

Crystallization of Fiber-Reinforced Poly(phenylene Sulfide) Composites. I. Experimental Studies of Crystallization Rates and Morphology

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SYNOPSIS

The isothermal crystallization from the melt of unreinforced poly(phenylene sulfide) (PPS) and of model carbon, aramid, and glass-fiber-reinforced PPS composites was studied by differential scanning calorimetry and optical microscopy. Crystallization was studied as a function of temperature, and the fiber contents in the composites were varied over a wide range. The results indicate that the influence of fibers on PPS crystallization is not only fiber specific, but also strongly dependent on the surface treatment (size). In general, fiber-reinforced systems crystallized faster than unreinforced (PPS), and the degree of crystallinity was less under comparable crystallization conditions. It was also observed that the rate of crystallization was enhanced in those systems which exhibited transcrystallinity in thin PPS film/single fiber composites as compared to those systems which did not exhibit transcrystallinity. Furthermore, the degree of crystallinity showed a nonlinear crystallization temperature dependence for those systems that exhibited transcrystallinity.

INTRODUCTION

The properties of fiber-reinforced composites based on semicrystalline polymers are determined in part by the crystalline structure and the degree of crystallinity of the thermoplastic matrix. Poly(phenylene sulfide) (PPS), a high performance semicrystalline thermoplastic polymer, is used extensively in composite applications, and it is necessary to have an understanding of how fibers embedded in the resin influence the crystallization process.

Although the crystallization of PPS has been studied quite extensively,^{1,2} relatively few publications have dealt with the influence of fibers on PPS crystallization. Zeng and Ho,³ using polarized light microscopy to investigate the PPS morphology, observed that single carbon or glass fibers in thin films of PPS exhibited a nucleating effect. Lopez and

Wilkes⁴ indicated that carbon fiber surface roughness influences the extent of transcrystallinity and that transcrystallinity is favored at lower crystallization temperatures. They also observed that transcrystallinity increased with decreasing PPS molecular weight. Waddon et al.⁵ and Johnson and Ryan⁶ also reported on the nucleating effects of fibers during PPS crystallization. Jog and Nadkarni⁷ reported on the isothermal crystallization kinetics of a 40% glass-fiber-filled PPS, which was observed to crystallize 15–25% faster than the unfilled PPS and to have a lower degree of crystallinity. Karger-Kocsis and Friedrich⁸ observed that the crystallinity of carbon- and glass-reinforced PPS was higher than that of the neat resin, which is inconsistent with the findings of Jog and Nadkarni, and also with the results of our previous work⁹ and the work discussed in this publication. Kenny and Maffezzoli¹⁰ report that carbon fibers have no detectable effect on the total amount of crystallinity developed in the PPS matrix during cold crystallization, and suggest that the carbon fibers delay the cold crystallization process. They also report that, during melt crystallization, the presence of carbon fibers decreases the

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degree of crystallinity and slows down the crystallization process. In terms of the influence of fibers on the thermal transitions of PPS, Ma et al.¹¹ reported that the glass transition temperature occurs 5°C higher and the crystallization temperature 7°C higher in a 63% carbon-fiber-filled system than in the neat resin. Jog and Nadkarni⁷ also reported a 6°C increase in the crystallization temperature of a 40% glass-fiber-filled PPS. Kenny and Maffezzoli¹⁰ conclude that carbon fibers do not substantially affect thermal transitions, although no data are presented. In our own previous studies we have dealt with the crystallization kinetics of some commercial PPS prepregs containing glass, carbon, and aramid fiber reinforcements.⁹ Carbon and aramid fibers decreased the crystallization half-times, the aramid fibers having a more pronounced effect. The glass fibers affected the crystallization half-times only at the higher crystallization temperatures. In all of the composites, the fibers depressed the degree of crystallinity. We have also reported on the effects of embedded fibers on the glass transition temperature of PPS.¹² We have shown that in several systems the T_g was lower when the reinforcing fibers contained a sizing material on the fiber surface than when the fibers were unsized. The lower T_g values are presumably due to plasticization of the PPS by a component of the size.

In this paper we present the results of a systematic isothermal crystallization kinetic study of a series of model composites based on carbon, aramid, and glass fibers. We deal with crystallization from the melt and with the influence of fiber type, fiber content, and surface finish (size) on the rate of crystallization, degree of crystallinity, and crystalline morphology.

EXPERIMENTAL

Model composites were prepared by a compression molding procedure using Ryton PPS resin in film form supplied by Phillips Petroleum. The PPS film was of the same grade as that used in the commercial prepregs discussed previously.⁹ The reinforcing fibers were unsized and sized AS-4 carbon fibers supplied by Hercules Inc., graphitized Thornel T300 carbon fibers supplied by Amoco Performance Products, unsized and sized Kevlar 49 aramid fibers supplied by E. I. du Pont de Nemours Co., and water-sized (unsized) and "PPS-compatible" sized glass fibers supplied by Owens-Corning Fiberglas Corp.

We used differential scanning calorimetry (DSC) to quantify the kinetics of crystallization and the

degree of crystallinity for our model systems as we did for the commercial prepregs previously studied.⁹ The DSC scans were collected on a Perkin-Elmer DSC-4 and analyzed with Laboratory Microsystems software and software created in-house. The general procedure was to heat the DSC sample to 330°C for 10 min to achieve complete melting and destruction of residual PPS nuclei. The sample was then quenched in the DSC equipment at 320°C/min to the isothermal temperature of interest, and the partial area under the crystallization exotherm was monitored as a function of time. This provided data for volume fraction crystallinity as a function of time; the crystallization half-time is defined as the time at which the extent of crystallization is 50% complete. The degree of crystallinity was calculated by dividing the heat of crystallization (area under the crystallization exotherm) by the heat of crystallization for 100% crystalline PPS, which was taken to be 19 cal/g based on the work of Brady.¹³

RESULTS AND DISCUSSION

Carbon Fiber Composites

The crystallization half-time (inversely related to the rate of crystallization) vs. isothermal crystallization temperature for several carbon fiber reinforced systems is shown in Figure 1. The crystallization half-time increases (decreasing crystallization rate) with temperature for unreinforced PPS as well as for all the carbon fiber systems studied. This is to be expected since the rate of crystallization will decrease with decreasing degree of undercooling from the melt. Also evident in Figure 1 is the effect of the carbon fiber reinforcement on the crystallization process. The presence of the carbon fibers enhances the rate of crystallization as demonstrated by the lower crystallization half-times at each of the temperatures studied. The graphitized Thornel fibers enhanced the rate of crystallization the most, while the unsized AS-4 fibers were most similar to the Phillips prepreg. Presumably, the fiber surface provides additional nucleation sites and heterogeneities, which lead to an increased overall rate of crystallization. However, since the specific surface areas of the systems studied are approximately the same, the additional surface area alone is not a sufficient explanation for the individual trends we observe. It is apparent that the type of fiber surface plays an important role in determining the level of interaction with the crystallizing polymer. For the Thornel system, the graphitization treatment would

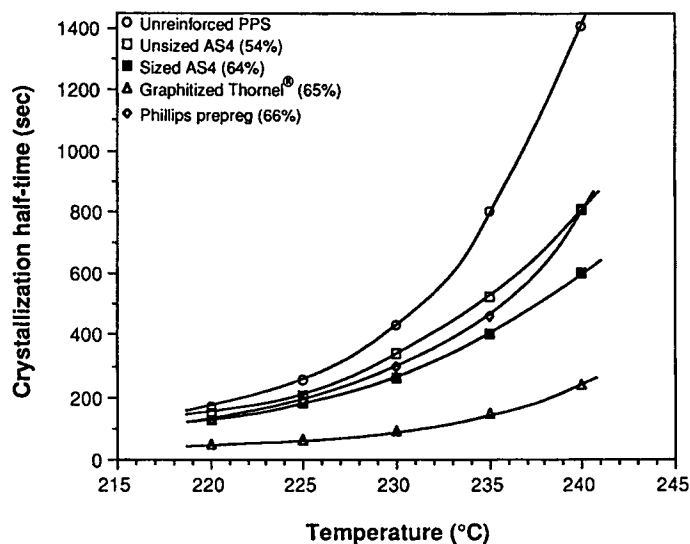


Figure 1 Crystallization half-time vs. isothermal crystallization temperature for unreinforced PPS, carbon-fiber-reinforced PPS model composites, and carbon fiber commercial prepreg. The highest fiber content samples are presented for each of the carbon fiber model composites.

seem to produce a surface that is highly attractive to the PPS, thereby leading to an enhanced rate of crystallization. With regard to the AS-4 systems, the sizing appears to produce a surface more attractive to the PPS than the unsized surface. Another possibility may be that the sizing interacts with the PPS, enhancing the mobility of the polymer near the fiber surface and leading to a higher rate of crystallization. This hypothesis is supported by the results of glass transition studies in which we observed lower T_g values for PPS reinforced with sized AS-4 fibers than for PPS reinforced with the unsized AS-4 (see Table I and Ref. 12). Presumably this is due to plasticization of the PPS by a component of the size that has diffused from the fiber surface into the matrix.

Our interpretations of the crystallization kinetics in terms of the nucleation capabilities of the fiber surfaces are supported by the morphological observations shown in Figure 2. Separate model experiments involving single fibers in thin PPS films to reveal the PPS morphology near the fiber surface show that the graphitized Thornel fiber, which caused the highest degree of rate enhancement, induced the most extensive transcrySTALLINE region. The sized AS-4 fibers, which caused an intermediate degree of rate enhancement, induced a less well-developed transcrySTALLINE region. The unsized AS-4 fibers did not induce transcrySTALLINITY.

In Figure 3 are shown the degree of crystallinity values as a function of the crystallization temperature for the carbon fiber systems. The unreinforced

Table I Transition Temperatures of Unreinforced PPS Film and Carbon-Fiber-Reinforced Systems^a

| | T_g (°C) | T_c (°C) | T_m (°C) |
|---------------------------|------------|--------------------|--------------------|
| PPS | 88.1 ± 0.2 | 132.6 ± 0.3 | 273.9 ± 0.1 |
| Commercial prepreg (66%) | 86.5 ± 0.6 | 127.3 ^b | 274.6 ^b |
| Unsized AS4 (54%) | 92.0 ± 1.1 | 144.6 ± 2.6 | 269.4 ± 1.9 |
| Sized AS4 (64%) | 89.8 ± 0.8 | 130.3 ± 0.1 | 273.4 ± 1.0 |
| Graphitized Thornel (65%) | 91.0 ± 0.4 | 137.7 ± 3.2 | 269.1 ± 1.3 |

^a Model composites were quenched from 330°C before heating at 10°C/min. The as-received PPS film and prepreg were heated from 25 to 330°C at a rate of 10°C/min.

^b Denotes result of only one sample.

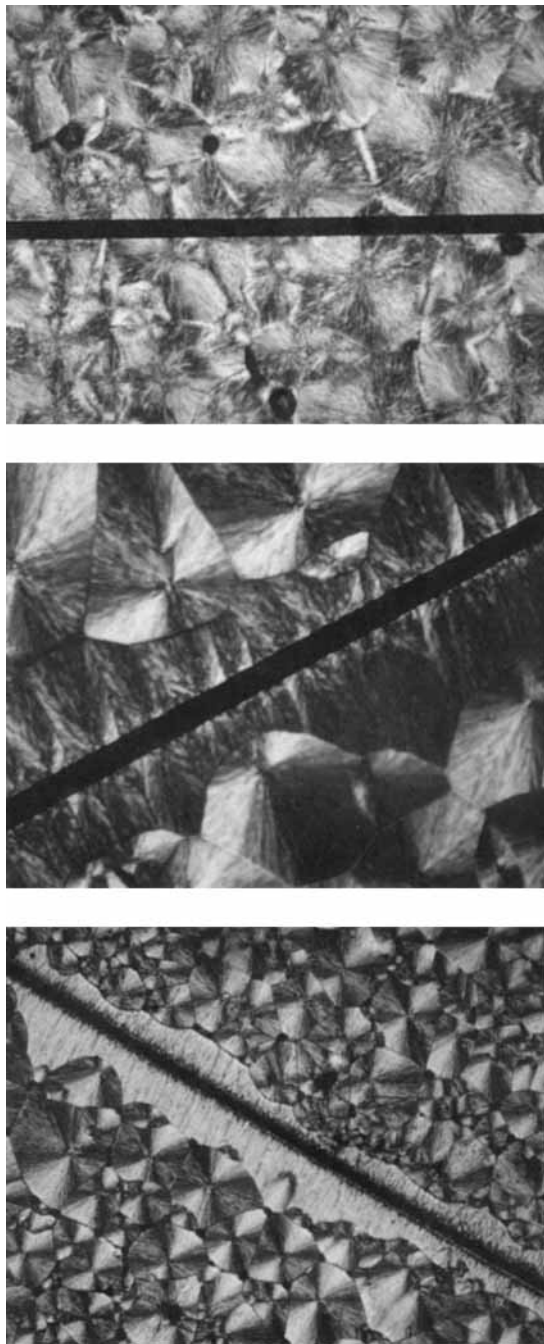


Figure 2 Morphology of model thin PPS film/single carbon fiber composites viewed through a polarizing light microscope Magnification: (a) unsized AS-4, 360 \times ; (b) sized AS-4, 570 \times ; (c) Thornel, 225 \times .

PPS exhibits the highest degree of crystallinity at each temperature, and the degree of crystallinity increases with temperature in a linear manner. The carbon-fiber-reinforced systems have lower degrees of crystallinity, the values for the unsized AS-4 and

the Phillips prepreg also increasing linearly with temperature. Both the sized AS-4 and the graphitized Thornel exhibit nonlinear temperature dependence: The sized AS-4 system exhibits a small minimum, whereas the Thornel data suggest that a minimum in the degree of crystallinity occurs at a higher temperature than those studied. For all the systems, the degree of crystallinity follows a trend inverse to the rate of crystallization. At faster crystallization rates, more impurities are trapped and imperfections generated in the growing crystals.

Some of the important thermal transition temperatures for these high carbon fiber model composites are shown in Table I. There is an increase in T_g in the model composites relative to the unreinforced PPS resin, but the increase is significantly less for the composite reinforced with the sized AS-4 than that reinforced with unsized AS-4. We ascribe this differential effect, and also the T_g depression of the commercial prepreg, to plasticization of the PPS by the size.¹¹ The crystallization temperature (T_c) of the PPS is also affected by the reinforcing fibers in a manner that would be expected from the T_g values. The melting temperatures of the model composites reinforced with unsized AS-4 and with graphitized Thornel are lower than for the other systems. This is consistent with the higher crystallization temperatures for these systems, which create a smaller temperature range during which secondary crystallization and crystallite perfection can occur.

Effects of Carbon Fiber Content

The fiber loading in the composite appears to play an interesting and complex role. Figure 4 shows crystallization half-time as a function of fiber content for the model carbon fiber systems. Note that these data are for a crystallization temperature of 225 $^{\circ}$ C, but similar trends were observed for all temperatures studied. The graphitized Thornel decreased the crystallization half-time for all contents, but the decrease was independent of the amount of fiber present in the composite. This would imply that there is a level of interaction between the polymer and the fiber surface above which no further enhancement can be achieved. The sized AS-4 system had a relatively minor effect on the crystallization half-time, although the effect was somewhat stronger at higher crystallization temperatures as was shown in Figure 1. The most anomalous behavior was observed for the unsized AS-4 system, which exhibited a strong maximum in the crystallization half-time at intermediate fiber contents. This max-

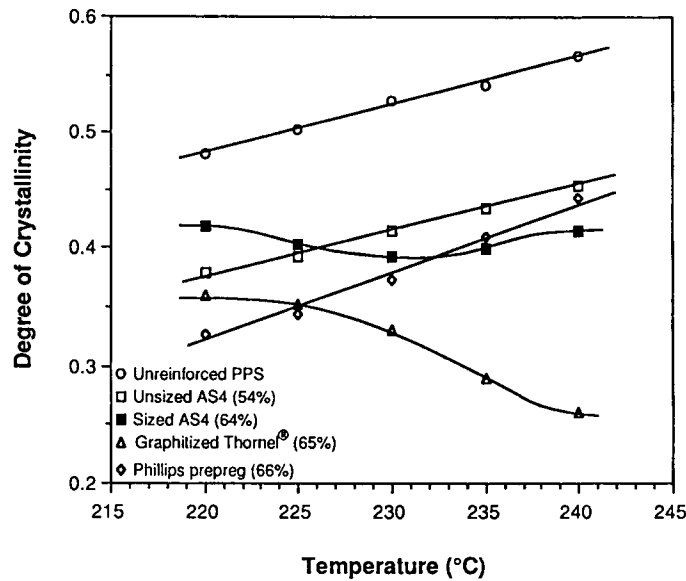


Figure 3 Degree of crystallinity vs. isothermal crystallization temperature for carbon-fiber-reinforced PPS model composites and the carbon fiber commercial prepreg. The data for the model composites represent the samples with the highest fiber content.

imum indicates that at intermediate contents the fibers interfere with the crystallization process, thereby leading to slower rates of crystallization. A possible explanation for this phenomenon, shown schematically in Figure 5, is that low and intermediate concentrations of the fibers decrease the mobility and ordering of the polymer chains, whereas,

at higher fiber contents, the average interfiber spacing becomes smaller, and the polymer chains between the fibers are forced to align and become somewhat ordered in the melt. This increase in ordering enhances both the nucleation and crystal growth stages of the polymer crystallization process. Interestingly, the sized AS-4 systems do not exhibit

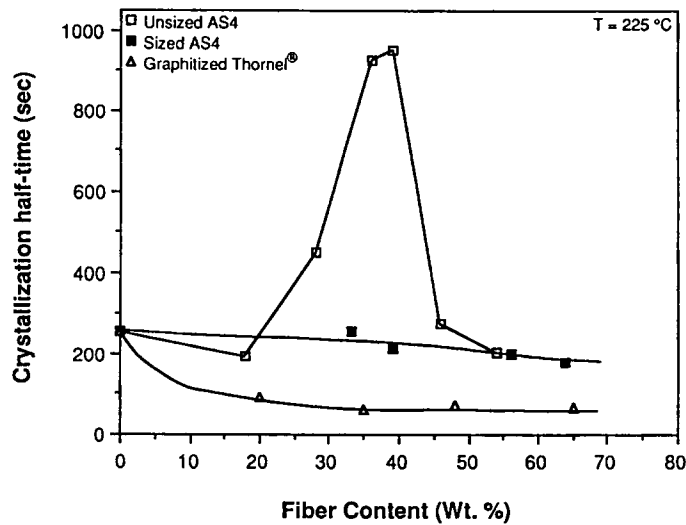


Figure 4 Crystallization half-time vs. fiber loading for carbon-fiber-reinforced PPS model composites at a crystallization temperature of 225°C. Similar trends were observed at other crystallization temperatures studied.

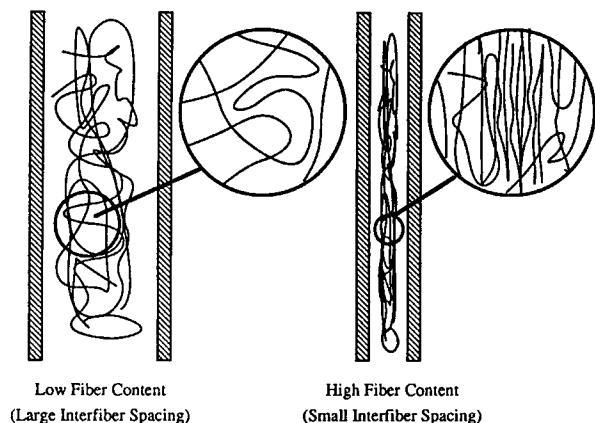


Figure 5 Schematic representation of the effect of interfiber spacing on the conformation of the polymer chains. At high fiber contents the polymer chains are more extended and sections of polymer chains may become aligned.

this phenomenon, suggesting that the sizing enhances the mobility of the polymer chains, which is also indicated by the T_g data.

Since the intermediate fiber contents for the unsized AS-4 system resulted in long crystallization half-times, we were able to crystallize composites of those fiber contents at lower temperatures than were needed for the other systems. Crystallization at high temperatures, however, usually took much longer, and the crystallization exotherms were very broad, making analysis difficult. In Figure 6 are shown

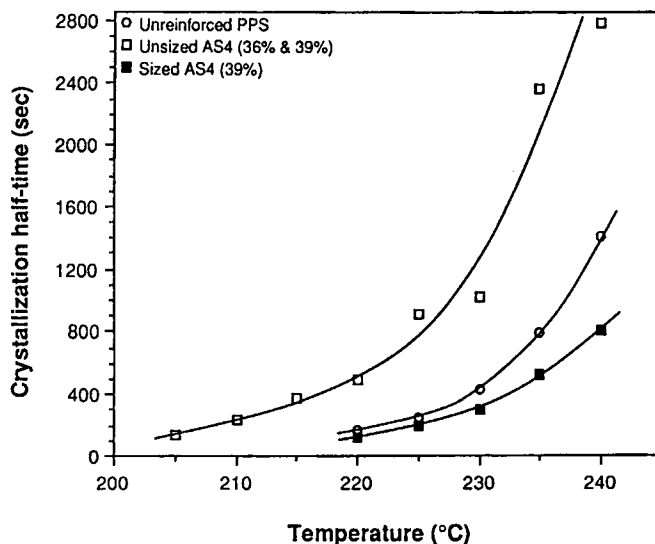


Figure 6 Crystallization half-time vs. isothermal crystallization temperature for the most nearly equal intermediate fiber contents of the PPS carbon fiber model composites.

the crystallization half-times versus crystallization temperature for the samples with 39% sized and unsized AS-4 fiber. The half-times for the unsized AS-4 are higher at all temperatures than for either the sized AS-4 or the unreinforced PPS.

Degree of crystallinity as a function of fiber content is shown in Figure 7. It appears that, for these systems, the degree of crystallinity drops off at higher fiber contents. The unsized AS-4 has a drop-off at lower fiber content than either the sized AS-4 or the graphitized Thornel. The drop-off in degree of crystallinity can be rationalized by considering the interfiber spacing and the rate of crystallization at higher fiber contents. Since the rate of crystallization is enhanced and the fiber spacing is small, the crystallites would be hampered during the growth process, resulting in a lower degree of crystallinity.

Aramid Fiber Composites

Crystallization half-times as a function of crystallization temperature for several aramid fiber reinforced systems are shown in Figure 8. As in the case of the carbon fiber systems, the data presented are for the most nearly equal high fiber content model composites, with the commercial prepreg and the unreinforced PPS shown for comparison. It is apparent that the presence of the aramid fiber strongly enhances the rate of crystallization (decrease in crystallization half-time), especially at the higher

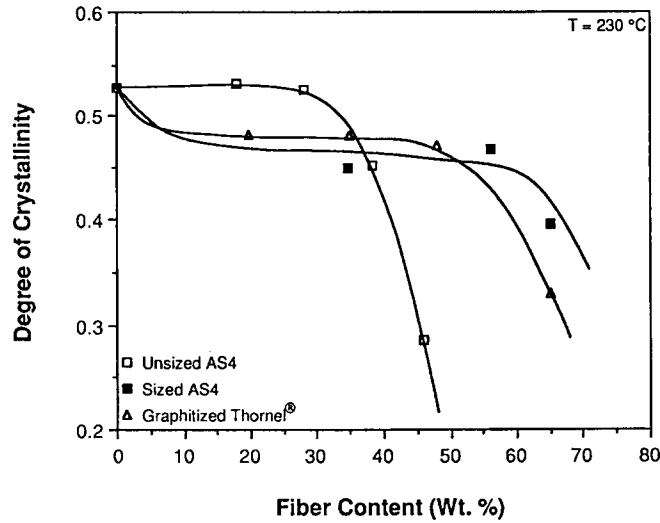


Figure 7 Degree of crystallinity vs. fiber loading for carbon reinforced PPS model composites at a crystallization temperature of 230°C. Similar trends were observed for each of the crystallization temperatures studied.

crystallization temperatures. It is of interest to note the similarity between the behavior of the sized Kevlar 49 system and the commercial prepreg. Both had enhanced crystallization rates compared to the unsized Kevlar 49 system. Presumably, the sizing applied to the aramid fiber surface is responsible for the enhancement difference. Since the interfacial contact areas for the unsized and sized aramid fiber

systems are the same, the observed rate enhancement by the sized aramid fibers can be due either to a difference in the nucleation densities of the sized fiber surfaces or to an increase in the mobility of the PPS polymer chains (or both). In Figure 9 are shown the results of single fiber morphology characterizations, indicating that both sized and unsized aramid fibers induce a well-developed transcrystal-

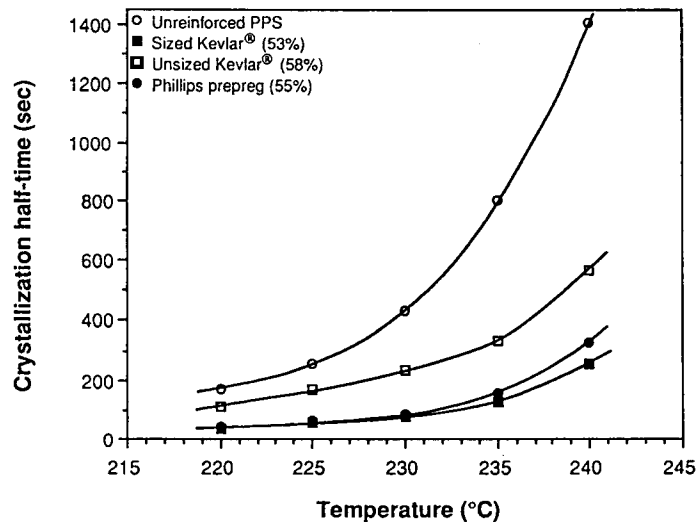


Figure 8 Crystallization half-time vs. isothermal crystallization temperature for unreinforced PPS, aramid fiber-reinforced PPS model composites, and aramid fiber commercial prepreg. The most nearly equal high fiber content samples for each of the model composites are presented.

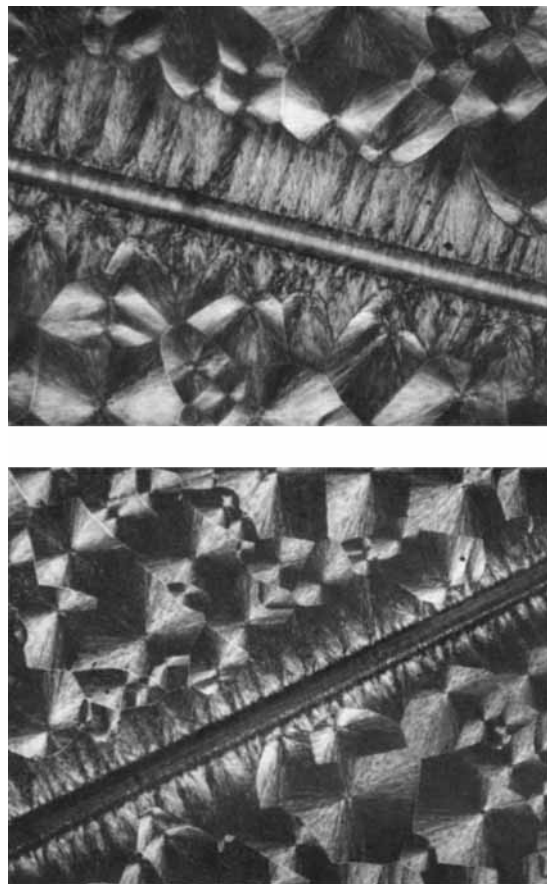


Figure 9 Morphology of model thin PPS film/single aramid fiber composites viewed through a polarizing light microscope (magnification 360 \times). (a) Unsized, (b) sized.

line structure and that the nucleating abilities of the unsized and sized aramid fiber surfaces are qualitatively similar. We therefore conclude that the sized aramid fibers interact with the PPS matrix in such a way that the molecular mobility of the PPS chains is enhanced. This is consistent with our T_g data, which are summarized in Table II. Again the

observed depressions of T_g for the sized model composite and the commercial prepreg correlate well with the lower crystallization temperatures for these systems.

Our results for the degree of crystallinity of the aramid fiber composites are shown in Figure 10. Both the sized and unsized Kevlar 49 model fiber composites as well as the commercial prepreg exhibit a nonlinear dependence on crystallization temperature. We associate the nonlinear temperature dependence in these and also in the carbon systems (Fig. 3) with the formation of transcrystalline morphologies. The data for the sized Kevlar 49 systems are similar to those for the commercial prepreg, suggesting that the same type of sizing was used. Also evident in Figure 10 is the effect of the sizing treatment on the degree of crystallinity. The lower degree of crystallinity for the unsized Kevlar-reinforced composite would appear to contradict the crystallization half-time data, and must be associated with the relatively large T_g depressions in the case of the sized aramid and commercial prepreps.

In Figure 11 are shown the crystallization half-times at a crystallization temperature of 240 $^{\circ}$ C as a function of aramid fiber content. After the initial increase in crystallization rate (decrease in half-time), higher fiber contents appear to have relatively minor effects on the kinetics. The corresponding degree of crystallinity data are shown in Figure 12. Although both the sized and unsized aramid-fiber-reinforced composites have significantly lower degrees of crystallinity than the unreinforced PPS, the sizing material appears to play a complex role and allows a higher degree of crystallinity to be achieved at higher fiber contents.

Glass Fiber Composites

Crystallization half-times for the commercial prepreg and the model composites prepared using un-

Table II Transition Temperatures of Unreinforced PPS Film and Aramid-Fiber-Reinforced Systems^a

| | T_g ($^{\circ}$ C) | T_c ($^{\circ}$ C) | T_m ($^{\circ}$ C) |
|--------------------------|-----------------------|-----------------------|-----------------------|
| PPS | 88.1 \pm 0.2 | 132.6 \pm 0.3 | 273.9 \pm 0.1 |
| Commercial prepreg (55%) | 83.1 \pm 0.6 | 119.7 \pm 0.4 | 276.1 \pm 0.3 |
| Unsized Kevlar (58%) | 90.3 \pm 0.9 | 132.4 \pm 3.2 | 274.3 \pm 2.2 |
| Sized Kevlar (53%) | 86.0 \pm 0.7 | 126.8 \pm 1.5 | 275.5 \pm 0.4 |

^a Model composites were quenched from 330 $^{\circ}$ C before heating at 10 $^{\circ}$ C/min. The as-received PPS film and prepreg were heated from 25 to 330 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min.

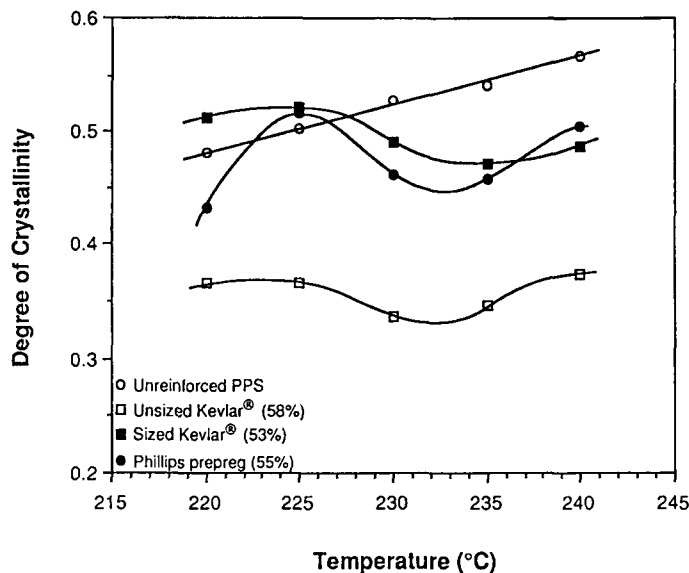


Figure 10 Degree of crystallinity vs. isothermal crystallization temperature for unreinforced PPS and aramid-reinforced PPS systems.

sized (water-sized) and “PPS compatible” sized glass fibers are shown as a function of isothermal crystallization temperature in Figure 13. The presence of glass fibers in the PPS matrix decreases the crystallization half-time relative to the unreinforced PPS at higher crystallization temperatures, but at lower crystallization temperatures the glass-fiber-reinforced systems had higher crystallization half-

times than the unreinforced PPS. Although this effect is unexpected, the occurrence of the crossover in each of the three systems suggests that the phenomenon is real and not an artifact. The effect of the sizing on the crystallization half-time is also apparent in Figure 13. Although the effect is small, it does appear that the sizing increases the crystallization rate at the higher crystallization tempera-

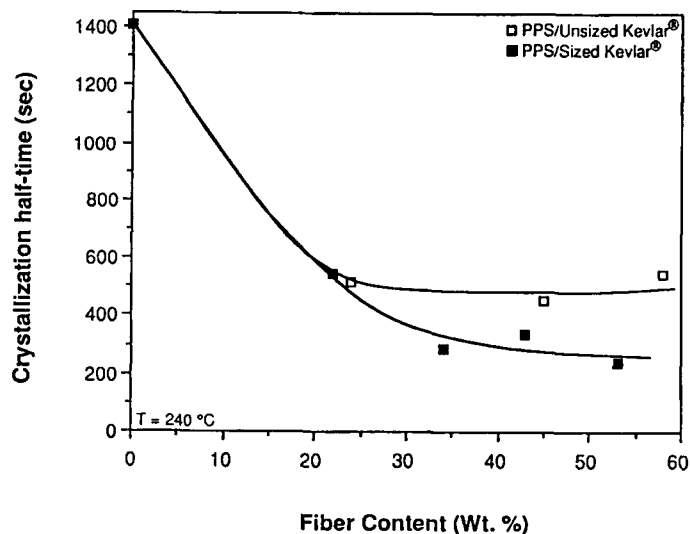


Figure 11 Crystallization half-time vs. fiber content for aramid-fiber-reinforced PPS model composites at a crystallization temperature of 240°C. Similar trends were observed at all crystallization temperatures studied.

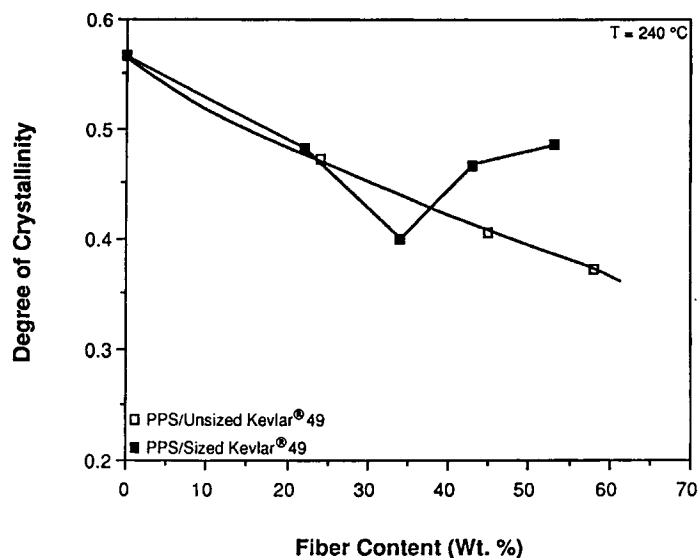


Figure 12 Degree of crystallinity vs. fiber content for aramid-reinforced PPS model composites at a crystallization temperature of 240°C. Similar trends were observed at the other crystallization temperatures studied.

tures. When these data are compared to our results for the carbon and aramid fiber systems, it is evident that the degree of rate enhancement due to the glass fibers is much less, indicating that there is relatively limited interaction between the glass fiber surfaces and the PPS. Morphological characterization of single glass fibers in a thin PPS film matrix (Fig.

14) also indicates that the nucleation density of the glass fiber surface is low, as evidenced by the lack of transcristallinity.

Data for the degree of crystallinity for the glass-fiber-filled model composites versus isothermal crystallization temperature are shown in Figure 15. With the exception of the sized glass system, the

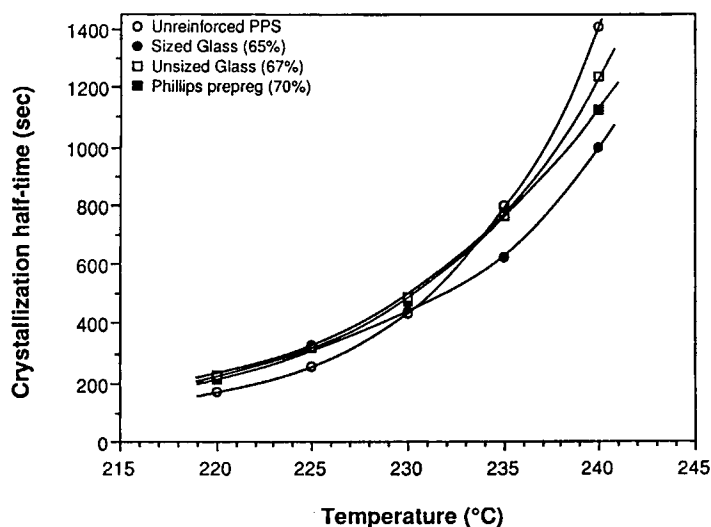


Figure 13 Crystallization half-time as a function of isothermal crystallization temperature for unreinforced PPS, glass-reinforced PPS model composites, and glass fiber commercial prepreg. The most nearly equal high fiber content samples of each of the model composites are shown.

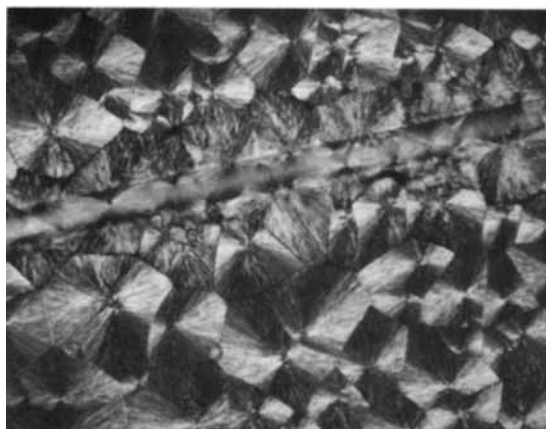


Figure 14 Morphology of model thin PPS film/single glass fiber composites viewed through a polarizing light microscope Magnification: (a) un-sized, 360 \times ; (b) sized, 570 \times .

degree of crystallinity increases linearly with temperature. The reason for the lack of temperature dependence for the sized glass system is not clear, but is probably due to a complex interaction between the effects of the fiber reinforcement and the sizing material.

The thermal transitions of the glass reinforced systems are summarized in Table III. There is a small increase in T_g relative to unreinforced PPS, and there is no specific effect of the size. The crystallization temperatures are also shifted, but in a complex way. As shown in Figure 16, we observed two overlapping crystallization exotherms for the glass reinforced systems. For the un-sized (water-sized) fibers, the high temperature peak at 136.5 $^{\circ}\text{C}$ was the more dominant, whereas, for the sized fibers, the low temperature peak at 130.1 $^{\circ}\text{C}$ was the more dominant. This indicates that the "PPS compatible" size enhances molecular mobility of the PPS, but apparently not adequately to depress the T_g .

CONCLUSIONS

Our results indicate that the influence of fibers on the crystallization of PPS is not only fiber-specific, but also strongly dependent on the surface treatment (size). In general, fiber-reinforced systems crystallized faster than unreinforced PPS, and the degree of crystallinity was less under comparable crystal-

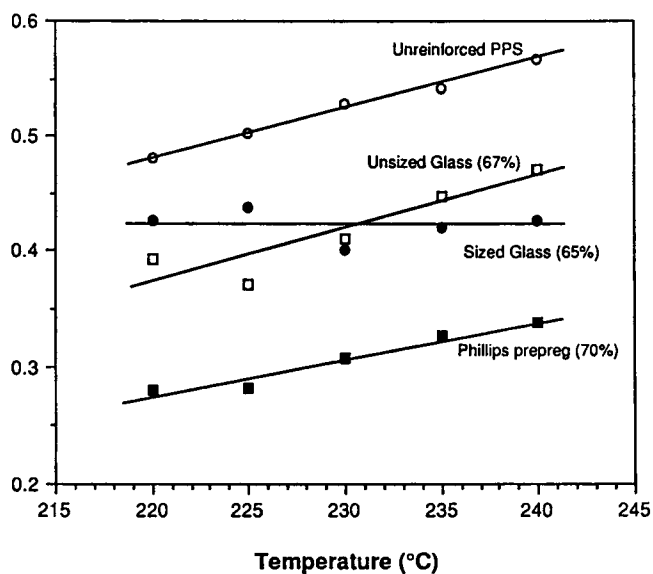


Figure 15 Degree of crystallinity as a function of isothermal crystallization temperature for unreinforced PPS and glass-fiber-reinforced PPS systems.

Table III Transition Temperatures of Unreinforced PPS Film and Glass-Fiber-Reinforced Systems^a

| | T_g (°C) | T_c (°C) | T_m (°C) |
|--|------------|--------------------------|-------------|
| PPS | 88.1 ± 0.2 | 132.6 ± 0.3 | 273.9 ± 0.1 |
| Commercial prepreg (70%) | 85.4 ± 0.3 | 126.8 ± 0.3 | 275.2 ± 0.6 |
| Water sized (unsized) glass (67%) "PPS compatible" | 89.3 ± 0.1 | 136.5 ± 0.4 ^b | 272.7 ± 0.5 |
| sized glass (65%) | 89.4 ± 0.7 | 130.1 ± 1.1 ^c | 272.4 ± 1.1 |

^a Model composites were quenched from 330°C before heating at 10°C/min. The as-received PPS film and prepreg were heated from 25 to 330°C at a rate of 10°C/min.

^b Denotes peak contains a low temperature shoulder.

^c Denotes major peak temperature reported; a second, smaller peak at higher temperatures overlaps major peak.

lization conditions. The most notable exceptions were model composites containing intermediate fiber content levels of unsized AS-4 carbon fibers, which had reverse effects, and the glass reinforced systems, which had relatively minor effects. We also observed that those systems that exhibited transcrystallinity, namely, sized and unsized Kevlar, sized AS-4, and

graphitized Thornel, enhanced the crystallization rate more than those systems which did not. Furthermore, the degree of crystallinity showed a non-linear crystallization temperature dependence for those systems that exhibited transcrystallinity. A kinetic analysis and modeling of our data will be presented in Part II.

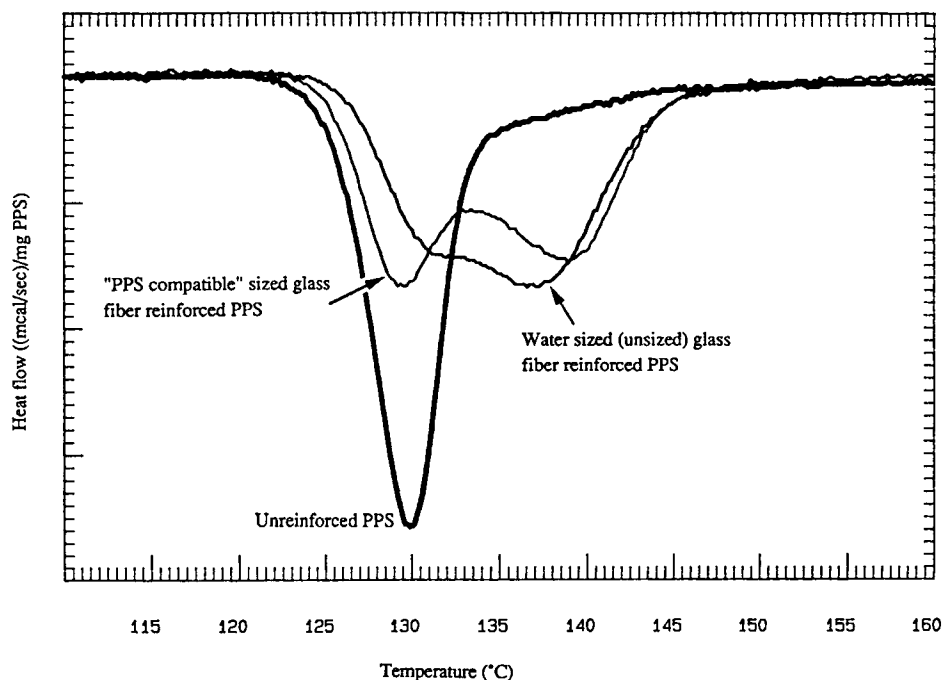


Figure 16 Crystallization behavior of unreinforced and glass-fiber-reinforced PPS model composites. Samples are heated at 10°C/min after quenching from 330°C melt temperature.

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