Effect of block copolymer architecture on compatibility: 3. Epoxidized styrene–butadiene block copolymers with polystyrene/chlorinated polymer blends

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The compatibilizing efficiency of epoxidized styrene–butadiene block copolymers [E(S-*b*-B)] of varying architecture for the immiscible polystyrene (PS)/chlorinated polymer (CP) blends [poly(vinyl chloride), chlorinated polyethene] was examined. The copolymers were a diblock (ESB), a three-arm star (ESB)$_3$ and a random ESBR. The techniques applied were dynamic mechanical analysis and tensile testing of specimens prepared from solvent casting. Compatibilizing efficiency was found to depend on the degree of epoxidation of the butadiene unit in the copolymer, which in turn relates to the degree of chlorination of the CP, and also on the CP/PS ratio in the ternary blend and the molecular architecture of the E(S-*b*-B) compatibilizer. Other things being equal, this efficiency varies as: ESB>(ESB)$_3$>ESBR; thus it parallels the behaviour of the E(S-*b*-B) towards the CP in the binary blends. The same holds true for the degree of epoxidation of the E(S-*b*-B). This is in agreement with recent theoretical compatibilizing efficiency predictions and relates to the relative strength of the interaction parameters among blend constituents. Use of appropriate values for these parameters allowed the determination of the spinodal, approximating successfully the immiscibility gap of the ternary. This procedure could only be applied to the PS/ESBR/CP system, since ESBR, unlike the other E(S-*b*-B) copolymers, is not microphase separated.

(Keywords: compatibilization; structure; ternary blends)

INTRODUCTION

It is well known that due to thermodynamic limitations only a few polymer pairs are miscible. Though progress has been made to increase this number by polymer modification[1,2], compatibilization has also been achieved by the addition of a third component; hence the importance of ternary blends in polymer technology[3-5]. These systems are important not only because by choosing a suitable composition a miscible system is obtained[6-8], but more often because when interfacial tension is reduced and good adhesion ensured, they combine the integrity of the miscible systems and the property diversification of an alloy[5,9].

Block copolymers have often been used as compatibilizers and considerable progress has been made to understand the importance of various molecular parameters determining their action[4,10-12]. Some of these act as emulsifiers[13,14], others 'anchor' together blend partners by the athermal mixing of their blocks with the chemically similar partner[15-17] or by mixing through enthalpic interaction[18]. This last class is of considerable interest since by suitably modifying the compatibilizer molecule one can vary the degree of interaction and hence the degree of compatibilization.

Recent literature on this type of ternary includes the work of Park *et al.*[19] who reported improved adhesion of hydrogenated styrene–butadiene–styrene (SBS) to polystyrene (PS) with the addition of poly(epichlorohydrin) (PEC) claiming an enthalpic interaction of PEC with PS. Also ternaries consisting of miscible binaries were reported[20] to be immiscible at certain compositions. This has been attributed to the asymmetry of binary interactions or the '$\Delta\chi$ effect'. Fayt and Teyssie reported on the compatibilizing action of hydrogenated poly(butadiene-*b*-methyl methacrylate) [P(B-*b*-MMA)] in binary blends of polyethylene (PE)/acrylonitrile–butadiene–styrene (ABS) and PE/poly(styrene-*co*-acrylonitrile) (SAN)[21]. Similarly, the improved adhesion of SBS/SAN with P(S-*b*-MMA) or P(B-*b*-MMA) may be explained by the athermal mixing of the PS blocks and the enthalpic interaction of SAN with the MMA block[22]. The compatibilizing action of SBS in the methyl poly(phenylene oxide)/SAN binary has been investigated thermally and morphologically[23]. A ternary analogous to our system combining the effects of athermal and enthalpic interactions was reported by Akiyama and Jamieson[24]. They examined the morphology of a PS/SAN blend compatibilized with a P(S-*b*-MMA) copolymer. Changing the AN content of the SAN component varies its degree of enthalpic interaction with the MMA block of the compatibilizer. Other such ternaries have been cited in recent papers[8,25] and in the review by Utracki[26].

This paper covers experimental findings for such a ternary blend comprising PS, poly(vinyl chloride) (PVC) [or chlorinated PE (CPE)] and epoxidized poly(styrene–

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butadiene) copolymers of differing architecture: an ESB, $(ESB)_3$ and ESBR, i.e. a diblock, a three-arm star and a random copolymer. The parameters that may be controlled in such a blend to modify the degree of interaction are: the degree of the copolymer epoxidation (*DE*), the degree of chlorination of the homopolymer, the molecular architecture of the epoxidized copolymer and the PS block length influencing its miscibility with the PS homopolymer. This last factor was not examined since the PS used had a sufficiently small number-average molecular weight compared to that of the PS block ensuring its incorporation into the latter.

Taking into account the above parameters the specific aims of this study were: (i) to find the minimum required amount of compatibilizer (epoxidized copolymer); (ii) to assess the influence of the homopolymer ratio [PS/chlorinated polymer (CP)] on compatibilization; and (iii) to determine the influence of the compatibilizer architecture on its effectiveness. As a primary diagnostic property to assess compatibility, use was made of the dynamic viscoelastic properties. Determination of tensile properties was also used since good elongation properties are an indication of (at least) mechanical compatibility.

EXPERIMENTAL

Details of the materials used were reported in Part 2 of this series[27]. Similar instrumentation and procedures were also used. Films from blends were cast using a common solvent (2-butanone, chloroform) in Teflon-coated pans and evaporating at a slow rate at ambient temperature. Final drying to constant weight was carried out at 60°C in a vacuum oven. A total of ~30 ternaries were investigated[28] examining the molecular parameters cited above.

RESULTS

Dynamic mechanical properties

To interpret the dynamic mechanical analysis (d.m.a.) relaxations in the blends one should keep in mind that due to the small PS content in the copolymers and the particular solvents employed, only a single relaxation (E'') is evident — that due to the elastomer phase. Epoxidation raises the glass transition temperature (T_g) and hence moves E''_{max} upwards on the temperature scale. The same effect is caused by the CP if it is miscible with the epoxidized copolymer. In immiscible systems both T_gs (of the epoxidized system and of the CP) are discernible. Incorporation of the PS homopolymer may not change the spectrum unless it saturates the block and phase separates giving an additional relaxation; similarly, when the amount of copolymer is too small to incorporate the PS homopolymer present. Examination of the thermomechanical spectra leads to the following conclusions:

1. incorporation of the PS homopolymer into the PS block seems to adversely affect the interaction of the epoxidized block copolymer with the CP (*Figures 1* and *2*). At similar compositions and *DE* the corresponding binary blends were found to be completely miscible[27,29]. No such effect was observed for the PVC ternaries (*Figure 3*). Of interest is the considerable shift of the T_g of the PS homopolymer when it cannot be incorporated completely into the

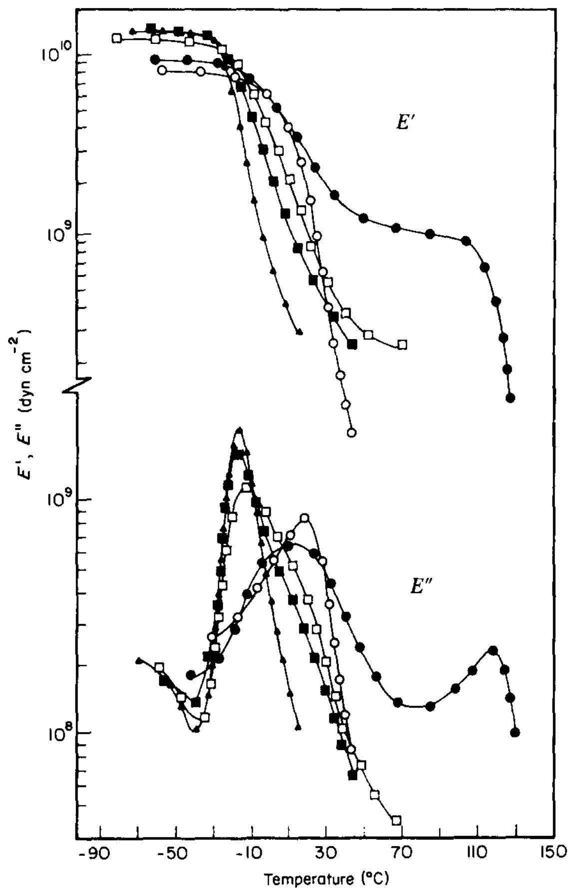


Figure 1 D.m.a. spectra of CPE(48)/ESB(42)/PS blends. CPE(48)/PS ratio = 1/1. (○) CPE(48). PS (wt%): (●) 15; (□) 30; (■) 45; (▲) 60

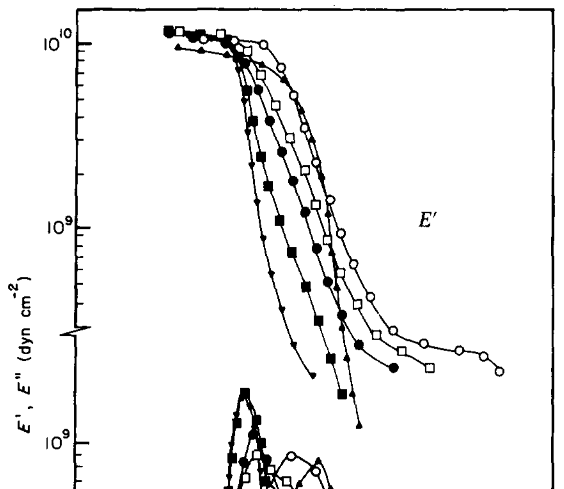


Figure 2 D.m.a. spectra of CPE(48)/$(ESB)_3$(42)/PS blends. CPE(48)/PS ratio = 1/1. (▲) CPE(48). PS (wt%): (○) 10; (□) 30; (●) 45; (■) 60; (▼) 75

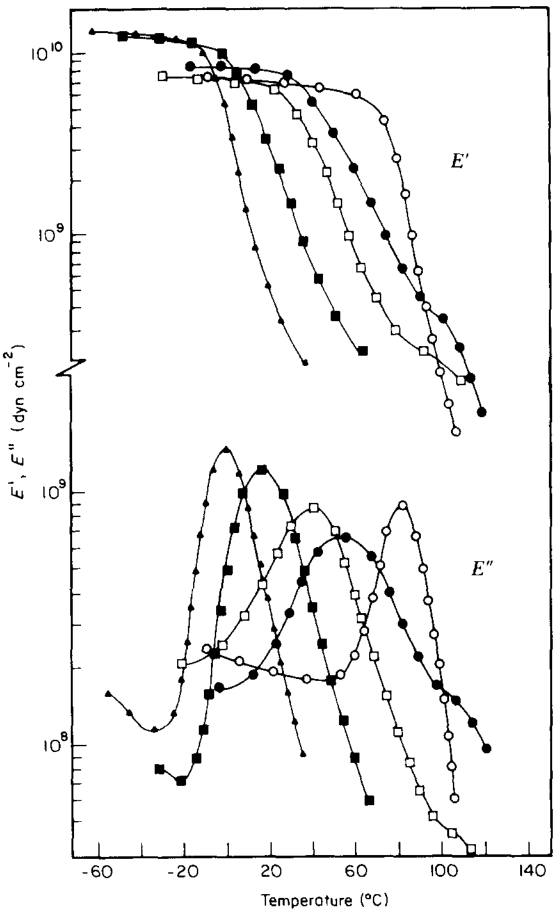


Figure 3 D.m.a. spectra of PVC/ESB(42)/PS blends. PVC/PS ratio = 1/1. (○) PVC. PS (wt%): (●) 15; (□) 30; (■) 45; (▲) 60

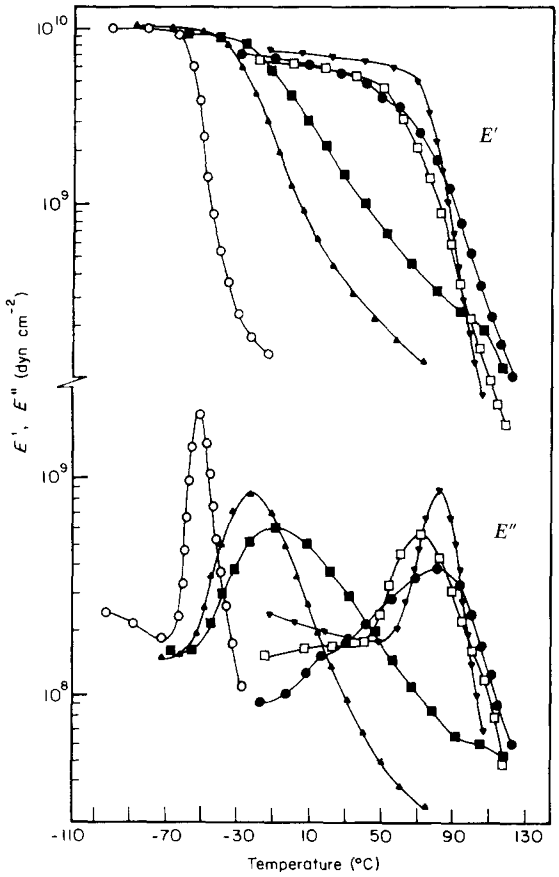


Figure 4 D.m.a. spectra of PVC/ESB(29)/PS blends. PVC/PS ratio = 1/1. (▼) PVC; (○) ESB(29). PS (wt%): (□) 5; (●) 15; (■) 45; (▲) 60

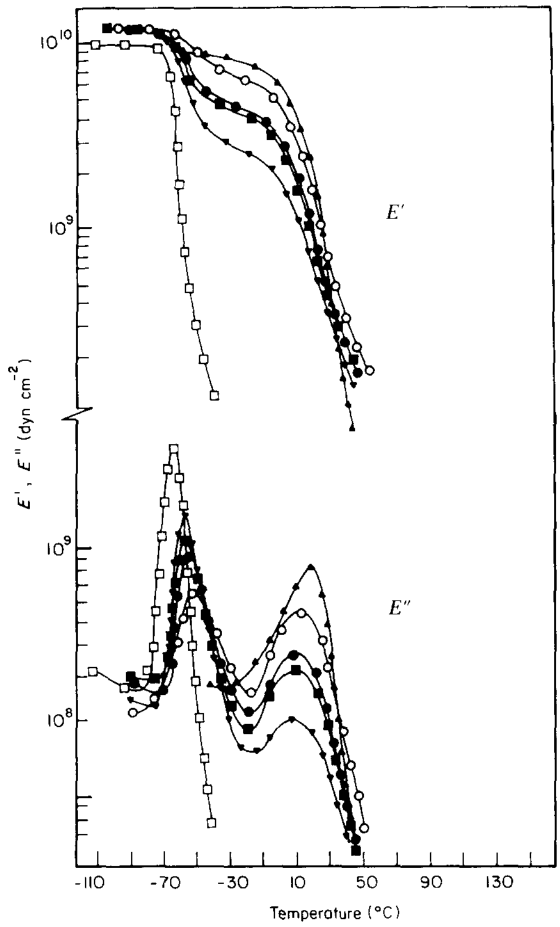


Figure 5 D.m.a. spectra of CPE(48)/ESB(16)/PS blends. CPE(48)/PS ratio = 3/1. (▲) CPE(48); (□) ESB(16). PS (wt%): (○) 15; (●) 30; (■) 45; (▼) 60

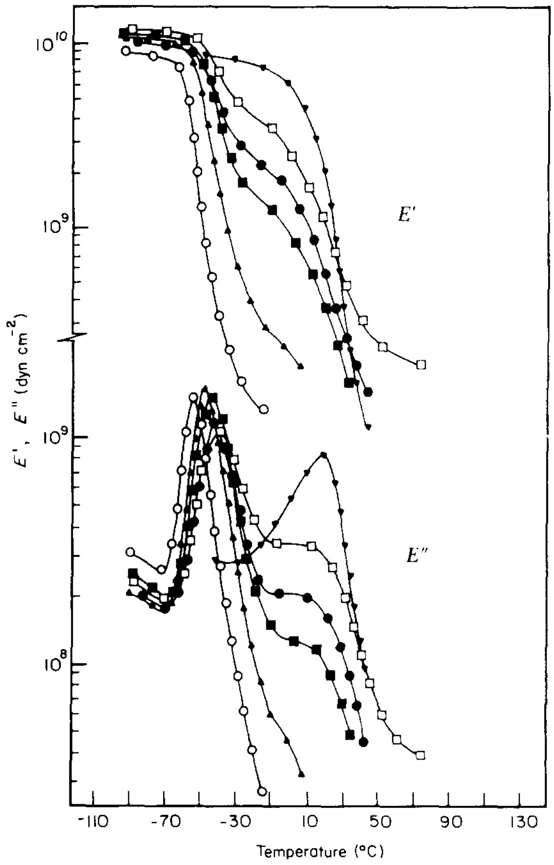


Figure 6 D.m.a. spectra of CPE(48)/(ESB)$_3$(21)/PS blends. CPE(48)/PS ratio = 1/1. (▼) CPE(48); (○) (ESB)$_3$(21). PS (wt%): (□) 30; (●) 45; (■) 60; (▲) 75

copolymer because of the low concentration of the latter;

2. as before[27,29] the *DE* is of paramount importance in bringing about compatibilization [cf. *Figures 3* and *4* for PVC/PS and *Figures 1* and *5* to *2* and *6* for CPE(48)/PS blends];
3. increasing the degree of chlorination requires increased *DE* to obtain a compatible system; this is an effect of the miscibility behaviour of the binary blends[27,29]. In the ternary, strong enthalpic mixing facilitates the athermal mixing of components (PS into the PS block). Evidence is given in *Figures 1* and *3*;
4. the effect of molecular architecture in the case of binaries has been explored in the companion paper[27] where it was demonstrated that structure simplicity favours miscibility. This is also shown in *Figures 3* and *7* and *1* and *2* where $(ESB)_3$ epoxidized to a higher degree is less effective than ESB. *Tables 1* and *2* give the compatibility behaviour of the ternaries investigated as determined by d.m.a. A distinction is made between compatible and miscible, the latter term being more appropriate for the ternaries involving the random copolymer (see below). Block copolymers are themselves microphase separated, hence the term compatible is more appropriate.

Tensile properties

From the large amount of data available[28] only certain figures are shown to support the following generalizations:

1. ultimate properties, tensile strength (σ_b) and elongation at break (ε_b), are satisfactory even in the case of some partially compatible blends (cf. *Figures 8* and *9* and *10* and *11*);
2. the ratio of the homopolymer concentration critically affects ultimate tensile properties. Properties deteriorate (σ_b and ε_b drop) when the ratio of PS/CP increases. This is also evident in partially compatible blends (cf. *Figures 10* and *12*, to *13* and *14* and *15* and *16*). This is in agreement with d.m.a. results on compatibilization, reported in *Tables 1* and *2*;
3. significant amounts of compatibilizer may be required to improve properties. This is possibly due to compatibilizer migrating into the CP component[3]. In some cases excessive amounts of compatibilizer may lead to property deterioration (*Figures 10* and *11*). This is attributed to the increase of stiffness of the rubbery component due to its mixing with the CP;

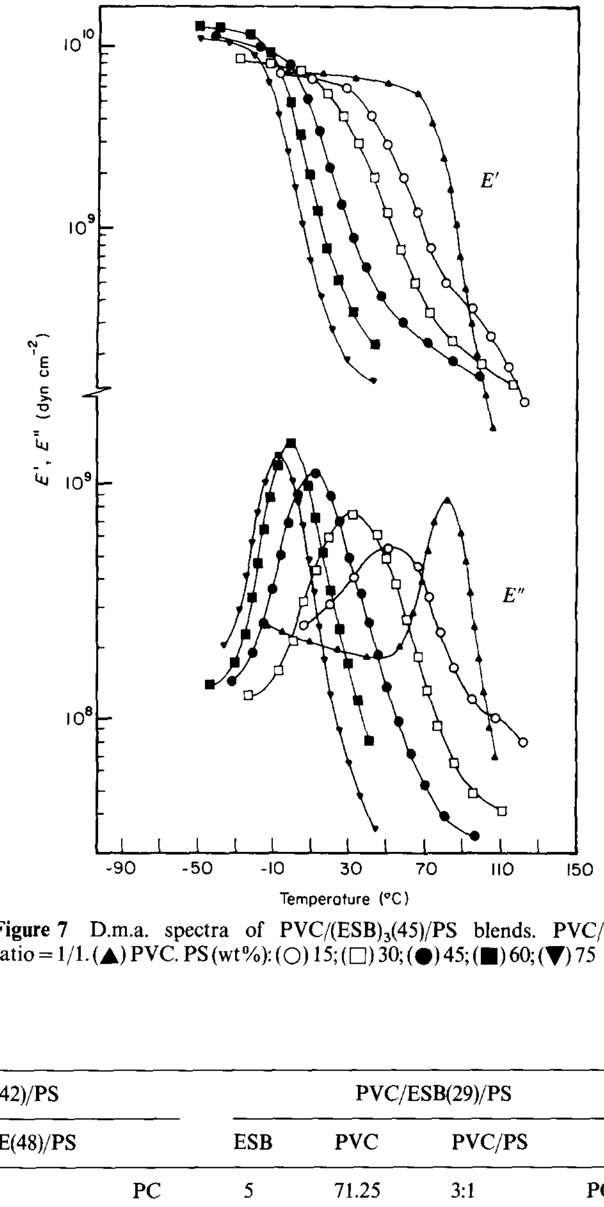


Figure 7 D.m.a. spectra of PVC/$(ESB)_3$(45)/PS blends. PVC/PS ratio = 1/1. (▲) PVC. PS (wt%): (○) 15; (□) 30; (●) 45; (■) 60; (▼) 75

Table 1 Compatibility behaviour of ternary blends[a]

PVC/ESB(42)/PS				CPE(48)/ESB(42)/PS				PVC/ESB(29)/PS			
ESB	PVC	PVC/PS		ESB	PVC	CPE(48)/PS		ESB	PVC	PVC/PS	
5	71.25	3:1	C	5	71.25	3:1	PC	5	71.25	3:1	PC
15	63.75		C	15	63.75		C	15	63.75		PC
30	52.50		C	30	52.50		C	30	52.50		PC
45	41.25		C	45	41.25		C	45	41.25		C
								60	30.00		C
5	47.50	1:1	NC	5	47.50	1:1	NC	5	47.50	1:1	PC
15	42.50		PC	15	42.50		PC	15	42.50		PC
30	35.00		C	30	35.00		PC	30	35.00		PC
45	27.50		C	45	27.50		C	45	27.50		PC
60	20.00		C	60	20.00		C	60	20.00		C
5	23.75	1:3	NC	5	23.75	1:3	NC	5	23.75	1:3	NC
15	21.25		PC	15	21.25		NC	15	21.25		NC
30	17.50		C	30	17.50		PC	30	17.50		NC
45	13.75		C	45	13.75		PC	45	13.75		PC
				65	8.75		C	65	8.75		PC

[a] Compositions in wt%. C, compatibilized; PC, partially compatibilized; NC, incompatible

Table 2 Compatibility behaviour of ternary blends[a]

PVC/(ESB)$_3$(45)/PS				PVC/ESBR(40)/PS				CPE(48)/ESBR(40)/PS			
(ESB)$_3$	PVC	PVC/PS		ESBR	PVC	PVC/PS		ESBR	CPE(48)	CPE(48)/PS	
5	71.25	3:1	C	5	71.25	3:1	PM	5	71.25	3:1	IM
15	63.75		C	15	63.75		PM	15	63.75		PM
30	52.50		C	30	52.50		M	30	52.50		PM
45	41.25		C	45	41.25		M	45	41.25		M
60	30.00		C	60	30.00		M	60	30.00		M
15	42.50	1:1	PC	10	45.00	1:1	IM	10	45.00	1:1	IM
30	35.00		C	30	35.00		M	30	35.00		PM
45	27.50		C	45	27.50		M	45	27.50		M
60	20.00		C	60	20.00		M	60	20.00		M
75	12.50		C	75	12.50		M	75	12.50		M
20	20.00	1:3	PC	10	22.50	1:3	IM	10	22.50	1:3	IM
45	13.75		PC	30	17.50		M	30	17.50		PM
60	10.00		PC	45	13.75		M	45	13.75		PM
75	6.25		C	60	10.00		M	60	10.00		M
				75	6.25		M	75	6.25		M

[a] Compositions in wt%. C, PC and NC as in *Table 1*. M, miscible; PM, partially miscible; IM, immiscible

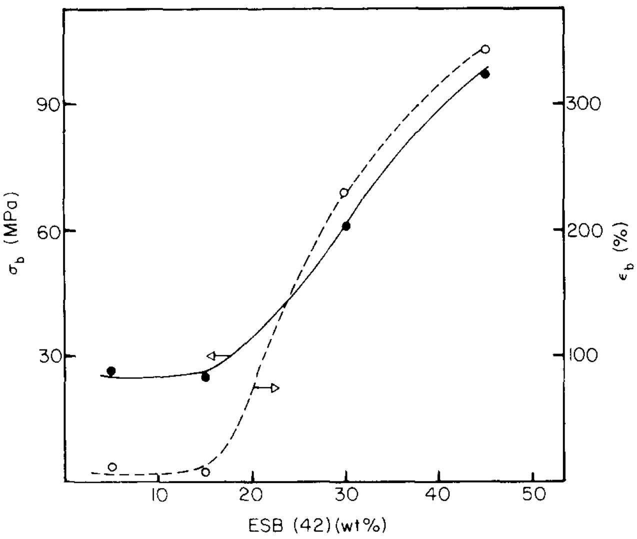


Figure 8 Ultimate properties of PVC/ESB(42)/PS blends. PVC/PS ratio = 3/1

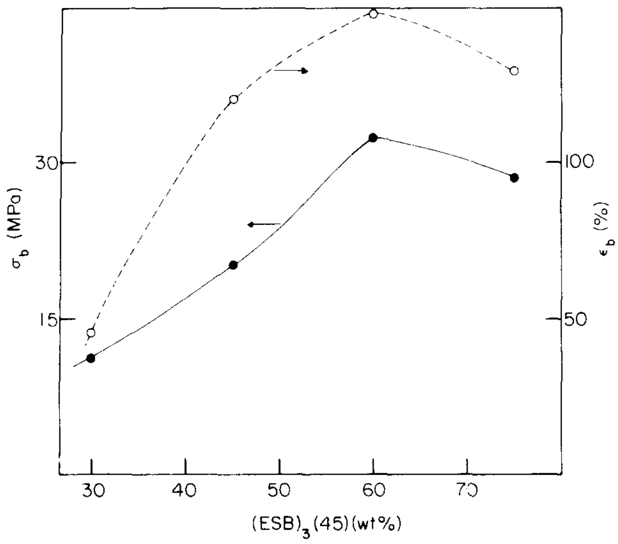


Figure 10 Ultimate properties of PVC/(ESB)$_3$(45)/PS blends. PVC/PS ratio = 1/1

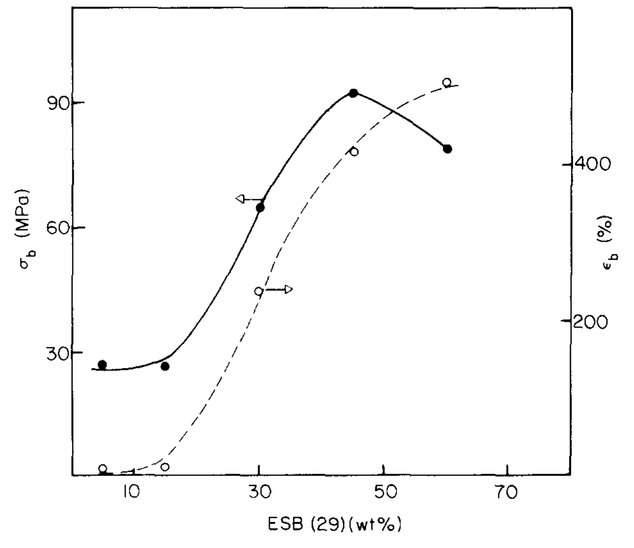


Figure 9 Ultimate properties of PVC/ESB(29)/PS blends. PVC/PS ratio = 3/1

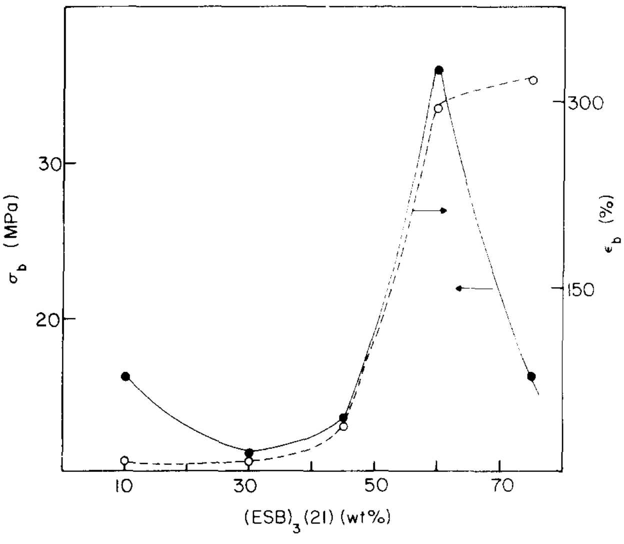


Figure 11 Ultimate properties of PVC/(ESB)$_3$(21)/PS blends. PVC/PS ratio = 1/1

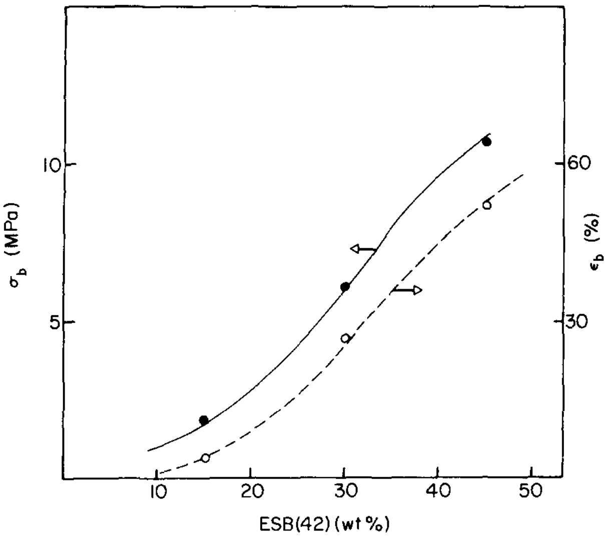


Figure 12 Ultimate properties of PVC/ESB(42)/PS blends. PVC/PS ratio = 1/3

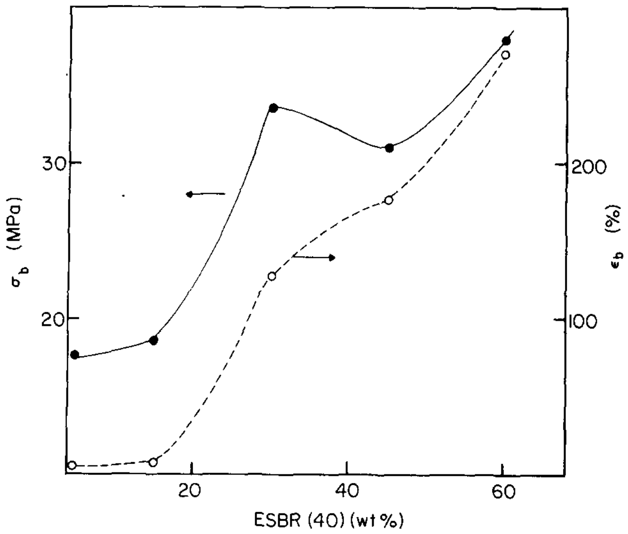


Figure 15 Ultimate properties of PVC/ESBR(40)/PS blends. PVC/PS ratio = 3/1

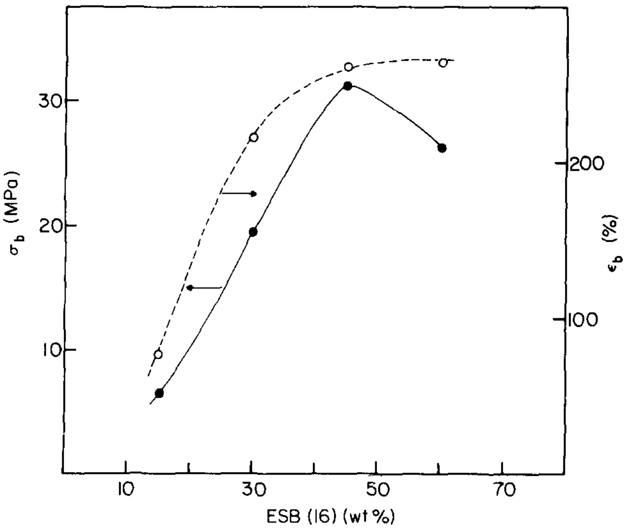


Figure 13 Ultimate properties of CPE(48)/ESB(16)/PS blends. CPE(48)/PS ratio = 3/1

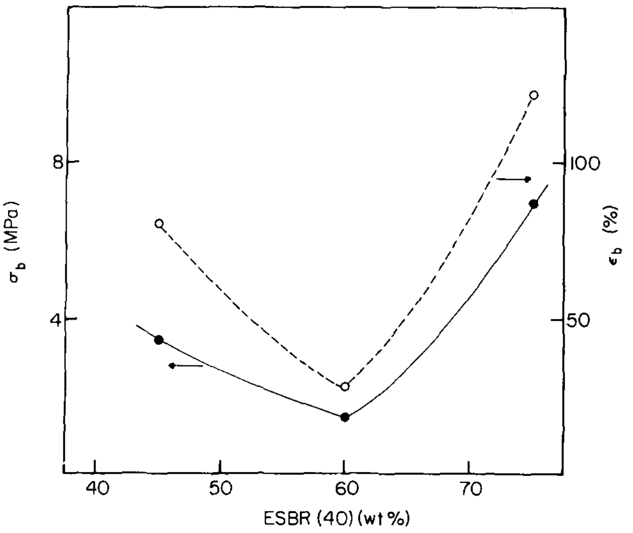


Figure 16 Ultimate properties of PVC/ESBR(40)/PS blends. PVC/PS ratio = 1/3

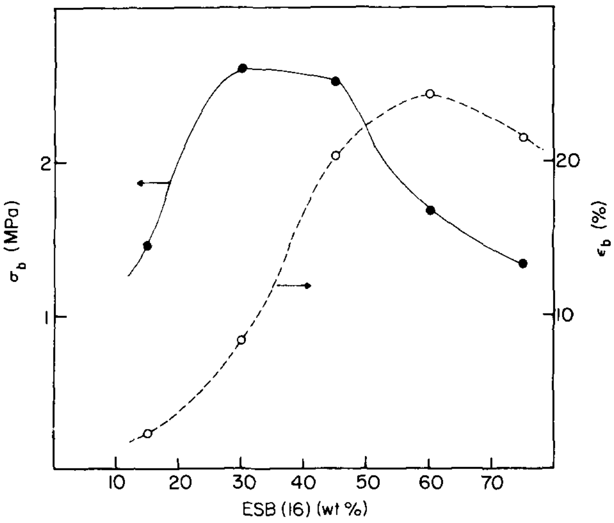


Figure 14 Ultimate properties of CPE(48)/ESB(16)/PS blends. CPE(48)/PS ratio = 1/3

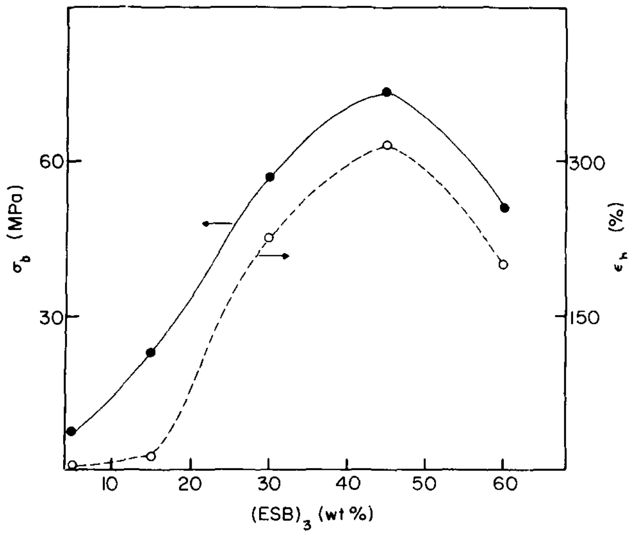


Figure 17 Ultimate properties of PVC/(ESB)$_3$(45)/PS blends. PVC/PS ratio = 3/1

4. *Figures 8*, *15* and *17* show the influence of architecture on the compatibilizing effectiveness. This decreases according to: ESB > $(ESB)_3$ > ESBR.

The compatibilizing behaviour of ESB is marginally superior to that of $(ESB)_3$. This has also been observed in the binary blends[27]. One should also keep in mind that the mechanism of compatibilization in the case of ESBR is different from that of the modified block copolymers. The latter act by 'anchoring' the homopolymers together while ESBR, a random copolymer, being considered[12] a 'homogeneous' polymer, may give a miscible system at those compositions where the binary interaction parameters bring it into the binodal region of the phase diagram.

DISCUSSION

In these blends epoxidized block copolymers may be represented by A-*b*-X added to an immiscible binary A/B (in this case PS/CP). Theory[11] and experimental evidence[24] support the view that when A is the minor phase in the binary, the emulsifying power of the block copolymer (e.g. ESB) is increased by a strong exothermic interaction between B and X (corresponding here to CP and EPBD block, respectively). This is valid when the A and B repulsion (PS–CP in our case) is weak. The interaction parameter between PS–PVC and PS–CPE may be calculated using Krause's scheme[30]. This is plausible since no exothermic specific forces are expected for these pairs. The basic equation to obtain the interaction parameter between monomer units of polymers 1 and 2 is given by:

$$\chi_{12}=\frac{V_r}{RT}(\delta_1-\delta_2)^2 \qquad (1)$$

where V_r is the reference volume and δ_i the solubility parameter of polymer *i*. Solubility parameters reported by Coleman *et al.*[31] were used: $\delta_{PS}=9.50$, $\delta_{PVC}=9.90$ and $\delta_{CPE(48)}=9.17$ $(\mathrm{cal\,cm^{-3}})^{1/2}$. The reference volume is taken as the molar volume of the smallest unit in the blend, the exact values being 41.3, 44.8 and 98.0 $\mathrm{cm^3\,mol^{-1}}$ for CPE(48), PVC and PS, respectively. The values obtained with equation (1) were $\chi_{PS/PVC}=0.012$ and $\chi_{PS/CPE(48)}=0.037$ at 25°C, using in each case the appropriate V_r. In the companion paper[27] the polymer–polymer interaction parameter was determined between the epoxidized hydrogenated PBD (EHPBD) and CPE(48). Depending on the degree of epoxidation this was found to lie in the range -0.1 to -0.03. A negative interaction parameter is also expected between EHPBD and PVC. Thus our system bears close analogy to the system studied by Akiyama and Jamieson[24]. The relative strengths of the interactions between PS/CP and EHPBD/CP explain the good emulsifying properties of the copolymer since good tensile properties were established even in systems where because of the low *DE* they were partially compatible. It also explains the improved properties of blends when PS is the minor phase, i.e. when the ratio of CP/PS = 3/1 (see previous section). In the case of miscible systems obtained by the proper ratio of the oxirane/CHCl units[29], in addition to emulsification, good mechanical behaviour is attained by the favourable enthalpic interaction between the EPBD segment and the CP ensuring its anchoring by dissolution into this complementary dissimilar component. In the case of the random copolymer (since this is not microphase separated and behaves like a homogeneous component), miscibility prediction is possible using thermodynamic theory to calculate spinodals as shown by Patterson *et al.*[32] and Su and Fried[33]. Using the Flory–Huggins theory the relevant equations are given by:

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

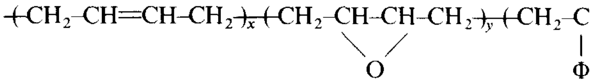
with $\chi_i=(\chi_{ij}+\chi_{ik}-\chi_{jk})/2$. In equation (2), m_i is the number of segments of homopolymer *i* and χ_{ij} is the interaction between segments *i* and *j*. [In the literature it is referred to as the Scott–Tompa interaction parameter[32] and is related to the Flory χ_{ij} by χ_{ij}(Scott–Tompa) = χ_{ij}(Flory)/m_i.] m_i is calculated using the expression:

$$m_i=\frac{M_i}{\mu}\frac{V_i}{V_r} \qquad (3)$$

where M_i is the number-average molecular weight of component *i*, and μ and V_i are the molecular weight and molar volume of the structural unit of polymer *i*, respectively; V_r is the reference volume equal to the molar volume of the smallest structural unit among the components in the ternary, in our case CPE(48) or PVC. Interaction parameters were calculated using the solubility parameter approach[30] and molar additivity constants given by Van Krevelen[34]. The solubility parameter of the copolymer was calculated assuming it to be the mean of the values of its monomers weighted as their volume fraction ϕ_i:

$$\delta_{cop}=\Sigma\delta_i\phi_i \qquad (4)$$

For ESBR a linear structure was assumed:



$$\text{-(-}CH_2\text{–}CH{=}CH\text{–}CH_2\text{-)-}_x\text{-(-}CH_2\text{–}\underbrace{CH\text{–}CH}_{O}\text{–}CH_2\text{-)-}_y\text{-(-}CH_2\text{–}\underset{\Phi}{\underset{|}{CH}}\text{-)-}_z$$

and in our case $\phi_x=0.513$, $\phi_y=0.230$ and $\phi_z=0.257$. Various pertinent data were taken from references 34 and 35 and calculation gave $\delta_{ESBR(40)}=9.19$ $(\mathrm{cal\,cm^{-3}})^{1/2}$. In the case of CP/ESBR the interaction should be exothermic and the interaction parameter should be in the range reported[27]. The values of interaction parameters employed to predict the spinodal for the ternary CPE(48)/ESBR(40)/PS are given in *Table 3*. Calculation of the segmental interaction parameter of EHPBD presents some difficulty since the basic structural unit should not be identified with the formula unit but with the 'minimum' structural unit that may crystallize. This was reported by Burfield[36] to consist of at least 10 carbon atoms. Hence our basic formula molecular weight should be increased by a factor of 2.5. The interaction parameter χ_{12}(Flory) using the melting temperature depression technique is calculated using the expression[27]:

$$\chi_{12}=-\frac{\Delta H_f^\circ V_{2u}}{RV_{1u}}(\text{slope}) \qquad (5)$$

Table 3 Molecular parameters used in the calculation of the spinodal for the CPE(48)/ESBR(40)/PS ternary at 25°C

Component	V_r (cm^3 mol^{-1})	d (g cm^{-3})	M_i	χ_{ij}^{seg}	δ_i (cal cm^{-3})$^{1/2}$
CPE(48) (1)	41.3	1.27	1160	-1.2×10^{-4}(1-2)	9.17
ESBR(40) (2)	66.0	1.02	2534	6.7×10^{-3}(2-3)	9.19
PS (3)	98.0	1.05	251	7.8×10^{-3}(1-3)	9.50

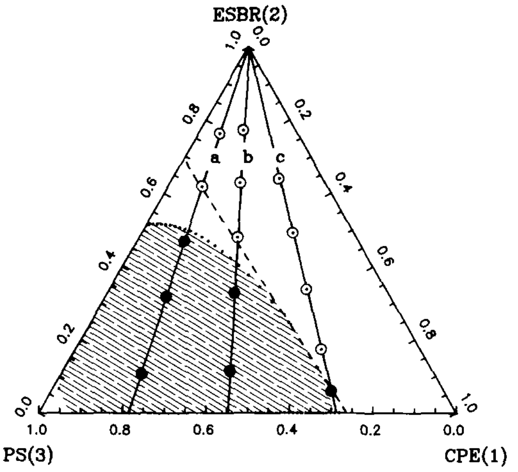


Figure 18 Phase diagram of ternary blends. Spinodal defines region of instability (shaded area). (○) Miscible and (●) immiscible or partially compatibilized compositions experimentally determined. Points on lines a, b, c correspond to ternaries with CPE(48)/PS ratio = 1/3, 1/1, 3/1, respectively. (--) Spinodal drawn with $\chi_{23}=0.0067$ (see text). Coordinates in volume fraction

where ΔH_f° is the molar heat of fusion of the crystalline component, V_u is the molar volume of the structural unit and subscripts 1 and 2 stand for the crystalline and amorphous component, respectively. If the molecular weight, and hence ΔH_f° (determined experimentally), is increased by a factor of 2.5, it does not follow that V_{1u} will be increased by the same factor, e.g. for a randomly jointed chain since $V=KM^{1/2}$, the molar volume will be increased by a factor of $(2.5)^{1/2}=1.58$. Taking this into account, the χ_{12} reported before[27] will increase in absolute value (−0.15). Application of equation (3) with $M_i=81\,000$ g mol^{-1} (ref. 27), $\mu=155$ g mol^{-1}, $V_i=100$ cm^3 mol^{-1} and $V_{rCPE(48)}=41.3$ cm^3 mol^{-1}, gives $\chi_{ESBR/CPE}^{seg}=-1.2\times10^{-4}$.

Other interaction parameters are expected to be positive since no specific forces are involved. These were calculated using equation (1). *Figure 18* shows the spinodal defining the region of instability and approximating the experimentally determined immiscibility gap. In *Figure 18* the χ_{23} parameter used was equal to 0.0045 to agree with the experiment. Taking into account the approximations involved in calculating solubility parameters, the prediction is satisfactory. *Figure 18* also predicts the influence of the CP/PS ratio on the miscibility of the ternary, i.e. increasing the CP/PS ratio favours miscibility. It should be noted that the spinodal is strongly dependent on the value of the positive interaction parameters (χ_{13} and χ_{23}). This has been pointed out by Su and Fried[33] in the case of a partially miscible blend compatibilized by a third component. A several-fold change of χ_{12} does not affect the miscibility gap as long as it is negative.

CONCLUSIONS

The compatibilizing ability of block copolymers is reduced as the structure changes from linear to branched. In our case the marginal difference between the ESB and $(ESB)_3$ may be attributed to strong enthalpic interactions masking the entropic factor determined by the molecular architecture.

Epoxidized styrene–butadiene block copolymers are versatile compatibilizers for binary blends consisting of an electron accepting polymer and a component miscible athermally (or enthalpically) with PS. Depending on the relative strengths of the interaction parameters among blend constituents, the composition of the immiscible binary blend may influence the compatibilizing efficiency of the copolymer.

Construction of spinodals is shown to be a useful procedure to predict miscibility behaviour in ternary systems involving homopolymers and/or random copolymers.

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