Effect of block copolymer architecture on compatibility: 1. Epoxidized styrene–butadiene copolymers with chlorinated polymers

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The compatibility behaviour of epoxidized styrene–butadiene (SB) block copolymers of varying architecture with chlorinated polyethylene at two degrees of chlorination (36 and 48 wt%) and with poly(vinyl chloride) was investigated over the complete composition range. The copolymers were two diblock (SB) copolymers differing in their degree of purity and a multiarm block copolymer $(SB)_n$. For comparison, data obtained previously with an epoxidized (E) triblock (ESBS) were also used. Other parameters examined were the degree of epoxidation to attain miscibility and the degree of chlorination. The techniques used were dynamic mechanical analysis, differential scanning calorimetry and tensile testing. It was demonstrated that epoxidized SB (ESB) is more miscible with chlorinated polymers than ESBS or $E(SB)_n$ with the same degree of epoxidation. Also $E(SB)_n$ is better in this respect than ESBS. The level of impurities (homopolymers and SBS) accompanying commercial samples of SB did not impair the tensile properties of these blends. The degree of chlorination was found to determine the required degree of epoxidation to obtain a miscible system.

(Keywords: structure and miscibility; epoxidized diblock copolymers; epoxidized multiarm block copolymers; chlorinated polyethylene blends; poly(vinyl chloride) blends)

INTRODUCTION

The use of block copolymers in polymer blending technology is diverse and of increasing importance. These speciality polymers can modify homopolymer mechanical properties[1,2] (e.g. increase toughness) and compatibilize homopolymer blends by affecting the size and stability of the dispersed phase[3–6] by enhancing interface adhesion. In the past a considerable amount of theoretical[7–9] and experimental[10–12] work has been directed to the elucidation of the phase behaviour and properties of block copolymer–homopolymer blends as a function of blend composition. To maximize their efficient use considerable research has also concentrated on the effect of the block chemical structure as a primary factor determining mutual miscibility or emulsification in binary or ternary blends. In this endeavour the desirable end effect is attained by the athermal dissolution of the homopolymer in the chemically identical block[12–14] or by specific interaction with a 'complementary dissimilar' block[4,15,16].

To date, however, little has been published on the effect of block copolymer architecture on blend miscibility or compatibilization. Past work related to this area includes that of Riess *et al.*[17] who concluded that diblock copolymers are more effective than triblock copolymers in dispersing two homopolymers. Also of relevance are the findings of Teyssié and co-workers[14] which indicate that a tapered diblock is more efficient than a pure diblock in compatibilizing low density polyethylene (LDPE)/polystyrene (PS) blends. This topic is also addressed by the experimental work of Jiang *et al.*[18] who indicated that the miscibility of polyisoprene (PI) in the PI–PS block copolymer decreases in the order diblock > triblock > four-arm star. These findings were rationalized by consideration of the entropy loss due to restriction of junction points at the interface. More recent work by Faust *et al.*[19] compared the miscibility of linear and star block PS copolymer with poly(vinyl methyl ether) (PVME). Miscibility *per se* is not affected. It was determined however that a fraction (0.27) of the internal core styrene units were sterically hindered from interacting with PVME molecules.

In this paper we examine the miscibility of poly(vinyl chloride) (PVC) and chlorinated polyethylene (CPE) with an epoxidized (E) linear styrene–butadiene (SB) diblock copolymer (ESB). Molecular parameters examined include chlorine content (degree of polarity) and degree of epoxidation (*DE*). Some results obtained with an SB commercial product of lesser purity are also reported to demonstrate the degree of differentiation. The results are compared with those of an ESBS/PVC blend reported previously[20]. Some preliminary findings and comparisons are also made with blends obtained with these chlorinated polymers and an epoxidized multiarm (or branched) $E(SB)_n$ block copolymer. In this system the effect of block copolymer architecture on miscibility was expected to be most pronounced, since the EB units interacting with the chlorine-containing partner would be shielded by the inert styrene blocks. This work is part of a more extensive investigation[21] aimed at determining the effect of block copolymer architecture and of other chemical structural parameters involved in compatibilization studies[16] of ternary blends.

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Table 1 Molecular characteristics of the polymers used

Sample	Acronym	Source	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
Poly(vinyl chloride)	PVC	EKO Chemicals Co.	36000	2.07
Chlorinated PE (48 wt% Cl)	CPE(48)	Aldrich Europe	61000	2.50
Chlorinated PE (36 wt% Cl)	CPE(36)	Aldrich Europe	–	–
SB diblock[a]	SB(P)	Phillips	189000	1.92
SB diblock[b]	SB(S)	Shell	79000	1.24
$(SB)_n$ multiarm[c] (branched)	SB(Br)	Shell	189000	1.98
SBS triblock[d]	SBS	Aldrich	53000	–

All block copolymers contained 30 wt% styrene

[a] Experimental product with ~95% purity

[b] Commercial product with a reported purity of ~80%

[c] Commercial product

[d] Taken from reference 20 for comparison. In copolymer products gel permeation chromatography analysis in tetrahydrofuran indicated a small percentage of homopolymers due to premature termination and a higher molecular weight product due to the coupling reactions of the diblock 'living anion'

EXPERIMENTAL

The materials used are listed in *Table 1*. Epoxidation was carried out with the *in situ* formation of performic acid in toluene solution (5 wt% solids) using an excess (110%) of the epoxidizing agent: an equimolar mixture of formic acid and hydrogen peroxide (H_2O_2). After the addition of H_2O_2 at 0°C, the temperature was allowed to rise and was maintained at 20°C for the duration of the epoxidation reaction. Other details of the procedure have been described previously[20,22]. *Figure 1* gives the degree of block copolymer conversion with time at 20°C. No significant differentiation is evident though the molecular structure of the copolymers differs. The results can be rationalized[23] considering the extended coil conformation of the starting copolymers in the dilute solution in a good solvent and the small size of the performic acid reactant. These findings are also an indication that the number of polybutadiene (PB) arms at the core of the branched copolymer is small.

Epoxidized polymers were characterized using ^1H nuclear magnetic resonance (n.m.r.), ^{13}C n.m.r., Fourier transform infra-red (*FT*i.r.) and volumetric analysis. The absence of ^1H n.m.r. absorptions at 3.2–3.3 and 3.8 ppm indicated the absence of diol and furan rings, respectively. Similarly no infra-red (i.r.) absorptions were detected for the above groups at 3430 and 1067 cm^{-1}. In this work more weight was given to n.m.r. analysis since at higher degrees of conversion neighbouring oxirane groups may affect chemical analysis results through side reactions, leading to higher member rings.

To identify samples, the degree of epoxidation calculated for the total polymeric material is given in parentheses following the epoxidized polymer (*Table 1*). Thus, ESB(P)(29)/10PVC refers to a 10 wt% PVC blend with a 29 mol% ESB block copolymer from Phillips.

Blends were prepared by dissolving in a common solvent (butanone-2 for PVC and chloroform for CPE), removing solvent and drying to constant weight at 50°C in a vacuum oven. Dibutyl tin dilaureate (2 wt%) was added as a thermal stabilizer. Films were prepared by compression moulding between Teflon sheets (150–170°C depending on composition, 15 MPa for 30 s) and quenching at 0°C. No difference in dynamic mechanical analysis (d.m.a.) spectra was detected between films prepared using this procedure and films prepared by solvent casting when the latter were adequately dried. The d.s.c. measurements on pure epoxidized copolymers were carried out in a nitrogen atmosphere using a Du Pont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was made with indium standard and the sample weight was 20 mg. This technique was not used for blends since it could not detect broadened peaks or their small shifts.

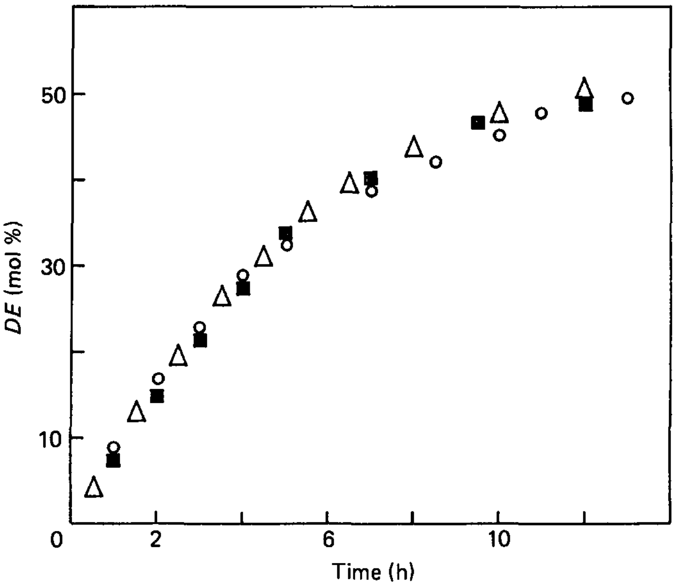

Figure 1 Degree of epoxidation *versus* time at 20°C of: (○) SB(P); (■) SB(S); (△) SB(Br). Analysis performed using n.m.r.

The d.m.a. 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). The specimen dimensions were 3.0 × 0.25 × 0.03 cm^3.

Tensile tests were performed according to ASTM D 882 at 23°C using a J.J. Tensile Tester type T5001 and film strips with dimensions 6.0 × 1.20 × 0.05 cm^3. Data reported were obtained at a crosshead speed of 50 cm min^{-1}.

*FT*i.r. spectra were obtained using a Nicolet 60 SX spectrometer and ^{13}C n.m.r. measurements were carried out using a Bruker AC300 spectrometer.

RESULTS

Introduction of the oxirane unit causes chain stiffening leading to a glass transition temperature (T_g) increase. Given the linear relationship[20,24] between T_g and the degree of epoxidation a calibration curve may be constructed to determine the latter quantity. Relevant data are given in *Figure 2* for the copolymers studied. The similar slopes for the straight lines are an indication of the similarity of the PB block main chain microstructure. As in previous work[20] due to the small PS content in these thermoplastic elastomers, only the low temperature PB main relaxation could be detected at the frequency used. As a practical miscibility criterion the composition dependence of the main relaxation of the blend components was examined[25].

Dynamic mechanical properties

Though d.m.a. spectra are available[21] for all copolymer blends only those pertaining to ESB(P) are given here. At low degrees of epoxidation (16 mol%), see E'' spectrum in *Figures 3–5*, all pairs are immiscible. However, a small shift associated with the EPB segment is discernible in the region of high contents of the epoxidized component. Increasing the degree of epoxidation to 29 mol% leads to miscible ESB(P)/CPE blends (*Figures 6* and *7*), however, ESB(P)/PVC is partially miscible (*Figure 8*) even at this higher degree of epoxidation (33 mol%). These observations lead us to conclude that: increased amounts of the epoxidized component cause miscibility limited to this composition range; and increased levels of chlorination require increased levels of epoxidation to obtain miscible blends.

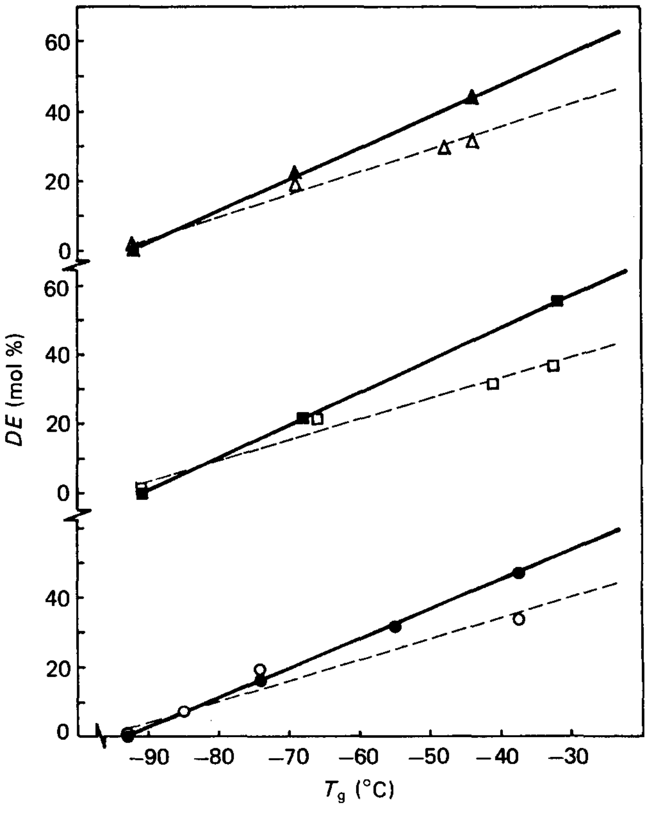

Figure 2 Effect of epoxidation on T_g of: (○, ●) SB(P); (□, ■) SB(Br); (Δ, ▲) SB(S). Closed symbols, n.m.r.; open symbols, chemical analysis. The T_g was determined by d.s.c.

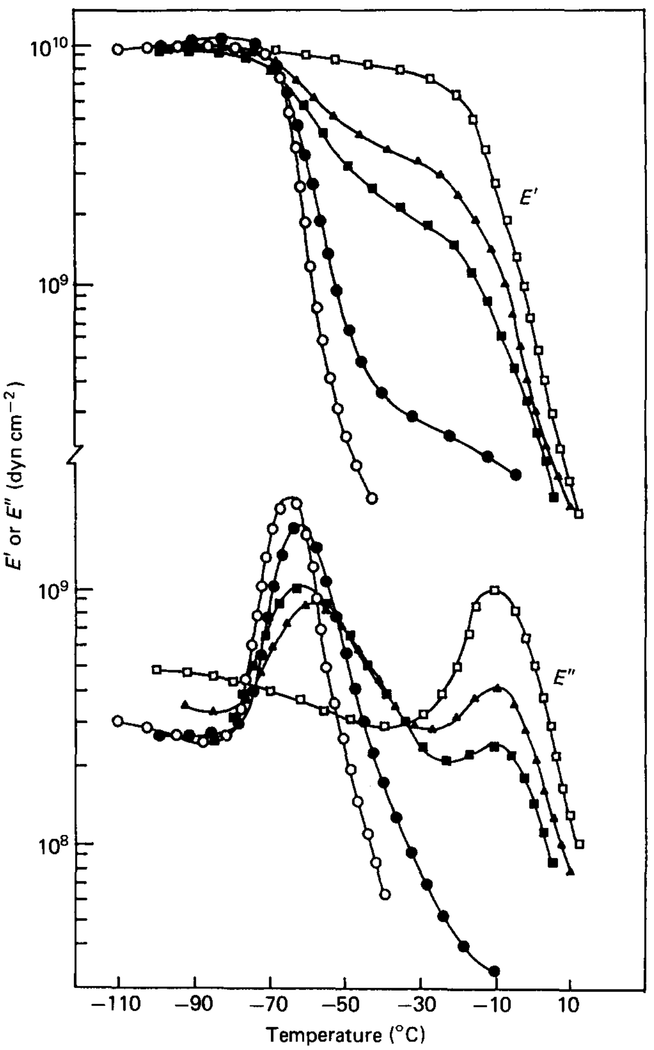

Figure 3 Thermomechanical spectra of ESB(P) (16)/CPE(36) blends: (○) 100/0; (●) 75/25; (■) 50/50; (▲) 25/75; (□) 0/100

Comparison of *Figure 8* with the results on epoxidized triblock ESBS(34)/PVC blends (ref. 20, Figure 3) indicates that the diblock ESB(P) (33) at a comparable degree of epoxidation is more soluble with PVC.

Analysis of the d.m.a. data obtained with the ESBS(Br) at various degrees of epoxidation and the three chlorinated polymers allows us to define their miscibility behaviour (*Table 2*). Specifically it is to be concluded that: with a higher degree of chlorination a higher *DE* is required to bring it into solution; and the branched block copolymer is less effective than the diblock in solubilizing a given chlorinated polymer. Thus in *Table 2* it is seen that some ESB(Br)(34) compositions (increased levels of CPE and PVC) are not miscible while the linear diblock ESB(P) could solubilize CPE(36) and CPE(48) at lower degrees of epoxidation (29 mol%) (*Figures 6* and *7*). The effect can be attributed to the shielding provided by the inert PS shell surrounding the epoxidized inner core of ESB(Br). Comparison of ESBS(34)/PVC (ref. 20, Figure 3) with the d.m.a. spectra of ESB(Br) (34)/PVC (*Figure 9*) shows that, contrary to expectation, the modified branched copolymer is more soluble in PVC than ESBS. Additional work is in progress[21] to explain this behaviour using a star block copolymer with a well defined architecture.

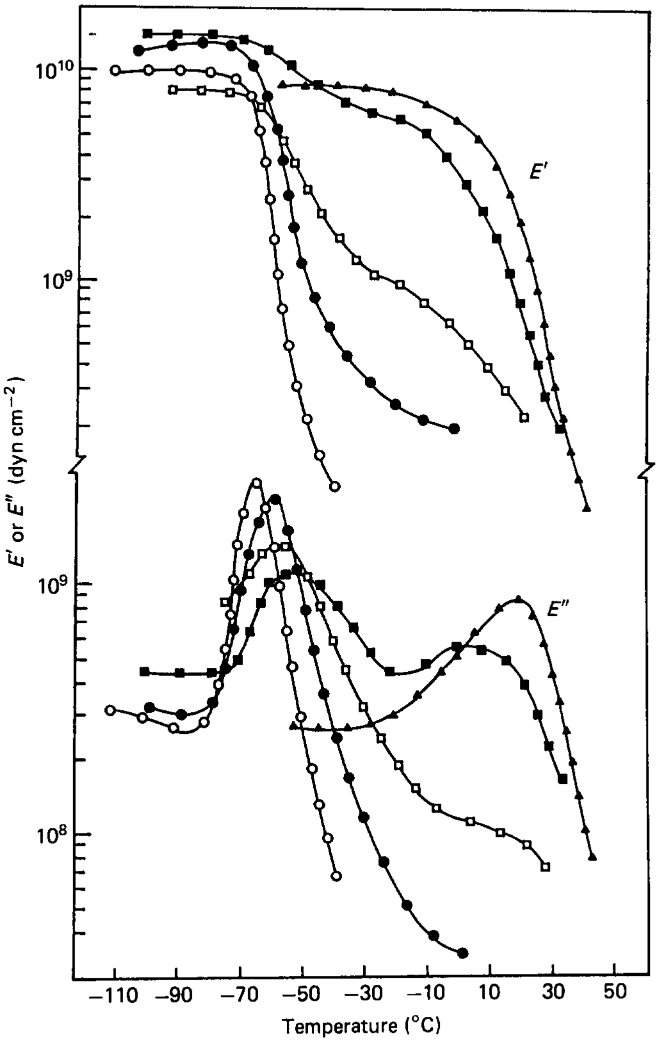

Figure 4 Thermomechanical spectra of ESB(P) (16)/CPE(48) blends: (○) 100/0; (●) 75/25; (□) 50/50; (■) 25/75; (▲) 0/100

The results on miscible blends were analysed using various blend T_g–composition relationships proposed for such systems. Best fit was obtained with the Gordon–Taylor relationship[26]:

$$T_{gb} = T_{g1} + k\frac{W_2}{W_1}(T_{g2} - T_{g1}) \qquad (1)$$

where indices b, 1 and 2 refer to the blend, the rubbery and the chlorinated components, respectively, W_i is the weight fraction of component i and k is a fitting constant.

Tensile properties

Figure 10 gives the stress–strain properties of ESB(P) (33)/PVC blends. Due to the high extensibility of most compositions, engineering stress was converted to true stress assuming affine deformation. Inspection of the data confirms the reinforcement of the unmodified diblock by the polar and bulky oxirane units. Introduction of a miscible chlorinated component further stiffens the material increasing ultimate stress. *Figures 11* and *12* correlate ultimate properties with the *DE* at three compositions for the ESB(P)/PVC and ESB(P)/CPE 48, respectively. It is seen that ultimate properties pass through a maximum at a *DE* of ~35 mol%. This is the result of two competing factors. As the *DE* increases the rubbery component is being reinforced by the increase of chain polarity. At high *DE* steric factors predominate impeding free chain rotation thus reducing elongation. To these effects the stiffening of the chlorine-containing component is superimposed. A similar behaviour is shown by the ESB(P) (34)/CPE(36) blends thus allowing us to conclude that: the optimum balance of ultimate properties is obtained at the intermediate epoxidation levels (35 mol%); the improved elastomeric properties of the epoxidized diblock copolymers are conserved in the blends even at semicompatible compositions (*DE* 16–33 mol%); at constant *DE* (~35 mol%), optimum blend stress and strain values are obtained at ~50 wt% Cl. At higher degrees of chlorination (PVC) a good combination of ultimate properties is obtained with increased amounts of the modified rubber. Comparison of stress–strain properties with the results of ESBS(34)/PVC blends (ref. 20, Figure 8) indicates that the epoxidized triblock has somewhat better properties (supports higher loads), however, the elongation properties at low rubber contents are poor.

Finally in *Figure 13* a comparison is made of the stress–strain properties of PVC blends using the two

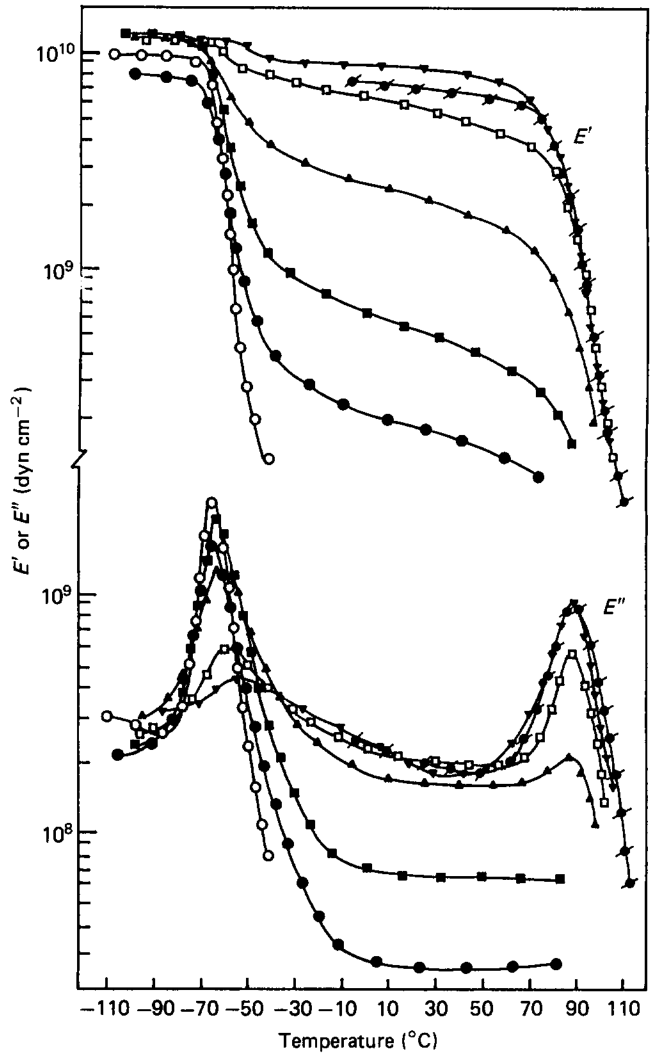

Figure 5 Thermomechanical spectra of ESB(P) (16)/PVC blends: (○) 100/0; (●) 87.5/12.5; (■) 75/25; (▲) 50/50; (□) 25/75; (▼) 12.5/87.5; (⊘) 0/100

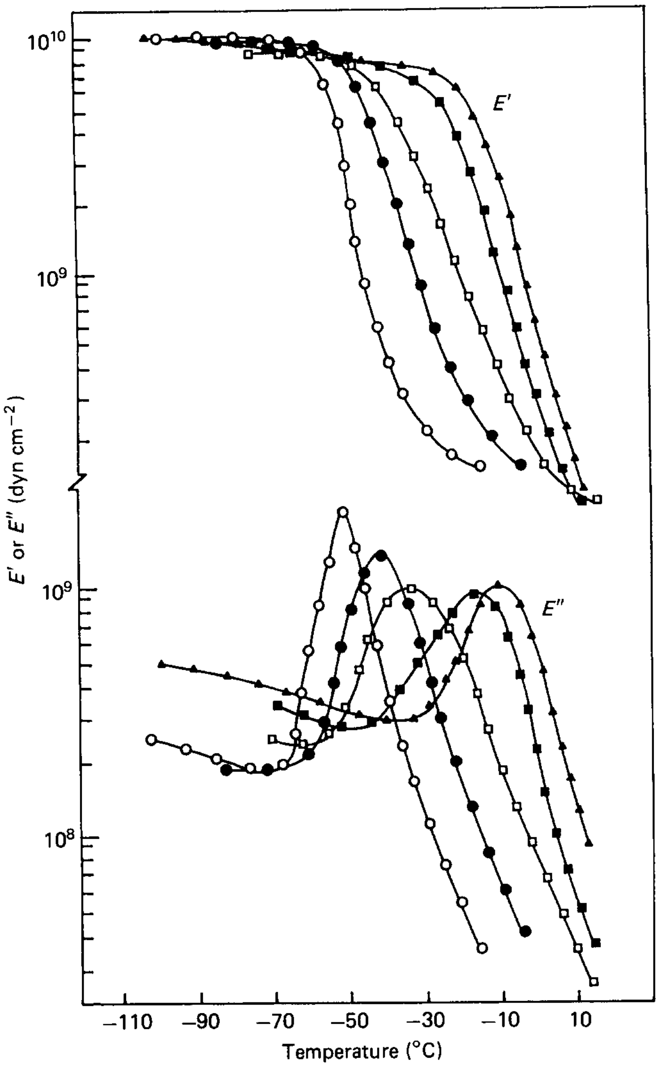

Figure 6 Thermomechanical spectra of ESB(P) (29)/CPE(36) blends: (○) 100/0; (●) 75/25; (□) 50/50; (■) 25/75; (▲) 0/100

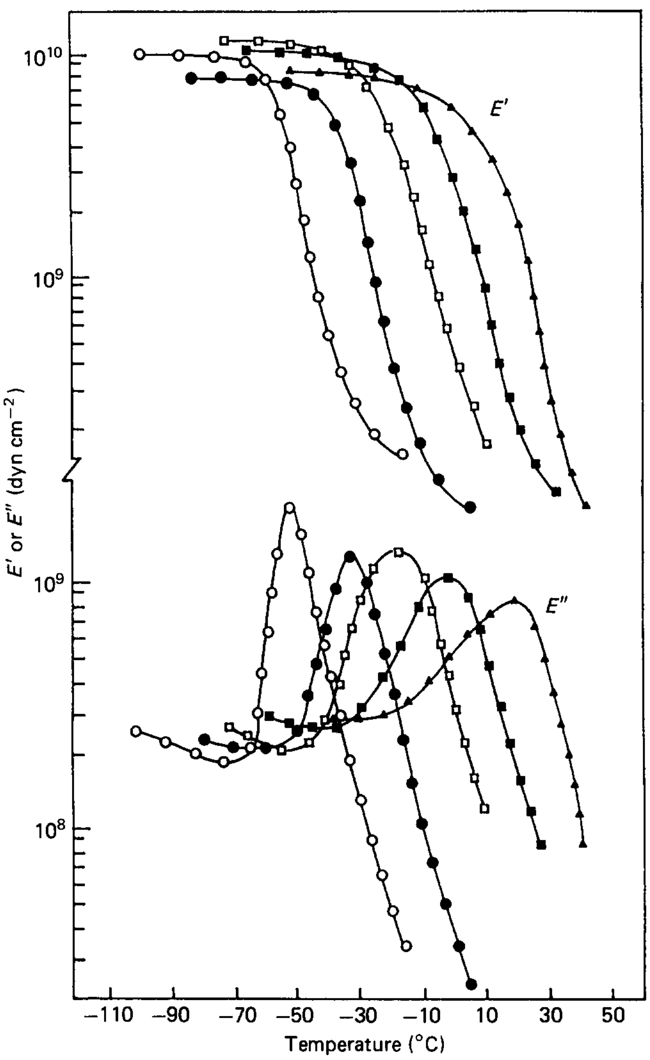

Figure 7 Thermomechanical spectra of ESB(P) (29)/CPE(48) blends: (○) 100/0; (●) 75/25; (□) 50/50; (■) 25/75; (▲) 0/100

Table 2 Compatibility chart of ESB(Br) blends

Degree of epoxidation (mol%)	CPE(36) (wt%)			CPE(48) (wt%)			PVC (wt%)		
	25	50	75	25	50	75	25	50	75
12	IM	IM	IM	IM	IM	IM	IM	IM	IM
21	–	PM	–	–	PM	–	PM	PM	PM
34	M	M	PM	M	M	PM	M	M	PM
47	–	–	–	–	–	–	M	M	M
50	–	–	–	M	M	M	M	M	M

M, miscible; PM, partially miscible; IM, immiscible

types of epoxidized diblock copolymers; ESB(P) (33) and ESB(S) (33). The latter has ~20 wt% impurities (PS and SBS). The results indicate, as above, higher load bearing capacity and extensibility of the latter product. Also, d.m.a. data (not reported) of the 50/50 blend with PVC at similar *DE* values are comparable to those in *Figure 8* for the ESB(P)(33)/PVC blends. One may thus conclude that the aforementioned impurities are not detrimental to the property and miscibility performance of ESB(S) blends. In fact, tensile properties are possibly improved because of the SBS presence as an 'impurity' accompanying the diblock copolymer.

DISCUSSION

The molecular origin leading to a partial shift of the low temperature relaxation in these blends (*Figures 3–5*) may be traced to a specific interaction between the oxirane ring (proton acceptor) and the chlorinated polymers.

This is supported by the exothermic interaction of low molecular weight analogues: tetrahydrofuran with chlorinated solvents[27]. Indeed a strong interaction involving the oxirane ring was detected using *FT*i.r. *Figure 14* shows the shift to lower wavenumbers of the absorption of the *trans*-oxirane ring[28] of ESB(Br) at

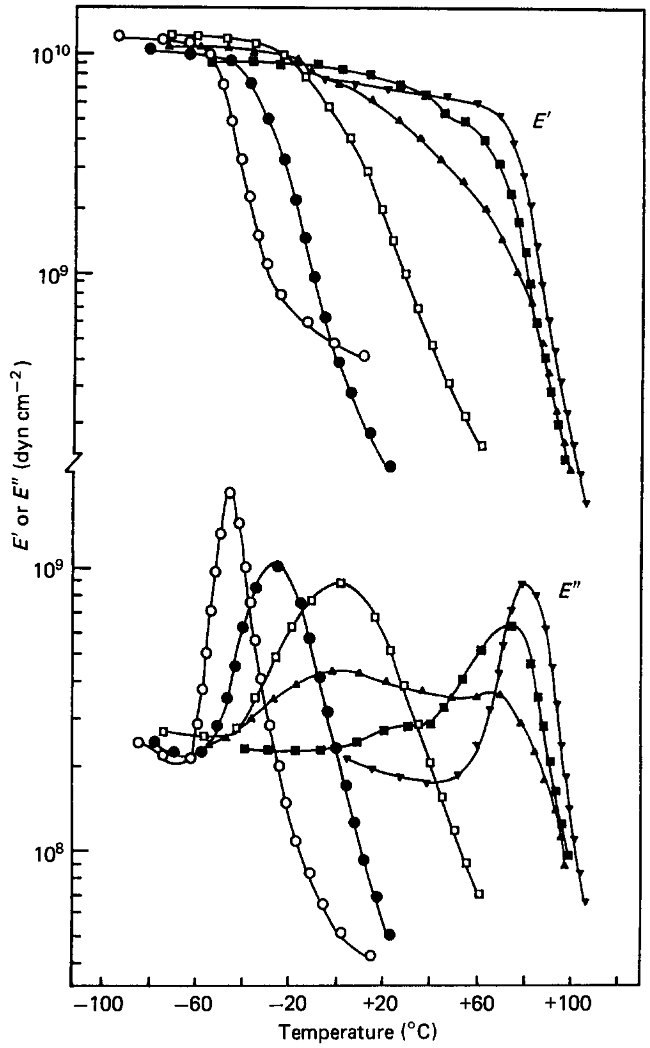

Figure 8 Thermomechanical spectra of ESB(P) (33)/PVC blends: (○) 100/0; (●) 75/25; (□) 50/50; (▲) 25/75; (■) 12.5/87.5; (▼) 0/100

~890 cm^{-1} with increasing amounts of PVC in their blends. This shift can be attributed to a weakening of the C–O stretching vibration due to a weak association with the chlorinated partner. In d.m.a. spectra, at low oxirane levels (16 mol%), a portion of the chlorinated component is solubilized, the result being a composite system consisting of a miscible blend corresponding to high proportions of ESB (its T_{gb} shifted upwards) and the rest of the chlorinated polymer maintaining its original T_g. This composition-dependent miscibility increases leading to a completely miscible blend when the oxirane content reaches a certain value characteristic for a given degree of chlorination.

Analysis of the data on partially miscible blends allows the determination of the minimum mole ratio (oxirane)/(CHCl) necessary for the onset of miscibility. Use was made of the T_{gb}–composition dependence assuming equation (1). The ratios determined are (oxirane)/(CHCl), 1.4 for CPE(36) and CPE(48) and 0.5 for PVC. These results indicate that the oxirane ring interacts more strongly with PVC and are in qualitative agreement with the findings on low molecular weight analogues[27] and the analysis of T_{gb} data using equation (1). *Figure 15* gives the T_{gb} variation of ESB(P) blends with PVC and CPE(48). The corresponding values of the empirical constant are 1.1 and 0.66. The curvature for the PVC blends is characteristic of specific interactions leading to chain association and modulus enhancement[29]. A further analysis was also made using the modified Gordon–Taylor equation along the lines suggested in the work of

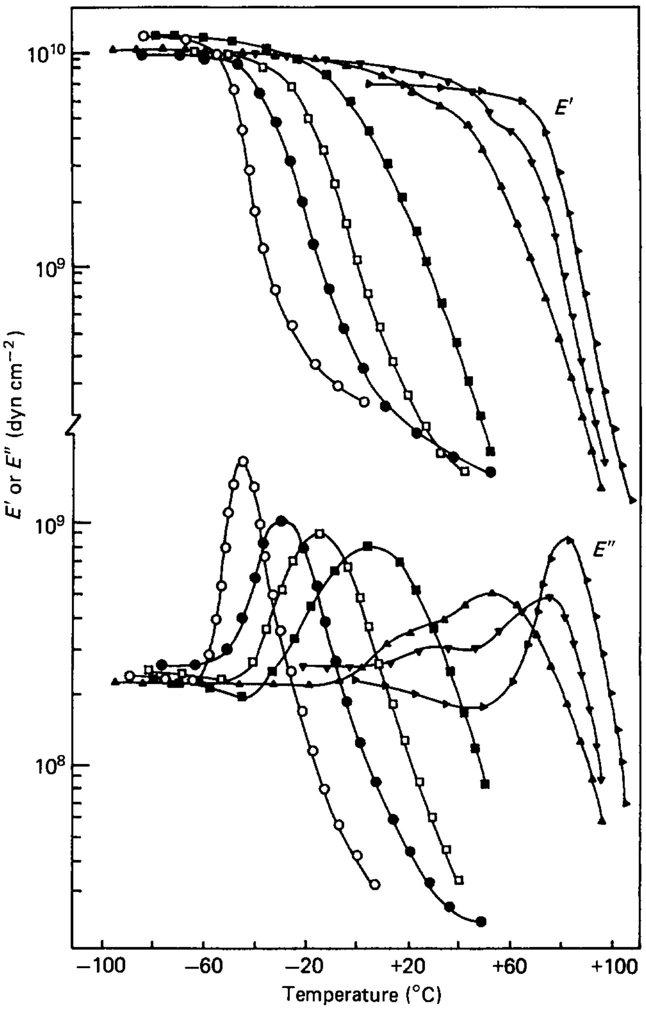

Figure 9 Thermomechanical spectra of ESB(Br) (34)/PVC blends: (○) 100/0; (●) 87.5/12.5; (□) 75/25; (■) 50/50; (▲) 25/75; (▼) 12.5/87.5; (▶) 0/100

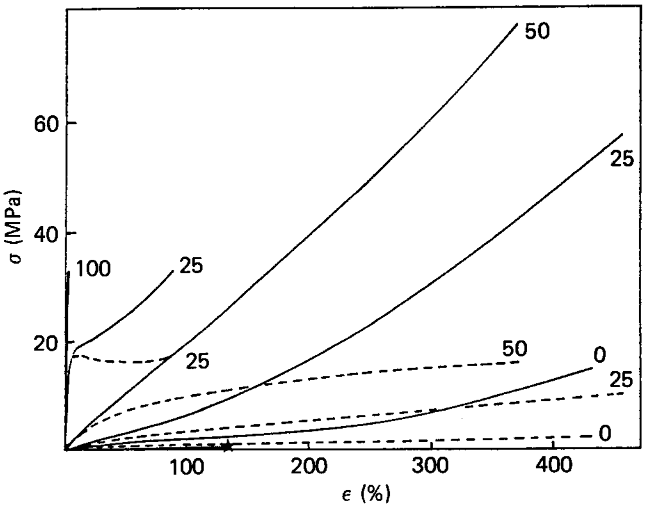

Figure 10 Stress–strain properties of ESB(P) (33)/PVC blends: (---) engineering stress; (———) true stress assuming affine deformation. Numbers next to curves indicate weight percentage of PVC. (-*-) Non epoxidized SB(P)

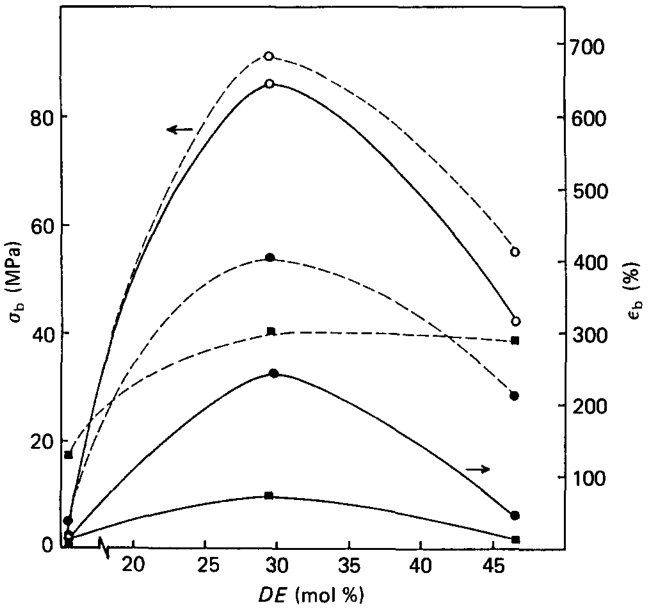

Figure 11 Ultimate tensile properties of ESB(P)/PVC blends: (○) 75/25; (●) 50/50; (■) 25/75

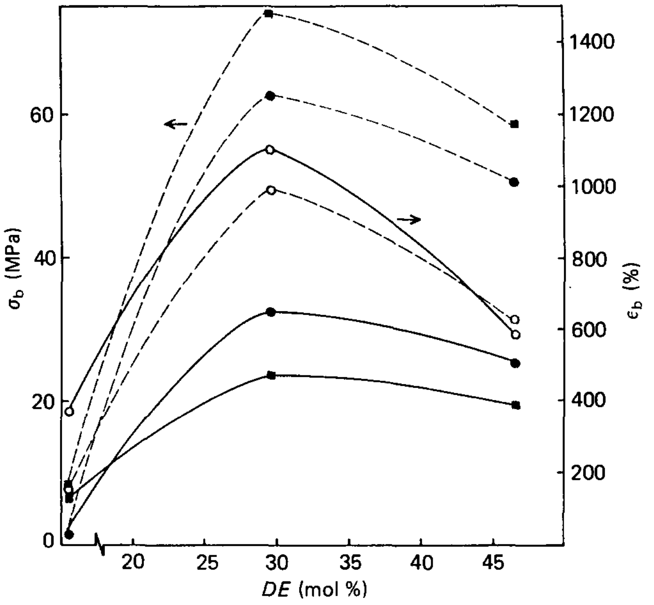

Figure 12 Ultimate tensile properties of ESB(P)/CPE(48) blends: (○) 75/25; (●) 50/50; (▲) 25/75)

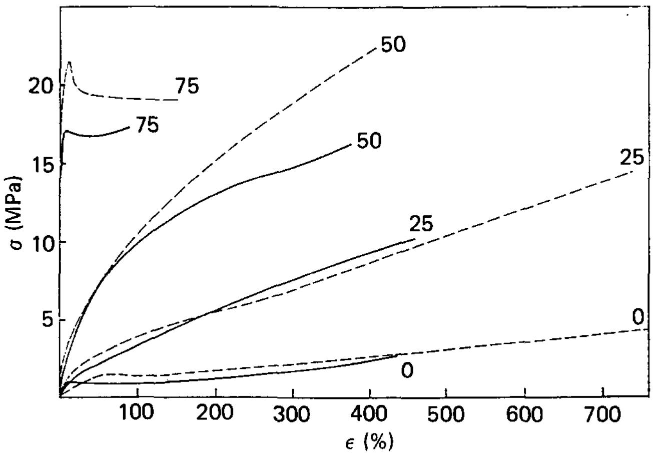

Figure 13 Comparison of stress–strain properties of ESB(P) (33)/PVC (——) and ESB(S) (33)/PVC (---). (Engineering stress values are given.) Numbers next to curves indicate weight percentage of PVC

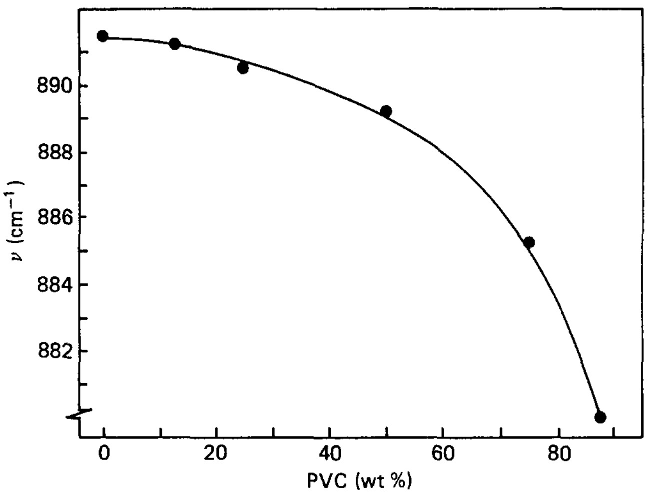

Figure 14 Composition dependence of *FT*i.r. absorption at 891.4 cm^{-1} of ESB(Br) (34)/PVC blends

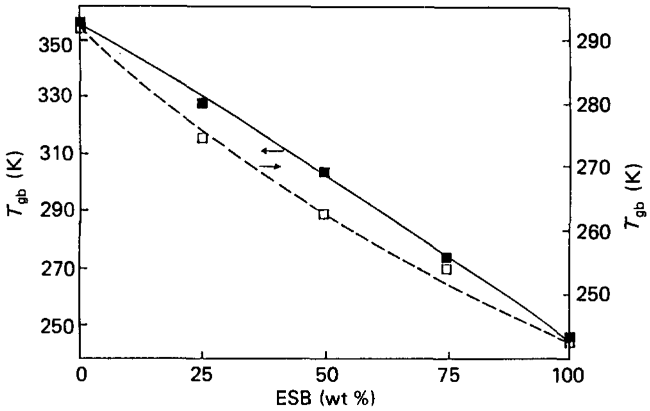

Figure 15 Composition dependence of T_{gb} blends: (■) ESB(P) (47)/PVC; (□) ESB(P) (47)/CPE(48)

Schneider *et al.*[30,31]. Consideration of contact interaction energies allows generalization of equation (1) to a virial form:

$$(T_{gb} - T_{g1})/(T_{g2} - T_{g1}) = (1 + K_1)W_{2c}^2 + K_2 W_{2c}^3 \quad (2)$$

where the corrected weight fraction is given by

$$W_{2c} = KW_2/(W_1 + KW_2) \quad (3)$$

with $K = \rho_1 T_{g1}/\rho_2 T_{g2}$.

Density values for ρ were obtained by calculation[32]. The terms K_1 and K_2 have been related to molecular energetic parameters through:

$$K_1 = K_1^*/(T_{g2} - T_{g1}) \quad \text{and} \quad K_2 = K_2^*/(T_{g2} - T_{g1}) \quad (4)$$

where K_1^* depends essentially on the interaction energy difference between hetero and homo contacts and K_2^* to the effects on the binary contact energies of the molecular surrounding[31]. A least squares regression analysis using equation (2) gave $K_1^* = 123$ and $K_1^* = 32$ for the ESB(P) (47)/PVC and ESB(P) (47)/CPE(48) blends, respectively, again in support of a higher interaction for the PVC blends. The corresponding values for K_2^* were 89 and 121. This may be interpreted to mean that the energetic effects of changing the surroundings in the neighbourhood of the ESB(P) in the CPE(48) blends is larger than in the PVC system [equation (3) in ref. 31]. Though this seems plausible in view of the higher degree of ordering in the latter system, additional compositions need to be analysed to obtain a valid generalization.

CONCLUSIONS

At constant *DE* ESB is more compatible with chlorinated polymers than ESBS and ESB(Br). Thus a copolymer architecture dependent differentiation in miscibility has been established.

There is a minimum mole ratio of (oxirane)/(CHCl) units for the onset of miscibility. For compositions with a lower oxirane concentration incompatibility sets in. In the blends studied, optimum tensile properties are attained for intermediate *DE* values.

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