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Compatibilization of chlorinated polyethylene/poly(vinyl chloride) blends with epoxidized natural rubber

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A ternary blend consisting of chlorinated polyethylene (CPE), poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) was investigated to define the miscibility regime. The techniques used were mainly dynamic mechanical analysis and tensile testing. In this ternary blend where ENR plays the role of the compatibilizer, it was established that different amounts are required to cause miscibility for different ratios of CPE/PVC; the highest at equal concentrations of the chlorinated components. Depending on the PVC/CPE ratio and the amount of compatibilizer, a wide spectrum of mechanical properties was obtained. Based on the single glass transition temperature data, a ternary phase diagram was constructed and the results were found to correlate well with the spinodal curve calculated for this system using a modified version of the Flory–Huggins lattice theory suitable for ternary blends.

(Keywords: ternary blends; ternary phase diagram of polyblends; compatibilization of blends; epoxidized natural rubber; chlorinated polyethylene/poly(vinyl chloride) blend)

INTRODUCTION

Ternary blends are gaining an important share in the field of polymer property diversification through blending. From the practical viewpoint these systems offer the possibility of extending the list of miscible or mechanically compatible blends frequently utilizing scrap or recycled plastic material[1]. Theoretically their study offers the possibility to explore the important principles governing the compatibilization of immiscible or nearly miscible blends[2–4].

Work on ternaries prior to ca. 1977 are listed in the review by Krause[5]. Kwei and coworkers[6] are credited with the first systematic study of a miscible blend involving poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) compatibilized with poly(vinylidene fluoride) (PVF_2). Since then the list of ternaries investigated has been considerably enlarged. In these blends the constituents are pairwise miscible, or a compatibilizer is added to induce miscibility (acting as a common solvent) and/or to improve adhesion between the main partners by modification of interface properties. Among the latter, which constitute the vast majority of ternary systems, we cite the study of Wang and Chen[7] where nitrile rubber was used to compatibilize the poly(vinylidene fluoride-*co*-vinyl chloride)/poly(vinyl chloride) (PVC) blend.

In the same class belongs the extensive work reviewed by Teyssié and coworkers[2,3] involving poly(styrene) (PS)/poly(ethylene-*co*-propylene) rubber (EPDM) with poly(styrene-*b*-hydrogenated isoprene) as compatibilizer, PS/PVC with poly(methyl methacrylate-*b*-styrene) or poly(ε-caprolactone-*b*-styrene) as compatibilizer and PVF_2/ polyolefins with hydrogenated PMMA/polydiene block copolymers as compatibilizer.

Cowie and Lath[8] compared the predicted and determined miscibility ranges of a ternary consisting of poly(styrene-*co*-acrylonitrile) (SAN)/poly(methyl methacrylate-*co*-acrylonitrile) (MMA-AN)/poly(styrene-*co*-methyl methacrylate) (S-MMA), using the copolymer–copolymer miscibility theory[9]. Much work in this area has also been reported by Paul, Barlow and coworkers, who investigated compatibilization of high-density polyethylene (HDPE)/PS blends[10,11] and HDPE/poly(phenylene ether) copolymers[11] using as a compatibilizer hydrogenated styrene–butadiene–styrene block copolymer. The same group have also reported on the compatibilization of poly(carbonate) (PC)/SAN using aliphatic polyesters[12].

Phase diagrams of ternary systems were also reported by Nishi and coworkers for the PS/poly(vinyl methyl ether)/poly(ε-caprolactone) (PCL)[13] and for the SAN/PC/PCL blend[14]. An experimental investigation of the miscibility and morphology of the ternary PVC/SAN/PMMA was published by White and coworkers[15].

Recently, the ternary (consisting of miscible binaries) of PMMA/poly(epichlorohydrin)/poly(ethylene oxide) was investigated by Paul, Barlow and coworkers[16]. This listing, by no means complete, does not include ternaries reported in the patent literature.

In past work we have demonstrated the effectiveness of epoxidized polyhydrocarbons to produce miscible polymers, e.g. PVC[17], chlorinated polyethylene (CPE)[18], chlorinated polypropylene (CPP)[19] and with proton-donating polymers[20]. This work was extended to include epoxidized poly(butadiene-*co*-styrene) (ESBR) and poly(butadiene-*b*-styrene) (ESBS) as blend partners with PVC[21], ESBS also being an effective compatibilizer for

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the immiscible PS/PVC system[22]. In the present study we report on the miscibility ranges of the ternary CPE/epoxidized natural rubber (ENR)/PVC. Both PVC and CPE are commodity plastics, the latter serving as a flexibilizer for PVC. Though CPE has a limited compatibilizing capacity in PVC/PE blends[23], its degree of miscibility (if any) with PVC has not been published as of today. In the work of Doubé and Walsh[24,25] on the miscibility of PVC/CPE, the structure and composition of CPE used differed from the product used in the present study; see the last section. Unpublished work referred to in ref. 26 indicates that the system is immiscible in the intermediate composition range. Thus it was of interest to explore the compatibilizing action of ENR on the basis of its demonstrated miscibility with PVC[17] and CPE[18]. This ternary offers many parameters to be optimized, e.g. the level of compatibilizer and the levels of epoxidation and chlorination to attain miscible or mechanically compatible blends. The present report covers the composition–miscibility–property parameters using sufficiently epoxidized and chlorinated components to ensure that the constituent binaries are miscible. Ternaries with partners of a lesser degree of chlorination and epoxidation will be the subject of a future report.

EXPERIMENTAL

The PVC used was an unplasticized product obtained from EKO Chemicals Co., Greece. G.p.c. measurements in tetrahydrofuran (THF) gave $\bar{M}_n = 36\,000\ \mathrm{g\,mol^{-1}}$ and a polydispersity index $I = 2.1$.

Epoxidized natural rubber had a degree of epoxidation of 50 mol% (ENR50). It was reported[27] that epoxidation proceeds in a random manner and that the *cis* configuration is maintained. ENR was donated by the Malaysian Rubber Producers Research Association Laboratory, Hertford, UK. G.p.c. measurements of ENR50 in THF gave $\bar{M}_n = 5.5 \times 10^4\ \mathrm{g\,mol^{-1}}$ and $I = 4.7$.

CPE containing 48 wt% chlorine (CPE48) was obtained from Aldrich–Europe, Belgium. D.s.c. measurements showed that it was amorphous. G.p.c. measurements in THF gave $\bar{M}_n = 6.1 \times 10^4\ \mathrm{g\,mol^{-1}}$ and $I = 2.5$.

Ternary blends were prepared by dissolving the components in a common solvent (THF). A PVC stabilizer (dibutyltin dilaurate, 2 wt% calculated on PVC) was added to the blend solution. After evaporating the solvent the blends were dried in a vacuum oven at 60°C to constant weight. Films were prepared by hot pressing between Teflon sheets at 150–180°C (depending on composition) and 15 MPa and quenching at 0°C. Three series of compositions were prepared depending on the weight ratio of PVC/CPE48, namely 1:1, 1:3 and 3:1. In reporting compositions, weight percentage of the constituents will be denoted in the order PVC/ENR50/CPE48.

Thin films by melt pressing on the microscope slide 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 20 mg and heating rate was 10°C min^{-1}. The first heating cycle to 120°C was followed by quenching to 0°C to determine T_g. Dynamic viscoelastic data, loss tangent tan δ and complex modulus $|E^*|$ were obtained at 110 Hz using a direct reading viscoelastometer (Rheovibron, model DDV II-C, Toyo-Baldwin). Specimen dimensions were $3 \times 0.3 \times 0.07\ \mathrm{cm^3}$.

Tensile tests were performed according to ASTM D 882 at room temperature and at crosshead speed of 20 cm min^{-1} using a J.J. Tensile Tester. Dimensions of film strips were $6.0 \times 1.20 \times 0.05\ \mathrm{cm^3}$.

RESULTS

Phase-contrast microphotography was inconclusive and could not establish homogeneity. This had been observed before in miscible blends[18,28] containing CPE. Therefore, emphasis was given to mechanical testing and d.s.c.

Mechanical properties of binary blends

Binary blends of ENR50/CPE48 and ENR50/PVC are miscible throughout the composition range[17,18]. Though from unpublished work on CPE48/PVC one might infer that the blend is immiscible[26], some blends at the extremes of the composition range were studied to define better the immiscibility gap of the ternary. The results are summarized in *Figures 1* and *2* in terms of dynamic mechanical and ultimate tensile properties data. It is seen that at high levels of CPE48 binary blends are miscible or nearly so. At intermediate and PVC-rich compositions there are two distinct relaxations attributable to the blend components and characteristic of an incompatible blend.

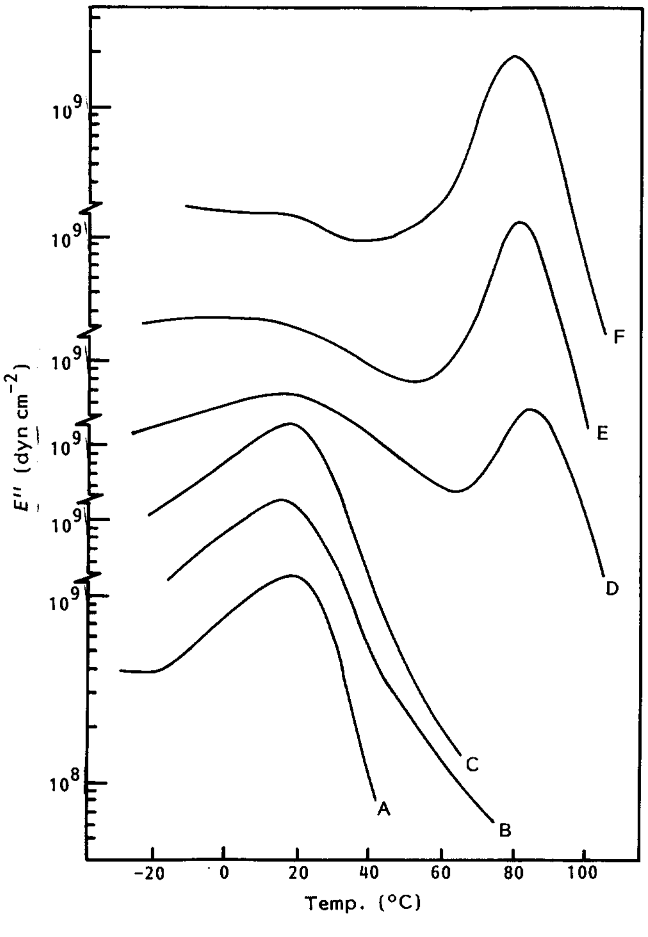

Figure 1 Thermomechanical spectra (E'' data) of binary PVC/CPE48 blends: (A) 0/100; (B) 10/90; (C) 20/80; (D) 50/50; (E) 90/10; (F) 95/5

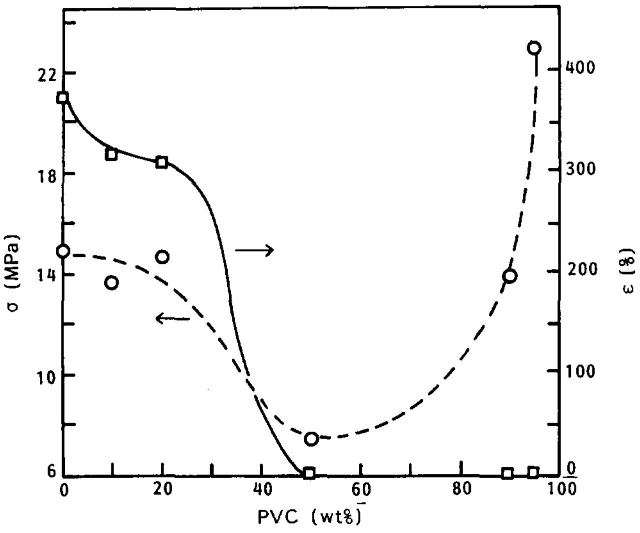

Figure 2 Ultimate properties of binary PVC/CPE48 blends

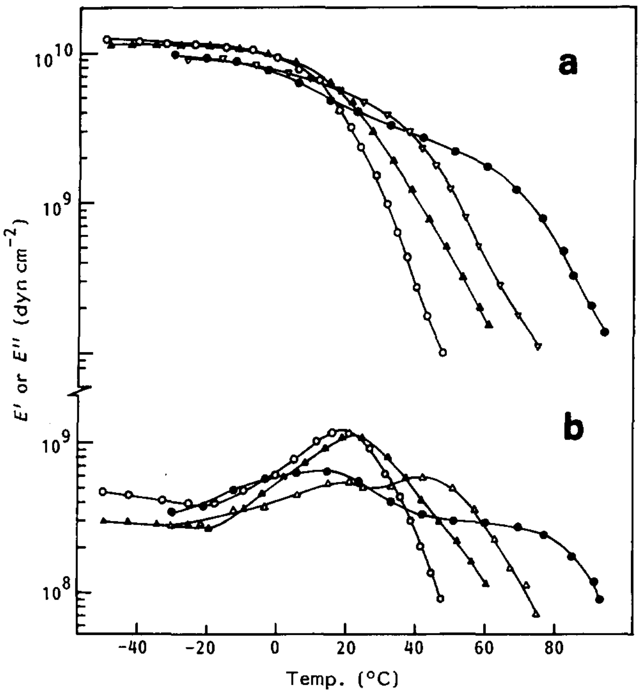

Figure 3 Thermomechanical spectra PVC/ENR50/CPE48 blends: (●) 47.5/5/47.5; (△) 40/20/40; (▲) 35/30/35; (○) 30/40/30

Mechanical properties of ternary PVC/ENR50/CPE48 blends

Compositions 47.5/5/47.5, 40/20/40, 35/30/35, 30/40/30. These blends contain PVC/CPE48 in the ratio 1:1. The dynamic mechanical analysis (d.m.a.) spectra, see *Figure 3b* (loss modulus E'' data), indicate separate relaxations of the main components at low ENR50 contents. At increased levels of the compatibilizer these approach each other and coalesce. Dynamic moduli E' data essentially support this transition in behaviour from a two-phase 47.5/5/47.5 to a homogeneous ternary at ENR50 levels higher than 20%; see *Figure 3a*. Stress-strain properties in *Figure 4* show no plastic yield and increased elongation and toughness as the level of ENR50 rises. Significantly, only 5% of the compatibilizer suffices to increase elongation at break ε_b to over 100%; see also *Figure 5* where ultimate properties are recorded. It is noteworthy that ultimate strength also goes up as the amount of ENR50 increases.

Compositions 23.7/5/71.3, 22.5/10/67.5, 20/20/60, 15/40/44. In these the PVC/CPE48 ratio is 1:3. The d.m.a. spectra in *Figure 6b* show that the PVC relaxation has almost vanished already at ENR50 levels of ~10%. The E' data, see *Figure 6a*, show reinforcement at the 22.5/10/67.5 composition (see below). Stress-strain properties are shown in *Figure 7*. The behaviour in *Figure 6* is more evident in the tensile properties data given in *Figure 8* where it is seen that, while ε_b is increasing with ENR50, ultimate strength σ_b passes through a maximum. This is of practical consequence since it optimizes the cost/performance parameter of this ternary in terms of tensile properties; compare *Figures 5, 8* and *10*. This synergism has been attributed very often to increased packing of chains due to strong molecular interactions or segment associations[29].

Compositions 71.3/5/23.7, 67.5/10/22.5, 60/20/20, 45/40/15. In these blends the PVC/CPE48 ratio is 3:1. In *Figure 9* the d.m.a. spectra again indicate the transition from a heterophase to a homogeneous blend. It is noteworthy that at low levels of compatibilizer, where blend components form separately a binary with ENR50, the main relaxations may maintain their position (or both move to lower temperatures); compare CPE48 relaxation

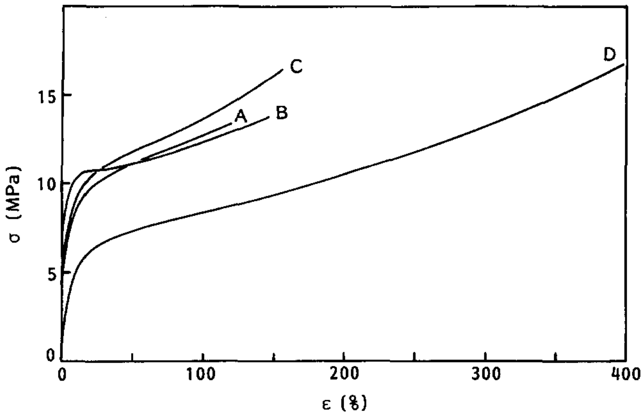

Figure 4 Stress-strain properties of PVC/ENR50/CPE48 blends: (A) 47.5/5/47.5; (B) 40/20/40; (C) 35/30/35; (D) 30/40/30

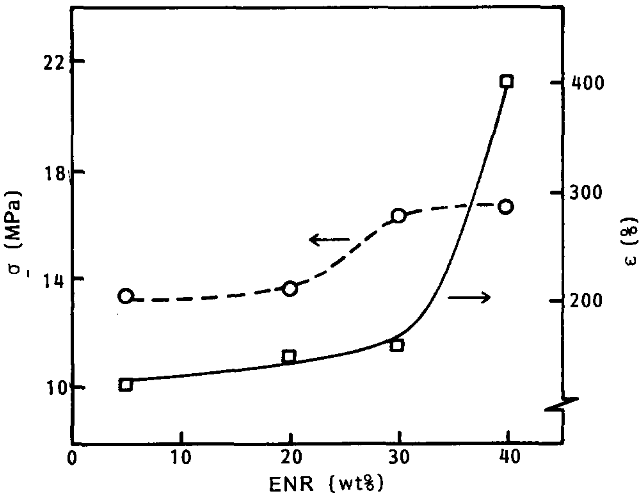

Figure 5 Ultimate properties of ternary blends with PVC/CPE48 1:1

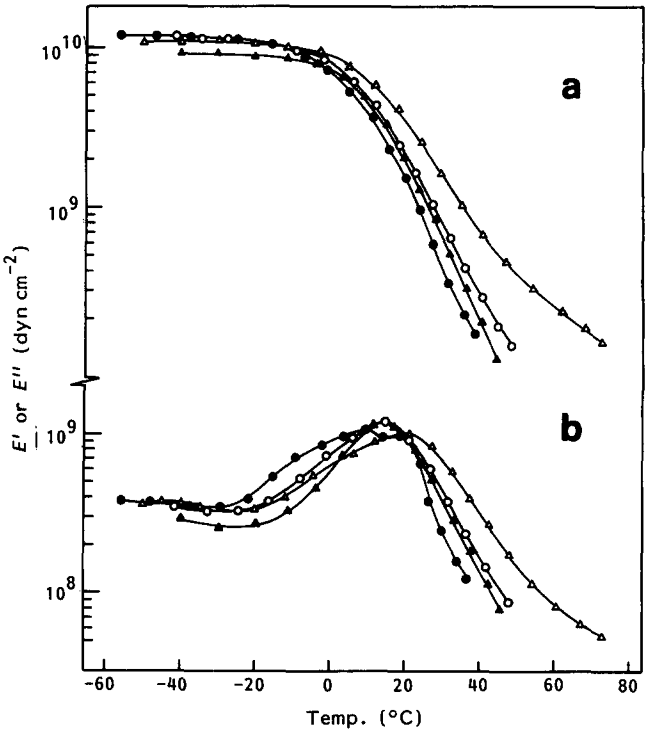

Figure 6 Thermomechanical spectra of PVC/ENR50/CPE48 blends: (●) 23.7/5/71.3; (△) 22.5/10/67.5; (○) 20/20/60; (▲) 15/40/45

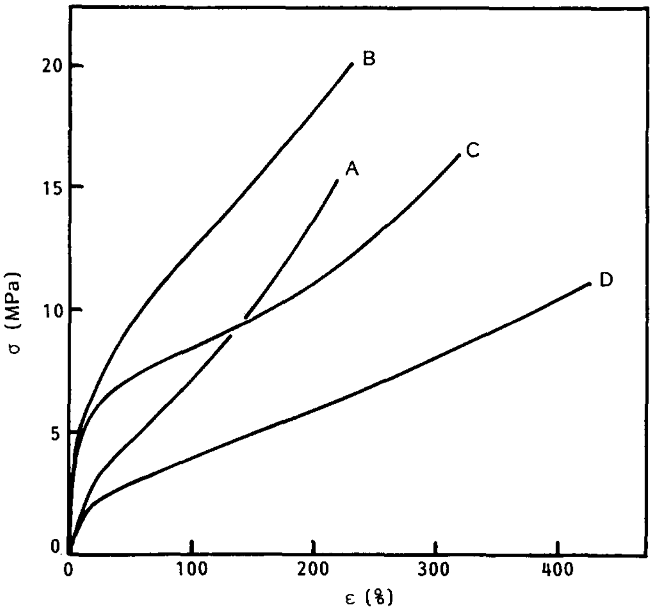

Figure 7 Stress–strain properties of PVC/ENR50/CPE48 blends: (A) 23.7/5/71.3; (B) 22.5/10/67.5; (C) 20/20/60; (D) 15/40/45

at 71.5/5/23.7 and 60/20/20 compositions in *Figure 9a*. Stress–strain properties in *Figure 10* are characteristic of a plastic material even at increased amounts of compatibilizer.

DISCUSSION

In assessing the miscibility of ternary blends one should be aware of the eventuality that, depending on composition and the T_g of the blend constituents, the possibility exists that the T_{gb}–composition curves of the binaries may cross each other. Thus the single T_{gb} of the ternary may not be the result of true miscibility but of an overlap of the T_{gb} of the two binaries[12]. This is not the case in the present system since the two thermoplastics, PVC and CPE48, have widely differing T_g (approximately at 80 and 20°C, respectively) and their binaries with ENR50 (with T_g at approximately −20°C[19]) give T_{gb}–composition curves that are not expected to cross[17,18]. An additional safeguard would be the study of tensile properties. A miscible ternary would have superior properties than a mixture of two incompatible binaries. Also, the examination of the ternary T_{gb} as a function of the compatibilizer at various ratios of PVC/CPE48 is different depending on this ratio; see *Figure 11*. We note that depending on

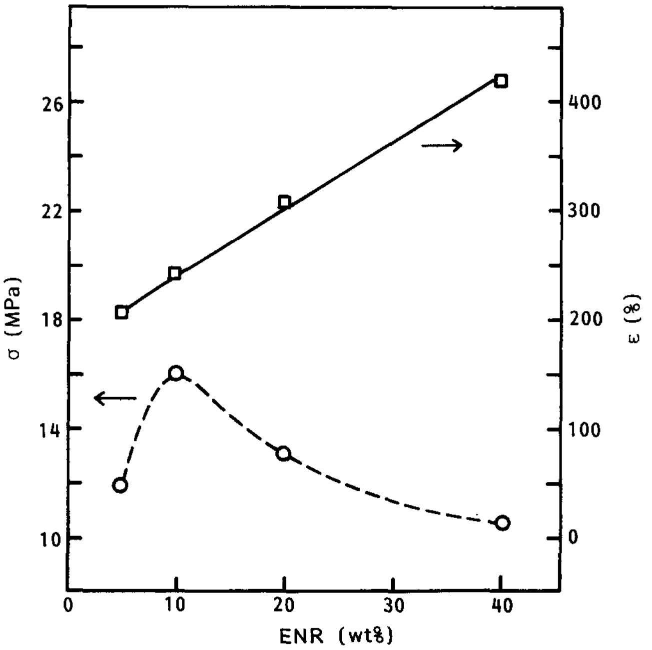

Figure 8 Ultimate properties of ternary blends with PVC/CPE48 1:3

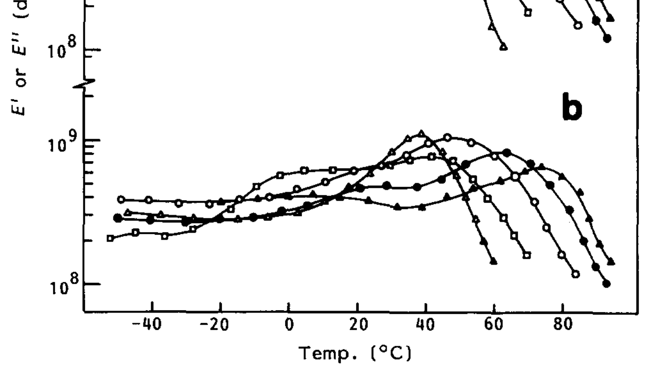

Figure 9 Thermomechanical spectra of PVC/ENR50/CPE48 blends: (▲) 71.3/5/23.7; (●) 67.5/10/22.5; (○) 60/20/20; (□) 56.25/25/18.75; (△) 45/40/15

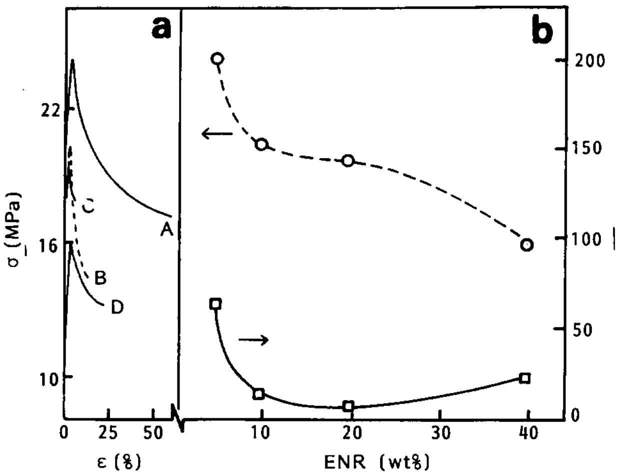

Figure 10 (a) Stress–strain properties of PVC/ENR50/CPE48 blends: (A) 71.3/5/23.7; (B) 67.5/10/22.5; (C) 60/20/20; (D) 45/40/15. (b) Ultimate properties of ternary blends with PVC/CPE48 3:1

this ratio different amounts of ENR50 are required to attain miscibility. This dissimilarity in the way the T_g are merging is also an indication that the single T_{gb} is not due to overlap[12].

Assuming additivity of free volume Kwei[6] suggested that for ternary amorphous miscible blends the following equation holds:

$$T_{gb} = \sum_i \phi_i T_{gi} \qquad (1)$$

where T_{gi} is the T_g of component i at volume fraction ϕ_i. In *Figure 12* a test of calculated and experimental T_{gb} values gave fair results. Deviations may be attributed to synergistic phenomena observed at certain compositions (see above) which lead to closer packing of chains. This could in principle violate the additivity of free volume[30], a necessary assumption for equation (1) to hold.

To rationalize this miscibility study an attempt was made to correlate the data with the thermodynamics of phase equilibria. In a recent paper Su and Fried[31] extended the Flory–Huggins lattice theory along the lines of Patterson's work[32] and phase diagrams of ternary blends were explored by simulating spinodals for various values of segmental interaction parameters. As noted by Patterson[32] spinodals are easier to calculate than binodals and for practical purposes they may serve equally well. Use was made of the equation for the spinodal of a ternary blend given by[31]:

$$\begin{aligned} m_1\phi_1 + m_2\phi_2 + m_3\phi_3 - 2[m_1m_2(\chi_1+\chi_2)\phi_1\phi_2 \\ + m_2m_3(\chi_2+\chi_3)\phi_2\phi_3 + m_3m_1(\chi_3+\chi_1)\phi_3\phi_1] \\ + 4m_1m_2m_3(\chi_1\chi_2+\chi_2\chi_3+\chi_3\chi_1)\phi_1\phi_2\phi_3 = 0 \qquad (2) \end{aligned}$$

with

$$\chi_i = (\chi_{ij} + \chi_{ik} - \chi_{jk})/2 \qquad (3)$$

Here m_i is the number of segments of homopolymer i and χ_{ij} the segmental interaction parameter between segments i and j. (In the literature it is referred to as the Scott–Tompa interaction parameter[32] and is related to the Flory χ_{ij} by $\chi_{ij} = \chi_{ij}(\text{Flory})/m_i$.) The interaction parameters between segments of ENR50/PVC and ENR50/CPE48 were calculated using the data of Pouchly and Biros[33] on the enthalpy of mixing of THF with PVC and low-molecular-weight chlorinated compounds. It was

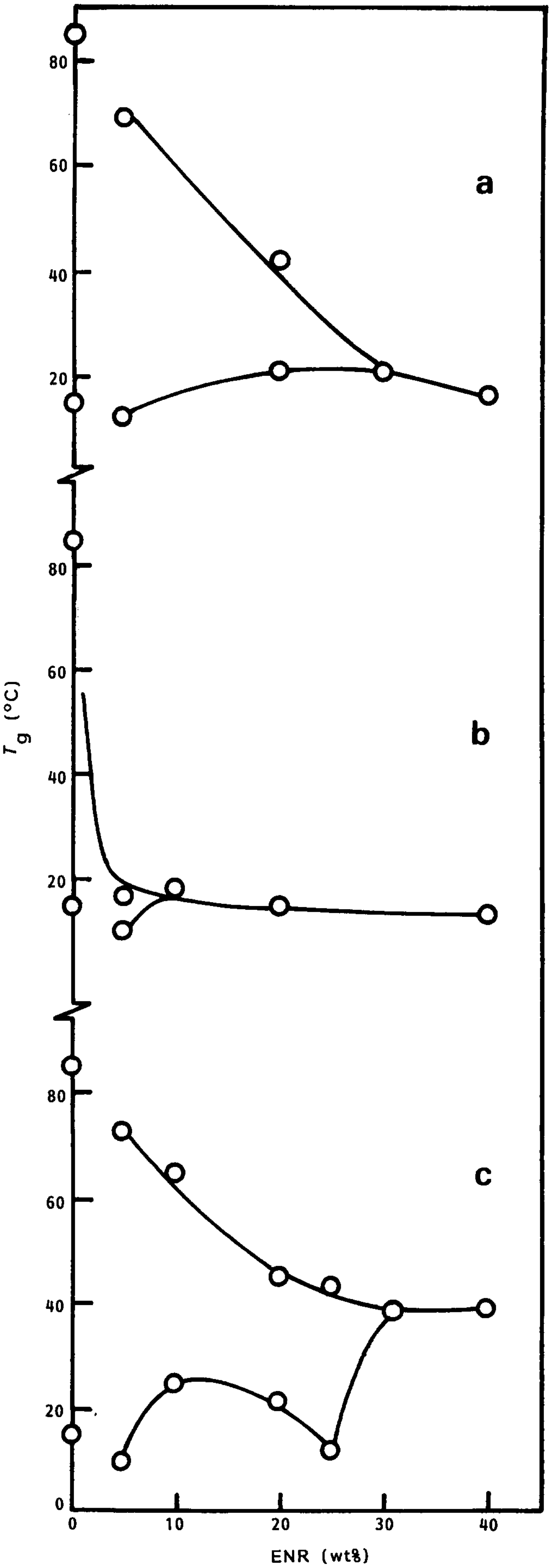

Figure 11 Composition dependence of T_g of ternary blends at various ratios of PVC/CPE48: (a) PVC/CPE48 1:1; (b) PVC/CPE48 1:3; (c) PVC/CPE48 3:1

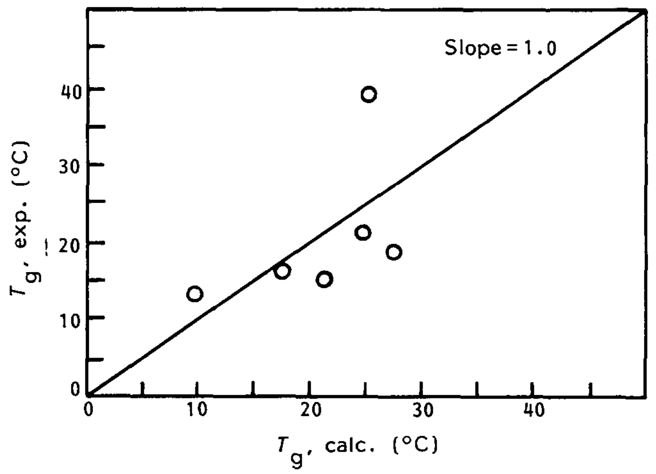

Figure 12 Comparison of glass transition temperatures of miscible ternary blends experimentally determined and calculated according to equation (1)

Table 1 Molecular parameters used in the calculation of the spinodal at 25°C

Component	V_r^a ($cm^3 mol^{-1}$)	d ($g cm^{-3}$)	m_i	χ_{ij} (Scott–Tompa)
PVC (1)	45.1	1.385	628	-0.0022^b (1–2)
ENR50 (2)	77.3	1.060	1354	-0.0008^b (2–3)
CPE48 (3)	41.3	1.250	1162	0.0034^c (1–3)

[a] Calculated from data in ref. 36
[b] Calculated from ref. 33; see text
[c] Using the spinodal curve; see text

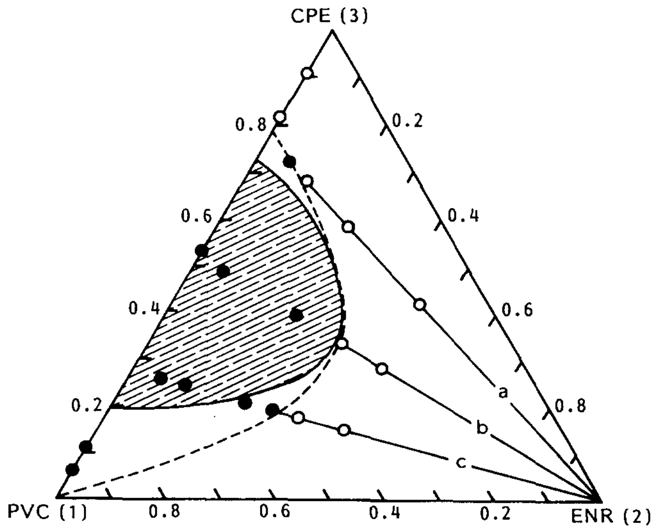

Figure 13 Phase diagram of ternary blends. Spinodal curve defines region of instability (shaded area). (○) Miscible compositions. (●) Immiscible or partially miscible compositions experimentally determined. Points lying on straight lines a, b, c correspond to ternaries with PVC/CPE48 ratio 1:3, 1:1, 3:1, respectively. (Coordinates in volume fraction)

assumed that segmental interactions primarily determine the enthalpy of mixing[34] and that χ_{ij} are composition-independent. A similar procedure using model compounds was followed with good overall results by Paul, Barlow and coworkers[35]. This calculation gave for the Scott–Tompa segmental interaction parameter $\chi_{12} = -0.0022$ and $\chi_{23} = -0.0008$. The reference volume[5] V_r used in the calculations was that of the basic unit of CPE48 (with the formula $-(CH_2)_{1.8}-(CHCl)_1-$ obtained from the overall chlorine content), since it was the smallest among the ternary components. Other pertinent data to be used in equations (2) and (3) are given in *Table 1*.

The χ_{13} used was determined by adjusting its value so that the spinodal enclosing the unstable region approximated the immiscibility gap determined by experiment; see *Figure 13*. We understand that this is an approximation since the binodal may diverge from the spinodal as one approaches the side of the triangle representing the CPE48/PVC binary. However, the experimental evidence we obtained on CPE48/PVC blends at the extremes of compositions confirms that this approximation represents data well. This value of χ_{13} is close to that reported by Doubé and Walsh[25], 0.0010 to −0.005, depending on blend composition. Closer agreement is not expected however, since CPE had a different structure. It had a 42wt% Cl content, 1% S as SO_2Cl groups and was prepared by solution chlorination. In our system CPE48 was prepared by suspension polymerization. This would lead to a less random distribution of Cl atoms along the chain. Also, their method was based on measurements using inverse phase chromatography. Our method is an indirect one based on ternary phase diagrams. It is relevant to note, however, that the spinodal is strongly dependent on the value of χ_{13}. The effect of the other two segmental interaction parameters is much smaller. This was pointed out by Su and Fried[31] for the case of a partially miscible blend (see figure 3 of ref. 31), compatibilized by a third component.

CONCLUSIONS

Epoxidized natural rubber may be used as an effective compatibilizer for binaries consisting of chlorinated polyhydrocarbons with chlorine content higher than ~48 wt%.

Ternaries obtained have useful mechanical properties already at low amounts of the compatibilizer.

Construction of spinodals may prove a useful procedure to correlate and predict miscibility data in blends and in certain cases extract values for interaction parameters valid in a ternary system.

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