Mechanical and Morphological Phase Behavior in Miscible Polyethersulfone and Polyimide Blends

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ABSTRACT: Phase behavior in the blends of polyimide (PI; Matrimid 5218) which is a condensation product of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 5(6)-amino-1-(4-aminophenyl)-1,3,3′-trimethylidone and polyethersulfone [PES; poly(sulfone bis(*p*-phenyl) oxide)] has been investigated by differential scanning calorimetry (DSC), tensile test, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Miscibility was obtained from an optically transparent film and a composition dependent single glass transition temperature (T_g) using DSC. Thermally induced phase diagram indicated LCST (lower critical solution temperature) type behavior. TGA measurement showed an increment in thermal stability and in weight retention in miscible blends. In mechanical measurement, the homogeneous 50/50 wt% blend showed the highest strain at break, yield stress and modulus, however these values were dramatically reduced after phase separation. Phase morphology was also observed by comparison to the domain growth in thermally induced phase separation using SEM and thereby this is a good agreement with the DSC and mechanical behavior.

KEY WORDS   Polyethersulfone (PES), Polyimide (PI) / Miscibility / Thermal Properties / Phase Behavior / Mechanical Properties / Phase Morphology /

Blends of high performance aromatic poly-(benzimidazole) (PBI) and various aromatic polyimides (PIs)[1-7] have been studied to identify their miscibilities. Some of the blends are miscible over a wide range of compositions and structural variations,[1-6] but some others are not miscible.[7] In most cases, miscibility was determined by the formation of optically transparent film, presence of a single composition dependent glass transition temperature (T_g), dynamic mechanical relaxational tan δ peak[4] relative to the T_g, and spectroscopic frequency shift[1,2,6] of functional groups in the constituents. Moreover, hydrogen bonding has been reported to be responsible for miscibility between carbonyl groups in PI and NH group in PBI.[2,3]

We have extended our investigation on the blends of an aromatic polyimide (PI; Matrimid 5218 of Ciba-Geigy Corporation) and an aromatic polyethersulfone (PES: Victrex grade 5200p of ICI American Inc.) for viability of the further application in high temperature materials. This system has been apparently transparent and given an opportunity to study the miscibility. Recently, Liang *et al.* studied thermal and rheological properties using the same blends system.[8] A composition dependent single glass transitions (T_g) and a narrow "processing window" have been observed. Moreover, rheological measurements in this range of compositions indicated that blending PES with PI increases the complex viscosity and the elastic modulus of the blends.

In the present investigation, the similar behavior was obtained in thermal study. Thus, in this article, thermal properties are compared to those obtained by Liang *et al.* In addition, a more systematic analysis of the mechanical and morphological phase behavior of the

blends is performed and discussed as a function of temperature.

EXPERIMENTAL

Materials

The chemical structures and names used in this study are listed in Table I. Polyethersulfone (PES, $M_n = 43000$, $M_w = 260000$) was used as-received powder and polyimide (PI: intrinsic viscosity of 0.5% N-methylpyrrolidone at 25°C; 0.65 dl g^{-1}, $M_n = 10000$, $M_w = 80000$) was also used as-received form. Both of the powder were dried in vacuum oven at 80°C for 2 days before sample preparation.

Sample Preparation

N,N'-Dimethylacetamide (DMAc; Aldrich, M_w 87.2, bp 164—166°C, $\rho = 0.937$) was used as a co-solvent. Homopolymers PES and PI were dissolved in DMAc by weight ratio and filtered. Homopolymer solutions (3 wt%) were mixed by the weight ratio and stirred at room temperature for 3 hours. For DSC measurements, powder specimens were prepared by a dropwise in ten-fold excess non-solvents, distilled water, or 40—70 μm thick films were cast from 3 wt% DMAc solution of the polymer mixtures on petri dishes under a nitrogen atmosphere at 80°C for 2 days. For SEM and tensile test, films of 50—100 μm thickness were cast from 3 wt% DMAc solution of the polymer mixtures by the same procedure described as the above. To exclude residual solvent, films were washed in distilled water at 80°C for 24 hours.

Powders and films were dried in vacuum oven under nitrogen atmosphere at 170°C for 5 hours and then further dried at their glass transition temperature (T_g) depending on blend composition for 3 hours. Specimens of 5 mm diameter disk for SEM analysis and ASTM-882 type for Instron tester were machined.
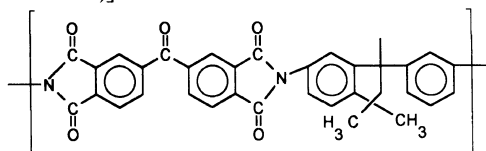
Analysis

Perkin-Elmer DSC-7 controlled by a Perkin-

Table I. Chemical structures of homopolymers

(A) Poly[sulfone bis(p-phenyl)oxide]
   [ICI Americas: Victrex PES ($T_g = 229$°C)]
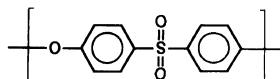
(B) Condensation product of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and 5(6)-amino-1-(4-aminophenyl)-1,3,3′-trimethylindane [Ciba-Geigy Corporation: Matrimide 5218 ($T_g = 324$°C)]

Elmer 7500PC was used to determine the apparent T_g's. Selected thermal histories were imposed to the specimens at desired temperature in DSC, annealing for 10 minutes, quenching to 50°C at 200°C min^{-1} and then rescanning up to 400°C. The heating rate was 20°C min^{-1} under nitrogen atmosphere. To obtain reproducibility, fresh samples were used for an every measurement and five measurements were averaged. Miscibility was determined by observing the composition dependent single T_g and phase boundary was obtained by a single or two T_g's according to the various annealing temperatures.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 from 50°C to 1000°C under nitrogen atmosphere at a heating rate of 10°C min^{-1}. Mechanical measurements were employed on an Instron model 4200 tester with PC. More than twenty measurements were averaged for each blend specimen with 50 mm min^{-1} crosshead speed and extensiometer in 60% relative humidity at 25°C. To study the difference in mechanical properties before and after phase separation, two different thermal histories were imposed to the specimens, at the temperatures where one or two-phase regimes exist (these two temperatures were predetermined from the DSC measurements).
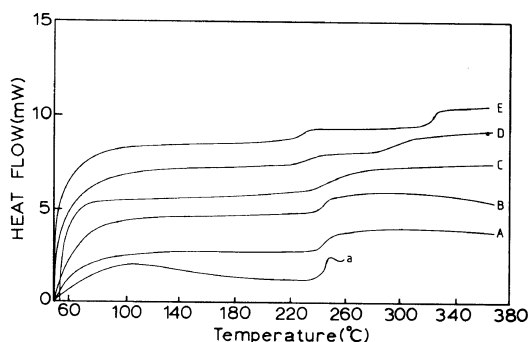
Figure 1. Representative DSC thermograms of PES/PI 50/50 wt% blend. (a): First scan up to 260°C. (A)—(E): Second scan up to 400°C after annealed at various temperatures followed by the first scan; (A) 260°C; (B) 270°C; (C) 280°C; (D) 290°C; (E) 330°C.

Phase morphology was studied using a JEOL-SEM (Model No. JSM-840A) on specimens of platinum polished surfaces. Before used on SEM, the specimens were annealed in preheated vacuum oven for 15 minutes at temperatures before and after phase separation (based on DSC study) followed by the same procedure used for mechanical Test.

RESULTS AND DISCUSSION

Thermal Properties and Phase Behavior

Structural thermal stabilities of homopolymers PES and PI are listed in Table II. $T_g(T_{g\ mid\ point})$, $\Delta T_g(T_g - T_{g\ onset})$ and ΔC_p (C_p difference at transition from glassy to rubbery region) are averages of several measurements from the second scan on DSC.

DSC thermograms of PES/PI, 50/50 wt% blend were plotted in Figure 1. Here, the specimen was scanned and annealed for 10 minutes at various temperatures, quench cooled to 50°C and then rescanned of up to 400°C. As shown in this figure, a single T_g was observed up to the annealing temperature at 280°C (one phase regime). As the annealing temperature is raised above 290°C, the two T_g's were observed and these values were close to the T_g's of the constituents. In this figure, curves A, B, C, D, and E show the second DSC

Table II. Thermal properties of the homopolymers

|	T_g's/°C	ΔT_g/°C	ΔC_p/J K^{-1}
PES	229	14	0.14
PI	324	14	0.15
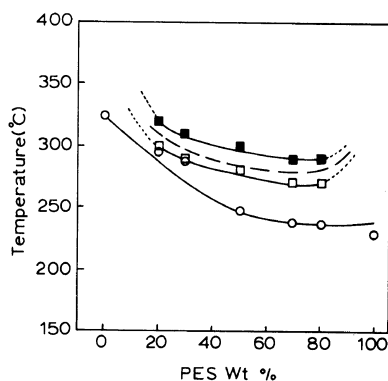
Figure 2. Glass transition temperatures (open circles, ○) of the PES/PI blends. Open (□) and solid squares (■) represent the annealing temperatures corresponding to a single and two T_g's, respectively. Broken line elucidates the phase boundary of the blends. Dotted lines depict the expected one (open square) or two (solid square) phase regimes beyond experiments.

thermograms after annealed at temperatures 260, 270, 280, 290, and 330°C, respectively, for the first scan. The only exception is the curve 1(a) which represents the first thermogram annealed at 260°C. In particular, curve C which is the second scan obtained after annealed at temperature 280°C, shows rather broad transition in comparison to the curve A or B where one-phase is obvious, and to the curve D or E where two phases take place. The behavior such as C or D, of which the transition is broad, may be observed in microphase separation.[9–11] A slight difference in T_g's between the first and the second scan (Figure 1 (a) and (A), respectively) was observed and this may be attributed by the residual solvent or moisture.[1,2]

T_g's of PES/PI blends in various compositions are tabulated in Table III. Figure 2, based on Table III shows a phase separation plot of
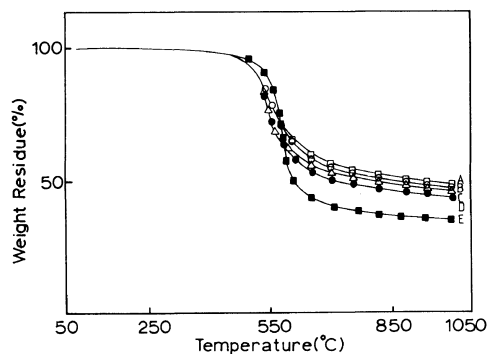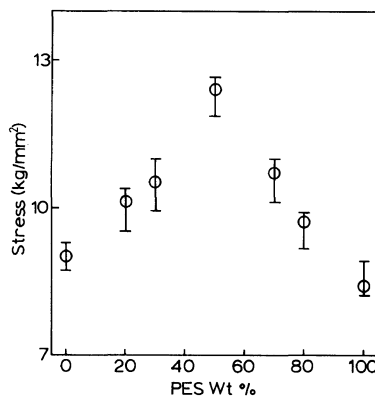
Figure 3. Weight residue of the homopolymers and the blends A, pure PI; B, PES/PI = 30/70; C, 50/50; D, 70/30; E, pure PES.
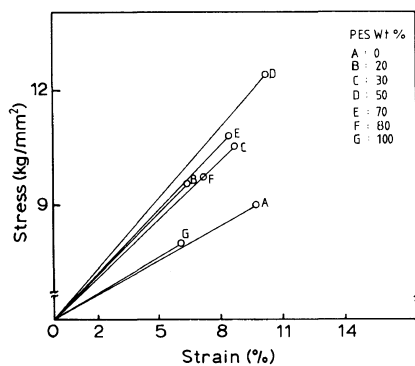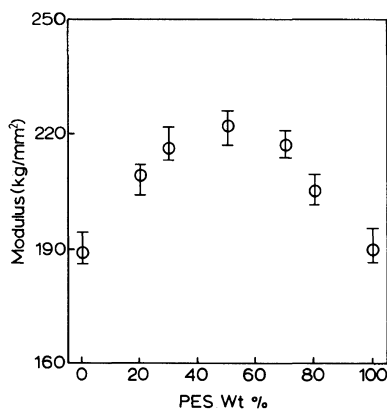

Figure 4. Stress-strain relationship of the pure PI (A), pure PES (G), and PES/PI blends (B) 20/80, (C) 30/70, (D) 50/50, (E) 70/30, (F) 80/20, measured at room temperature.

Figure 5. Yield stress of the homopolymers and the blends, figure shows the experimental deviations (bars) with average values (open circle).

Figure 6. Modulus of elasticity (Young's modulus) as a function of PES content.

PES/PI blend system derived from DSC data. This is not thermodynamically miscible system because the reverse phase behavior was not observed. In this figure, the open circles are T_g's of the homopolymers and of various blend compositions, and open and solid squares represent temperatures where one and two T_g's have been observed, respectively. Dotted lines are expected one or two phase regimes beyond the experimental results. Thus rough phase diagram was plotted with broken line between one and two T_g's. In this figure, one observes the reduced phase separation temperatures as the PES compositions are increased and the LCST type behavior where the two phases taken place in higher temperature. This is
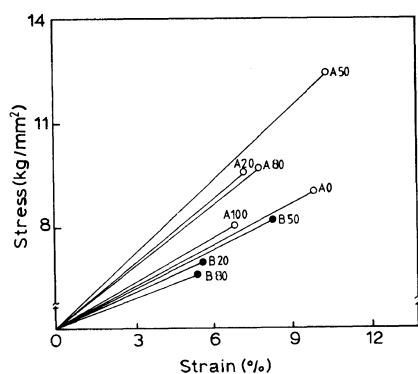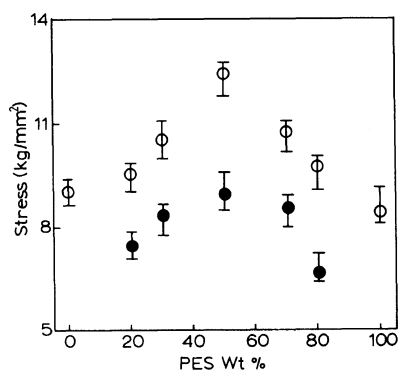
similar to the report of Liang *et al.*[8]

Weight loss and weight retention of the blends powder are depicted in Figure 3. Here, curves A, B, C, D, and E represent pure PI, PES/PI 30/70 wt%, 50/50, 70/30, and homopolymer PES, respectively. 5% weight loss was observed at 548°C for PES and at 522°C for PI. For the blends, it was not observed any particular weight retention during 5% weight loss. On the other hand, weight retention of PES at 1000°C is 33.9% while PI shows 50.5% of which PI shows better thermal stability at higher temperature. The increment in thermal stability and weight residue was observed for all blend compositions used. This synergistic

Table III. Glass transition temperature at various annealing temperature for the blend composition

	Observed T_g						
	Annealing temp						
PES wt%	260	270	280	290	300	330	350
0							324
20	284	290	295	299	299	231 307	229 320
30	272	283	287	286	236 305	231 317	230 322
50	246	247	247	233 296	233 306	231 317	230 322
70	238	238	233 309	232 317	231 322	230 322	230 322
80	236	237	233 310	233 315	230 320	231 322	231 324
100	229						

Table IV. Annealing temperature for mechanical and morphological phase behaviors

PES wt%	20	30	50	70	80
Before phase separation	300	290	280	270	270
After phase separation	320	310	300	290	290

Figure 8. Yield stress as a function of PES content after thermally treated at before (open circle) and after (solid circle) phase separation temperature.

Figure 7. Yield stress-strain of the homopolymers and the representative blends which were thermally treated at the temperatures before (A) and after phase separation (B). Numbers represent the PES content (%).
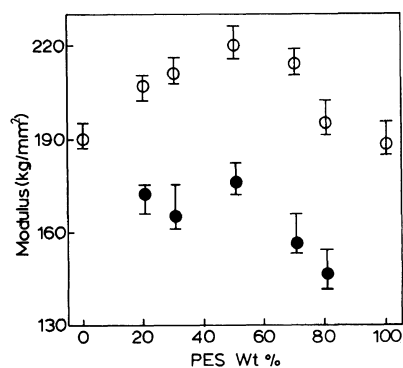
Figure 9. Modulus of the. PES/PI blends, which were thermally treated at before (open circle) and after (solid circle) phase separation temperature.
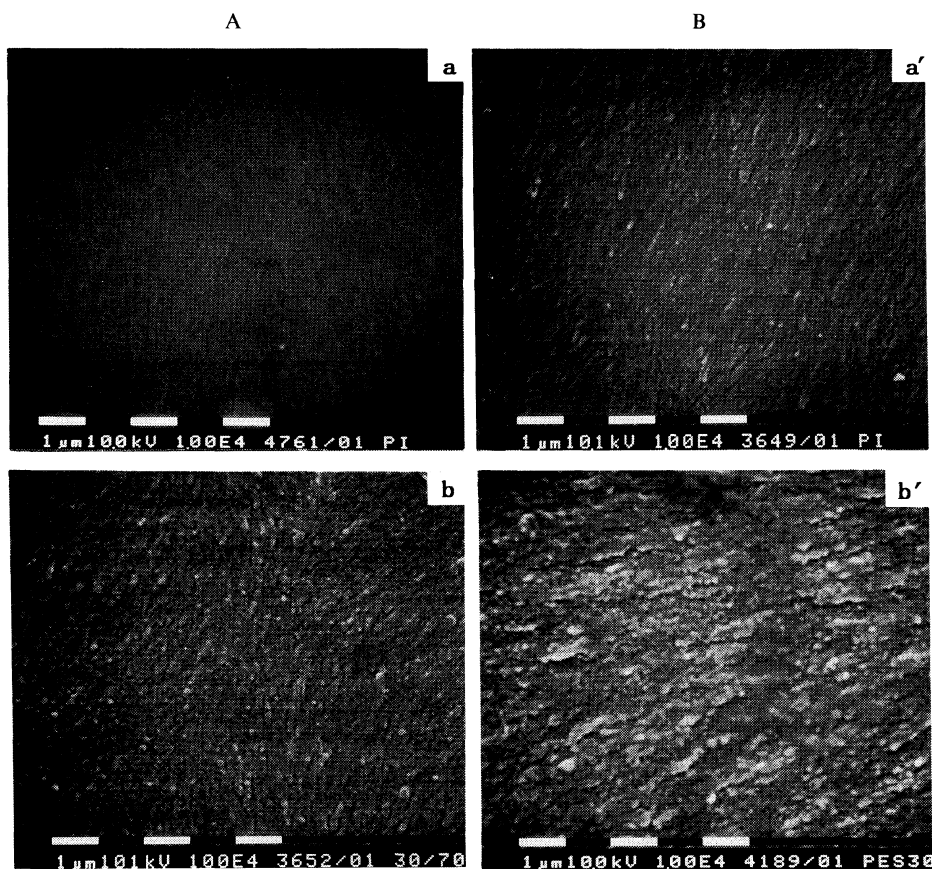
A   B

Fig. 10.

behavior may be obtained from specific intermolecular interactions between the constituents. The evidence of the specific interaction is under investigation and will be disclosed very soon.

Mechanical Behavior of Homopolymers and Their Blends

In Figure 4, stress-strain curves of the specimens were depicted and increased ductilities of the blends in comparison to those of homopolymers were observed. In particular, PES/PI, 50/50 blend shows the highest ductility by showing higher strain, which may be caused by specific intermolecular interaction. Figure 5 shows the relationship between yield stress and blend composition where stress of PES and

PI are $8.4 \, kg \, mm^{-2}$ and $9.0 \, kg \, mm^{-2}$, respectively. That of 50/50 blend shows the highest value of $11.9 \, kg \, mm^{-2}$. The rest of the blends are higher than homopolymer in stress.

The above observation is insufficient to represent miscibility because, in no matter heterogeneous system, the similar behavior would be observed to the results shown in this study.[12,13] As an example, the similar observation was obtained in sufficiently diffused heterogeneous sytem.[12]

To differentiate the typical behavior between homogeneous and heterogeneous system, the modulus of the blends were measured and those of PES and PI are $190 \, kg \, mm^{-2}$ and $189 \, kg \, mm^{-2}$, respectively, and those of PES/PI, $50/50 \, wt\%$ gives the highest value of 222

A   B
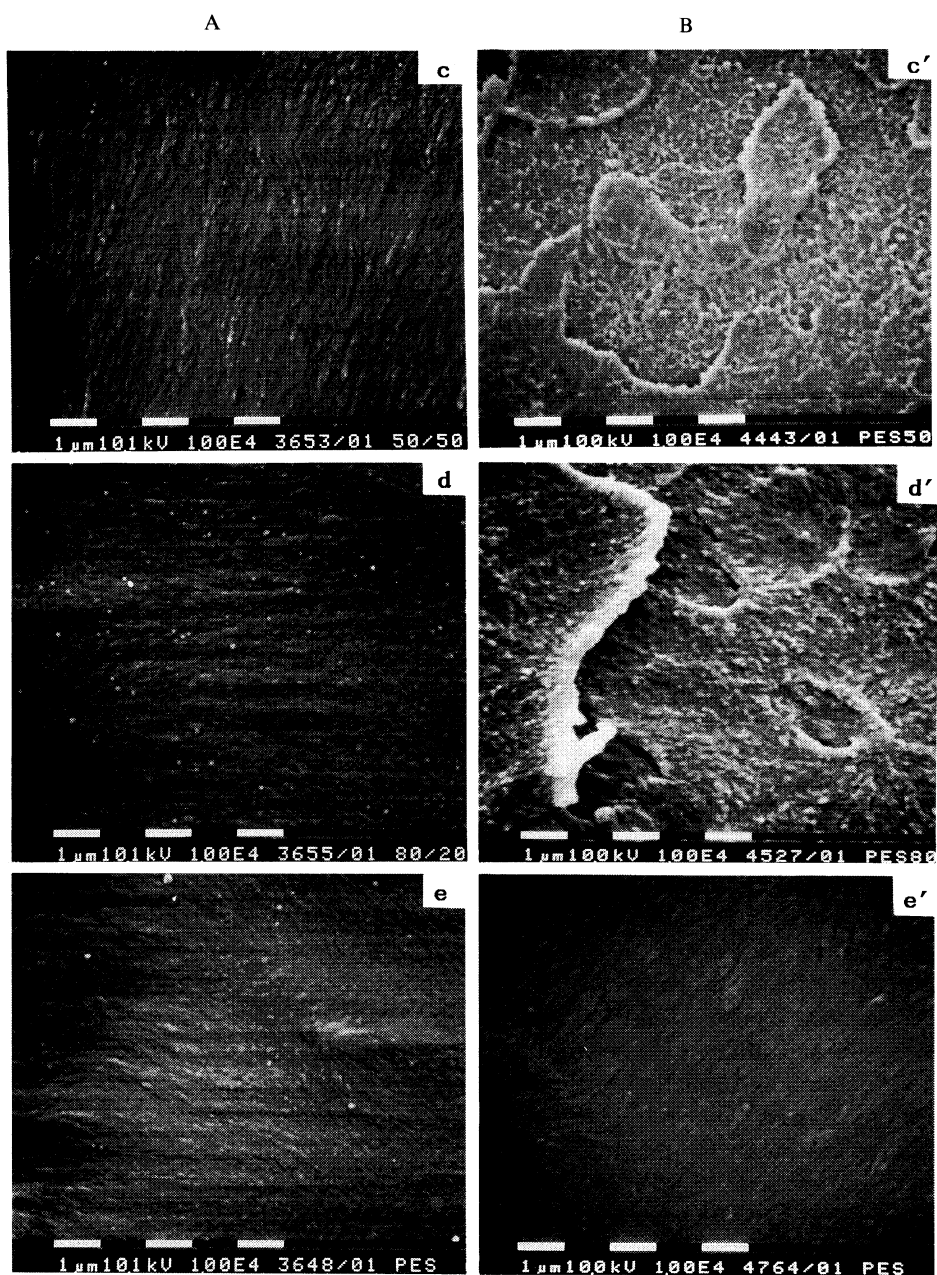
Figure 10. SEM photomicrographs of PES/PI blends (wave-like white portion represents the PES phase): (A), before phase separation; (B), after phase separation. a,a', pure PI; b,b', PES/PI = 30/70; c,c', PES/PI = 50/50; d,d', PES/PI = 80/20; e,e', pure PES.

kg mm^{-2} at room temperature. A synergetic convex type behavior was observed in modulus as well as in yield stress.

In polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blend system, 50/50 wt% blend showed the highest modulus due

to the specific interaction of π–π electron transfer between PS and PPO.[13] It was reported that the tendency of alignment in chain segment to produce maximum chain association causes stiffer chain and thereby it reduces the molecular mobility and raises modulus. In PBI/poly(etherimide) (PEI) blend system,[14] 70/30 wt% shows the highest modulus and this was interpreted as hydrogen bonding between the N–H group in PBI and the carbonyl group in PEI.[1,2] They reported that charge transfer complexation or π transfer complexation would be possible interaction which may not be ruled out. Such interactions may interfere molecular mobility resulting from raised modulus of the system.

In comparison to mechanical behavior between homogeneous (one-phase regime) and heterogeneous (two-phase regime) systems, two different temperatures which describe before and after phase separation in DSC annealing process (in Table IV) were imposed to the specimens for further test on Instron. Stress-strain curves of homopolymers and of representative blends are depicted in Figure 7. Ductilities of the phase-separated systems are dramatically reduced compared to those of the homogeneous blends as well as stress. This may be attributed to weakening or brokening intermolecular interaction which was formed in homogeneous blends. Tensile stress at rupture before and after phase separation is plotted in Figure 8 as a function of the blend compositions. Stress shown in one-phase system is reduced when the phase separation takes place. In particular, PES/PI, 20/80, 30/70, 70/30, and 80/20 wt% blends, the stress in phase separated system is lower than that of the two constituents. This may be observed when the system is incapable of sustaining the stress (stress failure) which is imposed to the system.

Modulus of the blends in homogeneous and heterogeneous systems are calculated and described in Figure 9, and the trend is similar to the previously observed in stress. Modulus

of phase-separated systems in the whole range of blend compositions are lower than those of homopolymers and this may be a result of stress failure in interface of concentrated domains with pure component. It needs further study to rationalize the behavior.

Phase Morphology

The same thermal histories which was given to the specimens for mechanical measurements were imposed for temperature dependent morphological investigation on SEM. Representative SEM photographs of the PES/PI blends heated at temperatures before and after phase separation are shown in Figure 10. Pictures A and B, respectively, represent the morphology observed at the temperature where before and after phase separation take place, and numbers on each picture describe the PES content in blends. In the pictures of section A, figures of PES/PI blends, (a) 0/100, (b) 30/70, (c) 50/50, (d) 80/20, (e) 100/0 exemplify that all the blend compositions are homogeneously mixed. PES and PI seem to be mixed in continuous phase. In section B, it is not obviously observed the difference in PES(e′) and PI(a′) between two differently imposed temperatures. However in Figure 10B-(b′), the fracture surface of 30/70 PES/PI, when the blend was heated above the phase separation temperature, the PES phase in a variety of sizes, emerges small portion of coalescence from the continuous PI phase, which describes phase separation. The change in morphology between 30% PES (Figure 10B-(b′)) and 50% PES (Figure 10B-(c′)) is dramatic. The blend 50/50 of PES/PI, exhibits further coalescence development in PES phase with continuous PI phase, here, it is observed rather rows of connected PES phase over PI. The continuity of the phase is also seen in Figure 10B-(d′) in 80/20. Phase separation is observed with thicker rows between two phases.

As shown in the above figure, domain formation for the phase separated system was clearly obtained and the observed domain size

of PES is increased, as the PES component is increased. This sort of observation is also obtained in the blend system of PBI/PEI blend.[14] Thus the morphologies observed by SEM agree well with the results from DSC or tensile test. From the SEM results, we may interpret the stress or modulus failure in phase separated systems, which is obtained from the measurements by Instron as followings. When high stress is imposed to the blend system at higher temperature, the stress strongly affects the interface, which is insufficient to sustain the stress followed domain formation due to a movement of each constituent. As a result, the phase separation firstly occurs at the interface between the two constituents and there will be a stress or modulus failure in the system. Phase diagram obtained from DSC study is in good agreement with the phase behavior shown in mechanical and morphological aspect.

CONCLUSIONS

1. Miscibility and phase behavior on the blends of PES/PI were carried out using DSC. TGA measurements showed an enhancement in weight loss and weight retention in blends.

2. Modulus and stress failure in the phase separated system was obtained and this may be rationalized by the weakening of the interaction in interface and by the domain formation due to phase separation.

3. Morphological phase behavior also shows a domain growth in phase separated system.

4. Mechanical and morphological phase behavior was investigated using the same thermal condition obtained as the DSC and showed in good agreement with the DSC results.

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