Compatibility of poly(vinyl chloride) with epoxidized copolymers of butadiene–styrene

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The compatibility of poly(vinyl chloride) (PVC) with epoxidized styrene–butadiene copolymers is examined at different levels of epoxidation. The copolymers modified were a random (SBR) containing 45 wt% styrene and a triblock (SBS) with 30 wt% bound styrene. Blends were examined in the complete composition range and the approximate levels of epoxidation to ensure blend miscibility were determined. Epoxidized SBS (ESBS) was more effective in miscibility compared with ESBR requiring a lesser degree of epoxidation (43 *versus* 46 mol%). Tensile properties of the ESBS/PVC blends showed the efficiency of ESBS as a polymeric plasticizer even at levels of epoxidation (*ca.* 35 mol%) where immiscibility sets in.

(Keywords: poly(vinyl chloride); miscibility of blends; polymeric plasticizer; epoxidized styrene–butadiene copolymers)

INTRODUCTION

Recent reviews in the area of polymer blends[1–3] indicate that an effective way to obtain miscible blends is to provide for suitable groups in the blend components leading to an exothermic enthalpy of mixing.

We have chosen this avenue in the past to obtain miscible systems utilizing the known hydrogen donor–acceptor capability of pairs such as the chlorinated polyhydrocarbons[4,5] and the cyclic ether[6] or epoxidized[7] polymers, respectively. Thus it was demonstrated that epoxidized natural rubber (ENR) forms miscible blends with poly(vinyl chloride) (PVC)[8] and chlorinated polyolefins[9,10]. For the same reason ENR was shown[11] to be miscible with polymeric resins (novolac) containing acidic hydroxyls. Realizing that epoxidation is a fairly straightforward polymer modification technique, it was applied to polybutadiene (PB) to assess the influence of microstructure and *MW* of the epoxidized PB on its effectiveness as a PVC polymeric plasticizer[12].

In the present work the miscibility behaviour of epoxidized styrene–butadiene random (ESBR) and triblock (ESBS) copolymers with PVC is examined, at various epoxidation levels in the complete blend composition range. The techniques used were dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.) and tensile testing.

This study had a larger scope than merely extending the list of miscible partners to such commodity plastics as PVC and chlorinated polyethylene (CPE); namely, had miscibility been attained, especially with ESBS, it would lead to compatibility studies of ternary blends[13,14] since ESBS, in principle, may serve as a compatibilizer for the incompatible PS/PVC pair[15].

EXPERIMENTAL

SBS copolymer had a 30 wt% (18 mol%) bound styrene content. G.p.c. analysis in toluene according to standard procedures[16] gave $\bar{M}_n = 5.3 \times 10^4\,\mathrm{g\,mol^{-1}}$. Thus the PS end-block was estimated to have $\bar{M}_{n,PS} = 8000\,\mathrm{g\,mol^{-1}}$.

The microstructure of the polybutadiene (PB) block was 31% *cis*-1,4, 33% *trans*-1,4 and 6 wt% vinyl. D.m.a. spectra suggest (see below) that it was a tapered block copolymer. SBR had 45 wt% bound styrene and $\bar{M}_v = 1.5 \times 10^5\,\mathrm{g\,mol^{-1}}$ from viscometry measurements in toluene. The butadiene microstructure was 15% *cis*-1,4, 33% *trans*-1,4 and 7 wt% vinyl. Both polymers were obtained from Aldrich, Europe. G.p.c. measurements in tetrahydrofuran gave, for PVC, $M_n = 2.7 \times 10^4\,\mathrm{g\,mol^{-1}}$ and $\bar{M}_w/\bar{M}_n = 1.9$.

Epoxidation was carried out in toluene solution (2 wt% solids) using an excess (130%) of the epoxidizing agent: an equimolar mixture of formic acid and hydrogen peroxide. The chemistry of the epoxidation reaction using the *in situ* formation of peroxyformic acid has been discussed before[17,18]. *Figure 1* gives the degree of SBR conversion with time at three temperatures, under the experimental conditions used. The reaction is favoured at higher temperatures. However, use of lower temperatures and low reactant concentrations minimizes undesirable side-reactions (oxirane ring opening and formation of higher cyclic products). Epoxidized polymers were characterized as before[12] using i.r., n.m.r. and elemental analysis. In this report the degree of epoxidation calculated

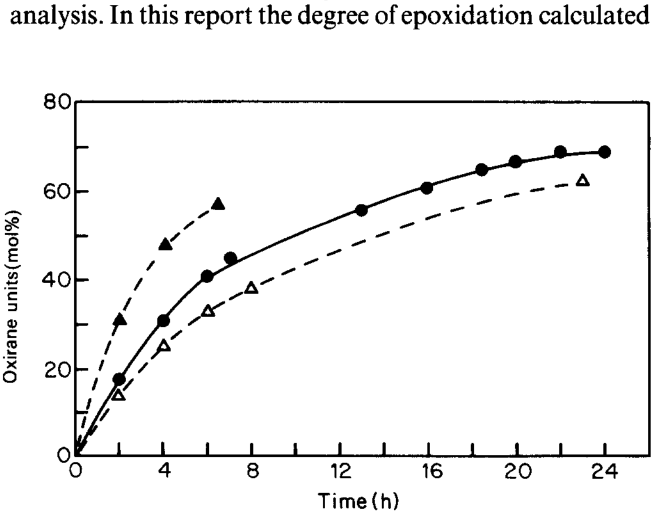

Figure 1 Degree of SBR conversion with time at 15°C (△), 20°C (●) and 30°C (▲) (mol% oxirane calculated on polybutadiene)

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on total polymeric material is given in parentheses following the epoxidized polymer while the numeral preceding PVC (designated as P) will denote the blend composition. Thus ESBS(34)/10P refers to a 10 wt% PVC blend with 34 mol% (based on total starting material) epoxidized SBS. Where obvious, P will be omitted.

Blends were prepared by dissolving the components in a common solvent (butanone-2), solvent removal and drying to constant weight at 50°C in a vacuum oven. A PVC stabilizer (2 wt% of dibutyltin dilaureate calculated on PVC) was added to the blend solution. Blends were compression moulded into films at 150–170°C (depending on composition) and ~15 MPa for 1 min and quenched at 0°C.

D.s.c. measurements were carried out in a nitrogen atmosphere using a Du Pont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was made with an indium standard and sample weight was ~15 mg. The heating cycle applied was: 25°C → −100°C → 150°C (1 min) → −100°C → 100°C. T_g was determined during the last heat scan.

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) and the procedure described before[8]. Specimen dimensions were $3.0 \times 0.25 \times 0.03$ cm^3. Tensile tests were performed according to ASTM D882 at 27°C, using a J.J. Tensile Tester type T5001 and film strips with dimensions $6.0 \times 1.20 \times 0.05$ cm^3. Data reported were obtained at a crosshead speed of 40 cm min^{-1}.

RESULTS AND DISCUSSION

Figure 2 gives the T_g variation of both copolymers with oxirane content (calculated on total copolymer). For the ESBS, T_g is taken as the main low-temperature relaxation associated with the PB phase; see d.m.a. spectra in *Figure 3*. Inspection of *Figure 2* indicates the relatively larger stiffening effect of the oxirane group in ESBS compared to ESBR. This is understandable considering the already stiffened SBR chain due to the phenyl groups. Thus the addition of the polar oxirane rings has an increased effect when introduced into the unsubstituted domains of SBS.

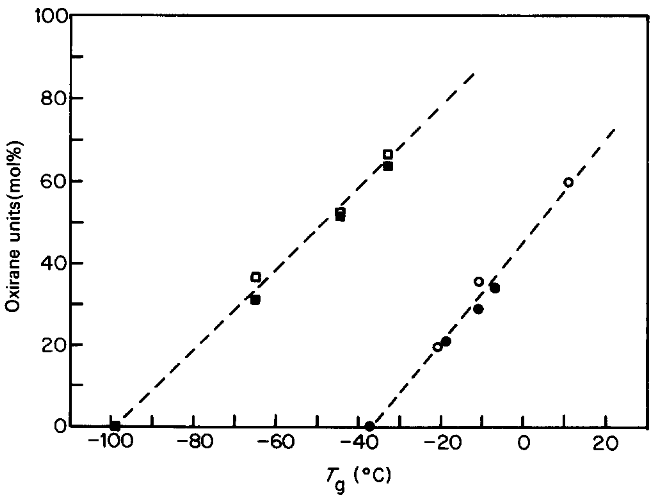

Figure 2 Effect of epoxidation on T_g of SBS (■, □) and SBR (●, ○). Filled symbols, n.m.r.; open symbols, elemental analysis. T_g obtained with d.s.c.

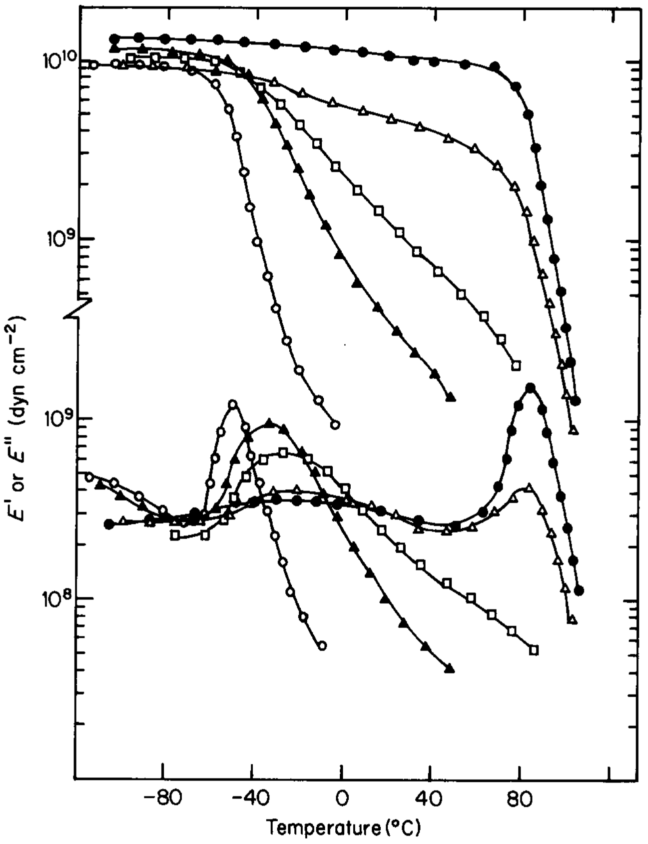

Figure 3 Thermomechanical spectra of ESBS(34)/PVC blends: (○) 100/0; (▲) 75/25; (□) 50/50; (△) 25/75; (●) 0/100

As a miscibility criterion only the composition dependence of the main relaxation associated with T_g was considered, as is the commonly accepted technique[19]. Other local-mode relaxations were also observed in the vicinity of −100°C (see *Figures 3, 4* and *7*), but these are ill defined and most probably are associated with the butadiene component of the copolymers[20].

Dynamic mechanical properties

The d.m.a. spectra of ESBS(34)/PVC and ESBS(43)/PVC blends are given in *Figures 3* and *4*, respectively. The lack of the PS relaxation in pure SBS leads us to believe that there is randomization of styrene in the thermoplastic elastomer. This is supported by the findings of Allen and coworkers[21], which show that (other molecular parameters being kept constant) randomization reduces and eliminates the PS relaxation as the block character is diminished. *Figure 3* indicates that blends are semicompatible at increased levels of ESBS(34). Even at the 50/50 composition, the PVC relaxation is hardly discernible. Increasing the degree of epoxidation to 43% gives miscible blends, as shown in *Figure 4*, where the regular shift with composition of a single blend T_g (T_{gb}) is evident; see also *Figure 5* where data with a higher level of epoxidation of ESBR(46) have also been included. At 43% epoxidation T_{gb} variation is below the weight-average line and is well represented by the Fox equation[22]. At higher epoxidation levels (46%), an S-shaped dependence on composition is observed at high ESBR levels. Similar findings were reported on PVC/ENR blends[8] and in miscible blends[23] where the existence of hydrogen bonding was established independently. It is suggested that these specific interactions may also be active in

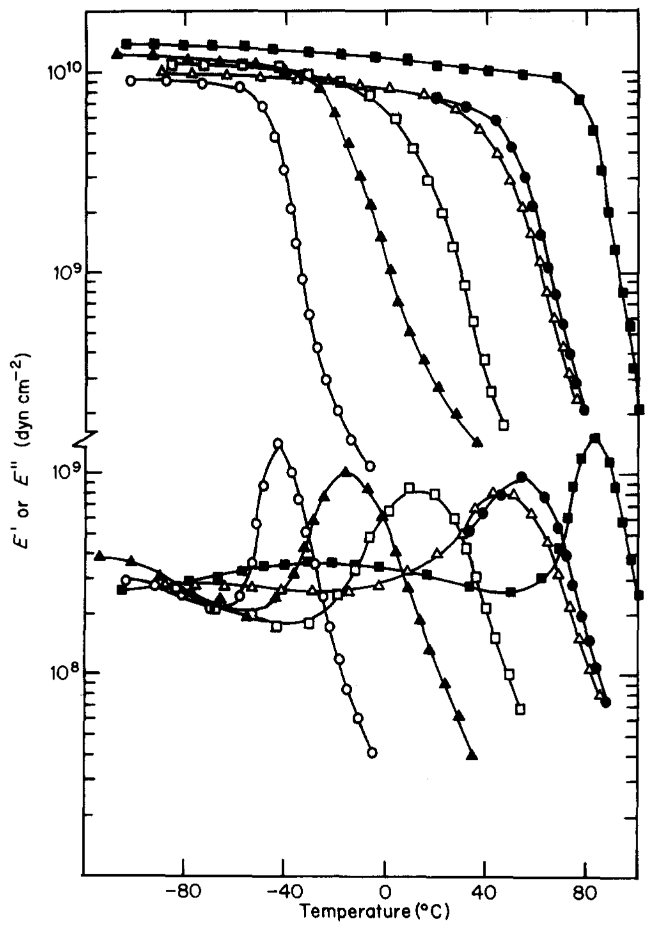

Figure 4 Thermomechanical spectra of ESBS(43)/PVC blends: (○) 100/0; (▲) 75/25; (□) 50/50; (△) 25/75; (●) 10/90; (■) 0/100

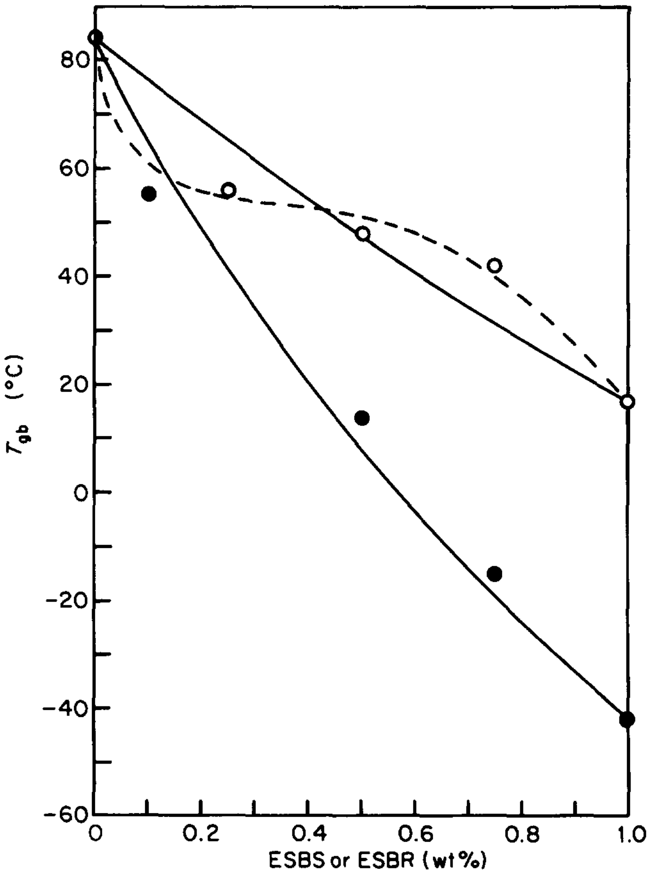

Figure 5 T_{gb} dependence on composition of blends: (●) ESBS(43)/PVC; (○) ESBR(46)/PVC. Data obtained with d.m.a. (E''_{max}). Full curves, Fox relationship; broken curves, Kwei relationship, $T_{gb}=(w_1T_{g1}+kw_2T_{g2})/(w_1+kw_2)+qw_1w_2$, with $k=0.11$, $q=110$

ESBR(46) blends, since it was reported that ENR itself may be hydrogen bonded[24]. This explains why the sigmoid T_{gb} variation appears at high concentrations of oxirane rings.

The results for ESBS/PVC blends are summarized in *Figures 6* and *7*. At the 38% level of epoxidation blends are incompatible and the two component peaks are discernible. This is further supported from the sigmoid variation of the dynamic modulus of the blends, indicating a two-phase system (see *Figure 6*). However, the spectra do indicate considerable interaction between components; consider the significant shift of the PVC relaxation to lower temperatures. Increase of the degree of SBR epoxidation to 46% yields a miscible blend (see *Figure 7*).

Consideration of the miscibility behaviour of ESBS and ESBR with PVC suggests that ESBS is more miscible at comparable degrees of epoxidation. This may be the result of a higher availability of the oxirane ring to interact with PVC when not interspersed among bulky phenyl groups (as is the case for ESBR). Our findings[12] also indicate that at comparable degrees of epoxidation EPB is less miscible with PVC than ESBS or ESBR. This may be explained qualitatively by invoking copolymer–copolymer miscibility theory[2,52] and the mutual repulsion between the styrene unit and an adjacent oxirane (Ox) ring in ESBR or ESBS (note that there is considerable randomization of styrene in SBS). This repulsion is expected in analogy to styrene–acrylonitrile units in

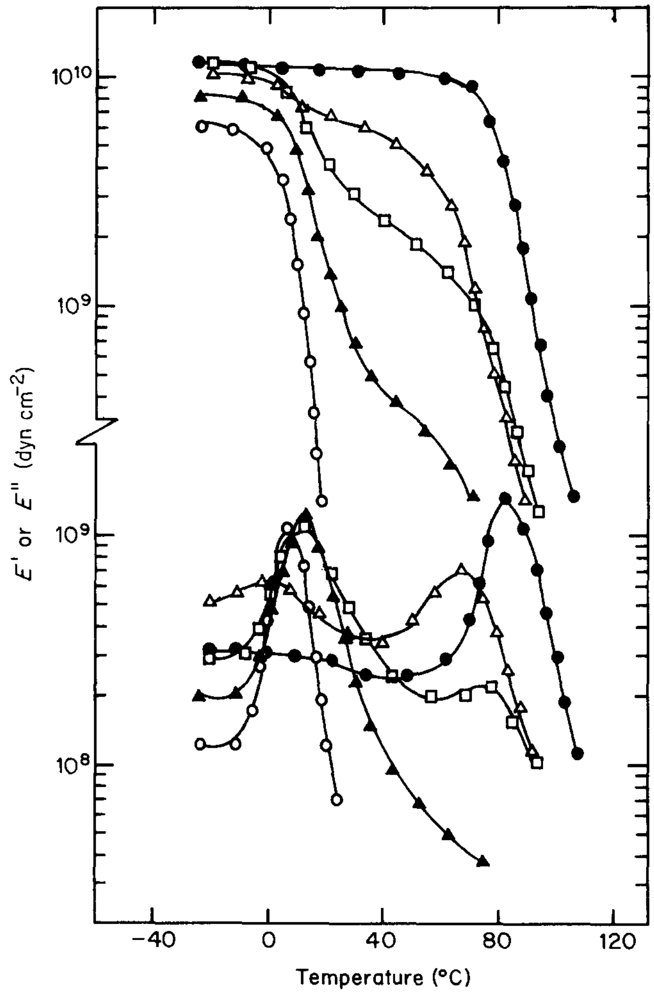

Figure 6 Thermomechanical spectra of ESBR(38)/PVC blends: (○) 100/0; (▲) 75/25; (□) 50/50; (△) 25/75; (●) 0/100

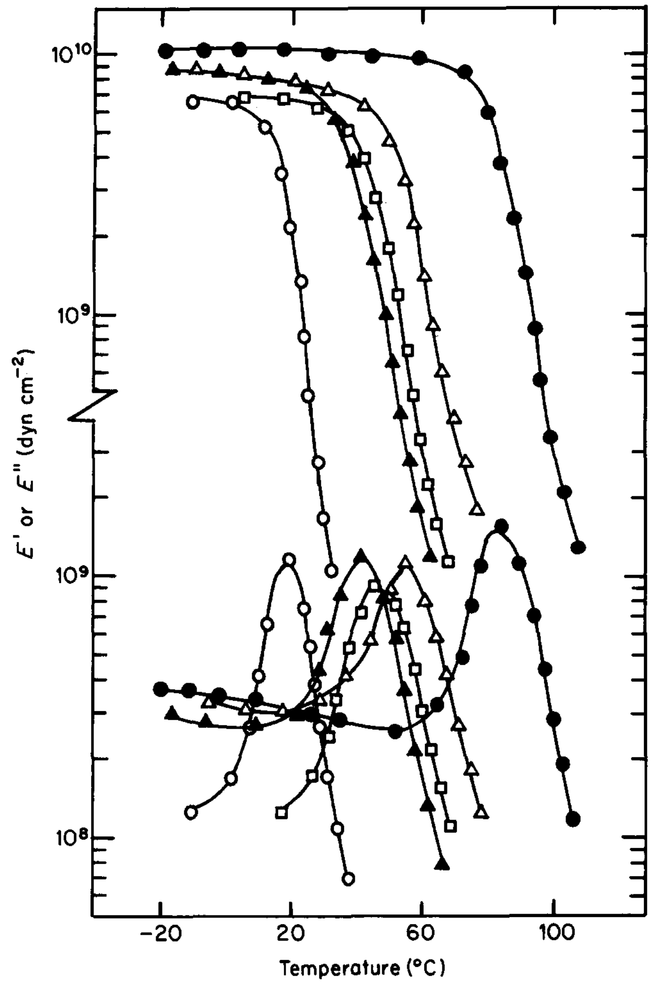

Figure 7 Thermomechanical spectra of ESBR(46)/PVC blends: (○) 100/0; (▲) 75/25; (□) 50/50; (△) 25/75; (●) 0/100

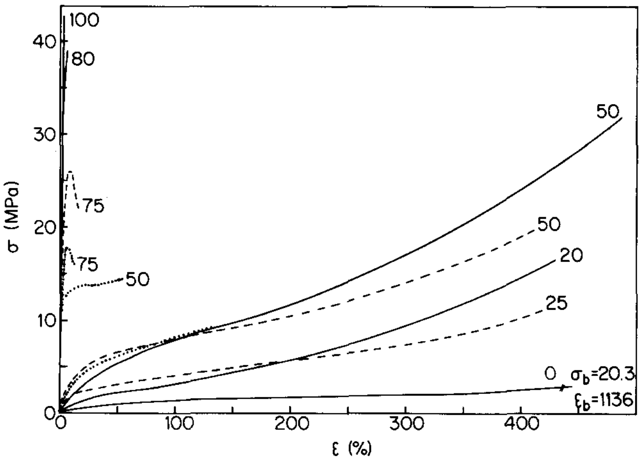

Figure 8 Stress–strain properties of blends: (···) ESBR(38)/PVC; (– – –) ESBS(34)/PVC; (——) ESBS(49)/PVC. Numbers next to curves indicate PVC percentage

the corresponding copolymer (SAN) where a positive segmental interaction parameter was determined[26], $\chi_{AN/S} = 0.17$.

Considering the similar proton-accepting character of the oxirane group, $\chi_{Ox/S}$ should also be positive and more so than $\chi_{Ox/B}$. This should induce mixing of ESBR (or ESBS) with PVC more so than mixing of EPB. It is pertinent to note that the styrene group exerts a stronger influence on the oxirane group compared to the unsubstituted hydrocarbon chain[27]. Quantitative application[10] of the copolymer–copolymer miscibility theory[2,25] to test the miscibility prediction was not made because of the complicated microstructure of ESBR. Another reason dissuading us from doing so was the possibility that specific forces were active in the ESBR/PVC blends.

Tensile properties

These data are given in *Figure 8* for some ESBS/PVC and ESBR/PVC blends at two levels of epoxidation. The results indicate the superior properties imparted to plasticized PVC by ESBS compared to ESBR (at high rubber levels). This can be attributed to the self-reinforcing character of the ESBS, which is retained in the blends. In general, increasing the degree of epoxidation is expected to increase strength and reduce ultimate elongation. This is the consequence of decreasing chain flexibility with the introduction of stiff and polar oxirane units. For effective PVC plasticization, ESBS and ESBR should be used at levels comparable to those used in polymeric plasticizers[28]. It is important and of practical consequence to note that, though ESBS(34)/PVC blends are not miscible on the basis of the d.m.a. results, their tensile properties are quite satisfactory and comparable to miscible compositions.

CONCLUSIONS

SBS and SBR epoxidized at levels higher than ~40 mol% give miscible blends with PVC.

ESBS gives blends with excellent tensile properties and can serve as a polymeric plasticizer even when partially miscible with PVC.

Phenyl substitution at moderate levels seems to enhance the miscibility behaviour of epoxidized polyhydrocarbons with PVC.

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