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Thermal and Rheological Properties of Miscible Polyethersulfone/Polyimide Blends

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SYNOPSIS

Blends of an aromatic polyethersulfone (commercial name Victrex) and a polyimide (commercial name Matrimid 5218), the condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindane, were studied by differential scanning calorimetry, dynamic mechanical analysis, and rheological techniques. The blends appeared to be miscible over the whole range of compositions when cast as films or precipitated from solution in a number of solvents. After annealing above the apparent phase boundary, located above T_g , the blends were irreversibly phase separated indicating that the observed phase boundary does not represent a true state of equilibrium. Only a narrow "processing window" was found for blends containing up to 20 wt % polyimide. Rheological measurements in this range of compositions indicated that blending polyethersulfone with polyimide increases the complex viscosity and the elastic modulus of the blends. For blends containing more than 10 wt % polyimide, abrupt changes in the rheological properties were observed at temperatures above the phase boundary. These changes may be consistent with the formation of a network structure (due to phase separation and/or crosslinking). Blends containing less than 10 wt % polyimide exhibited stable rheological properties after heating at 320°C for 20 min, indicating the existence of thermodynamic equilibrium.

Keywords: blends, polyethersulfone/polyimide, thermal and rheological properties of • polyethersulfone in miscible blends with polyimide • polyimide in miscible blends with polyethersulfone • rheology of polyethersulfone/polyimide blends • thermal properties of polyethersulfone/polyimide blends

INTRODUCTION

The modification of polymer properties through blending has been used increasingly to obtain inexpensive materials with improved characteristics. Polymer blends may be broadly classified into homogeneous (miscible) and heterogeneous (immiscible) blends. Homogeneous blends are relatively rare since the change in the combinatorial entropy of mixing of two high molecular weight polymers is negligible. The driving force for miscibility must then be provided by specific interactions between the polymers.¹ Nevertheless a number of miscible blends has been described. Novel polymer blends, consisting of aromatic polybenzimidazoles and ar-

omatic polyimides have been studied in our laboratory.²⁻⁴ Recently a new family of high-performance, miscible polymer blends consisting of polyimides and polyethersulfone has been discovered.⁵

Polyethersulfone (PES) (ICI Victrex) is a high-performance engineering thermoplastic with the structure

The phenyl groups are linked by thermally stable ether and sulfone groups. The extensively delocalized structure provides good resistance to oxidative degradation and retention of mechanical properties at high temperatures. The presence of ether oxygen linkages gives the polymer chain flexibility. Poly-

ethersulfone has been reported to be miscible with poly(ethylene oxide)^{6–10} and with phenoxy resin.¹¹

The polyimide (PI) (Ciba-Geigy Matrimid 5218) is a thermally stable and soluble thermoplastic with the repeat unit

Key properties of Matrimid 5218 are excellent high temperature resistance, toughness, good dielectric properties, low flammability, and high resistance to radiation and deformation under load at elevated temperatures. Blends of polyimides with a variety of homopolymers and copolymers have been reviewed by Adduci.¹²

EXPERIMENTAL

Materials

The polymers used in this study were the polyethersulfone, Victrex (grade 4800P) obtained from ICI America Inc. and the polyimide, Matrimid 5218 obtained from Ciba Geigy. Both "as-received" polymers were amorphous. Table I lists weight average, $\bar{M}_w$, and number average, $\bar{M}_n$, molecular weights, glass transition temperatures, T_g , and heat capacity increases, ΔC_p , at T_g .

Sample Preparation

Polyethersulfone is known to absorb moisture easily. Before use it was dried at 150°C for 4 h. The polyimide was used without preliminary drying. Both polymers were blended in a common solvent and then cast or coprecipitated producing films or powders, respectively.

To produce films, two solvents of substantially different boiling points were used, namely *N,N*-dimethylacetamide (DMAc) (bp = 166°C) and methylene chloride (CH₂Cl₂) (bp = 40°C). Solutions were cast onto Petri dishes and the solvent was removed by evaporating in dry N₂ at 70°C (DMAc) or in air at room temperature (CH₂Cl₂). Films cast from DMAc solution were washed for 7 days in hot water then dried for 7 days at 150°C in a vacuum oven. Films formed from CH₂Cl₂ solution were heated gradually to 200°C over a period of 10 h. The typical thickness of the films obtained by these procedures was 0.2–0.3 mm.

Powders were prepared by dissolving the blend constituents in CH₂Cl₂ and coprecipitating into a mixture of methanol and water (75:25, v/v). The residual CH₂Cl₂ was evaporated at 150°C for 12 h.

Thick films (in the form of disks) for rheological measurements were obtained by molding a stack of several thin films placed within a 25-mm diameter and 2-mm thick metal ring. Molding was carried out at a press temperature of 250–260°C with applied pressure 700 kg/cm² for 10–15 min.

Methods and Instrumentation

Thermal gravimetric analysis (TGA) was carried out with a Perkin-Elmer TGS-7 analyzer, in the temperature range 50–700°C at a heating rate of 10°C/min in an N₂ atmosphere.

Calorimetric measurements were performed with a Perkin-Elmer DSC-7 scanning calorimeter. A typical heating rate was 20°C/min.

The dynamic mechanical analyses were conducted using a Polymer Laboratories DMTA equipped with a high-temperature (500°C) head operating at a frequency of 1 Hz and a constant strain in a single-cantilever geometry. The thickness of the films was in the range of 0.1–0.2 mm. Data were collected at a heating rate of 4°C/min under N₂.

Table I. Characteristic Parameters of Blend Constituents

Polymer	$\bar{M}_n$	$\bar{M}_w$	DSC	
			T_g (°C)	ΔC_p (J/gC)
Polyethersulfone (Victrex)	22,000 ^a	~88,000 ^b	230	0.20
Polyimide (Matrimid 5218)	11,000 ^a	80,000 ^a	320	0.20

^a Manufacturer's data.

^b GPC in DMAc.

Rheological measurements were performed in a Rheometrics Dynamic Spectrometer in the parallel-plate mode. Frequency sweeps were carried out at temperature intervals of approximately 10°C from 265 to 325°C for pure PES and between 265°C and the corresponding phase separation temperatures for the blends. Parallel plate geometry was preferred to cone and plate geometry because the former is less sensitive to small variations in the gap due to thermal expansion of the plate fixtures. Nitrogen was circulated at all times in the environmental chamber to minimize degradation and chemical reaction in the blends.

RESULTS AND DISCUSSION

Physical Appearance of Blends

Blends cast from polymer solutions appeared as transparent yellowish to light brownish films. Coprecipitation from polymer solution produced a flakey yellow product which could be molded in a hot press to yield transparent films, similar in appearance to the cast films.

Thermogravimetry

It is known that solvent remaining in the sample after blending can act as a plasticizer, affecting both thermal and mechanical properties of the blend. Thus special care was taken to obtain "solvent-free" samples. The amount of residual solvent was determined by TGA of 100–400°C and the results are presented in Table II. The drying procedure applied proved to be effective; the amount of CH₂Cl₂ was reduced to below 0.5% and that of DMAc to below 1.5%. The difference between these two values is consistent with the large difference in the boiling

points of these solvents and may also indicate that there are differences in specific solvent-polymer interactions.

Glass Transitions

Both DSC and DMTA have become classical methods in the determination of miscibility. The phase structure of a blend is assessed by the number of glass transitions observed in the thermograms; while two transitions are a clear indication of phase separation, a single glass transition at a temperature intermediate between those of the pure components indicates miscibility.

In the present study, DSC measurements were performed with film, powder, and molded samples giving similar results. All the samples were analyzed between room temperature and 350°C.

Films cast from DMAc show aging phenomena similar to those observed by us in blends of polybenzimidazole with polyimide;¹³ thus, prior to DSC analysis it was necessary to heat the samples to the vicinity of the predetermined T_g and then cool to room temperature to provide uniform thermal histories. First-run DSC scans are shown in Figure 1. Only one well-defined glass transition lying between the glass transitions of the pure components and changing monotonically with composition was detected for each blend.

Figure 2 shows the temperature dependence of the loss factor ($\tan \delta$) for PES/PI blends during the first run. It is clear that a well-defined single $\tan \delta$ relaxation peak was obtained for each blend and the maximum in $\tan \delta$ (associated with T_g) is shifted to higher temperatures as the PI content increases. Consistent with these data are the results shown in Figure 3 where the temperature dependence of the storage modulus, E' , of the PES/PI blends is shown. In Figure 3 the decrease in E' occurring near T_g is shifted to higher temperatures with increasing amounts of PI. Thus the presence of a single glass transition observed in Figures 1–3 is a clear indication of a one-phase system, i.e., a miscible PES/PI blend.

Figure 4 gives a summary of the experimental T_g s measured by DSC and DMTA for films cast from CH₂Cl₂ and DMAc. Either a linear dependence or a negative deviation from linearity was observed. In general the T_g s of the blends obtained from DMAc were 5–10°C lower than those from CH₂Cl₂ probably because there was a slightly higher content of residual DMAc resulting in a more noticeable plasticization effect. The difference between the DSC and DMTA is attributed to the nature of the different

Table II. TGA of PES/PI Films Cast From Solutions in CH₂Cl₂ and DMAc

Ratio (wt %)	Weight loss in the 100–440°C interval (%)		
	CH ₂ Cl ₂	DMAc	(10°C/min heating rate)
PES/PI			
0/100	0.7	1.6	
20/80	0.5	1.8	
40/60	0.7	1.1	
50/50	0.5	1.2	
60/40	0.5	1.0	
80/20	0.3	1.2	
100/0	0.2	0.2

Figure 1. DSC scans for the blends and pure components. Curve 1, pure PES; Curve 2, PES/PI: 80/20 wt %; Curve 3, PES/PI: 60/40 wt %; Curve 4, PES/PI: 50/50 wt %; Curve 5, PES/PI: 40/60 wt %; Curve 6, PES/PI: 20/80 wt %; Curve 7, pure PI.

Figure 2. DMTA results for the different blends. Loss factor ($\tan \delta$) as a function of temperature for the blends and pure components. Curves are labeled as in Fig. 1.

Figure 3. DMTA results for the different blends. Storage modulus (E') as a function of temperature. Curves are labeled as in Fig. 1.

Figure 4. Glass transition temperatures (T_g) for the different blends. Experimental data have been applied to the Gordon-Taylor equation.¹⁴ k values are 0.95 for Curve 1 from DMTA and DMAc solvent, 0.59 for Curve 2 from DSC and MeCl₂ solvent and 0.52 for Curve 3 from DSC and DMAc solvent.

techniques and to the lower heating rate used in DMTA (4°C/min) compared to DSC (20°C/min).

The variation of the T_g in miscible blends as a function of blend composition can be described by several equations.¹⁴⁻²⁰ The Gordon-Taylor equation:¹⁵

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

is one of the most often used. Here T_g , T_{g1} , and T_{g2} are, respectively, the glass transition temperatures of the blend, polymer 1, and polymer 2; w_1 and w_2 are the corresponding weight fractions; and k is a constant which is usually taken as an indication of the strength of the interaction between the two polymers.

The data in Figure 4 can be described by the Gordon-Taylor equation with k varying between 0.95 and 0.52. A coefficient $k = 1$ is characteristic of weak interactions and was reported by Singh and Walsh²¹ for blends of polyether-sulfone with phenoxy resin. Schneider and Brekner²² found k between 1 and 0.40

for miscible [polystyrene/poly(vinyl methyl ether)] blends.

Weak intermolecular interactions in the present PES/PI blends are indicated by Fourier transform infrared (FTIR)²³ and solid-state nuclear magnetic resonance (NMR) studies²⁴ for samples cast from CH_2Cl_2 .

Phase Separation

The results of the first heat treatments described above indicate that the PES/PI blends are miscible. After heating to 350°C, samples were quenched to room temperature and heated again. The second-run DSC scans are presented in Figure 5 in which for every blend composition two well-resolved glass transitions are seen located close to the T_g s of the pure components.

Figures 6 and 7 show the $\tan \delta$ and E' curves of PES/PI blends obtained using DMTA during the second run. Two peaks in $\tan \delta$ corresponding to those observed for pure PES and pure PI (Fig. 6), and two stepwise decreases in E' (Fig. 7) can be seen. Thus it is obvious that phase separation occurs upon heating the samples to 350°C. Another indication of immiscibility in the present PES/PI blends

is that the film samples became cloudy after heating for 30 min above 300°C.

To determine the phase separation boundary, a series of annealing experiments was performed. On blends cast from CH_2Cl_2 each miscible blend was annealed for 20 min at a different temperature and analyzed by DSC upon heating. The lowest temperature for which two T_g s were detected was taken as the locus of the phase separation boundary. In Figure 8 the apparent phase boundary and T_g s for the PES/PI blends are shown. It is noteworthy that for higher PI contents the apparent phase boundary and the T_g s are of similar value, giving a very narrow "processing window" for the study of the reversibility of phase separation.

To determine whether it is possible to rehomogenize phase separated blends, such samples containing 20 wt % PI were annealed at different temperature between the phase separation boundary and the T_g . After a given annealing time the samples were quenched and the phase structure was assessed by DSC. In no case was remixing observed. Instead the DSC scans showed more pronounced phase separation with time; i.e., the glass transitions became sharper and were separated by a greater temperature range. The time required for this phenomenon to

Figure 5. DSC scans for the blends after heating to 350°C and quenching. Curves are labeled as in Fig. 1.

Figure 6. Loss factor ($\tan \delta$) as a function of temperature for phase-separated blends. Curve 1, 80/20 wt %; 2, 60/40 wt %; 3, 50/50 wt %; 4, 40/60 wt %; 5, 20/80 wt %.

Figure 7. Storage modulus (E') as a function of temperature for phase-separated blends. Curves are labeled as in Fig. 6.

Figure 8. Apparent phase boundary and T_g versus blend composition. ($\bullet$) two phase blend, ($\circ$) one phase blend.

occur ranged from 2 h at 270°C to 12 h at 250°C. This behavior implies that the one phase state shown in Figure 8 is not at equilibrium but is only a metastable state. Similar behavior was also observed for blends of polybenzimidazole with polyimide.¹³ For the present case, an investigation using a ternary polymer-polymer-solvent system confirmed phase metastability.²⁵

Rheological Measurements

Because of the small "processing window" described above, rheological measurements in this work were carried out only on blends containing less than 20 wt % PI. The measurements were made at various strains ranging from 1 to 7% to obtain torques that gave reliable signals. Within this range of deformation the response of the blends was within the linear viscoelastic region. Experimental measurements were repeated several times and the samples were replaced by new samples every 45 minutes. Measurements obtained from samples maintained for only a few minutes in the rheometer were compared with those that maintained for longer residence times to insure that chemical changes were not influencing the rheology. After the rheological measurements the samples that were run at tem-

Figure 9. Elastic shear modulus (G') versus frequency for pure PES and three different PI/PES blends. Reference temperature is 275°C.

Figure 10. Loss shear modulus (G'') versus frequency for the blends and conditions shown in Fig. 9.

peratures below those corresponding to the phase separation boundary were analyzed once more by DSC to confirm that no phase separation took place during the viscoelastic measurements. It was not possible to obtain rheological data for pure PI because this polymer degrades rapidly at the high temperatures required for softening.

The results obtained at various temperatures were expressed as a single function of frequency by performing time-temperature superposition shifts.

The elastic moduli (G') and the loss moduli (G'') measurements as a function of frequency for pure PES and PES/PI blends are shown in Figures 9 and 10 at a reference temperature of 275°C. The frequency range available for frequency-temperature superposition of the data decreases with increasing PI content because the shifting of data at high frequencies is limited by the increase in T_g with increasing PI content. Therefore, for the blends with higher PI contents it was not possible to obtain data at temperatures lower than the reference temperature because the measurements were too close to the blend T_g . In the low frequency region, the limitation is imposed by the decrease in temperature of the phase boundary with increasing PI content. Thus it was not possible to use high temperature data for time-temperature superposition because phase sep-

aration occurred. For this reason, the viscoelastic reference curves in Figures 11 and 12 were constructed using data obtained from 265 to 325°C for pure PES, from 265 to 285°C for the 95/5 and the 90/10 wt % PES/PI blends. The 80/20 wt % blend curves include data obtained only at the reference temperature. A single WLF shift factor a_t was found to apply for pure PES and for the 95/5 and 90/10 wt % blends:

$$\log a_t = 5.3 (T - T_g) / (95 + T - T_g) \quad (2)$$

From Figure 9 it is seen that as the PI content in the blend increases there is a gradual increase in the elasticity of the blends and the terminal zone moves toward lower frequencies. We believe that this is mainly a consequence of the composition dependence of the glass transition temperature. The loss modulus (G'') versus frequency curves in Figure 10 also show a monotonic increase in modulus and a shift of the terminal zone with increasing PI composition.

From G' and G'' the dynamic viscosity (η^*) was determined as shown in Figure 11. Within the limited frequency range accessible in our study it was only possible to reach the Newtonian plateau for the pure PES polymer and blends of the lower PI contents. The data show a significant increase in viscosity of more than one order of magnitude when 10 wt % PI is incorporated into the blend. The non-Newtonian region shows a considerable amount of shear thinning with similar power law behavior for the different blends.

Figure 12 shows the composition dependence of η^* at different shear frequencies. The data can be

Figure 11. Complex viscosity (η^*) versus frequency curves, calculated from G' and G'' measurements. Reference temperature is 275°C.

Figure 12. Composition dependence of the complex viscosity (η^*) at different shear rates.

fitted by straight lines linear in semilogarithmic plots indicating a simple relationship of the type

$$\eta_{\text{Blend}}^* = \eta_1^* w_1 \eta_2^* w_2 \quad (3)$$

in the range of compositions studied. Here η_{Blend}^* is the viscosity of the blend and η_i^* and w_i ($i = 1, 2$) are the viscosity and the mass fraction of the individual components.

We have also followed the phase separation process by rheological measurements. The samples were heated in the rheometer to the desired temperature above the phase boundary and the evolution of G' and G'' versus time were recorded at constant frequency and deformation. An example is shown in Figure 13 for the 90/10 wt % blend; similar behavior was observed for the 80/20 wt % blend. In Figure 13 the reduced elastic modulus (G'/G_0'), defined as the ratio between the elastic modulus at any time divided by the initial elastic modulus (G_0'), is plotted versus time at a constant frequency of 1 rad/s. Curves corresponding to 265, 275, 288, 300, and 320°C are shown.

When measurements were made at temperatures below the apparent phase boundary, which for the 90/10 wt % blend was approximately 282°C, no significant changes in the viscoelastic properties were observed, indicating a stable blend. At higher temperatures the modulus increased with time, slowly at temperatures close to the phase boundary and

Figure 13. Evolution of the reduced elastic modulus (G'/G_0) versus time at different temperatures. The data are for the 10/90 wt % PI/PES blend.

more rapidly at higher temperatures. In none of the experiments was it possible to reach a constant value for the modulus within a reasonable time. At the highest temperature (320°C) the experimental data showed a tendency to reach a plateau. We believe that this is a consequence not only of phase separation but also of chemical changes.

Phase separation occurred while heating disks of PES/PI blends of different compositions in the rheometer at temperatures above the phase boundary as indicated by DSC scans on small samples taken from the disks. The scans exhibited two glass transitions at 229°C and 320°C corresponding to the T_g s of the pure PES and PI.

To investigate further the physical and chemical changes occurring at high temperatures, some samples were annealed in the rheometer at 320°C for 20 minutes. The samples were then cooled in situ to the reference temperature of 275°C and new sets

of temperature and frequency sweeps were performed at temperatures of 265, 275, 288, and 295°C. Figures 14 and 15 show the results obtained for the 90/10 and 80/20 wt % PES/PI, respectively. A substantial change in the viscoelastic response of the blends was observed. The storage and loss moduli now exhibit a constant power law dependence on frequency of the type:

$$\begin{aligned} G'(\omega) &= S\omega^n \\ G''(\omega) &= D\omega^n \end{aligned} \quad (4)$$

where S and D are constants and n is the relaxation exponent which takes values $n = 0.33$ and $n = 0.14$ for the 90/10 wt % and 80/20 wt % PES/PI blends, respectively. This behavior, which is valid for five decades in frequency, has been shown to be typical of crosslinked polymers close to the gel point.²⁶⁻²⁹

Figure 14. Elastic (G') and loss (G'') shear moduli versus frequency after annealing the 10/90 wt % PI/PES blend at 320°C for 20 min. The reference temperature is 275°C.

The presence of an insoluble gel has also been confirmed by extracting the samples with CH_2Cl_2 . Small gel fractions between 0.10 and 0.30 have been obtained from 90/10 and 80/20 wt % blends. Infrared scans performed on the gel fractions of the samples

show changes in chemical structure and a higher concentration of PI in the gel fraction than in the original blend.

The samples of pure PES and the 95/5 wt % PES/PI blend with identical thermal histories were

Figure 15. Elastic (G') and loss (G'') shear moduli versus frequency after annealing the 20/80 wt % PI/PES blend at 320°C for 20 min. The reference temperature is 275°C.

quite stable showing no significant increase in G' and G'' with time.

CONCLUSIONS

The polyethersulfone, Victrex, and the polyimide, Matrimide 5218, form a miscible blend when mixed in a common solvent and cast or coprecipitated, but after heating a few degrees above the glass transition the blends become phase separated. The boundary thus obtained is not representative of equilibrium behavior. Miscibility in PES/PI blends must then be regarded as a metastable phenomenon in the blends achieved by relatively rapid solvent removal. Below the apparent phase boundary the blends with PI contents of 20% or less have sufficiently large "processing windows" and remain stable for periods of time compatible with processing requirements. Heating the blends at higher temperatures induces permanent changes in viscoelastic properties which are consistent with the incipient formation of a gel structure. Rheometry has been shown to be a very sensitive technique for detecting physical and chemical changes in these blends.

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