

24 h, and finally at 230°C for 24 h. A transparent film of about 60 μm thick was stored in a desiccator at room temperature. The film was annealed at 300°C for 12 h in a vacuum oven and 30/70 (by weight) PES/PA44I blend film was obtained. The neat polymer films of both PES and PA44I were prepared in a similar manner.

Measurements

Differential scanning calorimetry (DSC) was performed with a Shimadzu thermal analyzer DSC-41M at a heating rate of 20 °C min⁻¹ in nitrogen. Dynamic mechanical analysis (DMA) was carried out using a Toyoseiki Rheograph-Solid in the tensile mode at a frequency of 10 Hz and a heating rate of 2 °C min⁻¹ in air. Wide angle X-ray diffraction profiles were obtained for the film specimens on a Rigakudenki XG X-ray diffraction apparatus using nickel-filtered CuK α radiation (35 kV, 20 mA).

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for as-cast film of PES (curve A), PA44I (B), and 30/70 PES/PA44I blend (C). The blend has a single glass transition temperature (T_g) intermediate between those of the individual constituents. This single T_g behavior and optical transparency of the film mentioned above suggest a single-phase nature of the as-cast film of the PES/PA44I blend. The single-phase nature is also suggested by a single $\tan \delta$ peak in the DMA analysis (curve C in Figure 2).

A curve D in Figure 1 is the DSC thermogram at the second run after the first scan up to 350°C (curve C). Two T_g s are seen, indicating phase decomposition during the first run. To verify the phase decomposition, the transparent blend film was annealed at 300°C for 12 h and the annealed film was examined by DSC and DMA. In the DSC curve (E in Figure 1), although the annealed film exhibited no clear T_g of the aramid component probably

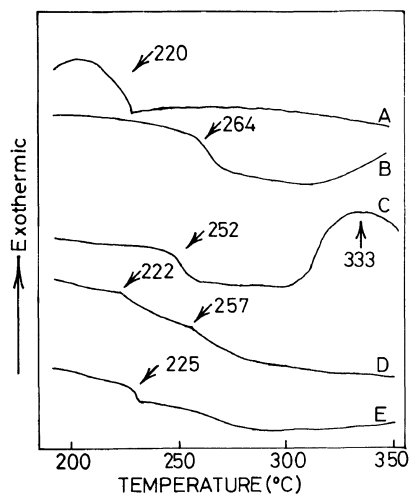


Figure 1. DSC curves for films of neat polymers and a 30/70 PES/PA44I blend at a heating rate of 20 °C min⁻¹: (A) PES, (B) PA44I, (C) as-cast blend of first scan, (D) as-cast blend of second scan, and (E) annealed blend.

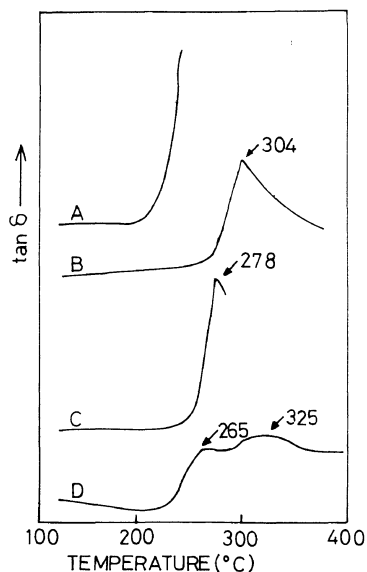


Figure 2. Temperature dependence of $\tan \delta$ for films of neat polymers and a PES/PA44I blend at a heating rate of 2 °C min⁻¹: (A) PES, (B) PA44I, (C) as-cast blend, and (D) annealed blend.

because of crystallization of the aramid, the film showed a T_g at 225°C based on PES component. In addition, the annealed film exhibited two T_g s in the DMA curve (D in

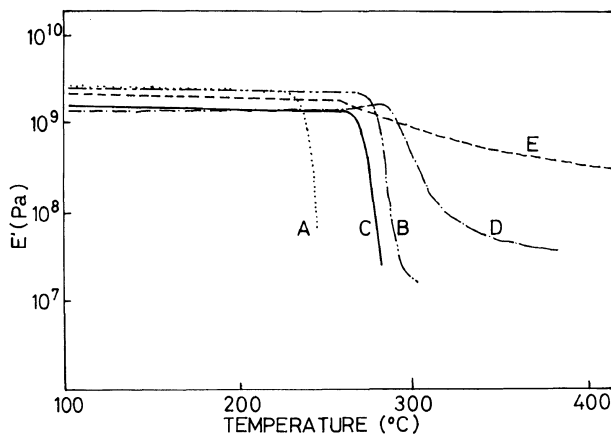


Figure 3. Temperature dependence of dynamic storage modulus for films of neat polymers and a PES/PA44I blend at a heating rate of $2^{\circ}\text{C min}^{-1}$: (A) PES, (B) PA44I, (C) as-cast blend, (D) annealed PA44I, and (E) annealed blend.

Figure 2). These results suggest phase separation to the constituent polymer phases.

Figure 3 shows the temperature dependence of dynamic storage modulus (E') for films of PES (A), as-cast PA44I (B), the as-cast PES/PA44I blend (C), the annealed PA44I (D), and the annealed blend (E). As expected from Figure 2, the unannealed blend film shows a glass-rubber transition at 240°C , whereas the annealed film exhibits a gradual decrease in the modulus, maintaining 350 MPa even at 400°C . Note here that the high temperature modulus of the annealed blend is well above the neat PA44I film annealed under the same condition.

A DSC curve for the as-cast blend film (curve C in Figure 1) also shows a clear exothermic peak due to crystallization at around 330°C , whereas no peak was detected in the curve for the neat PA44I film (curve B in Figure 1). A definite X-ray diffraction peak at $2\theta = 18^{\circ}$ was observed for the annealed blend film while the neat PA44I film annealed under the same conditions gave only an amorphous halo.

These results suggested that the crystallization of aramid is induced by the presence of PES; *i.e.*, blend-induced crystallization. The aramid seems to be a dormant crystalline

polymer. In other words, the crystallizability is latent but crystallization in neat aramid is not realized by annealing but is so in the presence of PES. This may be due to elevation of chain mobility by decreasing T_g on blending the low T_g component (PES). However, it is not sure whether the simple T_g (or mobility) argument is valid at present, because phase separation also takes place during annealing as mentioned above. That is, when the phase separation (liquid-liquid phase separation) precedes and crystallization follows, the aramid should be a dormant polymer, as in the case of neat aramid. Only in the opposite case, *i.e.*, when crystallization precedes, the T_g argument is applicable. The phase separation itself may induce crystallization. This seems plausible based on the current concept of polymer crystallization.⁷

To understand blend-induced crystallization behavior, we have to clarify kinetic aspects of both crystallization and phase separation, especially the competitive situation of the two rate processes. Kinetic results will be presented in near future.

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