The effect of a styrene–methyl methacrylate block copolymer on the morphological, rheological and mechanical properties of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(hydroxy ether of bisphenol A) (Phenoxy) blends

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The compatibilizing effect of styrene–methyl methacrylate block copolymer (SM) on blends of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and poly(hydroxy ether of bisphenol A) (Phenoxy) was examined in terms of phase structure and rheological and mechanical properties. Scanning electron micrographs show that the blends exhibit a more regular and finer dispersion when a small amount of the SM block copolymer is added. The interfacial tension between two immiscible polymers in the blends is estimated by applying various theories of emulsion models to the results of rheological measurements. The interfacial tension is significantly reduced when 5 wt% of the copolymer is added. Thermal analysis suggests that the added block copolymer is located at the interface of the PPE and Phenoxy. The blends exhibit remarkably enhanced toughness with the addition of a small amount of SM, which seems to be attributable to both dispersed particle size reduction and improved interfacial adhesion.

(Keywords: polymer alloy; PPE; Phenoxy; block copolymer; toughening; emulsion model; interfacial tension)

INTRODUCTION

Among multicomponent polymeric materials, polymer blends have recently been of considerable interest as the simplest route for combining the outstanding properties of different existing polymers[1–3]. Although many miscible polymer blends have been developed in the last two decades, there has recently been a great deal of interest in the study of the structure and properties of immiscible polymer blends, where each of the component polymers retains its own properties, combined into a final product that may display some new properties due to the particular phase morphology. Although an increasing number of miscible blends are reported in literature, most polymer pairs are virtually immiscible, thus leading to multiphase structure.

For immiscible polymer blends, coarse phase dispersion and coalescence together with poor adhesion between phases are the limiting factors in all applications. Therefore two structural requirements are necessary to secure adequate overall physico-mechanical behaviours of immiscible polymer blends. One is a proper interfacial tension, leading to phase size small enough to allow the blends to be considered as macroscopically homogeneous. The other is interphase adhesion strong enough to assimilate stresses and strains without disruption of the established morphology. These demands have been traditionally fulfilled by creating a practically irreversible morphology in the polymerization process itself, as illustrated by the examples of high-impact polystyrene (HIPS) and poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS). Recently, the physical and/or chemical interactions at the interface of immiscible polymer blends have been controlled by using copolymers (graft, block, or random copolymers) having segments capable of specific interactions and/or chemical reactions with the blend components.

The effect of (di)block copolymers on the phase structure of immiscible polymer blends has been investigated for many years. Early efforts concentrated on the blends of (di)block copolymers with homopolymers possessing repeat units identical with each segment of the copolymer[4–14]. More recently, the validity of the approach which uses A–C block copolymer as a compatibilizer to bridge the incompatibility gap between two polymers A and B (where polymer C is miscible with polymer B) has been reported[15–18]. However, there have been few reports on blends of two immiscible polymers (A and B) and a C–D (di)block copolymer, where A and B are miscible with C and D, respectively[19,20].

In fact, the mixing of a block copolymer with homopolymers having identical units is thermodynamically an athermal process. Several experimental investigations have shown that in this case the molecular weights of individual blocks of a copolymer must be equal to or higher than those of the corresponding homopolymers[21,22]. In contrast, when a block copolymer, whose blocks are chemically different but miscible with the corresponding

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polymers, is blended with two immiscible polymers, an exothermic interaction between miscible pairs exists. This interaction can be an important additional thermodynamic driving force for the solubilization of each block of a copolymer and the corresponding homopolymer, thus the compatibilizing effect of a block copolymer can be obtained irrespective of the molecular weight of the blocks of the copolymer[23].

In this study this concept is applied to the compatibilizing of immiscible blends of poly(2,6-dimethyl-1,4-phenylene ether)/poly(hydroxy ether of bisphenol A) (PPE/Phenoxy) using a styrene–methyl methacrylate block copolymer (SM), in which PPE and Phenoxy are miscible with polystyrene (PS) and poly(methyl methacrylate) (PMMA), respectively[24,25]. Phenoxy is an amorphous polymer which has some favourable properties, such as high rigidity, ductility, impact strength and creep resistance, which complement the shortcomings of PPE. In addition, due to the stable C–C and C–O–C bonds composing the main chain, Phenoxy shows very good chemical resistance, particularly to alkalis and acids[26]. Therefore the combination of PPE and Phenoxy can give mutually complementary properties, and desirable physico-mechanical properties can be obtained if a proper compatibilizing agent is used.

EXPERIMENTAL

Materials

The PPE and Phenoxy used in this study were commercial additive-free products. They were used as received without further purification. A styrene–methyl methacrylate diblock copolymer (SM) was synthesized by sequential anionic polymerization of styrene and methyl methacrylate using butyllithium as an initiator under a nitrogen atmosphere. *Table 1* lists the characteristics of the polymers.

Preparation of blends

All polymers were completely dried under vacuum before blending. Blends were prepared in the melt state at 270–290°C using a Rheomix 600 (Haake Buchler Instrument Inc., System 90 Torque Rheometer) for 10 min at 100 rev min^{-1}.

Methods

Thermal analysis was carried out using a Perkin–Elmer DSC7 under a nitrogen atmosphere. The instrument was calibrated using indium. A heating rate of 20°C min^{-1} was used, and the data obtained in a second heating experiment on a given specimen were collected.

Mechanically melt-blended samples were compression-moulded into sheets and then fractured at liquid-nitrogen temperature. The cryogenically fractured surface was coated with gold and observed with a scanning electron microscope (JEOL JSM-35) at an accelerating voltage of 25 kV.

The dynamic rheological properties of the blends were measured at 260°C on a Rheometrics mechanical spectrometer (RMS 800) with a parallel plate mode, under a nitrogen atmosphere. Samples with dimensions suitable for rheological measurement were cut out from the same sheet as used in the morphological observation. The parallel plate had a 2 mm gap and a radius of 12.5 mm. The strain was maintained at 5% for all of the samples.

Completely dried polymers were melt-mixed and injection-moulded on a Mini-Max Molder (CS-183MMV, Custom Scientific Instruments, Inc.). The injection temperature was 290°C. For all mechanical property measurements, the data given below were determined by averaging the results of three out of five specimens (maximum and minimum values were rejected).

RESULTS AND DISCUSSION

Morphology

The morphology changes in PPE/Phenoxy blends with the addition of SM are shown in *Figures 1* and *2*. The binary blends without block copolymer show the typical morphology of an immiscible mixture: very large, coarse, and irregular domains were formed (*Figures 1a* and *2a*). More regular and finer dispersion was observed when a small amount of SM was added (*Figures 1b, c* and *2b, c*), implying that the added SM plays a role as a compatibilizing agent. Even greater effects of compatibilization can be seen when about 10 wt% SM is added (*Figures 1d* and *2d*). It is worth noting that the ratio of the molecular weight of the PMMA block of SM to that of the Phenoxy is much less than unity. This fact suggests that an exothermic enthalpy of mixing for each polymer with the corresponding block of copolymer leads to an important additional thermodynamic driving force in the solubilization in the A/B/C–D system.

Thermal analysis

In order to play a proper role as an interfacial agent the block copolymer should be located at the interface of two immiscible polymers and each block of the copolymer should penetrate into the corresponding polymer domains. Therefore it is important to verify whether the block copolymer is suitably located at the interface and whether each block is dissolved in the corresponding domains. Information at the interfacial region in immiscible polymer blends can be obtained using various techniques, including electron microscopy, thermal transition analysis and more sophisticated

Table 1 Polymer characteristics

Polymers	Abbreviation	Source	M_w[a]	M_w/M_n[a]	T_g[b](°C)
Poly(2,6-dimethyl-1,4-phenylene ether)	PPE	Nippon Polyether Co.	45 000	2.06	216
Poly(hydroxy ether of bisphenol A)	Phenoxy	Union Carbide Co.	82 000	–	94
Poly(styrene-*b*-methyl methacrylate), 57 mol% St[c]	SM	Synthesized	92 000	1.80	105, 129

[a] Determined by g.p.c.
[b] Determined by d.s.c.
[c] Determined by elemental analysis (CHN)

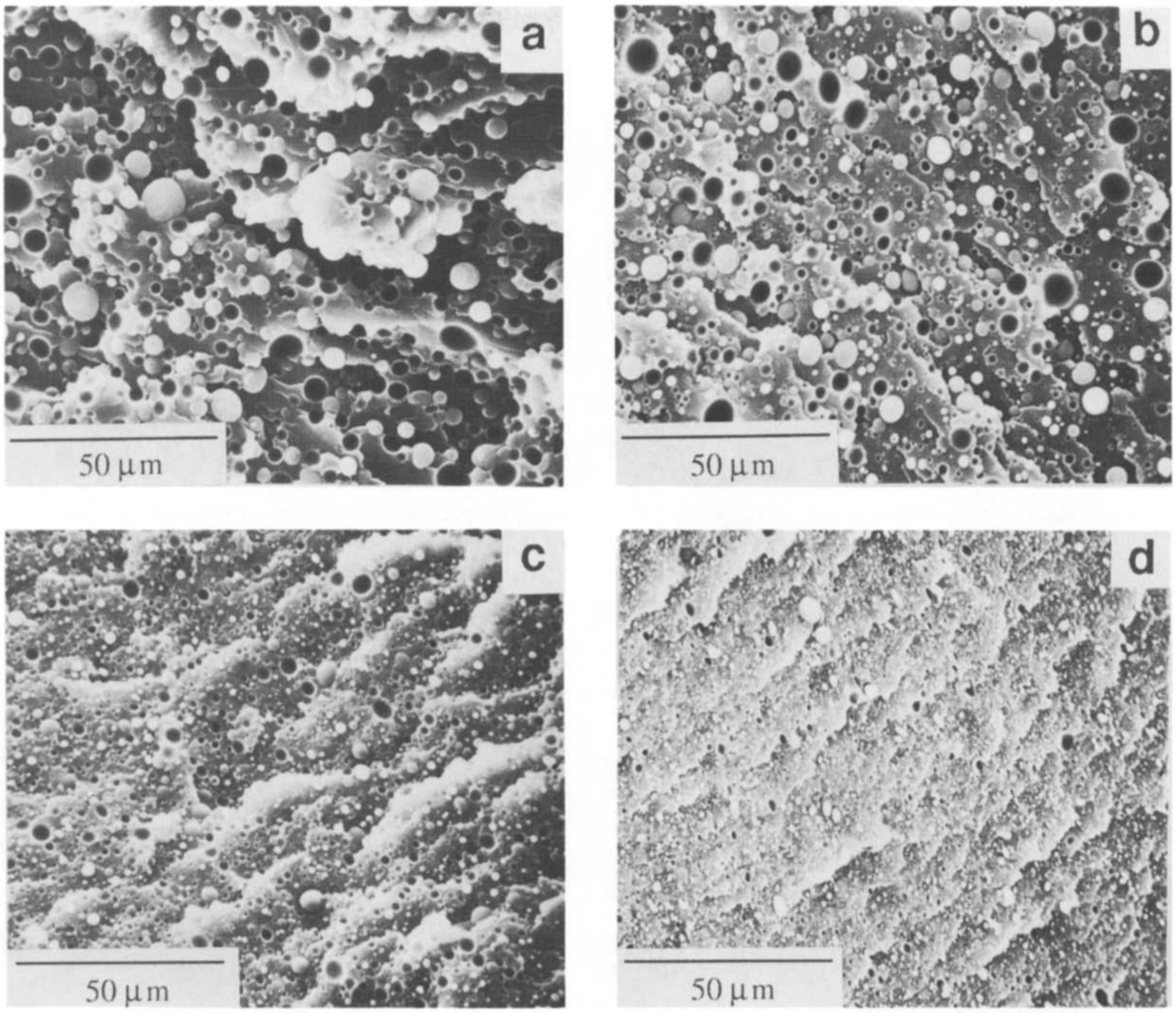

Figure 1 Scanning electron micrographs of 30/70 PPE/Phenoxy blends: (a) without block copolymer; (b) 3 wt% SM added; (c) 5 wt% SM added; (d) 10 wt% SM added

methods such as non-radiative energy transfer, forward recoil spectroscopy, secondary ion mass spectroscopy, neutron reflectometry, and so on. Although electron microscopy and more sophisticated techniques can give a direct view of the molecular situation at the interfaces with good detection resolution, the preparation of the specimen for these methods is somewhat difficult. On the other hand, the thermal analysis method can be used simply without such difficulties, although it gives indirect information. With the thermal analysis method, the location of the block copolymers can be elucidated by examining the composition of each phase. Thus d.s.c. is employed here to obtain information about the phase structure of the blends[20].

Figure 3 shows d.s.c. thermograms of PPE/SM binary blends. Two distinct glass transition temperatures (T_gs) at 105°C and 129°C are observed for the block copolymer, which correspond to the PS block and PMMA block of SM copolymer respectively (*Figure 3e*). For the PPE/SM binary blends, two T_gs are also observed, which means that the blends have a two-phase structure. When the amount of PPE in the binary blends is increased, the lower T_g of SM shifts to a higher temperature while the upper one exhibits no notable change. Since only the PS block of SM is miscible with PPE, the shift of the lower T_g of SM indicates that the PPE dissolves in the PS block of SM. Thus it can be suggested that the two-phase structure of the PPE/SM binary blends consists of a PPE/PS phase and a PMMA phase.

D.s.c. thermograms of SM/Phenoxy binary blends are shown in *Figure 4*. In contrast to *Figure 3*, the lower T_g of SM shows no change while the upper T_g of PMMA block shifts to a lower temperature with increasing amounts of Phenoxy in the blends. This result indicates that the SM/Phenoxy binary blends also have a two-phase structure: one is composed of PMMA/Phenoxy and the other of PS.

Figure 5 shows the effect of SM on the T_gs of PPE/Phenoxy blends. Without SM (*Figures 5a–c*), two distinct T_gs corresponding to those for the parent polymers are observed, indicating that they are immiscible. When SM is added (*Figures 5d–f*) the blends still display two T_gs. However, it is observed that the upper T_g shifts to lower temperatures and the lower to higher temperatures. This result reveals that all ternary blends involving a block copolymer have a two-phase structure as well: the PS block and PPE form one phase, and the PMMA block and Phenoxy form the other. Consequently, the above results show that the block copolymer is located at the interface of two immiscible polymers, PPE and Phenoxy, and each block of the copolymer penetrates into the corresponding homopolymer

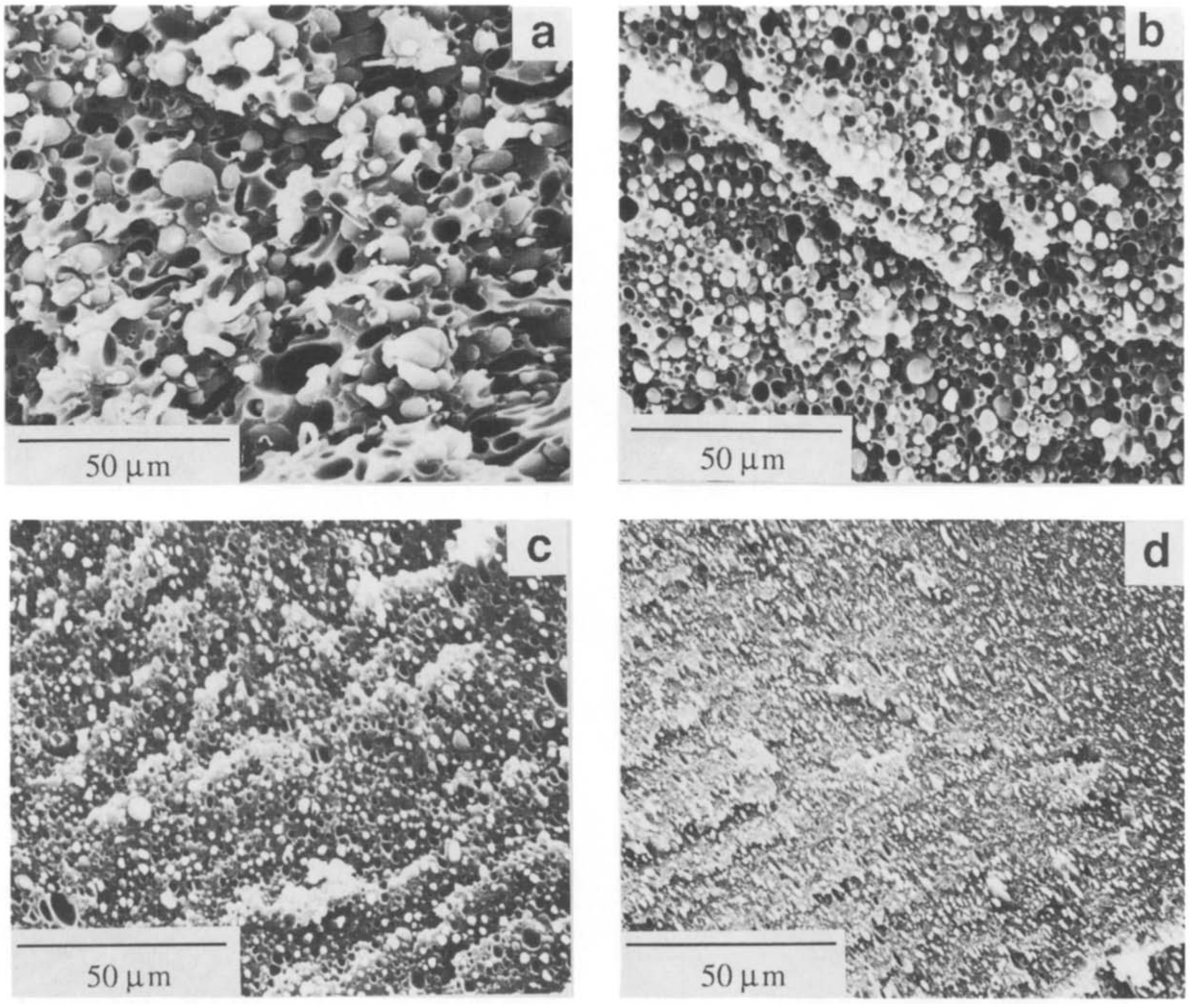

Figure 2 Scanning electron micrographs of 50/50 PPE/Phenoxy blends: (a) without block copolymer; (b) 3 wt% SM added; (c) 5 wt% SM added; (d) 10 wt% SM added

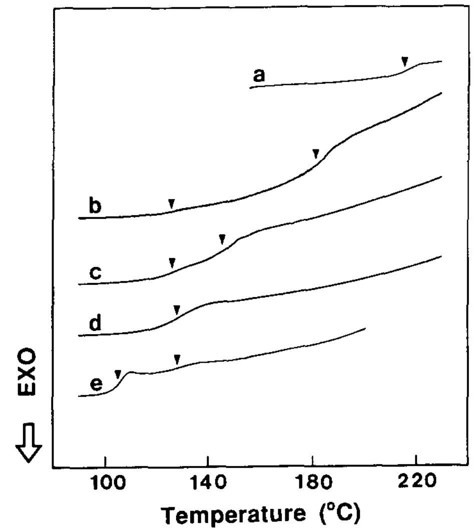

Figure 3 D.s.c. thermograms of PPE/SM blends: (a) PPE; (b) 70/30 PPE/SM; (c) 50/50 PPE/SM; (d) 30/70 PPE/SM; (e) SM

domains. However, the possibility that micelles of the diblock themselves will exist in either or both phases could not be excluded.

Rheological properties

Complex viscosities of 30/70 blends are plotted against frequency in *Figure 6*. In spite of the low viscosity of block copolymer, SM, the blends show an increase in viscosity with the addition of the block copolymer. This is probably due to the coupling effect of the block copolymer. In other words, when SM is added to the blends, it gives better adhesion between dispersed PPE and the Phenoxy matrix. Therefore the contribution of PPE to the blend viscosity becomes greater, which results in the increase of viscosity in the blend.

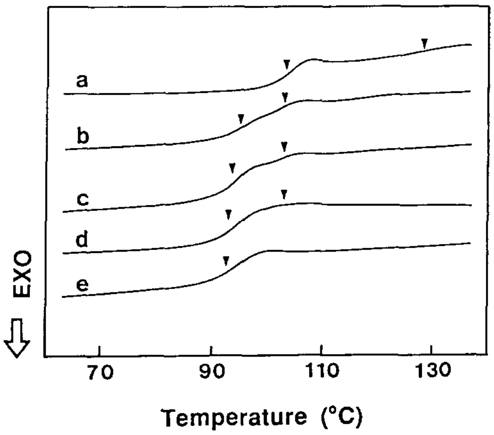

Figure 4 D.s.c. thermograms of SM/Phenoxy blends: (a) SM; (b) 70/30 SM/Phenoxy; (c) 50/50 SM/Phenoxy; (d) 30/70 SM/Phenoxy; (e) Phenoxy

The effect of SM on the complex viscosities of 50/50 blends is shown in *Figure 7*. In this case, the minor phase

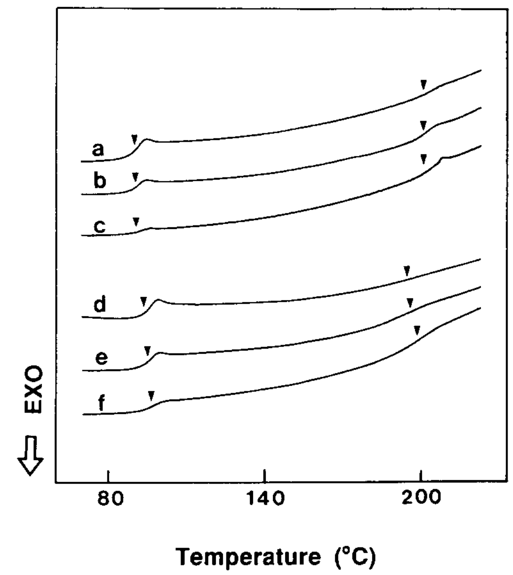

Figure 5 D.s.c. thermograms of PPE/Phenoxy blends: (a) 30/70; (b) 50/50; (c) 70/30; (d) 30/70 with 10 wt% SM; (e) 50/50 with 10 wt% SM; (f) 70/30 with 10 wt% SM

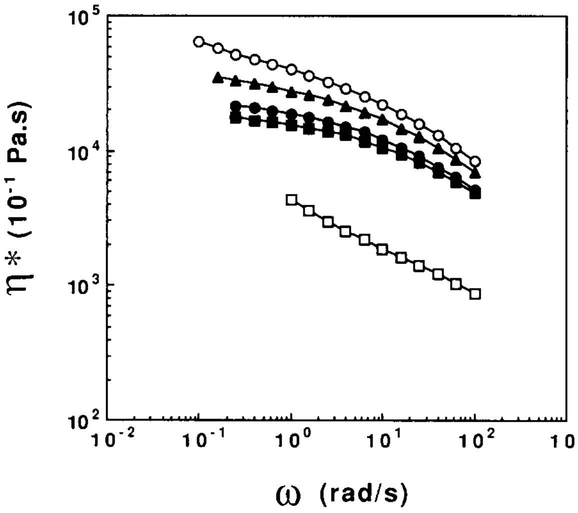

Figure 6 Complex viscosity *versus* frequency for 30/70 PPE/Phenoxy blends: (■) without block copolymer; (●) 3 wt% SM added; (▲) 5 wt% SM added; (○) 10 wt% SM added; (□) SM

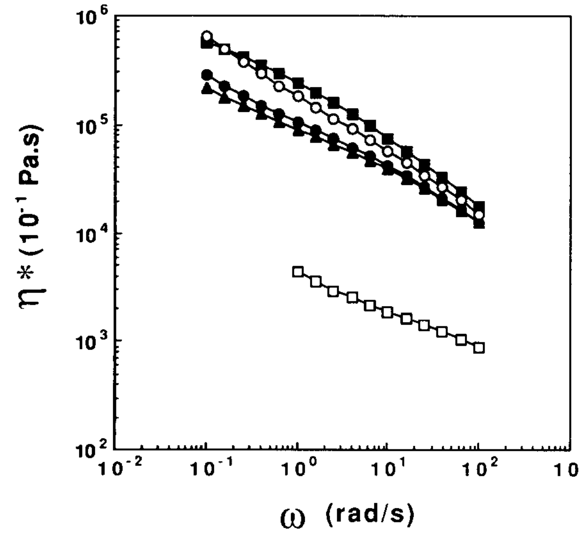

Figure 7 Complex viscosity *versus* frequency for 50/50 PPE/Phenoxy blends: (■) without block copolymer; (●) 3 wt% SM added; (▲) 5 wt% SM added; (○) 10 wt% SM added; (□) SM

is PPE since the viscosity ratio of PPE to PS is greater than unity. Some differences are observed when compared with the 30/70 blends. When 3 wt% or 5 wt% SM is added, the viscosity of the blend decreases as compared to the original blend. However, the viscosity increases again for 10 wt% SM. This behaviour can be explained as follows. A 50/50 PPE/Phenoxy binary blend has a somewhat interconnected phase structure (i.e. this blend composition is believed to be a threshold of a co-continuous phase structure in this system) as shown in *Figure 2a*. When 3–5 wt% SM is added (*Figures 2b, c*), a breakdown of the interconnected structure is observed with a clear dispersion of the minor phase which induces a decrease in viscosity. A further increase in SM (*Figure 2d*) results in better adhesion between PPE and Phenoxy similar to the case of 30/70 blends, hence the viscosity of the blend containing 10 wt% SM increases.

Comparison with model predictions

Characterization of the flow behaviour of heterogeneous systems has been an interesting field of research for many years. Numerous models have been developed in order to show the link between macroscopic behaviour of the system and microscopic interaction between the system components. A classic example is provided by Einstein's prediction of the viscosity of a fluid in which small solid spheres are suspended[27]. Taylor[28] proposed an extended theory including the case in which the spheres are liquid. Schowalter *et al.*[29] have applied Taylor's work to the case of deformable suspended droplets. They obtained a qualitative picture of the deformation process by considering a droplet of radius R immersed in a fluid with viscosity η_0, where the interfacial tension between the droplet and the surrounding fluid is σ. Brenner[30] has obtained the complete solution of this problem in the linear viscoelastic range of deformation. According to his results, the dynamic moduli of the dilute emulsions of Newtonian liquids for a small-amplitude dynamic shear experiment can be expressed as:

$$G'(\omega)=\frac{\eta_0^{0\,2}R\varphi}{80\sigma}\left(\frac{19K+16}{K+1}\right)^2\omega^2 \tag{1}$$

$$G''(\omega)=\eta_0^0\left[1+\left(\frac{5K+2}{2K+2}\right)\varphi\right]\omega \tag{2}$$

where η_0^0 is the zero shear viscosity of the matrix, K is the ratio of zero shear viscosity of inclusions to the matrices (i.e. $K=\eta_i^0/\eta_0^0$), R is the radius of inclusions assumed to be monodisperse in size and σ is the interfacial tension. φ and ω are the volume fraction of inclusions and the frequency, respectively. Independently, Oldroyd[31,32] extended Taylor's analysis and made a calculation of the macroscopic elastic properties of an emulsion arising from the interfacial tension between the two phases. His calculation leads to the following expression for the complex modulus of the emulsions:

$$G^*=G_M^*\left(\frac{1+3\varphi H}{1-2\varphi H}\right) \tag{3}$$

where

$$H=\frac{4\sigma/[R(2G_M^*+5G_I^*)]+(G_I^*-G_M^*)(16G_M^*+19G_I^*)}{40\sigma/[R(G_M^*+G_I^*)]+2(G_I^*+3G_M^*)(16G_M^*+19G_I^*)} \tag{4}$$

where G^* is the complex modulus and φ, σ, and R designate the same parameters as given in equations (1) and (2). The indices M and I denote the matrix and the inclusion, respectively. Recently, Palierne[33] derived the linear viscoelastic modulus at an arbitrary concentration for polydisperse spherical inclusions. In this model both the matrix and inclusions are assumed to be viscoelastic. His result for dilute emulsions is expressed simply as follows:

$$G^* = G^*_{\mathrm{M}}\left(1+\frac{5}{2}\sum_i \varphi_i \frac{E_i}{D_i}\right) \tag{5}$$

where

$$E_i = 2(G^*_{\mathrm{I}} - G^*_{\mathrm{M}})(19G^*_{\mathrm{I}} + 16G^*_{\mathrm{M}}) + 8\sigma/[R_i(5G^*_{\mathrm{I}} + 2G^*_{\mathrm{M}})] \tag{6}$$

$$D_i = 2(G^*_{\mathrm{I}} - 3G^*_{\mathrm{M}})(19G^*_{\mathrm{I}} + 16G^*_{\mathrm{M}}) + 40\sigma/[R_i(G^*_{\mathrm{I}} + G^*_{\mathrm{M}})] \tag{7}$$

where φ_i is the volume fraction of type i grouped by the size of polydisperse inclusions.

A series of studies on the rheological properties of some immiscible polymer blends has been carried out by several investigators. Scholz *et al.*[34] applied the Schowalter model (an extension of Taylor's model) to the two-phase polypropylene and polyamide blends and Graebling *et al.*[35] applied the same model to the poly(dimethylsiloxane) and polyoxyethylene blends. Oldroyd's model was used to interpret the rheological behaviour of poly(dimethylsiloxane) and polyoxyethylene blends by Graebling and Muller[36] and PS and polyethylene blends by Brahimi *et al.*[37]. According to their results, unfortunately, the predictions from these emulsion models are found to be unsatisfactory in describing the actual rheological behaviour of all immiscible polymer blends. The stringent assumptions of those models which are inappropriate for immiscible polymer blends seem to be the main reasons for the discrepancies between the model predictions and the experimental results.

It is, however, interesting to note that the interfacial tensions (σ) can be estimated by comparing the equations of those models with values of the experimentally determined dynamic modulus, radius of inclusions and volume fraction. Generally, direct measurement of σ of polymer liquids or melts is very difficult due to their long equilibration time and the possibility of thermal degradation. Hence only a few techniques such as pendant drop and the tensiometric method are known to be suitable for polymer systems[38–40].

Applying zero shear viscosity (including the K values) and the average radius of inclusions determined from SEM micrographs at a specific blend ratio to the equation (1), the σ values which show the best agreement with the experimental data can be determined. Although the σ values determined by this method are not absolute, the order of magnitude of σ is meaningful. In addition, it is also important to investigate the relative changes in the σ values of the blends due to the compatibilization by adding copolymers[41].

Since both Oldroyd's and Palierne's models have σ terms in both the numerator and the denominator, they are less sensitive to the changes in interfacial tension than Schowalter's model. Hence, the σ values which show the best fit with the experimental data are obtained from equation (1) as a first step, then the predictions of equations (3)–(7) with the estimated σ values are compared with the rheological data of the experiment.

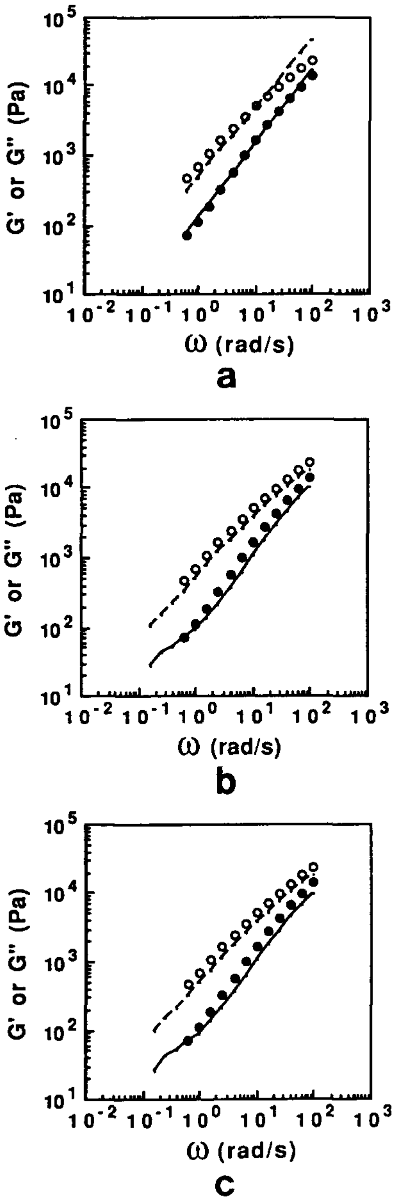

Figure 8 Comparison of the predictions of emulsion models (curves) with the experimental results (points) for the 10/90 PPE/Phenoxy blend: (a) Schowalter's model; (b) Oldroyd's model; (c) Palierne's model for dilute emulsions. Filled and open symbols represent G' and G'', respectively

Figure 8 shows the model predictions and experimental data of G' and G'' values of 10/90 PPE/Phenoxy blends. No significant differences were observed between the models of Oldroyd (*Figure 8b*) and Palierne (*Figure 8c*). Roughly, all models show similar results except for some deviation in the high-frequency range.

Theoretical values were then compared with the experimental data for 10/90 PPE/Phenoxy blend with 5 wt% SM as shown in *Figure 9*. In contrast to the results of *Figure 8a*, the predicted G'' values in *Figure 9a* show significant deviation from the experimental results. Unlike G' (equation (1)), G'' is independent of σ (equation (2)). The parameters affecting the G'' value are η^0_0 and K, which reflect the characteristics of the matrix. Therefore, in contrast to the result of *Figure 8a*, the poor fit of G'' shown in *Figure 9a* is attributed to the change in matrix properties arising from the interaction between PMMA and Phenoxy by the addition of SM. The models of

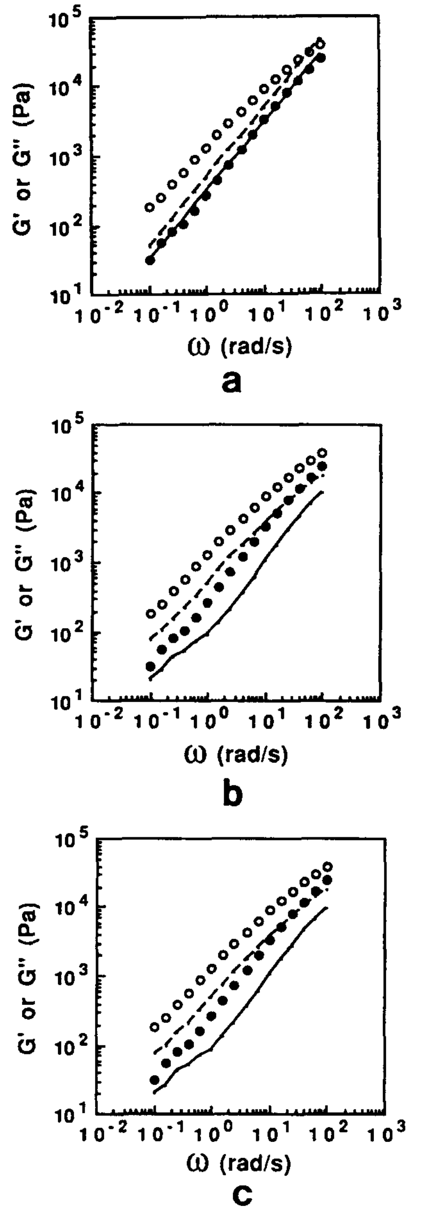

Figure 9 Comparison of the predictions of emulsion models (curves) with the experimental results (points) for the 10/90 PPE/Phenoxy blend with 5 wt% SM: (a) Schowalter's model; (b) Oldroyd's model; (c) Palierne's model for dilute emulsions. Filled and open symbols represent G' and G'', respectively

Oldroyd and Palierne show notable deviations in both G' and G''. However, the models' assumptions do not include any of the effects of interactions between the dispersed phase and the matrix. Considering the actual existence of the particle–matrix interaction, these deviations seem to be natural.

Table 2 lists various rheological parameters and characteristics of the inclusions used in this estimation. It also shows the estimated σ values obtained from *Figure 8a* (equation (1)). When 5 wt% SM is added, the interfacial tension of the blend is estimated as one order of magnitude smaller as compared with that of the blend without SM. This result falls in line with the SEM results (*Figures 1* and *2*), which show more regular and finer dispersion for the blends containing SM.

Mechanical properties

The effect of SM on the mechanical properties of PPE/Phenoxy blends is shown in *Figures 10–13*. The

Table 2 Rheological parameters, characteristics of dispersed domains and estimated interfacial tensions of PPE/Phenoxy blends[a]

Blends	η_0^0 [b] (Pa s)	K[c]	R[d] (μm)	φ[e]	σ[f] ($\times 10^{-3}$ N m^{-1})
10/90	380	2900	18	0.1	9.6092
10/90-5 wt% SM	380	2900	2.6	0.1	0.5699

[a] At 260°C
[b] Determined from the low-frequency limit of η' at 260°C
[c] $K = \eta_i^0/\eta_0^0$
[d] Determined from scanning electron micrographs
[e] Volume fraction in dispersed domains
[f] Estimated from equation (1); the error limit is 5%

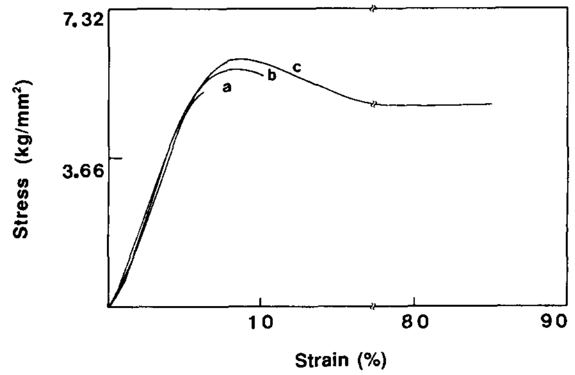

Figure 10 Representative tensile stress–strain curves of 30/70 PPE/Phenoxy blends: (a) without block copolymer; (b) 5 wt% SM added; (c) 10 wt% SM added

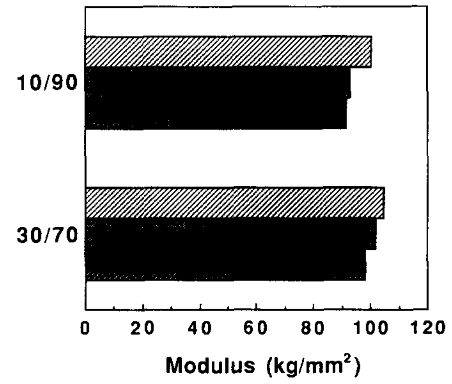

Figure 11 Tensile modulus of 10/90 and 30/70 PPE/Phenoxy blends: (▨) without block copolymer; (▩) 5 wt% SM added; (■) 10 wt% SM added

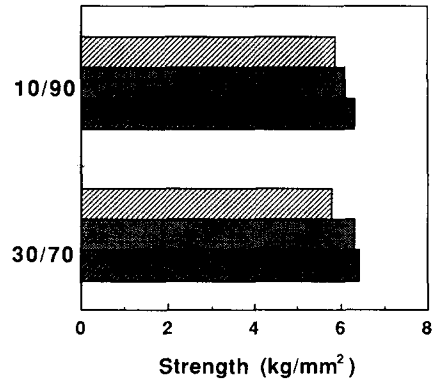

Figure 12 Tensile strength of 10/90 and 30/70 PPE/Phenoxy blends: (▨) without block copolymer; (▩) 5 wt% SM added; (■) 10 wt% SM added

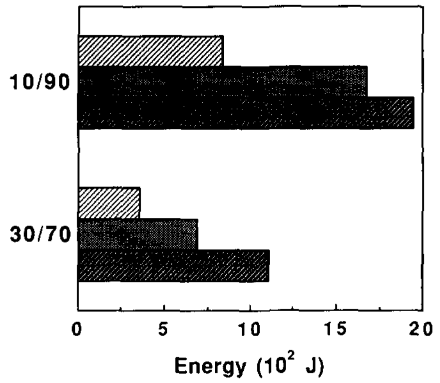

Figure 13 Fracture energy of 10/90 and 30/70 PPE/Phenoxy blends: (▨) without block copolymer; (▩) 5 wt% SM added; (■) 10 wt% SM added

stress–strain curves of 30/70 blends modified with the SM block copolymer are presented in *Figure 10*, and the changes in average values of modulus, strength and fracture energy obtained from the integration of stress–strain curves to the maximum stress of 10/90 and 30/70 blends are displayed in *Figures 11–13*. While the modulus decreases with the increasing amount of SM in the blend, both the tensile strength and the elongation at break increase notably. When 10 wt% SM is added to the 30/70 blend, the blend fails in a ductile manner at about 85% strain, and shows about a threefold increase in fracture energy. *Figure 14* shows the SEM micrographs of fractured surfaces after tensile tests. As compared with the fractogram of the blend without SM (*Figure 14a*), the micrograph of the blend with 10 wt% SM shows the characteristics of ductile failure (*Figures 14d, e*). A highly

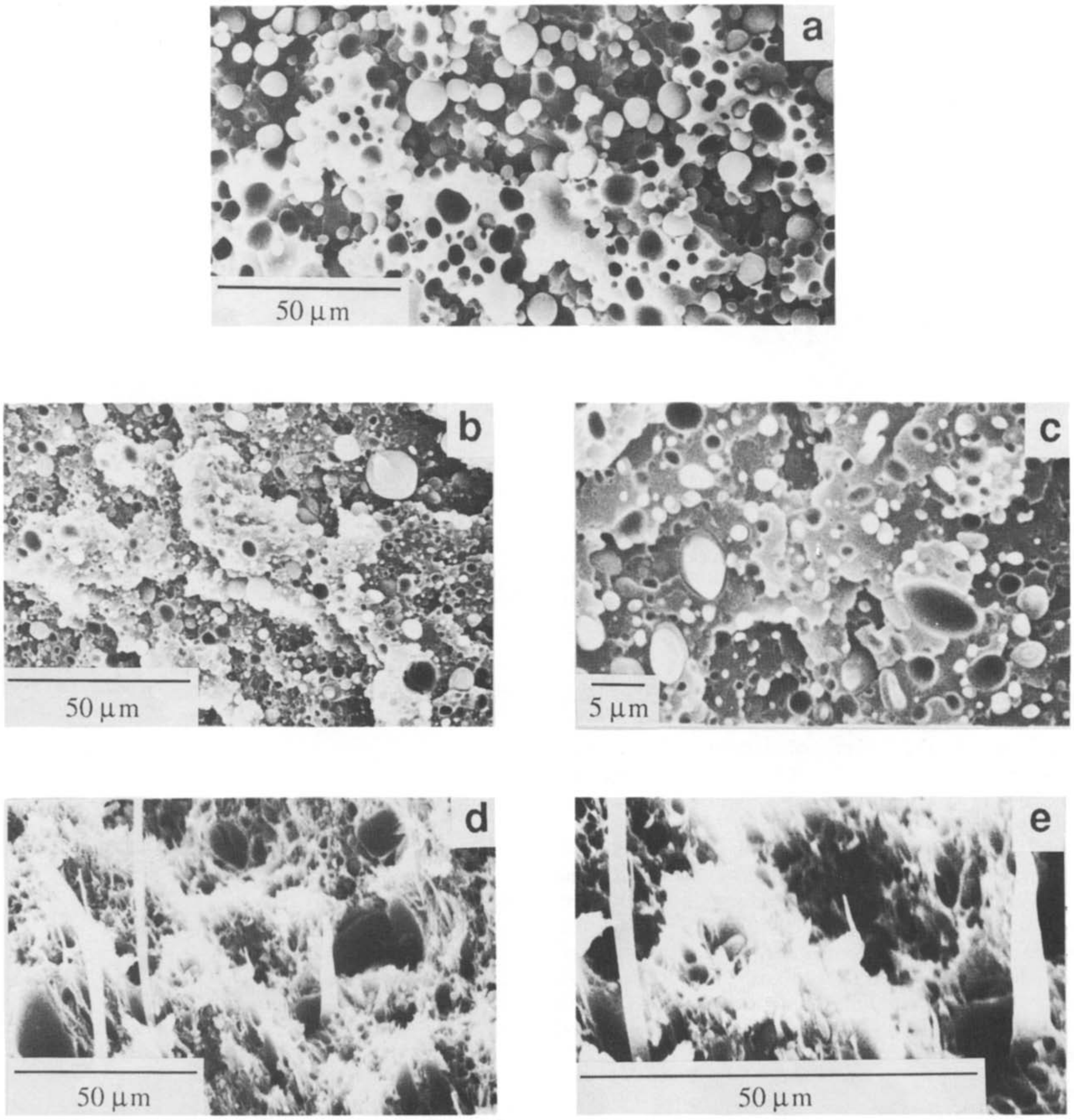

Figure 14 Scanning electron micrographs of 30/70 PPE/Phenoxy blends after tensile test: (a) without block copolymer; (b) 5 wt% SM added; (c) magnified feature of (b); (d) 10 wt% SM added; (e) magnified feature of (d)

elongated minor phase, which indicates the existence of interaction between dispersed phase and matrix, is observed along with the size reduction of the dispersed phase. It is believed that both particle size reduction and enhanced interfacial adhesion contribute to the improvement of the toughness of this blend system.

CONCLUSIONS

This study has focused on the compatibilizing effects of the C–D type block copolymer on blends of two immiscible polymers A and B using a styrene–methyl methacrylate block copolymer for the PPE/Phenoxy system. By means of several experimental techniques such as SEM, thermal analysis (d.s.c.), and measurements of mechanical and rheological properties, the effects of the block copolymer on the phase structure, rheological and mechanical properties of the immiscible blend system were investigated. Also, the effect of the block copolymer on the interfacial tension between the two immiscible homopolymers was examined by applying several theories of emulsion models to the measured rheological results.

More regular and finer dispersion was observed upon the addition of a small amount of SM to the PPE/Phenoxy blend. This suggests that the interfacial tension between the two immiscible polymers was reduced by the addition of copolymers. The molecular weight of PMMA block is lower than that of Phenoxy (i.e. $M_{\mathrm{PMMA}}/M_{\mathrm{Phenoxy}}=0.48$). This fact suggests that an exothermic enthalpy of mixing of each homopolymer and the corresponding block of copolymer leads to an important additional thermodynamic driving force for solubilization. Dependent on the blend ratios, different rheological behaviour was observed. Due to the coupling effect of SM copolymer, 30/70 blends showed an increase in viscosity with the addition of SM in spite of the low viscosity of SM. However, 50/50 blends showed a decrease in viscosity at low SM concentration, which is probably due to the breakdown of the interconnected phase structure. From the thermal analysis data of binary or ternary blends of PPE, Phenoxy and SM, it is believed that the location of SM is at the interface of two immiscible polymers, PPE and Phenoxy. By modifying with 5–10 wt% SM, the blends exhibit remarkably enhanced toughness. Both particle size reduction and the interfacial adhesion effect seem to contribute to the improvement of toughness in this blend system. When 5 wt% SM is added, the interfacial tension of the blend is estimated as one order of magnitude smaller as compared with that of the blend without SM, even though the theoretical predictions from the emulsion models do not always show a satisfactory agreement with the experimental results.

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