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Miscibility Behavior in Polyethersulfone/Polyimide Blends with and without Solvents

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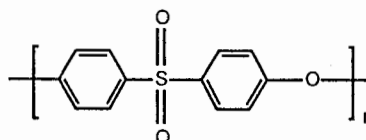
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Abstract: The miscibility behavior in blends of polyethersulfone (Vitrex PES) with the polyimide PI 2080, (the condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride [BDTA] and a 4:1 mixture of 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate) or with the polyimide XU 218 (the condensation product of BDTA and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindane) was investigated using differential scanning calorimetry, dynamic mechanical analysis and thermogravimetric analysis. The effects of solvents (dimethylacetamide, tetramethylene sulfone, dimethyl sulfoxide and 1-methyl-2-pyrrolidone) on miscibility were studied and one solvent, tetramethylene sulfone was found to have a plasticizing effect. In the absence of solvent, the equilibrium phase boundary for these blends was in the experimentally inaccessible region below the T_g -composition line. The phase boundary at zero solvent concentration was obtained by extrapolation using data collected in the presence of the plasticizer.

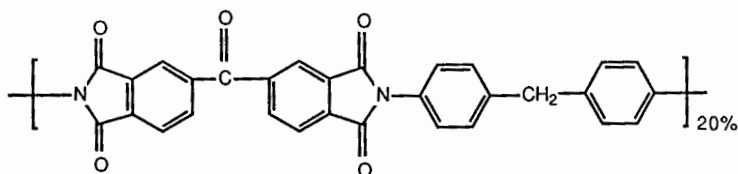
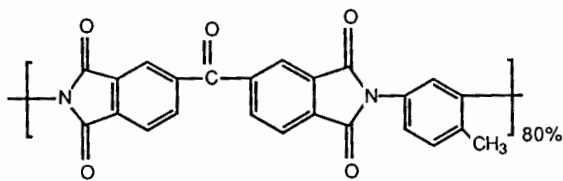
INTRODUCTION

In the last few years, high performance miscible polymer blends have attracted attention in the search for new materials at lower costs. Recently, two new families of high performance blends consisting of an aromatic polybenzimidazole and aromatic polyimides [1-3] and aromatic polyimides and polyethersulfone [4] have been reported. However, even though these blends appear to be miscible over the entire range of compositions, phase separation on heating above T_g is irreversible. This contribution describes the miscibility behavior in polyether-sulfone/polyimide PI 2080 and polyethersulfone/polyimide XU 218 blends with and without solvents.

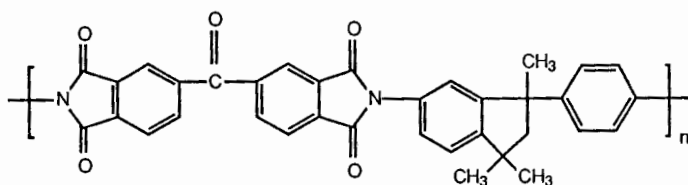
Polyethersulfone (PES) is a high performance engineering thermoplastic with the repeat unit:



The polyimide 2080 (PI 2080) is also a thermally stable polymer; its repeat unit is:



PI XU 218 has the repeat unit:



PES/polyimide blends are interesting for several reasons. First, little information about these blends is available in the literature although PES has been reported to be miscible with poly(ethylene oxide) [5,6] and with phenoxy resin [7]. Second, PES costs less than polyimide and has somewhat similar mechanical properties. Third, films of the blends have indicated that the brittle nature of pure PI is decreased by mixing with PES. Thus PES/PI blends offer a potential improvement over the pure materials.

Miscibility in polymer blends is controlled by thermodynamic factors such as the polymer-polymer interaction parameter [8,9], the combinatorial entropy [10,11], polymer-solvent interactions [12,13] and the "free volume" effect [14,15] in addition to kinetic factors such as the blending protocol, including the evaporation rate of the solvent and the drying conditions of the samples. If the blends appear to be miscible under the given preparation conditions, as is the case for the blends described here, it is important to investigate the reversibility of phase separation since the apparent one-phase state may be only metastable. To obtain reliable information about miscibility in these blends, the miscibility behavior was studied in the presence and absence of solvents under conditions which included a reversibility of phase separation. An equilibrium phase boundary was then obtained for the binary blend systems by extrapolating to zero solvent concentration.

EXPERIMENTAL

Materials

The polyethersulfone, Victrex PES, was supplied by ICI Americas, Inc. Its reported grade and molecular weight were 4800p and $M_n = 22,000$, respectively; its glass transition temperature was 230°C. PI 2080 ($T_g = 310^\circ\text{C}$) was supplied by Dow Chemical Co. PI XU 218 ($M_w = 80,000$, $M_n = 10,000$ -11,000, $T_g = 320^\circ\text{C}$) was obtained as a yellow powder from Ciba-Geigy.

The solvents, N,N-dimethylacetamide (bp = 165-166°C), tetramethylene sulfone (bp = 285°C), 1-methyl-2-pyrrolidone (bp = 202°C) and dimethyl sulfoxide (bp = 189°C) were all obtained from Aldrich Chemical Co.

Preparation

PES/PI 2080 Blends PES was dried for more than four hours at 150°C to remove residual water before use. Solutions (3 wt%) of the blends were prepared by dissolving the two pure polymer constituents in the desired ratio. Films of the blends were cast from these solutions on Pyrex glass dishes at 80-90°C under vacuum. To obtain solvent-free samples, the films were gradually heated to 240-250°C over a period of three days. To obtain samples of varying solvent contents, the films were dried at lower temperatures for shorter lengths of time. The solvent content of the samples was measured by thermogravimetric analysis.

PES/PI XU 218 Blends PES was dried as described above and pure PES and PI XU 218 were dissolved in the desired proportions in methylene chloride. Tetramethylene sulfone (TMS) was the only other solvent used in the blends containing PI XU 218. PES, PI XU 218 and TMS ternary mixtures were prepared by dissolving all three components in the desired proportions in methylene chloride at room temperature. Because TMS is a solid below 27°C, it was first liquified by heating and was then added dropwise to mixtures of PES and PI XU 218. Films were cast from solution on Pyrex glass dishes. Methylene chloride was evaporated by placing the dishes in a dessicator with a hole in the lid for several days and then by transferring the dishes to a fume hood. Final traces of solvent were removed under vacuum, annealing at 60°C for three days.

Measurements

Thermogravimetric analyses (TGA) were carried out using a Perkin-Elmer TGA-7 instrument. The temperature range was from 50 to 700°C and the heating rate was 20°C/min in a nitrogen atmosphere.

The glass transition temperatures of the pure polymers and the blends were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C/min for those samples not containing TMS and 10°C/min for samples containing TMS. All measurements were carried out under nitrogen. All samples except those containing TMS were encapsulated in the standard aluminum pans.

Dynamic mechanical thermal analyses were carried out using a Polymer Laboratories DMTA equipped with a high temperature (500°C) head operating at a frequency of 1 Hz and a constant strain, $\times 1$, in the single cantilever mode. The thickness of the PES/PI 2080 films was in the range of 0.1-0.2 mm and that of the PES/PI XU 218 films was 0.2-0.3 mm.

RESULTS AND DISCUSSION

A. Physical Appearance of the Blends

All polymer solutions were transparent and films cast from these solutions also appeared to be transparent; those containing PI 2080 were slightly yellow to light brown in color. The brittle nature of PI 2080 was improved by mixing with PES in that films of these blends qualitatively were more flexible than films of pure PI 2080.

B. Thermogravimetric Analysis

Since solvents present in blend samples can act as efficient plasticizers, the most important step in sample preparation is to eliminate residual solvent. Figure 1 and Table 1 show TGA results for several "solvent-free" PES/PI 2080 blends prepared in N,N-dimethyl acetamide (DMAc) and for PES/PI XU 218 blends prepared in methylene chloride. It is clear that for PES/PI 2080 blends the residual solvent contents at all blend compositions were less than 1 wt% after drying. For PES/PI XU 218 blends prepared without tetramethylene sulfone (TMS) there was no obvious decomposition above 300°C. Figure 1 also shows that with increasing PI 2080 content, the thermal stability of the blends increases as indicated by the gradual decrease in weight loss from 100°C to 700°C.

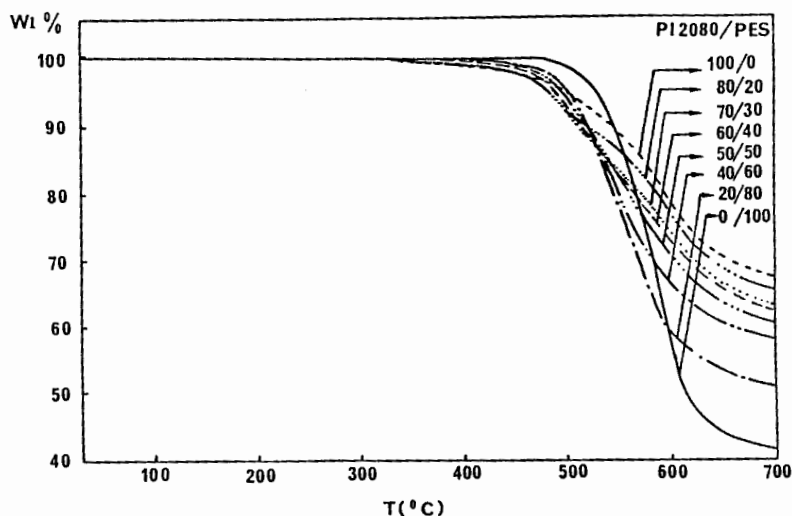


Figure 1. TGA curves for films of pure PES and PI 2080 and blends obtained by casting from DMAc solution. The films were previously dried at 245-250°C for 15 hr under vacuum.

Table I
TGA results for PES/PI 2080 and PES/PI XU 218 blends

blend composition wt% PES/PI 2080	weight loss (%) 100-400°C	weight loss (%) 100-700°C	onset of decomposition (°C)
100/0	0.90	35.7	463
90/10	0.76	36.0	446
80/20	0.61	39.5	442
70/30	0.79	38.6	439
60/40	0.79	41.7	442
50/50	0.54	43.8	450
40/60	0.42	47.4	448
30/70	0.19	47.3	456
20/80	0.14	50.7	450
10/90	0.19	55.8	467
0/100	0.11	58.8	483
PES/PI XU 218 wt%	weight loss (%) below 350°C	weight loss (%) at 300°C, 2 hr	
100/0	0.90	-	
80/20	0.60	0.20	
70/30	0.40	0.30	
60/40	0.90	0.40	
50/50	0.50	0.30	
40/60	0.40	0.30	
30/70	0.70	0.30	
20/80	0.50	0.20	
10/90	0.40		
0/100	0.50		

For PES/PI XU 218 blends prepared with TMS in methylene chloride, TGA results and elemental analyses indicated that TMS was not lost from the samples during drying (Figure 2). After several

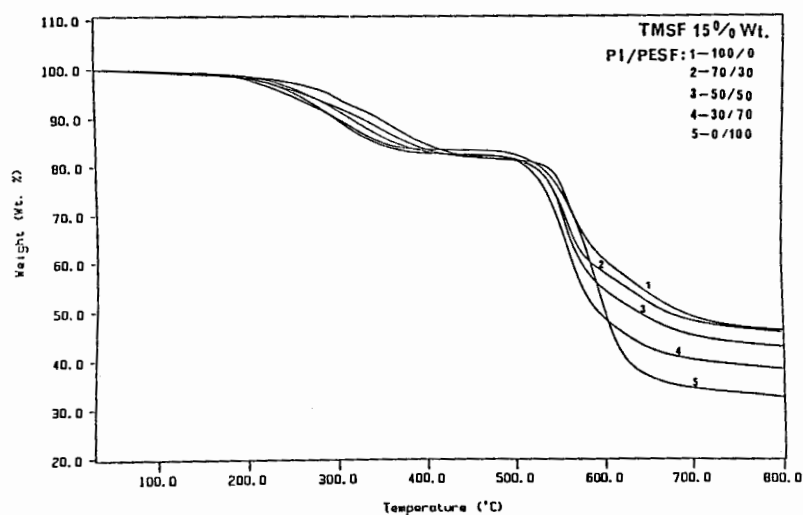


Figure 2. TGA curves of PES/PI XU 218 blends containing 15 wt% TMS.

C. Enthalpy Relaxation Phenomena

Since the thermal behavior of polymers is known to be sensitive to thermal history and traces of residual solvent and moisture, all samples were annealed at temperatures sufficiently high to remove solvent and moisture but low enough to prevent phase separation. In this way reproducible glass transition temperatures were obtained; all data presented are average values of at least three measurements.

Initial differential scanning calorimetry (DSC) scans of PES/PI 2080 blends always showed one or more enthalpy relaxation peaks while those of the PES/PI XU 218 blends showed one broad relaxation peak for each composition investigated. The relaxations observed for PES/PI XU 218 blends increased smoothly with increasing PI content.

The presence of enthalpy relaxation peaks may affect the determination of glass transition values. To erase a relaxation peak within the glass transition, the samples were heated to 10°C over T_g and then quenched at a rate of 320°C/min to 50°C. DSC curves were then recorded again with a heating rate of 20°C/min.

Figure 3 shows typical DSC curves for 80/20 wt% PES/PI 2080 blends. It can be seen that curves A, C and D display relaxation peaks while curves B and E correspond to scans obtained after the previous thermal history has been "erased". In addition, curves A, B and C indicate that the blends are

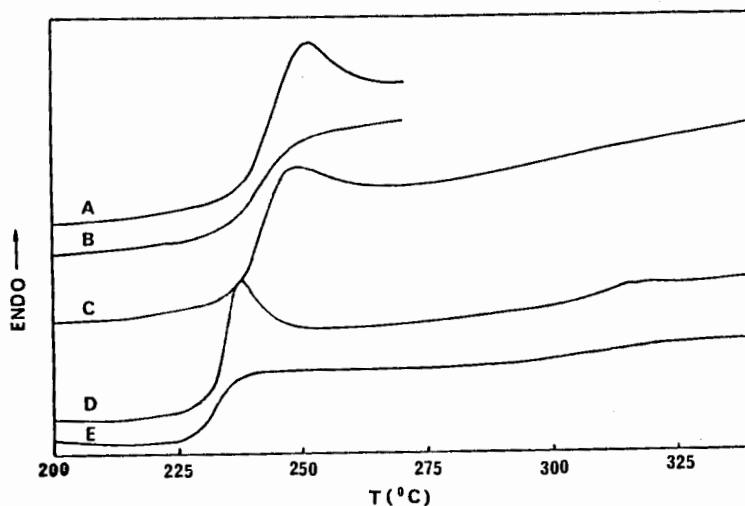


Figure 3. DSC curves for an 80/20 wt% PES/PI 2080 blend. One film was subjected to the following process in sequence: A: initial scan; B: after quenching from 270°C; C: after slow cooling from 270°C (1°C/min); D: after slow cooling from 350°C (1°C/min); E: after quenching from 350°C.

PES/PI XU 218 blends containing TMS exhibited lower T_g values as expected and always showed a single T_g , independent of TMS content. Figure 4 shows the glass transition temperatures (measured by DSC at 10°C/min) of the ternary mixtures as a function of TMS content and weight percent XU 218. The most notable effect on the reduction of T_g in the ternary blends (as compared to blends prepared without TMS) was observed with the initial addition of TMS.

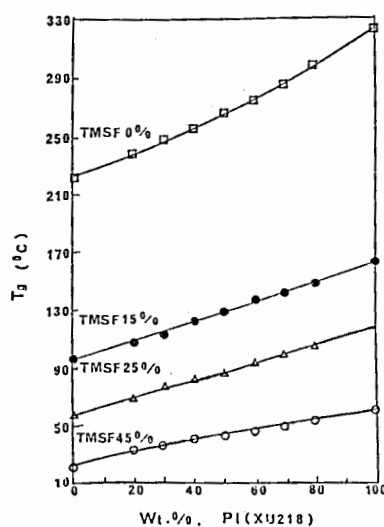


Figure 4. T_g -composition curves for PES/PI XU 218 blends containing different amounts of TMS.

D. Phase Behavior

The DSC and dynamic mechanical thermal analysis (DMTA) results obtained for solvent-free PES/PI 2080 samples after the thermal history had been "erased" and before phase separation had occurred show only one glass transition indicating that under these conditions PES is miscible with PI 2080 over all blend compositions. However, when solvent-free samples were first heated to 350°C (330°C for PES/PI XU 218 samples), then cooled and subjected to DSC and DMTA measurements, two T_g 's were always observed indicating that phase separation had taken place.

It is expected [16-18] that thermally induced phase separation can be reversed when polymer blends are annealed below their respective LCST's if the system is in equilibrium. However, in the present PES/PI systems, as in the PBI/PI systems [19], reversibility is not observed. It is obvious that the data presented above represent only apparent phase boundary curves. Because of the rigidity of the PES and PI chains, the mobility of the segments is limited and the system is highly viscous. The observed one-phase system corresponds to a homogeneous "frozen" structure formed from a solution of the constituents as the solvent evaporates. When relaxation times are sufficiently reduced, the chains have sufficient mobility to form a stable two-phase state. The location of the true phase boundary curve in the present case for PES/PI blends may lie below the T_g -composition line.

In Figure 5 it can be seen that the "window" between T_g and the apparent phase boundary for PES/PI XU 218 blends is narrow, especially when the PI content is greater than 60 wt%.

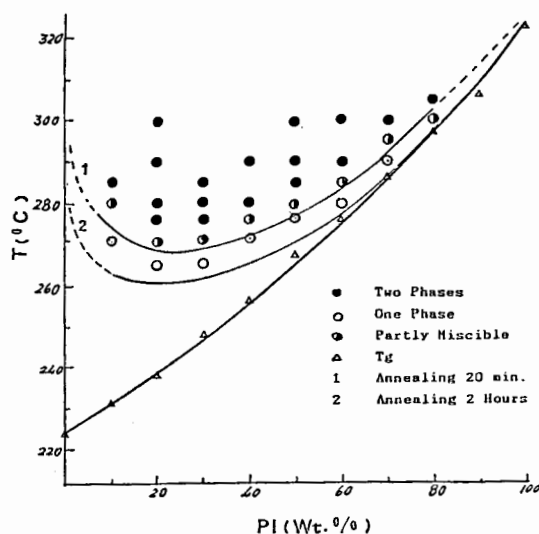


Figure 5. Apparent boundary curve for PES/PI XU 218 blends (without TMS).

E. Effects of Solvent on Phase Behavior

The addition of a compatible low molecular weight solvent to the PES/PI systems would have the effect of reducing the viscosity of the system and thus reducing the relaxation time of the segments. Therefore, a series of films of pure polymers and blends prepared in different solvents was subjected to DSC investigation. The results showed that the T_g values decreased with increasing solvent concentration. Figure 6 (pure PES) shows typical results.

Since TMS has a relatively high boiling point ($bp = 285^\circ\text{C}$) and showed a low extent of evaporation from the samples, it was used in the preparation of samples for further study.

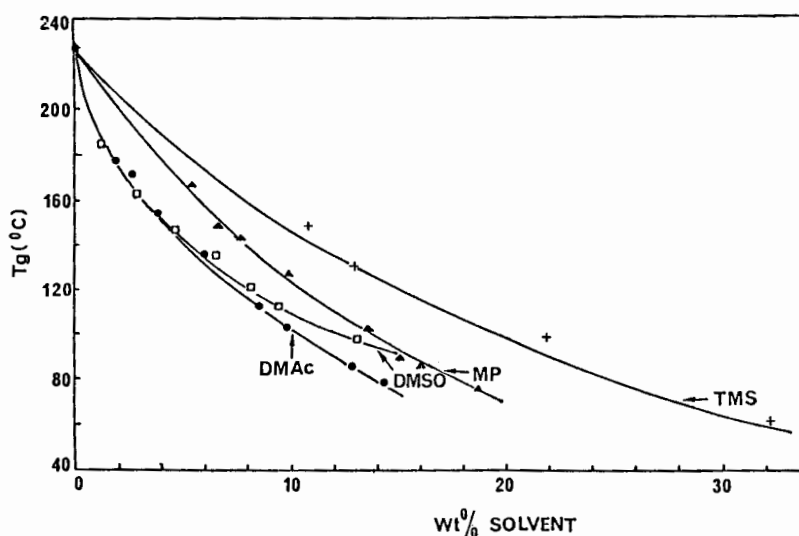


Figure 6. T_g as a function of solvent content for pure PES.

To determine the apparent phase boundaries in PES/PI blends with and without TMS a series of annealing experiments was performed. Each blend was annealed at a different temperature for 20 min for the system without TMS and for 10 min for the PES/PI/TMS ternary system and then analyzed by DSC. The lowest temperature for which two T_g 's were detected was taken as the location of the apparent phase separation boundary.

The effects of the addition of TMS are shown in Figures 7 and 8 for PES/PI XU 218 and PES/PI 2080 blends, respectively. The glass transitions and phase separation occur at lower and higher temperatures, respectively than in the absence of TMS and the "window" between the T_g -composition line and the apparent boundary curve is expanded.

As discussed above it is clear that the phase boundary curves obtained under these conditions are true equilibrium curves. Reversible phase separation was observed for PES/PI XU 218 blends at a TMS content of 25 wt% or greater and for PES/PI 2080 blends at a TMS content of 30 wt% or greater.

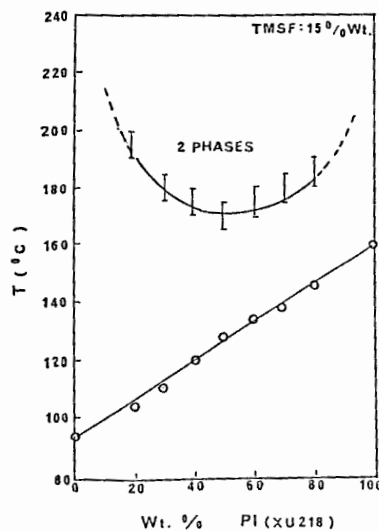


Figure 7. T_g -composition line and phase boundary curve for PES/PI XU 218 blends containing 15 wt% TMS.

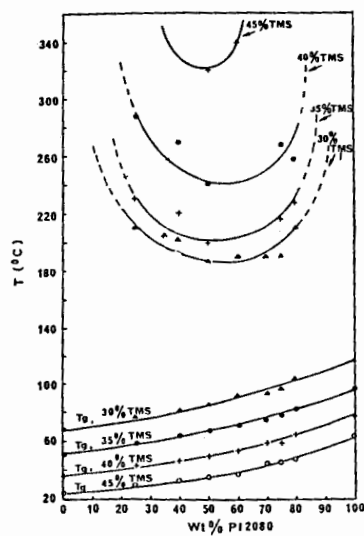


Figure 8. T_g -composition lines and phase boundary for PES/PI 2080 blends containing different amounts of TMS.

To obtain a true equilibrium phase boundary curve for solvent-free PES/PI blends, the data collected for samples containing different amounts of TMS were extrapolated to zero solvent content. For a 50/50 wt% PES/PI XU 218 blend a phase separation temperature of 140°C is obtained, a temperature lower than the blend T_g (267°C). Similar results are observed for PES/PI 2080 blends, Figure 9.

We note some similarities between the present PES/PI/TMS blends and the PMMA/SAN/DMP system reported by Bernstein et al. [20]. These authors found that phase separation in the PMMA/SAN system is not reversible but addition of 15 wt% or more of DMP induced reversibility. These effects were explained by the proposal that "equation of state" and "entropy of mixing" factors are working in opposition. In this system it is our belief that the reversible and irreversible processes merely reflect thermodynamic and kinetic considerations. The displacement of the phase boundary curve for the PES/PI/TMS system to higher temperatures is due to contributions to the free volume from TMS [21-23].

Crosslinking was not observed in annealing studies with PES/PI XU 218 blends; all samples with and without TMS could be dissolved in methylene chloride to form transparent solutions after thermally induced phase separation and annealing. However, PES/PI 2080 samples heated to 350°C several times could not be dissolved in DMAc suggesting that a network structure had formed.

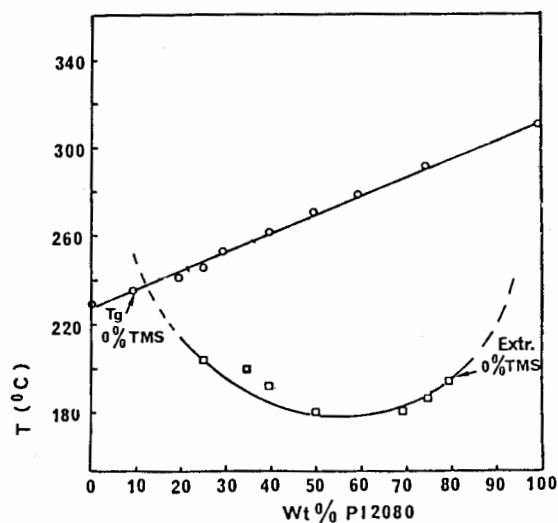


Figure 9. T_g -composition line and phase boundary for PES/PI 2080 blends extrapolated to zero TMS content.

CONCLUSIONS

The apparent miscibility in the PES/PI blends is due to the "frozen" structure of the mixture produced during the film preparation protocol. After the system is phase separated at a temperature above T_g it cannot revert to a one-phase mixture. Thus the structure of the blend samples is not thermodynamically stable; the equilibrium phase boundary for these mixtures must be below the respective blend T_g 's.

When tetramethylene sulfone was added to PES/PI blends the blend T_g 's were sufficiently depressed and the window between the phase boundary curve and the T_g -composition line was expanded so that equilibrium data could be obtained. At TMS contents greater than 25 or 30 wt% an equilibrium LCST could be detected which occurred at higher temperatures as the TMS content increased. Concurrently, the phase separation process became experimentally reversible.

ACKNOWLEDGEMENT

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