Compatibilization of poly(vinyl chloride)/ polystyrene blends with epoxidized styrene–butadiene–styrene block copolymers

John K. Kallitsis and Nikos K. Kalfoglou*
Department of Chemistry, University of Patra, 26110 Patra, Greece

(*Received 19 January 1989; revised 2 March 1989; accepted 9 March 1989*)

The effectiveness of epoxidized styrene–butadiene–styrene (ESBS) block copolymer as a polymeric compatibilizer for the incompatible polystyrene/poly(vinyl chloride) (PS/PVC) blend was investigated. ESBS at two epoxidation levels (34 and 49 mol% oxirane units) was used and the study covered mainly compositions with up to 30 wt% PS content in the ternary blends. The results support the view that ESBS can serve as a compatibilizer at these levels of epoxidation and when added in amounts in excess of ~5 wt%. Ternary blends may also have good elongation properties due to the thermoplastic elastomer character of ESBS.

(Keywords: compatibilization of blends; epoxidized styrene–butadiene–styrene block copolymers; miscible ternary blends)

INTRODUCTION

The study of ternary blends becomes increasingly important[1–3] with the incentive to discover new polymeric materials and/or develop practical and economic methods for recycling commodity plastics[4,5].

In past work we have demonstrated that compatible polymer blends can be obtained by combining poly(vinyl chloride) (PVC)[6], chlorinated polypropylene[7] or chlorinated polyethylene[8] with epoxidized polyisoprene (natural rubber) (ENR). Similar results were obtained with epoxidized polybutadiene (EPB) and in that work[9] the influence of *MW* and microstructure of EPB was examined. In the above systems miscibility was attributed to donor–acceptor[10] and/or dipole–dipole interactions[11]. In a more recent study[12] the miscibility behaviour of ENR with various phenolic resins was interpreted along similar lines.

This work has been extended to include the miscibility of PVC with epoxidized styrene–butadiene random (ESBR) and triblock (ESBS) copolymers[13]. Thus it was shown that both ESBR and ESBS epoxidized to a sufficiently high degree (above ~40 mol%) give miscible blends. At lower degrees of epoxidation, semicompatible blends with good tensile properties are obtained.

The present study explores the possibility of further extending the compatibilizing action of ESBS by adding polystyrene (PS) to the binary blend ESBS/PVC to obtain a ternary system. It was expected that the non-polar PS block of ESBS would mix with the added PS homopolymer while the EPB block would interact with the PVC component. Thus ESBS would serve as a compatibilizer to the incompatible PVC/PS pair. An analogy to the present system may be found in the work of Teyssié and coworkers, recently reviewed[14,15], who used PS–PMMA (poly(methyl methacrylate)) or PS–PCL (polycaprolactone) block copolymers to compatibilize PVC/PS blends. These and other references[16,17] summarize the salient parameters found to determine compatibility in ternary systems involving copolymers. It should be clarified that to obtain useful mechanical properties miscibility at the molecular level is not always required or sometimes even desirable. What is frequently of importance is the size of the dispersed phase determined by the action of the compatibilizer (ESBS in this study).

Blends were examined in the solid state at the optimum degree of epoxidation of SBS[13]. Other parameters taken into account were the PS/ESBS ratio and the *MW* of the PS homopolymer, since they affect the degree of PS miscibility into the PS block[17]. It was assumed that epoxidation would only slightly affect the mutual solubility of PS/ESBS.

Indeed, it is rational to expect that epoxidation would increase the polar character of the polybutadiene block of the SBS, thus decreasing its slight miscibility[18] with the polystyrene homopolymer (also a polyhydrocarbon). Therefore, the only avenue for the polystyrene solubilization would be by incorporation into the PS block of the ESBS to be examined in this work.

Though the aim of the study originally was to obtain miscible ternary blends, during the course of the investigation it was discovered that useful tensile properties were obtained even for partially miscible compositions where a lesser amount of ESBS was used. In fact, from the cost/performance viewpoint, these would be of more interest.

The techniques used were dynamic mechanical analysis (d.m.a.), tensile testing to assess large-deformation behaviour as well as optical (phase-contrast) and scanning electron microscopy (SEM).

EXPERIMENTAL

SBS was the same as used before[13] and was obtained from Aldrich, Europe. It had a 30 wt% bound styrene content, a $\bar{M}_n = 5.3 \times 10^4\,\mathrm{g\,mol^{-1}}$ and a nominal block *MW* of PS, $\bar{M}_{n,PS} = 8000\,\mathrm{g\,mol^{-1}}$. Because of tapering the actual *MW* of the PS block should be less. PS samples

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* To whom correspondence should be addressed

0032-3861/89/122258-07$03.00

of different *MW* were prepared by bulk polymerization using benzoyl peroxide. Based on property evaluation of PS/SBS blends, it was determined that the sample with the highest *MW* to be used in subsequent experimentation had an $\bar{M}_w = 6000\,g\,mol^{-1}$. (This is coded as PS6.) PVC was obtained from Aldrich, Europe. Its $\bar{M}_n = 2.7 \times 10^4\,g\,mol^{-1}$ and $\bar{M}_w/\bar{M}_n = 1.9$. Epoxidation of SBS was carried out as described before[13] and in this study SBS with 34 and 49 mol% oxirane units (based on total moles of starting material) was used. These epoxidized SBS will be designated as ESBS(34) and ESBS(49), respectively.

Blends were prepared by dissolving in a common solvent, tetrahydrofuran (THF), slow solvent removal in Teflon-coated pans 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. A blend series (with ESBS(34)) was also tested with cast films subsequently compression moulded at 150–170°C and ~15 MPa, followed with quenching at 0°C. No essential difference in their mechanical properties was detected.

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[6]. Specimen dimensions were $3.0 \times 0.20 \times 0.015\,cm^3$. Tensile tests were performed according to ASTM D882 at 27°C using a J.J. Tensile Tester type T5001 and film strips with dimensions $6.0 \times 0.7 \times 0.03\,cm^3$. Data reported were obtained at a crosshead speed of $40\,cm\,min^{-1}$.

Thin films deposited on slides were examined under a phase-contrast microscope (Orthoplan Leitz) with oil immersion ($n_e^{23} = 1.5180$) in bright field. For scanning electron microscopy the SEM used was a JEOL model JSM-35. Thicker specimens were prepared by solution casting. These were fractured at near-liquid-nitrogen temperatures.

RESULTS AND DISCUSSION

Mechanical properties of binary blends

The results for binary blends of the components constituting the ternary system PS–ESBS–PVC will be described first.

PS6/SBS blends. It is well established by theory[17] and experiment[19,20] that, to obtain a miscible PS/SBS blend, the homopolymer *MW* should not exceed the *MW* of the PS block of the SBS copolymer. In this case the weight fraction of the homopolymer dissolved was reported[19] to be ~0.30. Any excess is separated out as a distinct phase. To optimize the PS/SBS ratio we based our judgement on tensile properties of the blends and to a lesser extent on the visual observation of film clarity. The former (see *Figure 1*) indicate that up to 0.30 weight fraction (wt fr.) of PS can be added to the SBS component without significant impairment of the blend's ultimate properties and before turbidity sets in. D.m.a. results were not useful in this respect. The thermomechanical spectra indicate the appearance of a distinct PS relaxation (increasing in strength with the amount of added homopolymer). No shift of the main relaxations, of PB (at −85°C) and of PS (at 90°C), were observed. Once the maximum ratio of PS6/SBS was established, we proceeded to examine the PS6/ESBS(49) blends.

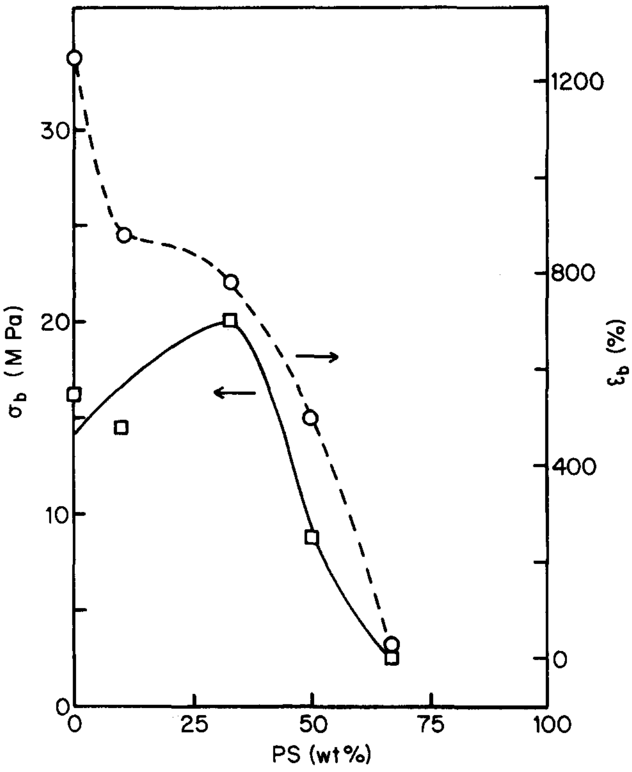

Figure 1 Ultimate properties of PS6/SBS blends

PS6/ESBS(49) blends. Previous work[13] established that, to obtain a miscible ESBS/PVC blend, the required degree of epoxidation is ~40 mol%. The d.m.a. data for the PS6/ESBS(49) blends are summarized in *Figure 2*, where a small upward shift of the epoxidized PB block relaxation is indicated: $\Delta T_g \simeq 9$°C for the 33/67 and 50/50 compositions. This, combined with the increase in the width of the PS relaxation (compared with PS6/SBS blends), may be interpreted to mean a limited solubility between the two components. Given the previous results, this should be traced to the SBS modification. In principle, the slight miscibility may be explained by invoking the 'repulsion effect'[21] between the phenyl groups and the oxirane units introduced into the SBS. More drastic effects are observed in the modulus E' variation, where the stiffening effect of the added homopolymer is apparent (see *Figure 2*).

Of more practical consequence is the tensile behaviour of the blends given in *Figures 3* and *4*. Judging from the ultimate properties in *Figure 3*, the 30/70 composition combines the highest amount of added PS with no loss of tensile strength. The σ–ε curves in *Figure 4* show the characteristic plastic yield at increased levels of PS (>0.30 wt fr.). At these levels it may well be that the tensile behaviour is determined by the PS separated out in the matrix. These findings are in substantial agreement with the findings of Shen and coworkers[19]. It is of relevance that up to the 33/67 composition no stress-whitening was observed during deformation.

ESBS(49)/PVC blends. This system has been described before[13]. At increased levels of epoxidation (≥43 mol%) it is miscible with PVC at all compositions. At lower degrees of epoxidation (34 mol%) miscibility was observed at increased levels of ESBS (>0.50 wt fr.). Good tensile properties were determined at all compositions at both degrees of epoxidation.

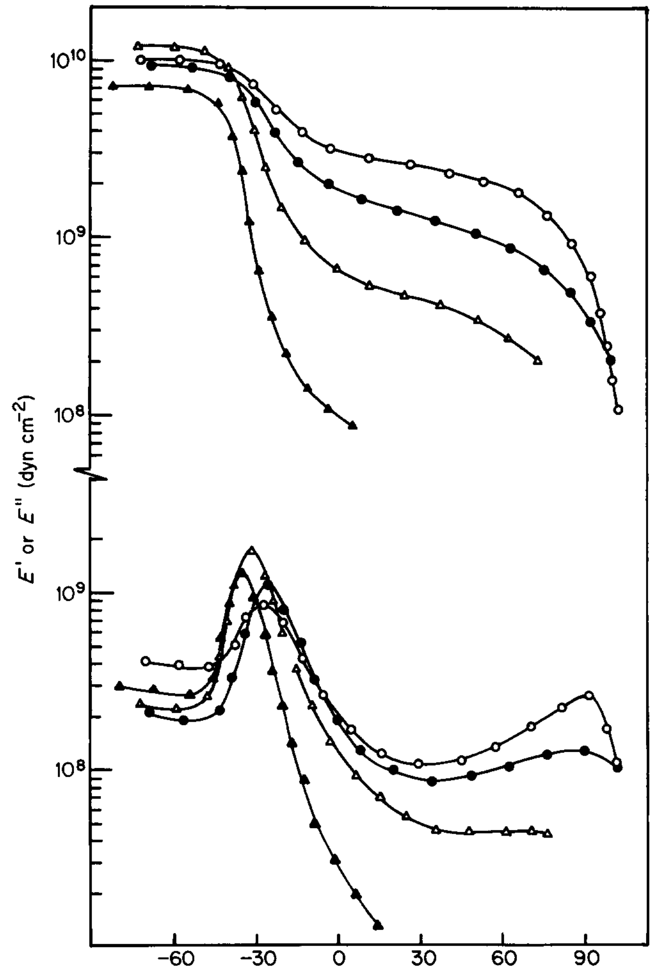

Figure 2 Thermomechanical spectra of PS6/ESBS(49) blends: (▲) 0/100; (△) 18/82; (●) 33/67; (○) 50/50

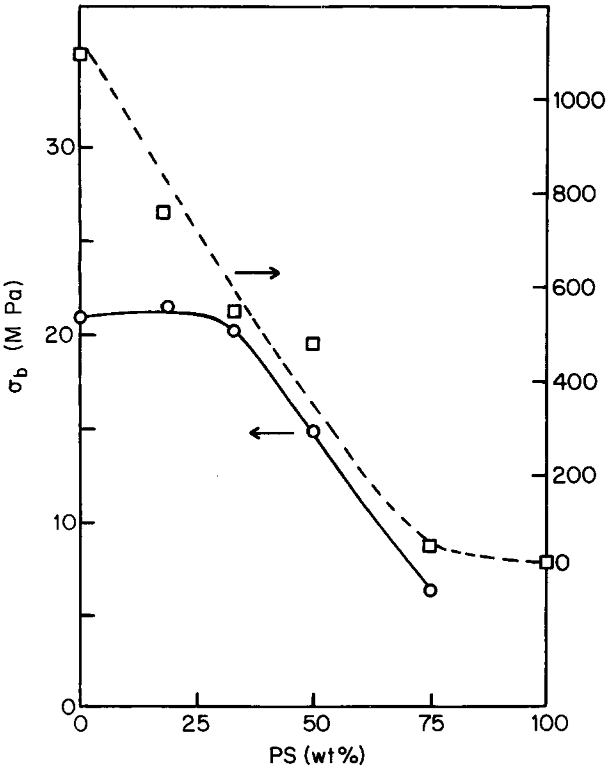

Figure 3 Ultimate properties of PS6/ESBS(49) blends

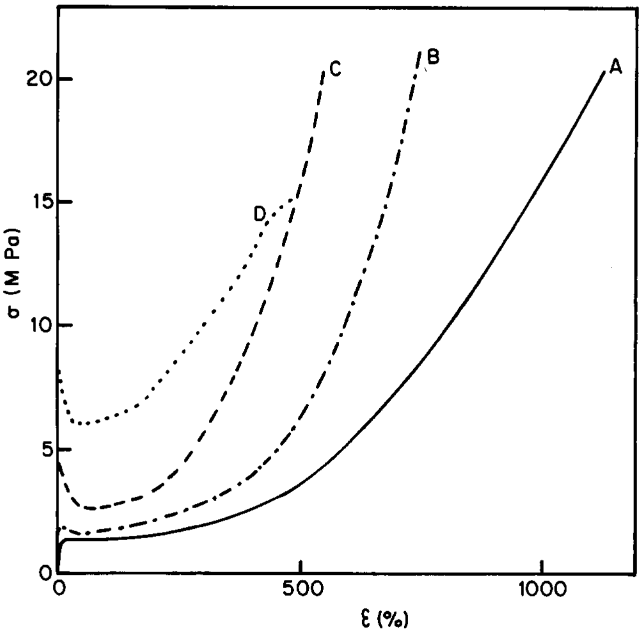

Figure 4 Stress–strain properties of PS6/ESBS(49) blends: (A) 0/100; (B) 18/82; (C) 33/67; (D) 50/50

Mechanical properties of ternary PS6/ESBS(49)/PVC blends

In this ternary, compatibilization of the incompatible PS6/PVC blend may in principle be attained by inclusion of the PS homopolymer into the PS block and by dissolution of the PVC by the ESBS epoxidized to a sufficient degree. A difficulty inherent in the analysis of the d.m.a. spectra is the proximity of the main PVC and PS6 relaxations, at 70°C and 90°C, respectively. Another limitation is the low strength of the PS relaxation at low levels of homopolymer (<20 wt%). Thus T_{gb} prediction using available relationships suitable for miscible ternary blends cannot be made. To ascertain compatibilization, tensile properties and morphological examination will be relied on. The following compositions (written in the same sequence of components—see above) were studied.

30/60/10, 20/40/20 and 10/20/70 blends. In these blends the PS6/ESBS(49) ratio was 0.5—the optimum practical value. The d.m.a. spectra are given in *Figure 5*. The composition with the highest PS amount shows two distinct relaxations, one due to PS (block plus added PS) at ~ 96°C and the low-temperature transition due to the miscible ESBS(49)/PVC binary blend at ~ -12°C. Decreasing the amount of PS6 gives a single relaxation changing almost linearly with the content of PVC. This is a consequence of the weak PS relaxation and its proximity to the PVC α transition.

Tensile properties are summarized in *Figures 6* and *7* as a function of composition. In *Figure 6* the ultimate properties of the incompatible PS6/PVC blend are included for comparison. It is seen that, contrary to the poor properties of the binary blend, the ternary system has improved tensile and ultimate properties at all compositions except at very high PVC contents (>70 wt%). *Figure 6* shows modulus synergism at the 10/20/70 composition. The phenomenon has been observed before in blends where an increase of packing due to strong interactions[22] or good adhesion[23] was obtained. The nominal stress–strain curves in *Figure 7* indicate yielding

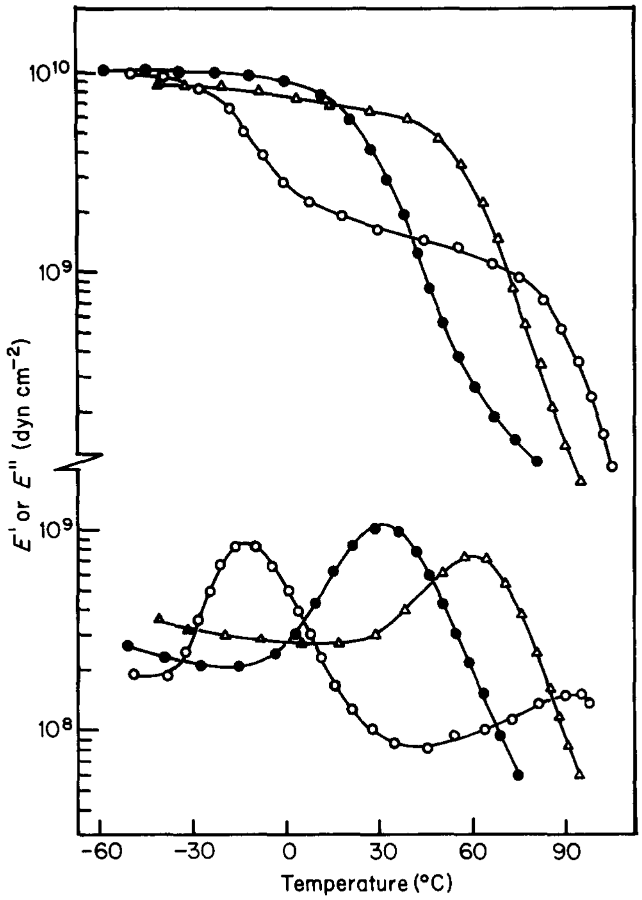

Figure 5 Thermomechanical spectra of PS6/ESBS(49)/PVC blends: (○) 30/60/10; (●) 20/40/40; (△) 10/20/70

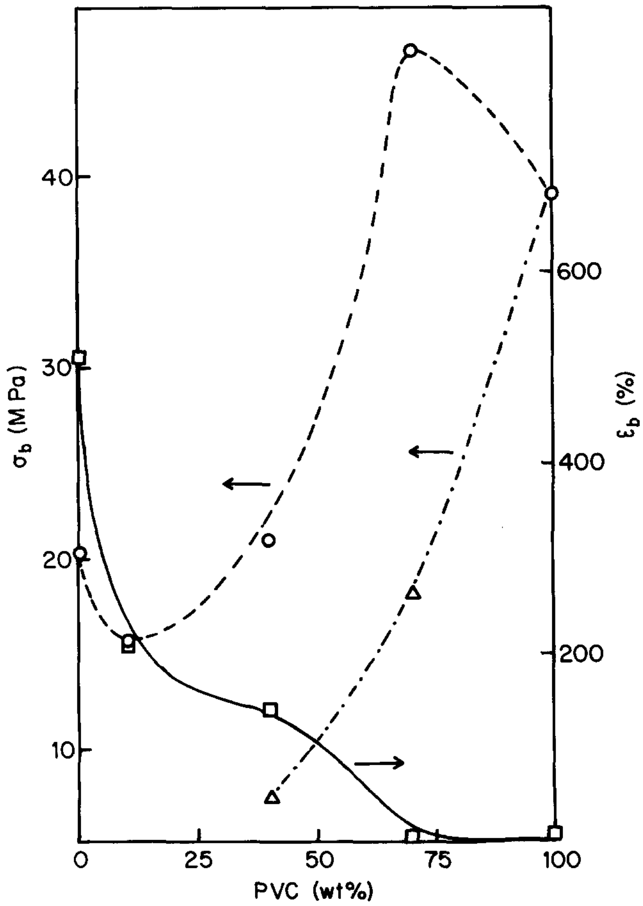

Figure 6 Ultimate properties of PS6/ESBS(49)/PVC with PS6/ESBS(49) 1:2: (△) binary PS6/PVC blends. For the binary only σ_b data are recorded because of high brittleness

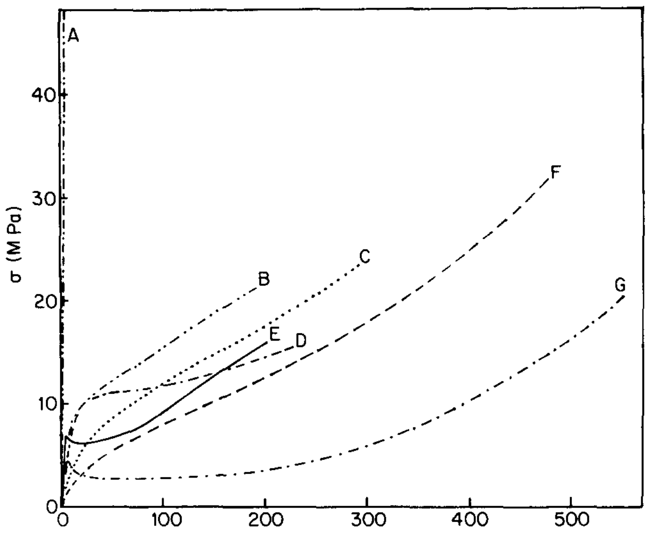

Figure 7 Stress–strain properties of PS6/ESBS(49)/PVC blends and their comparison with those of binary blends: (A) 10/20/70; (B) 20/40/40; (C) 10/45/45; (D) 40/30/30; (E) 30/60/10; (F) 0/50/50; (G) 33/67/0

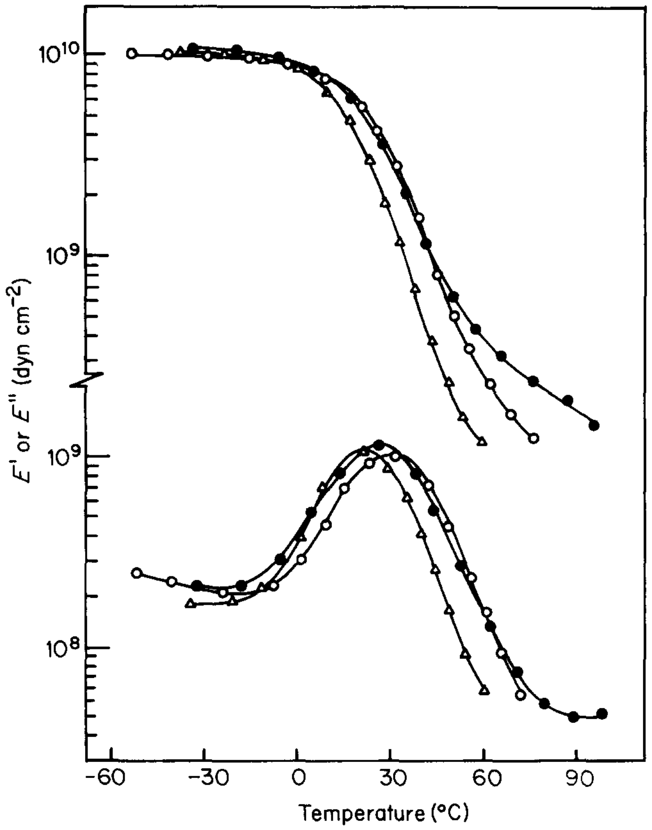

Figure 8 Thermomechanical spectra of PS6/ESBS(49)/PVC blends: (△) 10/45/45; (○) 20/40/40; (●) 40/30/30

at high PS6 compositions, good elongation at intermediate compositions and plastic response at the highest PVC level.

Compositions 10/45/45, 20/40/40 and 40/30/30. In these the ESBS(49)/PVC ratio is 1:1. The d.m.a. data in *Figure 8* indicate a gradual increase of T_{g_b} with decreasing ESBS(49) component in the blend. At high PS6 contents there is evidence of this component separating out in the matrix; see modulus differentiation at the 40/30/30 composition. Ultimate tensile properties are given in

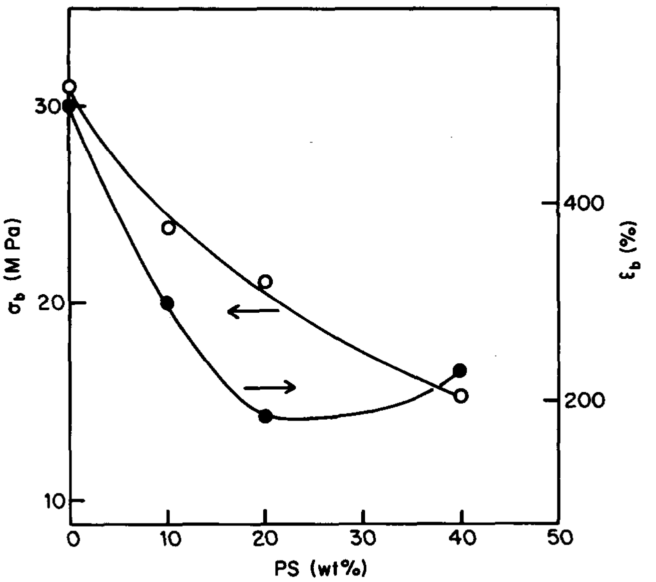

Figure 9 Ultimate properties of PS/ESBS(49)/PVC blends with ESBS(49)/PVC 1:1

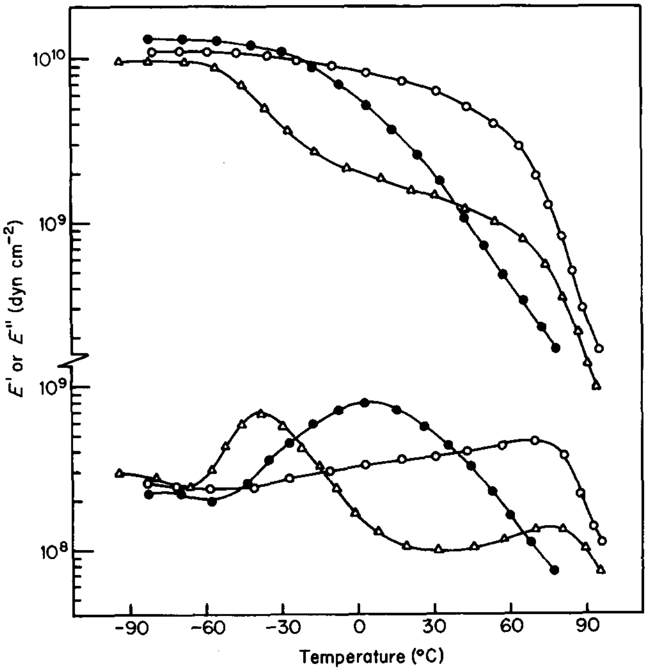

Figure 10 Thermomechanical spectra of PS6/ESBS(34)/PVC blends: (△) 30/60/10; (●) 20/40/40; (○) 10/20/70

Figure 9, where it is seen that good ultimate properties are obtained. It is of significance that ultimate elongation ε_b is stabilized even for blends with considerable PS6 content (20–40 wt%). The nominal stress–strain curves in *Figure 7* show elastic behaviour except for the 40/30/30 composition, where plastic behaviour sets in.

Mechanical properties of ternary PS(6)/ESBS(34)/PVC blends

In a previous communication it was reported[13] that, depending on blend composition, ESBS(34)/PVC are semicompatible. Thus it was of interest to examine whether useful ternary blends may be obtained using an SBS with this smaller degree of epoxidation. This product has a lower T_g and hence a higher flexibilizing action.

Ternary blends of PS6/ESBS(34)/PVC examined had the following compositions: 30/60/10, 20/40/40 and 10/20/70. Thus they can be compared with blends in the first case above. The d.m.a. spectra in *Figure 10* are distinctly different compared to the ESBS(49)-containing blends; compare with *Figure 5*. The dominant feature in the present spectra is the enhanced width of the relaxations characteristic of blend heterogeneity. As before, the PS6 relaxation is discernible in the 30/60/10 composition. Though the blends are semicompatible, ultimate properties in *Figure 11* indicate that ESBS(34) can be used as an effective compatibilizer in PS6/PVC blends with up to 50 wt% PVC; compare properties of the binary PS6/PVC with those of the ternary. At high PVC contents (70 wt%), the blends have poor elongation properties (ε_b) since it was shown[13] that at low ESBS(34) levels its blend with PVC is incompatible.

It should be added that the degree of epoxidation as a variable controlling the degree of polarity of the compatibilizer (hence its degree of interaction with the PVC component) is of particular importance. Thus it was demonstrated[24] that increased interactions may lead to an undesirable loss of the compatibilizer into the PVC phase while moderate interactions could in principle lead to a lower miscibility but an adequate concentration at the interphase to achieve good adhesion.

In order to examine the compatibilizing action of ESBS(49) at small concentrations, several compositions of ternary blends were tested for their ultimate properties (see *Figure 12*). Elongation (ε_b) was small—characteristic of a brittle plastic blend. This may be attributed to the low level of the rubbery component, which, though promoting good adhesion, loses its identity by dissolution into the PVC phase. At these ESBS(49) contents PVC is not sufficiently flexibilized. These blends show a modulus synergism. This has been also observed[15] in other compatibilized blends containing a tapered block copolymer with relatively short blocks, as in the present case.

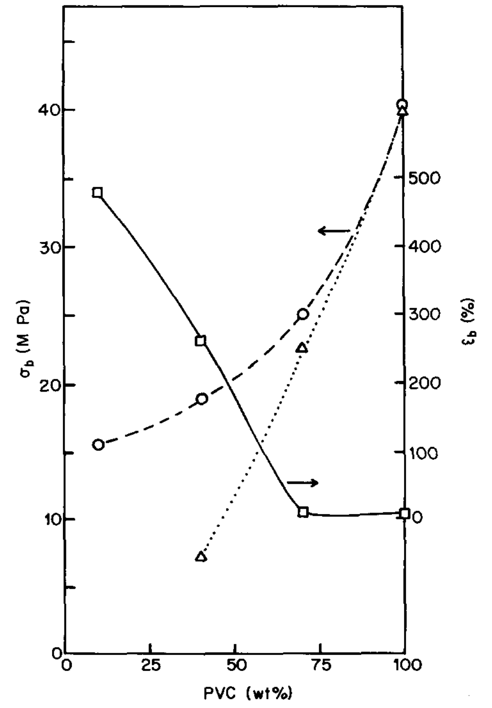

Figure 11 Ultimate properties of PS6/ESBS(34)/PVC blends: (△) binary PS6/PVC blends

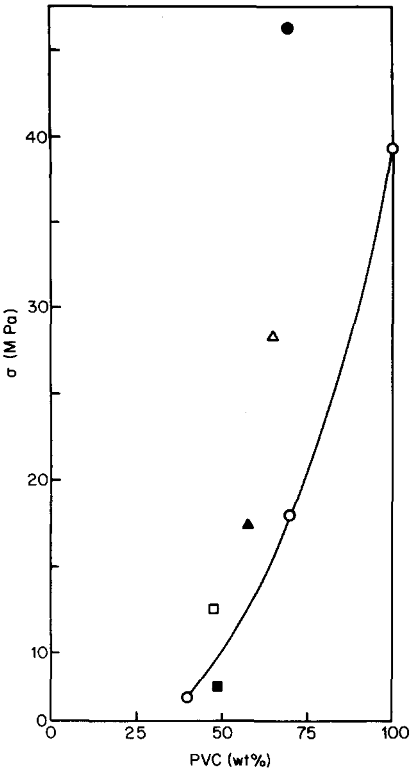

Figure 12 Ultimate strength of ternary blends at low ESBS(49) contents: (■) 49/2/49; (□) 47.5/5/47.5; (▲) 28/14/58; (△) 30/5/65; (●) 10/20/70; (○) binary PS6/PVC blends

However, the results[23] refer to a binary blend (PS/low-density polyethylene) involving non-polar interactions.

Morphology

The results on morphology are given in *Figures 13* and *14* for phase-contrast and SEM, respectively. In *Figure 13*, given[25] the refractive indices of PVC ($n_D = 1.539$) and PS ($n_D = 1.591$), at positive phase contrast, dark areas should correspond to the polystyrene phase. Both the PS6/PVC (*Figure 13a*) and PS/ESBS(49) (*Figure 13b*) show a coarse mosaic structure. In the nearly compatibilized PS6/ESBS(34)/PVC blend (*Figure 13c*) a finer dispersion is obtained and more so when ESBS(49) is used in increasing amounts (see *Figures 13d* and *13e*). In *Figure 13f*, addition of increased amounts of PS6 leads to a coarser morphology.

More direct and revealing information is obtained with the SEM technique, which proved invaluable in investigating blend compatibilization[24]. In *Figure 14a* the cryofracture surface of PS6/PVC displays the characteristic smooth cavities of poorly adhering components of an incompatible blend. Addition of 5 wt% ESBS(49) (see *Figure 14b*) drastically reduces the size of the dispersed phases by reducing interfacial tension. Further increase of the compatibilizer (20 wt%) (see *Figure 14c*) gives a blend exhibiting the characteristic ductile fracture surface. This is caused by strong interface adhesion—the result of increased miscibility between PS6 and PVC by means of the compatibilizing action of ESBS(49).

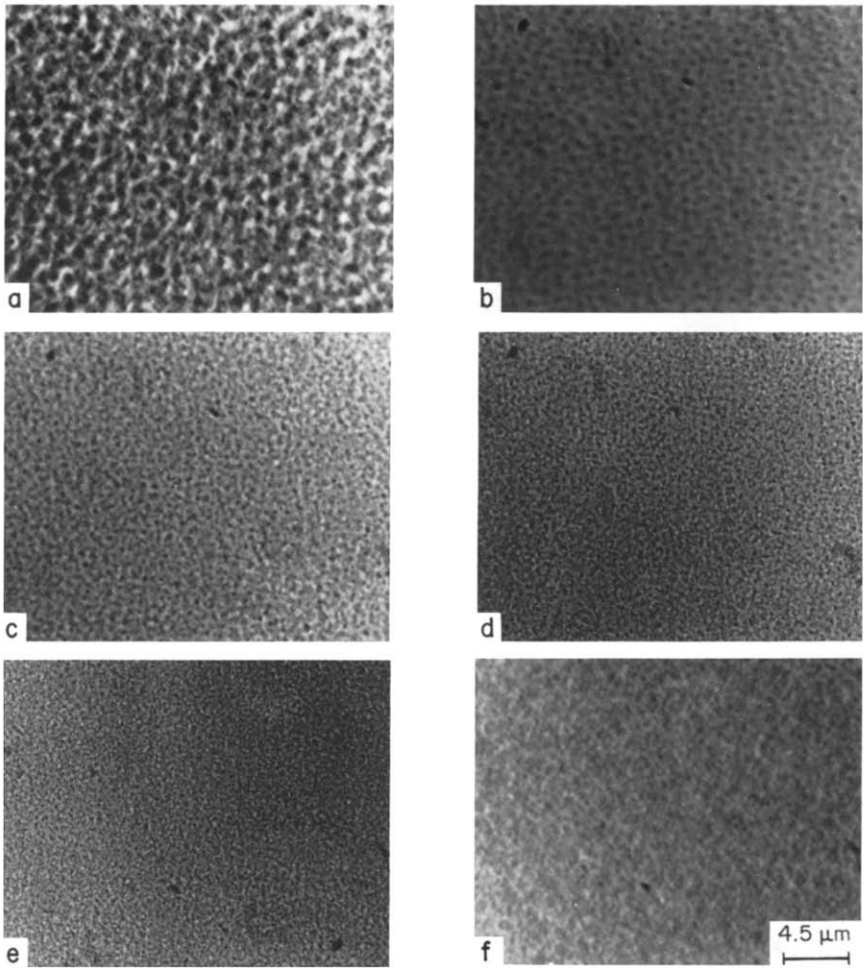

Figure 13 Phase-contrast micrographs of blends: (a) PS6/PVC, 60/40; (b) PS6/ESBS(49), 18/82; (c) PS6/ESBS(34)/PVC, 20/40/40; (d) PS6/ESBS(49)/PVC, 10/20/70; (e) PS6/ESBS(49)/PVC, 10/45/45; (f) PS6/ESBS(49)/PVC, 40/30/30

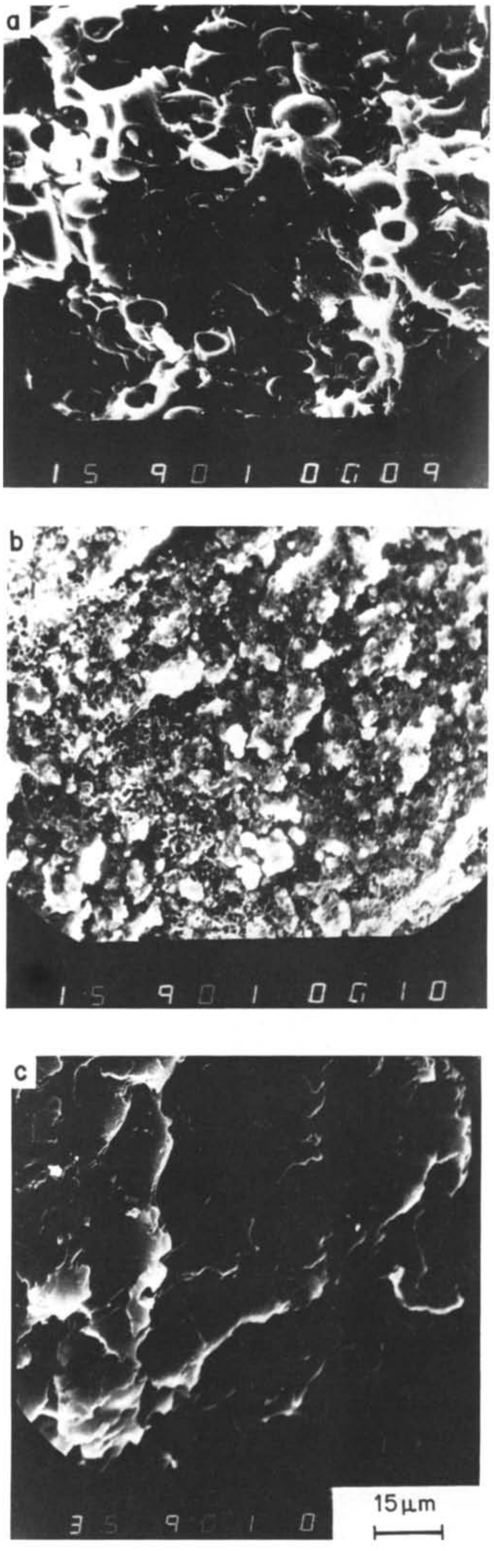

Figure 14 SEM micrographs of fracture surfaces of PS/ESBS(49)/PVC blends: (a) 30/0/70; (b) 30/5/65; (c) 40/20/40

CONCLUSIONS

Epoxidized SBS block copolymers can serve as an effective and inexpensive compatibilizer for PS/PVC blends and possibly other PS/(proton-donating polymer) blends.

Mechanical and morphological results are in essential agreement with similar ternary blends; however, in the present case the compatibilizer is readily available and at higher levels imparts to the blends the useful tensile properties of a thermoplastic rubber.

Compatibilization is dependent on the degree of PB epoxidation in SBS, and at reduced degrees of epoxidation miscible ternary blends may be obtained at moderate levels of PVC.

Work is in progress to optimize the compatibilizing action by examining molecular parameters such as copolymer architecture, PS block length and the intensity of interface interactions.

ACKNOWLEDGEMENTS

This work was supported in part by the Ministry of Industry, Energy and Technology, the General Secretariat of Research and Technology. Thanks are also due to Mr L. Kombotiatis of the Air Force Center for Technical Applications and Development for the SEM microphotographs.

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