Effect of block copolymer architecture on compatibility: 2. Epoxidized styrene–butadiene star block copolymers with chlorinated polymers

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The compatibility behaviour of an epoxidized styrene–butadiene three-arm block copolymer ($(ESB)_3$) with chlorinated polyethylene (CPE) at two degrees of chlorination (36 and 48 wt%) and with poly(vinyl chloride) was investigated over the complete composition range. The techniques used were dynamic mechanical analysis, differential scanning calorimetry and tensile testing. The results were compared with epoxidized block copolymer blends of different architectures, studied before: a linear ESB, a branched $E(SB)_n$ and an SBS. The results indicate that miscibility is reduced along the series $ESB > (ESB)_3 > E(SB)_n$, at the same level of epoxidation. Additional data on tensile properties on $(ESB)_3$ and $E(SB)_n$ blends are also reported. A method is also described to obtain epoxidized semicrystalline poly(hydrocarbons), which when blended with CPE showed a T_m depression. This allowed the determination of the interaction parameter χ_{12} of epoxidized poly(hydrocarbon)/chlorinated polymer using the well established method.

(Keywords: block copolymer architecture; epoxidized styrene–butadiene; chlorinated polymers)

INTRODUCTION

In a previous communication[1] the compatibility of epoxidized styrene–butadiene (ESB) block copolymers of varying architecture with chlorinated polyethylenes (CPE) and poly(vinyl chloride) (PVC) was examined.

In this work these binary systems are further examined using a well characterized three-arm block copolymer so that, together with the previous findings[1,2], a unified picture on the effect of architecture on compatibility may evolve. In addition to dynamic viscoelastic data, this paper includes additional tensile properties on these blends. Of central importance in polymer–polymer miscibility prediction is the determination of the interaction parameter χ_{12}. This has been achieved using the T_m depression method[3] and a semicrystalline epoxidized partially hydrogenated polybutadiene (PBD). This work was preliminary to an investigation on the effect of copolymer architecture in compatibilizing ternary blends[4].

EXPERIMENTAL

The materials used are reported in *Table 1*. Also listed are the materials studied before[1,2] and in the companion paper[4].

The epoxidation procedure using the *in situ* formation of performic acid and characterization of epoxidized products using ^1H n.m.r., ^{13}C n.m.r., *FT*i.r. and chemical analysis were identical to those described previously[1,2]. To identify samples the degree of epoxidation (*DE*) calculated for the total polymeric material is given in parentheses following the epoxidized polymer (*Table 1*). Thus $(ESB)_3(40)/CPE(48),25$ refers to a 25 wt% CPE(48) blend with a 40 mol% epoxidized three-arm SB block copolymer.

Blends were prepared by dissolving in a common solvent (butan-2-one for PVC, chloroform for CPE) and drying to constant weight at 50°C in a vacuum oven. Other preparative procedures on film preparation were similar to those reported before[1].

Dynamic mechanical analysis (d.m.a.) data at isochronous conditions (110 Hz), d.s.c. measurements and tensile testing were performed using the same instrumentation and under identical conditions as previously[1].

Hydrogenation of polybutadiene

To obtain a semicrystalline epoxidized poly(hydrocarbon) for the T_m depression measurements of blends, PBD was hydrogenated and in a second step epoxidized. Thus melting points were obtained at easily accessible temperatures. The procedure was as follows[5]. A solution of high *cis*-PBD (1% by weight) in xylene and tosyl hydrazone (TH) ($CH_3C_6H_4SO_2NHNH_2$) at a mole ratio ($>C{=}C<$)/(TH) = 1:1 was heated with stirring at 125°C for 1 h. The hydrogenated product obtained was precipitated in methanol and dried at 50°C *in vacuo*. ^1H n.m.r. analysis gave a degree of hydrogenation of 58 mol%, H(58)PBD. Epoxidation was performed as usual and products with two degrees of epoxidation were prepared: 30 and 42 mol% of the available double bonds. These will be identified as E(42)H(58)PBD and E(30)H(58)PBD, respectively.

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Table 1 Molecular characteristics of polymers used

Sample	Acronym	Source	$\bar{M}_n$ (g mol^{-1})^f	$\bar{M}_w/\bar{M}_n$
Poly(vinyl chloride)	PVC	EKO Chemicals Co.	36 000	2.07
Chlorinated PE (48 wt% Cl)	CPE(48)	Aldrich Europe	61 000	2.50
Chlorinated PE (36 wt% Cl)	CPE(36)	Aldrich Europe	21 150	1.82
SB diblock^a	SB(P)	Phillips Petroleum	246 000	1.08
SB radial (three-arm)	$(SB)_3$	Phillips Petroleum	189 000	1.92
SB diblock^b	SB(S)	Shell	79 000	1.24
$(SB)_n$ branched^c	SB(Br)	Shell	189 000	1.98
SBS triblock^d	SBS	Aldrich Europe	53 000	–
SBR random	SBR	Bayer-Polysar	106 770	4.43
Poly(butadiene), high-*cis*^{c}	PBD	Pirelli	194 000	2.10
Polystyrene^e	PS	–	11 000	1.15

All block copolymers contained 30 wt% styrene; SBR contained 23.75 wt% styrene

^{a} Experimental product with ~95% purity

^{b} Commercial product with a reported purity of ~80%

^{c} Commercial product

^{d} Taken from ref. 2 for comparison

^{e} Experimental product prepared by bulk polymerization

^{f} From g.p.c. analysis in tetrahydrofuran

G.p.c. measurements in tetrahydrofuran (THF) for a sample resembling the former product gave $M_n = 81\,000\,\text{g mol}^{-1}$ and $M_w = 139\,000\,\text{g mol}^{-1}$.

RESULTS

Dynamic mechanical properties

At low *DE* $(ESB)_3$ copolymers are immiscible with chlorinated polymers. To obtain complete miscibility the *DE* should exceed ca. 40 mol%. Thus at low *DE* the blends with CPE(48) and PVC are immiscible. A typical thermomechanical spectrum is given in *Figure 1*. Both the low- and high-temperature relaxations attributed to $(ESB)_3$ and CPE(48), respectively, are well defined and separated. Increasing the *DE* causes some differentiation between the two chlorinated blend partners (see *Figure 2*), the CPE(48) being nearly miscible. The two relaxations approach each other and there is a single broad peak at the 50/50 composition. This is not the case for the corresponding $(ESB)_3$/PVC blends. At higher *DE* both CPE(48) and PVC show complete miscibility (see *Figure 3*), and one observes a single relaxation shifting with composition along the temperature scale—a d.m.a. criterion for miscibility. Comparison of data with previous findings[1] indicates that the epoxidized SB(P) diblock (see *Table 1*) is compatible at lower *DE* than ESB(Br) or $(ESB)_3$. Already ESB(P)(16) shows a shift of the relaxations (E'') associated with T_g and ESB(P)(29) is completely miscible with CPE(48); see figures 4 and 7 in ref. 1. Space limitations do not allow inclusion of all the d.m.a. spectra available[6]. Thus the compatibility data are summarized in *Table 2* where, for comparison purposes, results from previous studies[1,2] have also been included. The essential experimental facts can be summed up as follows:

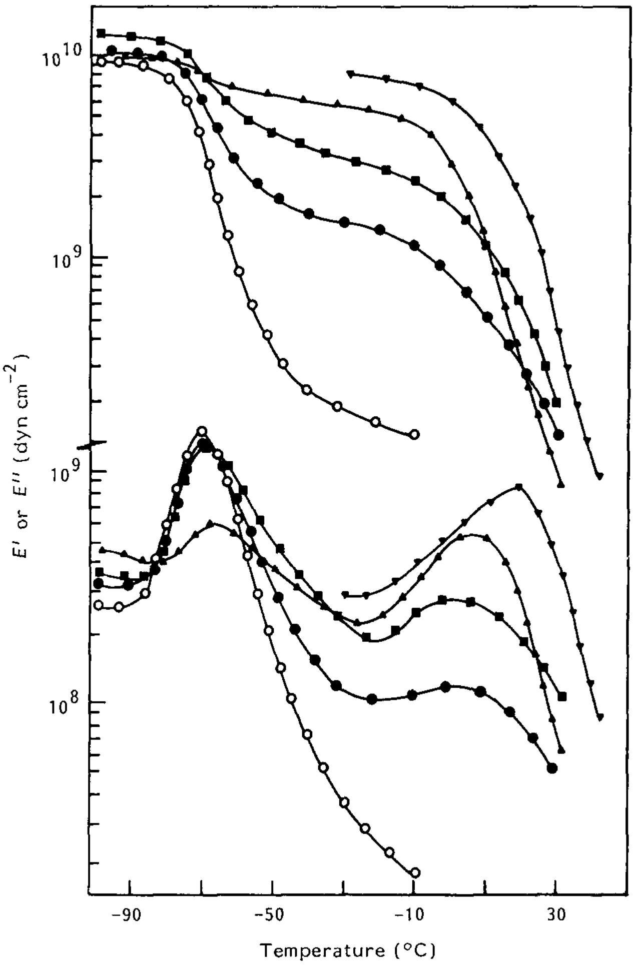

Figure 1 Thermomechanical spectra of $(ESB)_3(11)$/CPE(48) blends: (○) 100/0; (●) 75/25; (■) 50/50; (▲) 25/75; (▼) 0/100

(1) Increased amounts of an epoxidized copolymer may lead to a miscible blend.

(2) Increased chlorine contents in the chlorinated polymer requires increased *DE* of the copolymer. Thus a minimum mole ratio of oxirane groups to methylene chloride moieties to attain miscibility may be determined. This is (oxirane)/(CHCl) ≃ 1.4 for CPE(36) and CPE(48) and 0.5 for PVC.

(3) Other things being equal, branched copolymers showed smaller compatibility than diblock copolymers.

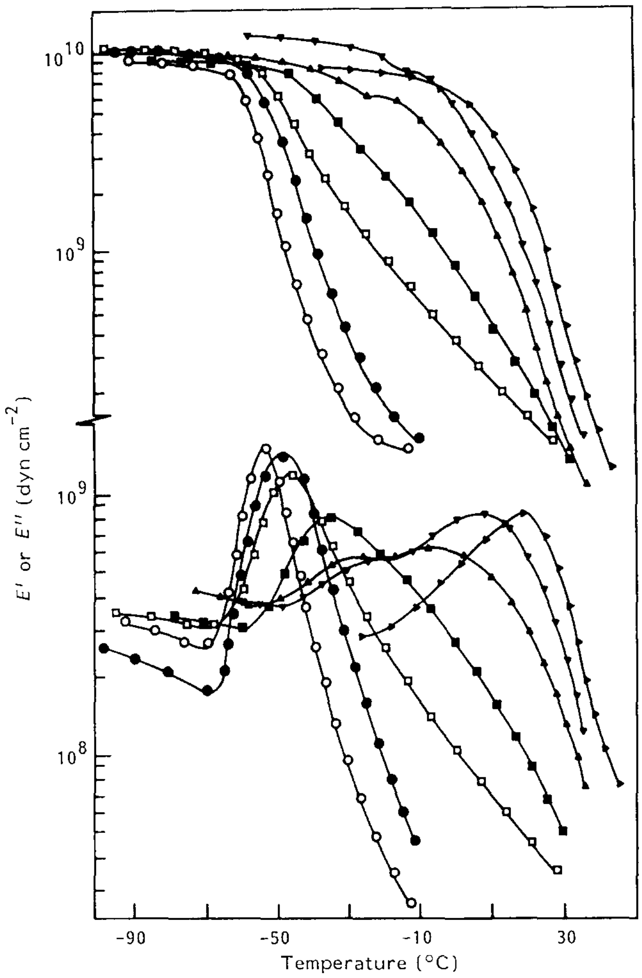

Figure 2 Thermomechanical spectra of $(ESB)_3(21)$/CPE(48) blends: (○) 100/0; (●) 87.5/12.5; (□) 75/25; (■) 50/50; (▲) 25/75; (▼) 12.5/87.5; (▶) 0/100

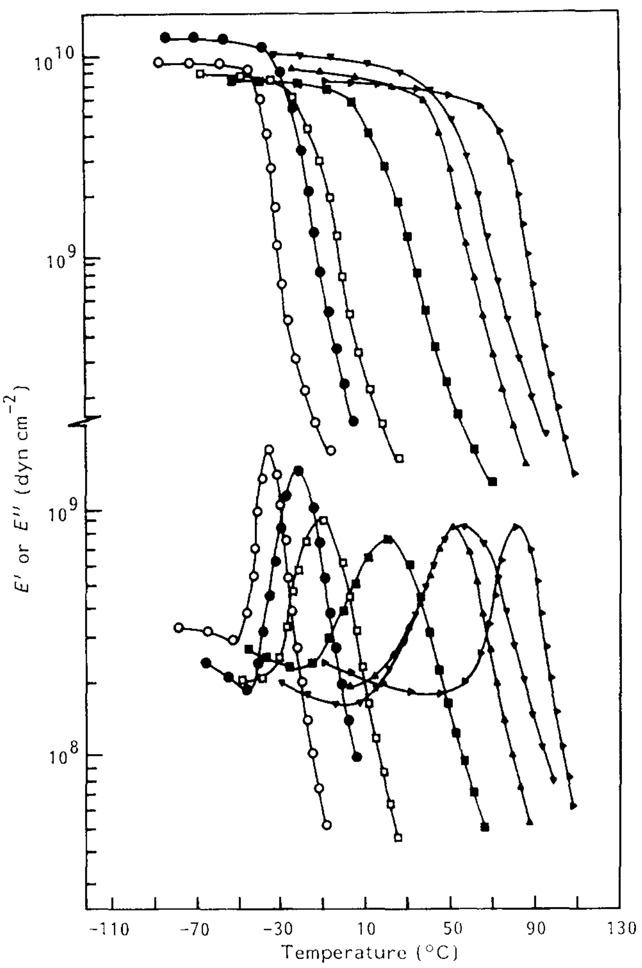

Figure 3 Thermomechanical spectra of $(ESB)_3(40)$/PVC blends: (○) 100/0; (●) 87.5/12.5; (□) 75/25; (■) 50/50; (▲) 25/75; (▼) 12.5/87.5; (▶) 0/100

Table 2 Compatibility chart of blends

Blends	Degree of epoxidation (mol%)	CPE(36) (wt%)			CPE(48) (wt%)			PVC (wt%)		
		25	50	75	25	50	75	25	50	75
(a) ESB(P)[1,6]	16	M	IM	PM	M	PM	PM	M	IM	IM
	29	M	M	M	M	M	M	M	M	PM
	33	–	–	–	–	–	–	M	M	PM
	47	–	–	–	M	M	M	M	M	M
(b) $(ESB)_3$	11	IM	IM	IM	IM	IM	IM	IM	IM	IM
	21	M	M	PM	M	M	PM	M	IM	IM
	40	–	–	–	M	M	M	M	M	M
(c) ESB(Br)[1]	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
(d) ESBS[2]	34	–	–	–	–	–	–	M	M	IM
	43	–	–	–	–	–	–	M	M	M

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

The compatibility behaviour of ESB(P) and $(ESB)_3$ may only be inferred indirectly since identical *DE* were not available. Comparison of figures 5 and 7 of ref. 1 indicates a higher width of the relaxation spectra for the $(ESB)_3$ product notwithstanding its higher *DE*. Contrary to expectation ESB(Br) shows comparable miscibility as linear ESBS[2].

The above results on the ability of ESB to yield miscible blends with chlorinated polymers indicate that this depends on their architecture and varies in the order:

$$\mathrm{ESB(P)} > \mathrm{(ESB)_3} > \mathrm{ESB(Br)} \simeq \mathrm{ESBS}$$

A qualitative explanation is given in the 'Discussion'.

Tensile properties

To examine the tensile behaviour critically, one should take into account the structure of the copolymer itself and the effect of the oxirane content on chain flexibility and on blend miscibility *per se*. It is well documented[7] that SB diblock copolymers have lower tensile strength compared to SBS copolymers. One would also expect that SB(Br) and $(SB)_3$ and their epoxidized homologues would also have improved tensile strength compared to SB since in the former products the PBD units are also anchored between the PS blocks. *Figure 4* compares the tensile properties between ESB(Br) and $(ESB)_3$ and of their PVC blends. It is evident that SB(Br) and ESB(Br) are stronger and have lower extensibility than $(SB)_3$ and $(ESB)_3$ owing to their higher degree of crosslinking. In blends, $(ESB)_3$ has improved properties not only because of a more uniform load distribution leading to higher extensibility but also owing to its higher compatibility with PVC (see previous section). *Figure 5* gives the ultimate properties of $(ESB)_3$/PVC blends at three compositions as a function of the *DE* of the copolymer. At low *DE* no significant diversification is evident since the system is immiscible at all compositions. Note, however, that no deterioration of properties is evident apparently because of strong chain association of blend partners. Increasing the *DE* leads to partial miscibility leading to increased 'incorporation' of PVC into the $(ESB)_3$. This combined with the stiffening effect of the oxirane content leads to higher load-bearing capacity. Extensibility also increases because of improved compatibility. At higher *DE* extensibility is reduced for the PVC-rich compositions since these miscible blends are stiffer owing to their high T_g value. Similar trends are observed with the ESB(Br)/PVC blends and also the ESB(P)/PVC blend reported before[1]. The effects in blends with CPE(48) and CPE(36) are only significant in the elastomer-rich compositions (see *Figure 6*). This is related to the fact that the T_g of the two blend components are not greatly different as in the case of the PVC blends.

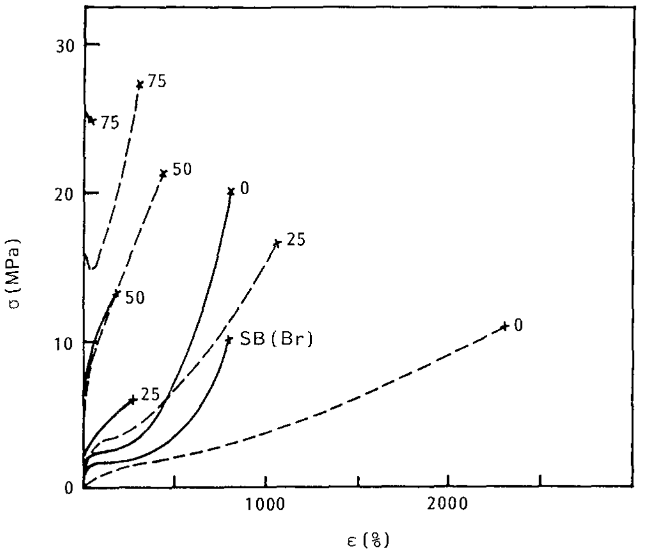

Figure 4 Stress–strain properties of ESB(Br)(21)/PVC (—) and $(ESB)_3(21)$/PVC (--) blends (σ is engineering stress). Numbers next to curves indicate weight percentage of PVC

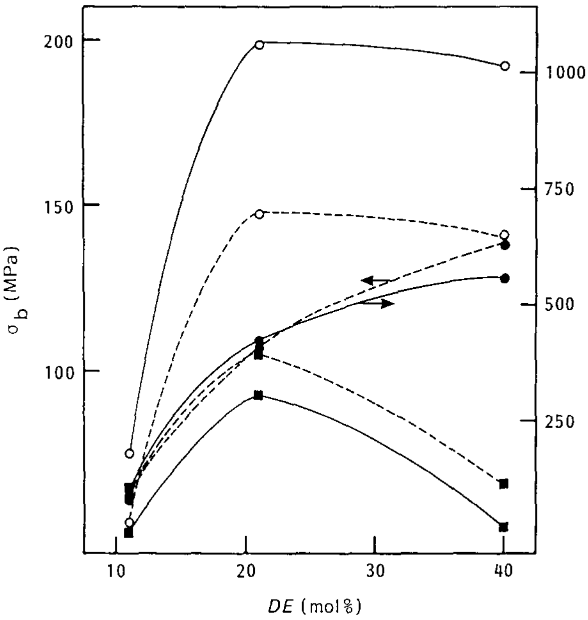

Figure 5 Ultimate properties of $(ESB)_3$/PVC blends: (○) 75/25; (●) 50/50; (■) 25/75

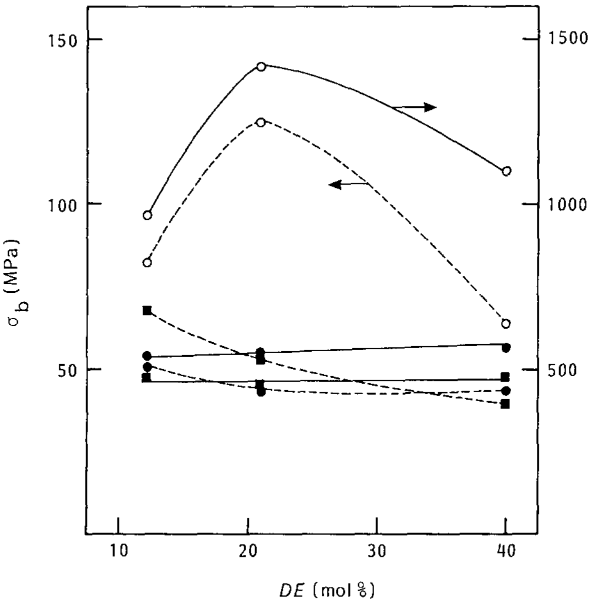

Figure 6 Ultimate properties of $(ESB)_3$/CPE(48) blends: (○) 75/25; (●) 50/50; (■) 25/75

Thermal properties

Ever since we discovered that epoxidized poly(hydrocarbons) may yield miscible blends with chlorinated[8] (and proton-donating[9]) polymers, we have sought to determine experimentally the oxirane/methylene chloride interaction parameter. A first attempt was made using PVC annealed at 140°C to increase its crystallinity and thus obtain a measurable T_m depression in blends. However, the effect was too small to yield measurable results. Next an attempt was made to epoxidize poly(*trans*-1,4-isoprene)[10], which already has substantial crystallinity and its T_m can be conveniently measured. It was found[6], however, that when sufficiently epoxidized to yield miscible blends (above ca. 30 mol%), its crystallinity was destroyed[6,10]. Finally, an attempt was made to hydrogenate high *cis*-PBD using the procedure described in the 'experimental' section. It has been established[11] that with the increase of the degree of hydrogenation (*DH*) the original high *cis*-PBD (with a T_g at $-104°C$ and T_m at $-24°C$) becomes amorphous at 16 mol% *DH*; H(16)PBD. Further hydrogenation changes T_g with no evidence of crystallinity; this appears at ca. 48 mol% *DH*, the H(48)(PBD) having a T_g at $-70°C$ and a T_m at 20°C. Thus one obtains an unsaturated poly(hydrocarbon) containing short polyethylene sequences established[11] by i.r. to be in the *trans*-1,4 conformation. The material has a conveniently located T_m and may be epoxidized to a sufficiently high *DE* to yield miscible blends without loss of crystallinity. Blends in the complete composition range were prepared with CPE(48) using H(58)PBD at two *DE* (see 'Experimental' part).

T_m determination using d.s.c. indicated considerable T_m depression in blends. To separate the morphology and thermodynamic factors leading to T_m reduction[12], the Hoffman–Weeks procedure[13] was applied by plotting T_{mb} (experimental melting point) vs. annealing temperature for all compositions; for example, see *Figure 7* for E(30)H(58)PBD/CPE(48) blends.

This analysis is based on the relation:

$$T_{mb} = T^{\circ}_{mb}(1 - 1/\eta) + T_c/\eta \qquad (1)$$

and yields the equilibrium T_m of the crystalline component in the blend (T°_{mb}) and in the pure state (T°_m). Here η is a lamellar thickening factor relating crystal thickness l_c to the initial l^* (i.e. $l_c = nl^*$), assumed to be independent of T_c[14]. The T°_{mb} values obtained are used to determine the interaction parameter χ_{12} (see below) and are summarized in *Tables 3* and *4*.

Table 3 Thermal properties of E(42)H(58)PBD/CPE(48) blends

Composition	T°_{mb} (K)	ϕ_2	$(1/T^{\circ}_{mb} - 1/T^{\circ}_m)/\phi^2 \times 10^3$
100/0	344.4(T°_m)	–	–
90/10	343.9	0.08	0.05
80/20	342.3	0.16	0.11
70/30	340.2	0.24	0.15
60/40	335.5	0.34	0.22
50/50	441.9	0.43	−1.11
40/60	436.3	0.53	−1.15
30/70	458.6	0.64	−1.13
20/80	481.2	0.75	−1.10
10/90	498.1	0.87	−1.03

Table 4 Thermal properties of E(30)H(58)PBD/CPE(36) blends

Composition	T°_{mb} (K)	ϕ_2	$(1/T_{mb} - 1/T^{\circ}_m)/\phi^2 \times 10^3$
100/0	338.0(T°_m)	–	–
90/10	336.8	0.08	1.27
80/20	334.9	0.15	1.79
70/30	332.1	0.24	2.16
60/40	329.8	0.33	2.22
50/50	366.8	0.42	−5.54
40/60	371.9	0.52	−5.19
30/70	377.9	0.63	−4.96
20/80	384.2	0.75	−4.75
10/90	391.4	0.87	−4.64

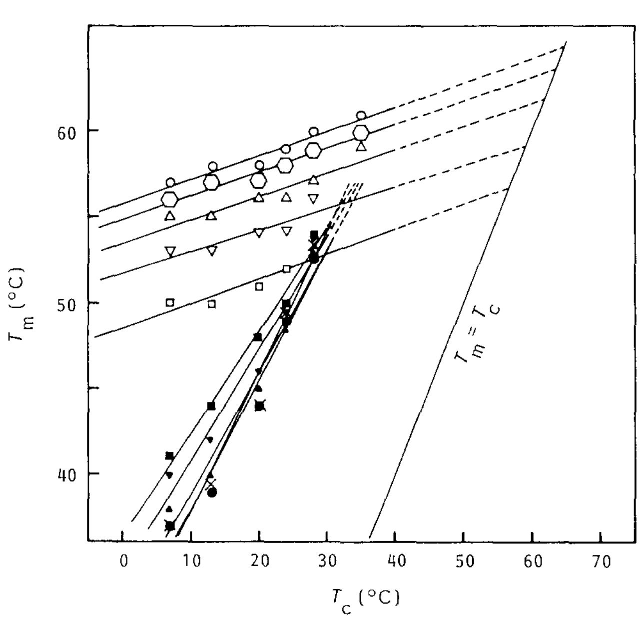

Figure 7 Hoffman–Weeks plots of E(30)H(58)PBD/CPE(48) blends: (○) 100/0; (○) 90/10; (△) 80/20; (▽) 70/30; (□) 60/40; (■) 50/50; (▼) 40/60; (▲) 30/70; (●) 20/80; (×) 10/90

DISCUSSION

As mentioned above, the origin of the miscibility of the epoxidized poly(hydrocarbons) may be attributed to the oxirane unit interacting with a complementary dissimilar partner. *FT*i.r. studies reported in the companion paper[1] showed a considerable shift of the oxirane absorption.

Use of the T°_{mb} equilibrium data (obtained as described above), relating the T_m depression to thermodynamic interaction, allowed the determination of the χ_{12} interaction parameter. The working equation is given by[3,15]:

$$\left(\frac{1}{T^{\circ}_{mb}} - \frac{1}{T^{\circ}_m}\right)\frac{1}{\phi_2} = -\frac{RV_{1u}}{\Delta H^{\circ}_f V_{2u}}\chi_{12}\phi_2 \qquad (2)$$

where ϕ_i is the volume fraction of polymer *i* and indices 1 and 2 refer to the crystalline and amorphous components in the blend, respectively; ΔH°_f is the heat of fusion of the perfect crystal and V_{iu} is the molar volume of repeat unit *i*. Application of equation (2) assumes that there are no entropic contributions to the T_m depression and that χ_{12} is composition-independent. The first assumption is valid because of the high molar mass of the components. It is recognized that the second may be assumed valid only as a first approximation in the composition range where the T_m vs. T_c plot is linear. To apply equation (2) one needs, in addition to T°_m, T°_{mb} and ϕ_2, the quantity ΔH°_f, which was not available in the literature. This was obtained by plotting experimental values of ΔH_f vs. T_m of E(H)PBD and extrapolating to T°_m to obtain ΔH°_f (see *Figure 8*). The ΔH°_f values thus determined were 6.25 cal g^{-1} and 7.06 cal g^{-1} for the E(30)H(58)PBD and E(42)H(58)PBD, respectively. The values are reasonable in view of the findings of Burfield and Tanaka on the heat of fusion of natural rubber[16], $\Delta H_f = 6.1$ cal g^{-1}. The molecular data used in equation (2) were calculated on the basis of the chemical structure of the epoxidized hydrogenated polybutadienes and the constants given by Krevelen[17]. For E(30)H(58)PBD $V_{1u} = 62.38$ cm^3 mol^{-1} and a segmental molecular weight $M = 59.96$ g mol^{-1}. For E(42)H(58)PBD

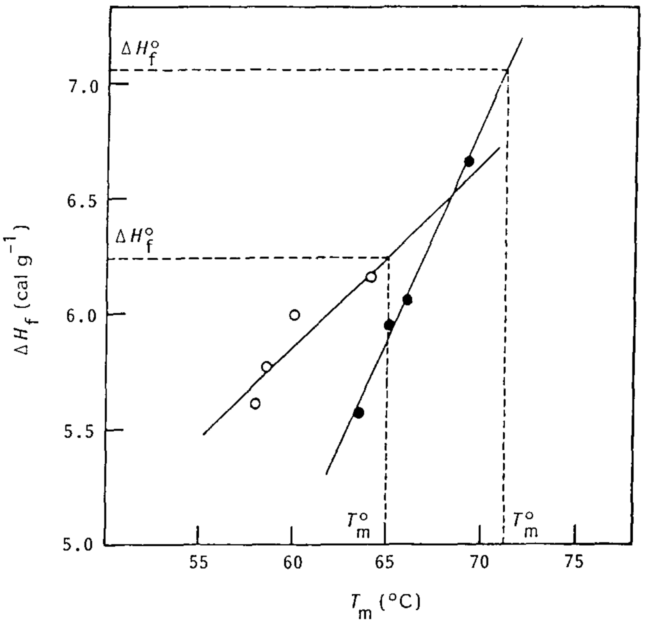

Figure 8 Determination of ΔH_f° of E(30)H(58)PBD (○) and E(42)H(58)PBD (●) polymers

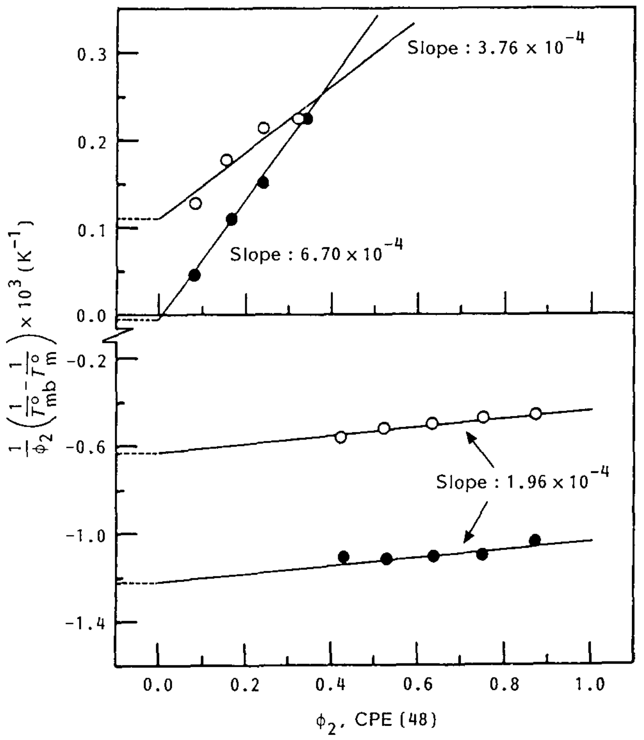

Figure 9 Determination of interaction parameter χ_{12} of blends: (●) E(42)H(58)PBD/CPE(48); (○) E(30)H(58)PBD/CPE(48)

$V_{1u} = 62.43\,\text{cm}^3\,\text{mol}^{-1}$ and $M = 61.88\,\text{g}\,\text{mol}^{-1}$. For the amorphous component CPE(48), molar volume was calculated to be $V_{2u} = 41.3\,\text{cm}^3\,\text{mol}^{-1}$. Use of the previous data and the slope obtained using equation (2) allowed the determination of χ_{12}. *Figure 9* gives two slopes obtained at different composition ranges where linearity exists. For blend E(30)H(58)PBD/CPE(48) $\chi_{12} = -0.05$ at ϕ, CPE(48) < 0.50; at other compositions $\chi_{12} = -0.03$. Similarly for the component with the higher *DE*, $\chi_{12} = -0.1$ and -0.03, in the above composition ranges. This is in agreement with the d.m.a. results indicating a miscibility dependence on the *DE* and blend composition. Such findings are not unusual; for example, in the polystyrene–poly(methyl methacrylate) (PS/PMMA) blend it was determined[18] that χ_{12} varies from 0.015 to 0.029 as the PMMA content increases. Analogous findings were reported for the poly(ethylene oxide)–poly(vinyl chloride) (PEO/PVC)[19] and poly(ethylene oxide)–poly(vinyl acetate) (PEO/PVAc)[20] blends.

As to the molecular origin of miscibility differentiation among the epoxidized block copolymers studied, it should be traced to the entropy loss ΔS_m during mixing, caused by locating their S–B junctions at the interface of the two blend partners. This 'ordering' decreases as $-\Delta S_m(\text{Br}) > -\Delta S_m(\text{3-arm}) > -\Delta S_m(\text{diblock})$. Consideration of the negative sign and the relative ΔS_m magnitudes and taking into account the basic thermodynamic function relating the Gibbs free energy G with entropy leads to:

$$\Delta G_m(\text{diblock}) < \Delta G_m(\text{3-arm}) < \Delta G_m(\text{branched}) \qquad (3)$$

This assumes that the enthalpic factor ΔH_m is comparable in the above series and not large enough to swamp the influence of the entropic factor. Our experimental findings in general seem to be in agreement with inequality (3) since ESB(P) is more miscible compared to ESB(3-arm) and this in turn more so than ESB(Br), other things being equal.

Phase-separated blends provide the opportunity for testing phenomenological mechanics models that relate modulus with blend morphology[21,22]. Of the various models available, Kerner's model in its complete version was tested[22]. This is given by:

$$E = E_c\left(\frac{\phi_d E_d}{(7-5\nu_c)E_c + (8-10\nu_c)E_d} + \frac{\phi_c}{15(1-\nu_c)}\right)\left(\frac{\phi_d E_c}{(7-5\nu_c)E_c + (8-10\nu_c)E_d} + \frac{\phi_c}{15(1-\nu_c)}\right)^{-1} \qquad (4)$$

where E is the dynamic modulus of the blend and indices c and d signify the continuous (matrix) and dispersed phase, respectively; ϕ_i is the volume fraction of phase i, and ν_c is the Poisson ratio of the composite, assumed to be real and equal to the arithmetic mean of their components weighted as their volume fraction. The model assumes strong adhesion between phases, a spherical shape for the dispersed inclusions with negligible interactions between them. To take into account the state of dispersion, Nielsen introduced[22] the concept of an effective volume fraction $\phi_{d,e}$ to replace ϕ_d. This is defined by:

$$\phi_{d,e} = \phi_d + \phi_d^2(1-\phi_m)/\phi_m^2 \qquad (5)$$

where ϕ_m is the maximum packing fraction of the dispersed phase. ϕ_m values for different dispersed particle shapes and states of dispersion are listed in ref. 22.

For the model's assumptions to hold, blends at low *DE* should be used (immiscible blends) at low rubber compositions. In *Figure 10* a comparison of *E* vs. *T* is made with values calculated using the parallel, the series phase connectivity and Kerner's model, and the experimental data[1] for the ESB(P)(16)/CPE(36) blend at low rubber concentration; $\phi_m = 0.512$ corresponding to close packing of spheres. *Figures 11* and *12* give similar comparisons at low and high rubber levels for the ESB(Br)(21)PVC system. At increased rubber levels the model fails since matrix inversion may take place. In

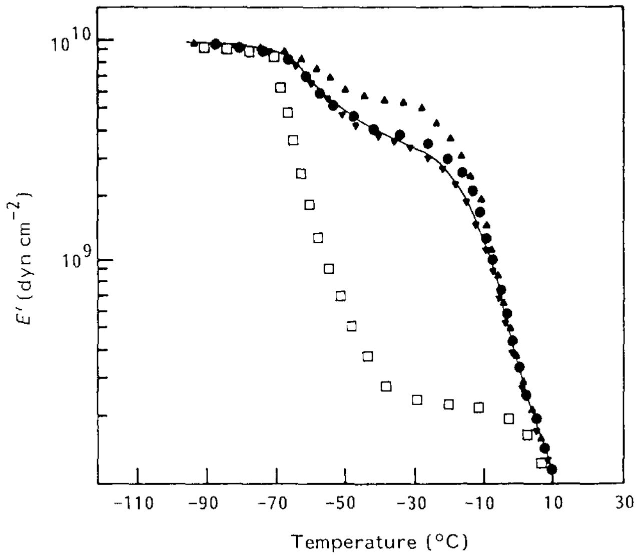

Figure 10 Comparison of calculated and experimental E modulus of ESB(P)(16)/CPE(36),75 blend: (—) experimental curve; (▲) phase connectivity in parallel; (□) in series; (●) equation (4) with $\phi_d=0.29$ and $\nu_c=0.42$; (▼) equation (5) with $\phi_m=0.512$

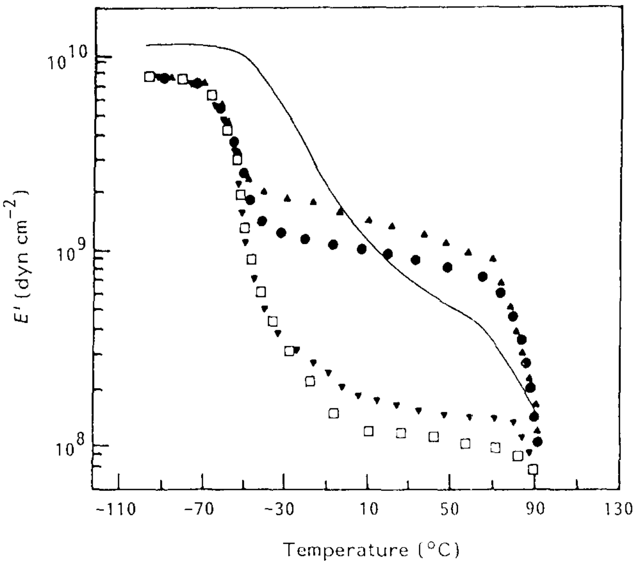

Figure 12 Comparison of calculated and experimental E modulus of ESB(Br)(21)/PVC(25) blend: (—) experimental curve; (▲) phase connectivity in parallel; (□) in series; (●) equation (4) with $\phi_d=0.80$ and $\nu_c=0.42$; (▼) equation (5) with $\phi_m=0.780$

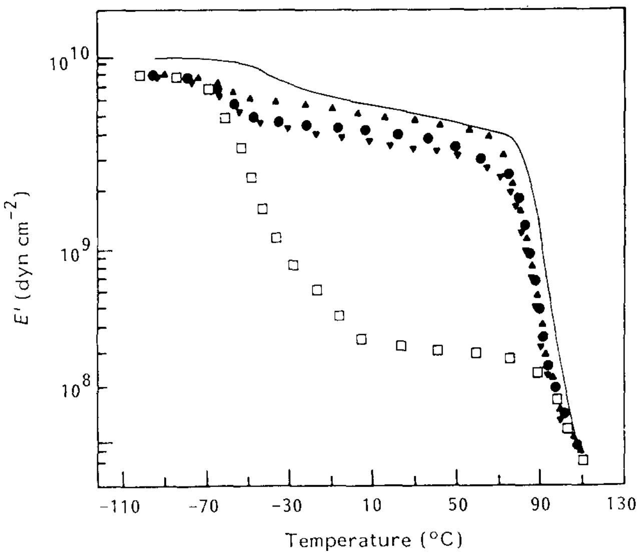

Figure 11 Comparison of calculated and experimental E modulus of ESB(Br)(21)/PVC(75) blend: (—) experimental curve; (▲) phase connectivity in parallel; (□) in series; (●) equation (4) with $\phi_d=0.31$ and $\nu_c=0.38$; (▼) equation (5) with $\phi_m=0.762$

general, taking into account the miscibility behaviour of the blends, one concludes that architecture does not play a role on the relative success of these phenomenological models since at certain compositions all failed. What is important is whether the assumptions for applying these models are validated: dispersed rubbery inclusions with strong adhesion to the matrix. In particular, in *Figure 12*, in addition to phase inversion, failure may also be caused by partial dissolution of the dispersed phase (see *Table 2*(*c*)). Overall, considering the fit obtained with the application of the $\phi_{d,e}$ concept, it does not offer any distinct advantage over the original Kerner equation. The ϕ_m values for the ESB(Br)/PVC blends correspond to elongated inclusions; however, to validate this conclusion a better fit should have been attained in the complete temperature range. It is worth noting that the simple parallel model allowing for maximum reinforcement is also applicable because segment–segment interactions can in principle align chains in parallel.

CONCLUSIONS

Miscibility of ESB with chlorinated polymers depends on copolymer architecture decreasing from the linear diblock to radial block copolymer, star and branched. This can be accounted for by the change in free energy ΔG_m caused because of the entropy reduction during the mixing process.

Mechanical properties at large deformations are governed by chain polarity (oxirane content) of ESB and of its degree of miscibility with the chlorinated partner. Even in partially miscible blends good tensile properties give evidence of strong interchain interactions. This is further supported by the negative value of the χ_{12} interaction parameter determined in closely related miscible blends.

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