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Tensile fracture morphology of polysulfone-poly(phenylene sulfide) blends

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SUMMARY

Melt-extruded and subsequently injection molded polysulfone (PSF) and poly(phenylene sulfide) (PPS) blends exhibit very good tensile properties, at least up to 35-50% by weight of PPS. The tensile strength at the lower PPS contents shows additive effect or slightly better and materials fail in ductile mode. Tensile fracture surfaces were investigated using scanning electron microscopy (SEM). The 20% PPS blend shows no apparent voids between phases with some pull-out or elongation of the dispersed phase. At 35% PPS, phase boundaries were not clear and very rough surface profiles were observed. Blends with high PPS content (>50%) usually fail in the brittle mode. The fracture morphology of systems failing with a brittle mode revealed an interfacial debonding phenomenon.

INTRODUCTION

Polysulfone (PSF) and poly(phenylene sulfide) (PPS) form phase separated blends at all compositions when solution or melt-blended (1,2). Polysulfone is an amorphous polymer while poly(phenylene sulfide) is a semi-crystalline polymer. Post-annealing of the blends after injection molding may further increase the degree of crystallinity of PPS depending on the molding conditions. In a previous paper (3), we reported that mechanical properties of the blends such as tensile strength and modulus increase after annealing at temperatures below the glass transition temperature (Tg) of PSF. The heat deflection temperature (HDT) of the blends also increases as a result of annealing. The increase in crystallinity of PPS due to annealing seems to further enhance the mechanical properties of the blend system. Tensile properties behave as if they are approximately additive for blends with low PPS content. The addition of PPS reduces the melt viscosity and improves the processibility of the blend system. As discussed previously (3), out-gassing of PPS at high temperature can cause a decrease in the molecular weight of PSF and hence account for the inferior tensile properties of the blend at high PPS content. In this note, scanning electron microscopy (SEM) has been used to investigate tensile fracture surfaces in order to further elucidate the correlation of tensile properties to the microstructure of the blends.

EXPERIMENTAL

Poly(phenylene sulfide) was obtained from Celanese Engineering Resins, Inc. designated as Fortron 214P. Polysulfone (Udel-1700) was supplied by Amoco Performance Products, Inc. Tensile specimens of the pure materials tested were supplied by the manufacturers. The PPS specimens received were in the high crystalline state.

The two components were vacuum dried at 110 °C for at least 16h prior to extrusion to remove residual absorbed moisture. A Haake Rheomex 254 single screw extruder was used to extrude the blends. Temperatures at different zones of the extruder ranged from 280 °C to 300 °C. The residence time of the melted materials in the extruder was estimated to be about 2 min. Composition of the blends were 10, 20, 35, 50, and 70 percent PPS by weight, with the balance being polysulfone.

Blend extrudates were predried at 110 °C in a forced air oven for at least 16h prior to injection molding. A BOY 50M injection molding machine was used to mold test specimens using an ASTM standard specimen mold. The temperature along the barrel was set at 290 to 327 °C for all blend compositions. The mold temperature was preset at 60 °C throughout all molding experiments. Only the injection pressure was changed for the different compositions. In general, the higher the PPS content, the lower the injection pressure required.

A United FM-30 electromechanical testing machine (United Calibration Corp., Garden Grove, CA, USA) was used to test the tensile properties of the blends at ambient temperature according to ASTM method D638. Type I injection molding specimens were used. A crosshead speed of 50.8 mm/min was employed throughout the investigation.

The morphologies of the fracture surfaces of the blends subjected to the tensile failure tests were examined with a Joel 840A SEM. The SEM was operated at 20 keV accelerating voltage and the micrographs were obtained using the secondary electron imaging (SEI) mode. All of the fracture surfaces observed by SEM had been previously coated with a thin conducting layer of carbon to prevent specimen charging by the electron beam.

RESULTS AND DISCUSSION

In general, a shear band developed at the beginning of the tensile test that was subsequently followed by a cold drawing in all the as-molded blend compositions except the 70% PPS blend. The 70% PPS blend failed in a brittle fracture mode. After annealing (160 °C for 2h), the blend specimens and the pure PSF failed after the shear band developed but without cold drawing up to a composition of 35% PPS. Blends with a composition above 35% PPS and the pure PPS, as received, failed by a brittle mode.

Figure 1 is a plot of yield stress (or stress at break) of the blends versus PPS content. Both as-molded and annealed test results are depicted. As shown in Fig. 1, at low PPS content, the as-molded and the annealed blends reveal a tensile strength close to an additive response with a ductile type of failure. A ductile failure mode is defined as resulting from a single, angled shear band which develops during the tensile test. The annealed specimen at 50% by weight of PPS exhibited a rupture stress below the value of the simple addition rule. The specimen failed in a brittle mode. Both as-molded and annealed 70%/30% (PPS/PSF) blend specimens failed in the brittle mode with tensile strengths below the simple additive response.

Figure 2 shows SEM micrographs of a portion of the tensile fracture surface of pure PSF (Figs. 2a,b) and pure PPS (Figs. 2c,d) as received. The fracture regions of both materials shown are beyond the slow fracture mirror region. The PSF fracture initiation started at one corner of the molded piece and proceeded in the slow fracture mode approximately one quarter of the distance accross the fracture face. The PPS fracture was initiated in the middle of the molded piece and the slow fracture (mirror) region extended circularly outward only 50 um. At low magnification, the PSF micrograph (Fig. 2a) shows approximately parallel fracture lines leading up to and surrounding an elliptical secondary fracture site. The parallel cracks resemble what is called a "mackerel pattern" fracture surface (4,5). At higher magnification (Fig. 2b), the crack edge contains structures that

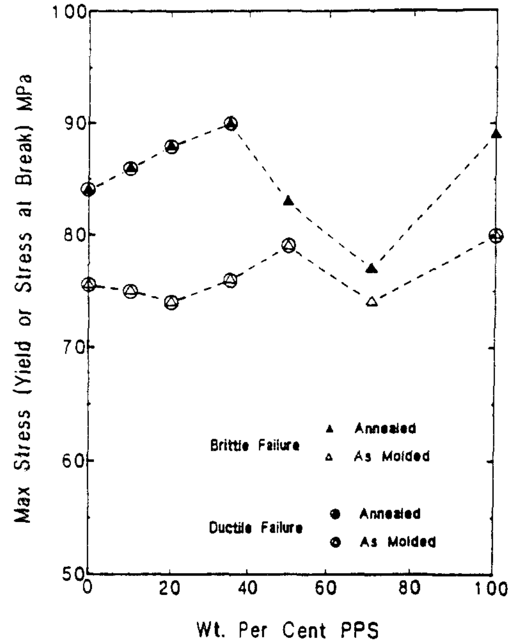

Figure 1 Plot of maximum stress versus PPS content of PPS/PSF blends. After Ref. 3

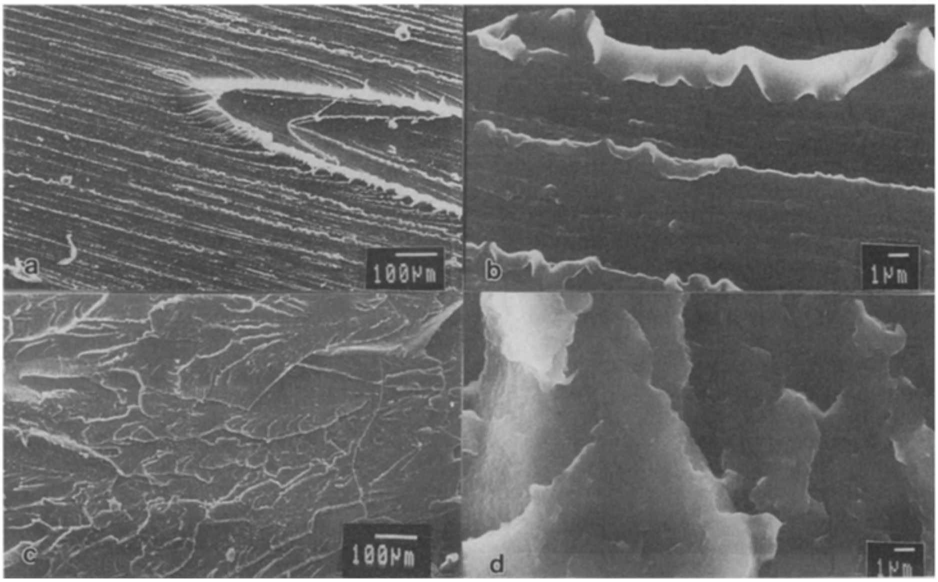

Figure 2 SEM micrographs of tensile fracture surfaces of PSF at low (a) and high (b) magnification and low (c) and high (d) magnification of PPS

appear to be drawn or melted along side the upper edge. The tensile fracture surface of PPS, also in the fast fracture region, is shown in Figs. 2(c,d). This region contains flake-like structures which when observed at higher magnification (Fig. 2d), show surface roughness with the fracture proceeding in different directions at different levels.

Figure 3 are SEM micrographs of the tensile fracture surfaces of the 10/90 (PPS/PSF) blends as-molded (Figs. 3a,b) and annealed (Figs. 3c,d). Figs. 3a and 3c show typical radiated crack river markings and a distinct semicircular secondary crack front as pointed out at location A (Fig. 3a) and B (Fig. 3c). At higher magnification, the dispersed PPS phase in the lighter zone within the primary fracture region of the as-molded blend is visible as drawn out light colored fibrils. In the same location (i.e. near the secondary crack front of the annealed sample, Fig. 3d) the morphology is similar to the pure PSF fracture morphology with no visible PPS phase. In between the river markings in all other areas of the primary and secondary fracture regions of as-molded and annealed samples, the fracture morphology is extremely smooth, practically featureless.

SEM micrographs of both as-molded and annealed tensile fracture surfaces of the 20/80 (PPS/PSF) blends at high magnification are shown respectively in Figs. 4(a,b) - and 4(c,d). Some areas of the as-molded specimen show highly drawn dispersed PPS phase fibrils with a fairly uniform size (Fig. 4a) while other areas show variable size dispersed PPS phase with only a few drawn fibrils (Fig. 4b). It should be noted that the

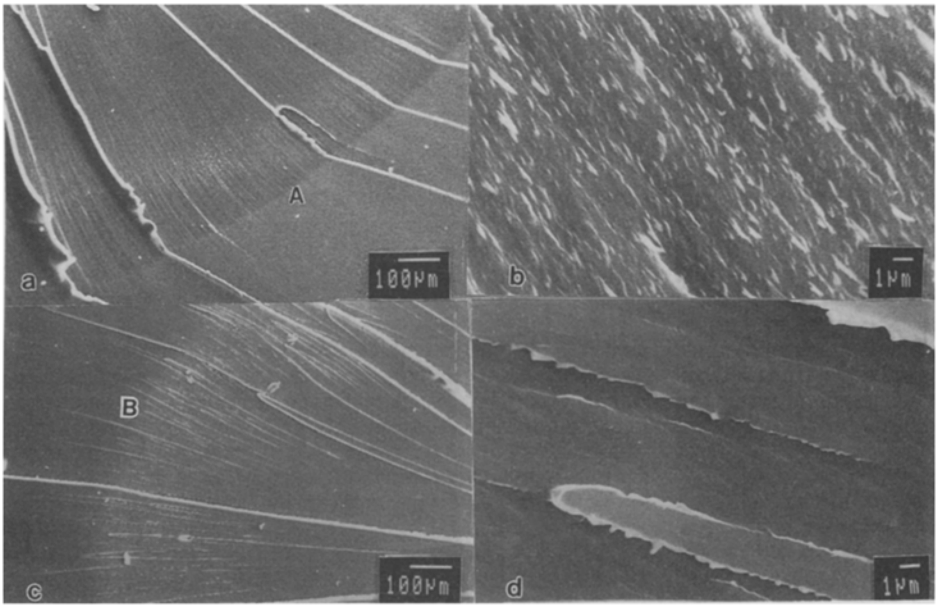

Figure 3 SEM micrographs of the tensile fracture surfaces of the 10/90 (PPS/PSF) blends (a,b) as-molded and (c,d) annealed

PPS fibrils in Figure 4a are blunt. The annealed fracture surface shows relatively few drawn fibrils (i.e. Fig. 4c and Fig. 4d). Even though some drawing effect can still be observed. As discussed in our previous paper (2), these fibrils may be due to noncrystallized PPS, which remains amorphous. In all cases, cavities are not observed around the dispersed PPS phase fibrils.

At a composition of 35/65 (PPS/PSF), the SEM micrographs (Figs. 5a-d) do not reveal any phase distinction. The micrographs of both as-molded (Figs. 5a,b) and the annealed (figs. 5c,d) show a feathery morphology in the primary (slow) fracture regions (Figs. 5a,c) and a very rough fracture surface with steps indicating large changes in direction of the fracture front as it progresses through the material in the fast fracture regions (Figs. 5b, and d).

At 50% PPS, some of the as-molded specimens failed with a brittle fracture mode while some failed in a ductile mode. Those specimens with ductile failure show a feathery morphology in the slow fracture region with a large incidence of drawing (Fig. 6a). In the fast fracture region with ductile failure, no PPS dispersed phase is observed and the fracture morphology is step-like (Fig. 6b). Note that Figs. 6a and b look reasonably similar to corresponding pictures in Figure 5. Those specimens that failed in a brittle mode (whether as-molded or annealed) show ribbon-like morphology in the slow fracture region (Fig. 6c). In the fast fracture region (Fig. 6d), there is ample evidence of cavitation or interfacial stress relaxation after passage of the crack front. Severe cracks between phases is obvious and interfacial adhesion is apparently poor in both brittle mode failure specimens.

Figure 7 shows the as-molded and the annealed SEM fracture surface micrographs of the 70% PPS blends. Transmission Electron micrographs (2) show that the dispersed phase in this composition is the PSF, as expected from its composition. SEM micrographs for both as-molded and annealed conditions in the slow fracture region (Figs. 7a and 7c, respectively) are similar to that of the pure PPS except that the mirror center has disappeared and relatively large inclusions were observed in both specimens. These inclusions probably serve as initiators for fracture. Cavitation (or interfacial debonding) around the dispersed (PSF) phases are observed. Figures. 7b, and 7d from the fast fracture region of both as-molded and annealed specimens also show similar morphology with cavitation. PPS phase inclusions inside the dispersed PSF phase are also observed particularly in the slow fracture region.

The brittle failure mode as indicated in Figure 1 may be partly explained by the presence of crack or cavities between phases as revealed in Figs. 6 and 7. The molecular weight reduction of the PSF in the 70% PPS blends cannot be ruled out as well (3,6). The tensile strength of the blends which fall close to the additive response are those without interfacial cracks as shown in Figs. 2 to 6. This phenomenon has been discussed in detail by Barlow and Paul (7,8).

CONCLUSIONS

The tensile fracture behavior of polysulfone and poly(phenylene sulfide) blends show both ductile and brittle failure, depending on blend composition and annealing. In the blends with higher PSF content, the tensile strength follows closely the simple

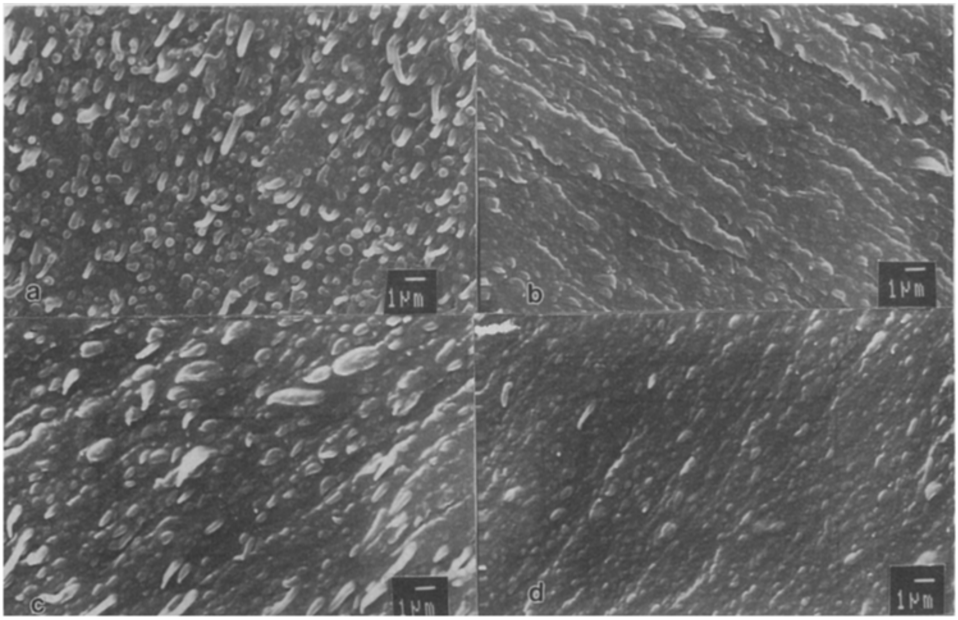

Figure 4 SEM micrographs of the tensile fracture surfaces of the 20/80 (PPS/PSF) blends (a,b) as-molded and (c,d) annealed

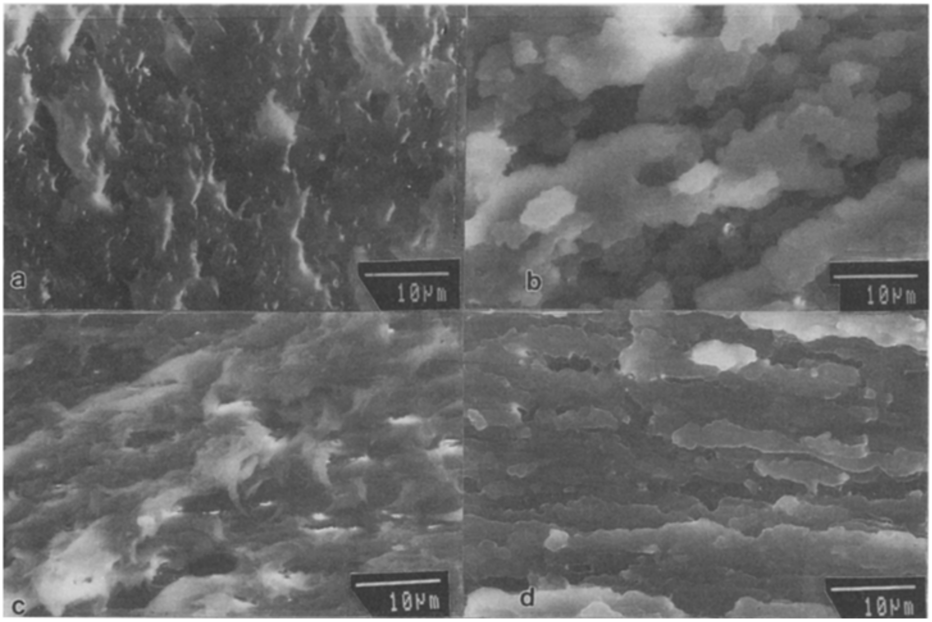

Figure 5 SEM micrographs of the tensile fracture surfaces of the 35/65 (PPS/PSF) blends (a,b) as-molded and (c,d) annealed

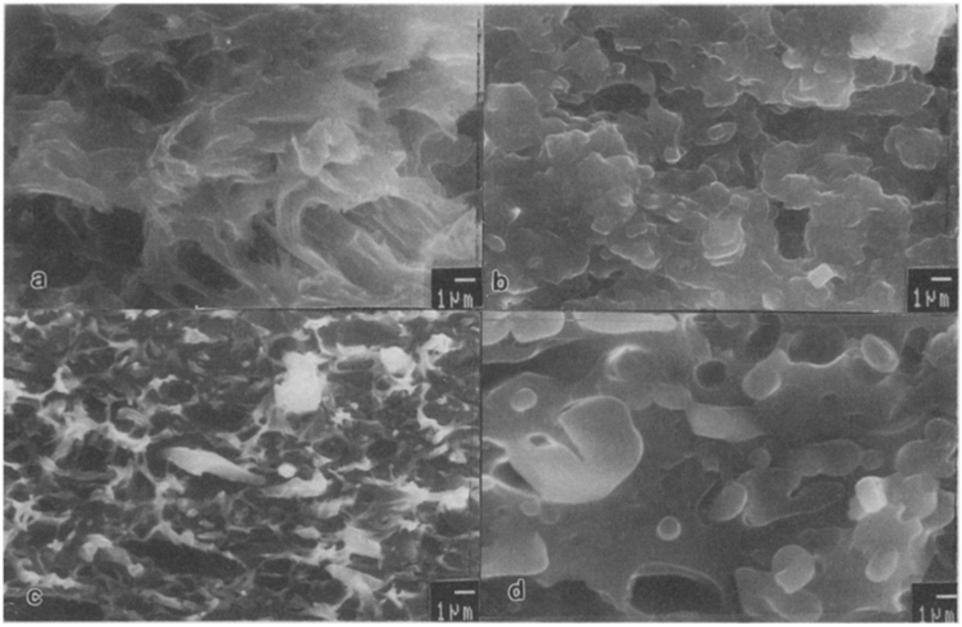

Figure 6 SEM micrographs of the tensile fracture surfaces of the 50/50 (PPS/PSF) blends (a) as-molded, slow fracture ductile failure (b) as-molded, fast fracture ductile failure (c) annealed, brittle failure (d) as-molded, brittle failure

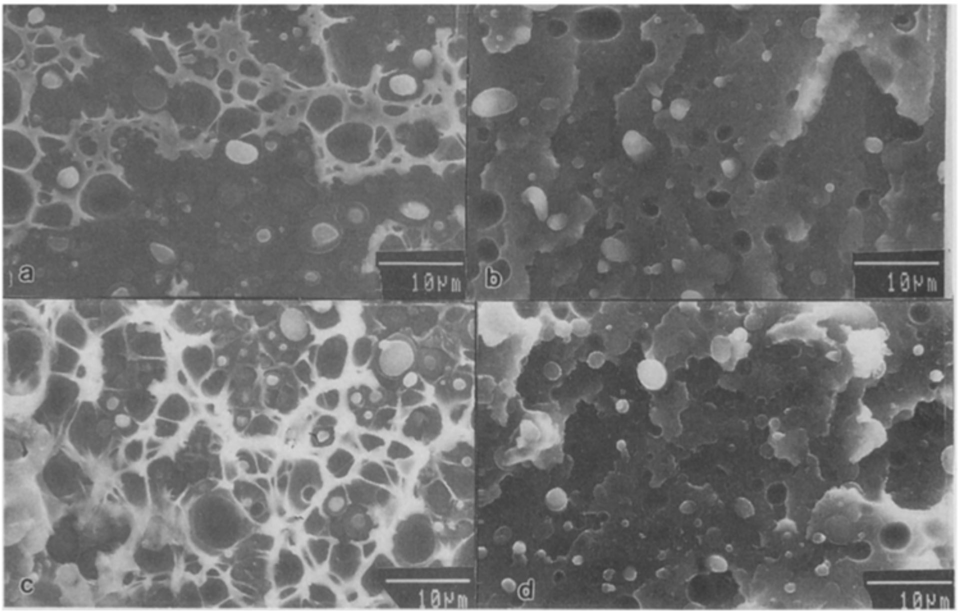

Figure 7 SEM micrographs of the tensile fracture surfaces of the 70/30 (PPS/PSF) blends of the slow fracture region (a) as-molded (c) annealed and fast fracture region (b) as-molded (d) annealed

rule of addition, both in the as-molded and annealed (160 ^{o}C for 2h) conditions. SEM fracture surface micrographs reveal that there are no apparent interfacial cracks or voids between phases in these compositions. Brittle failure specimens are associated with fracture surfaces exhibiting voids surrounding the dispersed phase.

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