy and Technology, the General Secretariat of Research and Technology.

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