Effects of Fibers on the Crystallization of Poly(phenylene Sulfide)

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Synopsis

The isothermal crystallization of unreinforced poly(phenylene sulfide) (PPS) and PPS filled with glass, carbon, and aramid fibers was studied by differential scanning calorimetry. The Avrami exponent and rate constant are reported, but the crystallization half-times were used to compare the effects of different fibers on the rate of PPS crystallization. The aramid and carbon fibers decreased the crystallization half-time with the aramid fiber having the most pronounced effect. The glass fibers affected the crystallization half-time only at the higher crystallization temperatures. The aramid filled PPS exhibited anomalous degree of crystallinity behavior in that the degree of crystallinity passed through a minimum as a function of temperature. The other systems all exhibited increasing degree of crystallinity with increasing crystallization temperature. Finally, the Avrami plot for the aramid filled PPS is not linear, and the data are fitted better with two linear regions indicating that two types of crystallization processes may be present.

INTRODUCTION

Poly(phenylene sulfide) (PPS) is a high-temperature, high-strength, semicrystalline, thermoplastic polymer that is finding increasing use as a matrix material in fiber-reinforced composites. The properties of a semicrystalline polymer, such as PPS, depend on the crystalline structure and the degree of crystallinity of the polymer. Therefore, a systematic study of the influence of different fibers on crystallization kinetics and structural morphology is essential to the understanding of how processing conditions influence the final properties of the composite. In this paper we wish to report the results of an isothermal kinetic study of unreinforced PPS and PPS reinforced with carbon, glass, and aramid fibers.

There are several published reports in the literature concerning the use of thermal analysis techniques to characterize the crystallization kinetics of PPS. Most of the data are recent and specific to unreinforced or glass-reinforced PPS. Jog and Nadkarni[1] have reported on the use of differential scanning calorimetry (DSC) to study the crystallization of unfilled and 40% glass-filled PPS. They used an Avrami analysis of their data and report that the maximum crystallization rate of both the unfilled and glass filled PPS occurs at 170°C. They also report a 15–25% reduction in crystallization time for the glass-filled PPS. In addition, the degree of crystallinity of the glass-filled polymer is noted to be less than that of the unfilled polymer. Lopez and Wilkes[2] used DSC to analyze the effect of molecular weight on the crystallization of unfilled PPS. They observed that the crystallization rate decreased as

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the molecular weight increased, although the effect was not large. They also reported that the maximum crystallization rate occurs at 170°C for samples with molecular weights of 24,000 and 49,000 and at 180°C for a sample with 63,000 molecular weight.

Bair et al.[3] examined the crystallinity gradients in injection-molded PPS. The maximum crystallization rate of PPS was found to occur at 205°C. However, Manzione,[4] using the data from Bair et al., claims that a better fit of his model for the crystallization of PPS in injection molding would be obtained if the PPS maximum crystallization rate were 180°C rather than the reported 205°C. To date, these are the only reported values on crystallization kinetics and maximum crystallization rate for PPS. With the exception of the Jog and Nadkarni paper, which deals with 40% glass-filled PPS, there are no published reports comparing the crystallization behavior of unfilled PPS with fiber-reinforced PPS. Therefore, we have undertaken a detailed study to compare the crystallization kinetics, degree of crystallinity, and maximum crystallization rate of PPS and PPS reinforced with carbon, glass, and aramid fibers, with the ultimate aim of relating crystallization behavior to composite morphology and physical properties.

BASIC CRYSTALLIZATION KINETICS

A typical isothermal DSC thermogram is shown in Figure 1. In an isothermal crystallization kinetics study, the heat flow to or from the DSC cell is measured as a function of time at a specified crystallization temperature. For the unfilled and fiber-filled PPS samples, the crystallization process is exothermic, and the total area under the crystallization exotherm is the heat of crystallization, ΔH_c. The degree of crystallinity, X, of the sample can be found by dividing its heat of crystallization by the heat of crystallization for 100% crystalline PPS:

$$X = \frac{\Delta H_c}{\Delta H_c \,(100\% \text{ crystalline})} \tag{1}$$
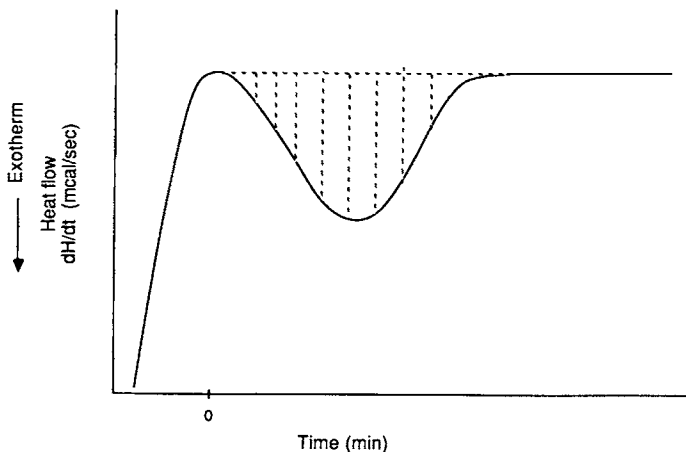

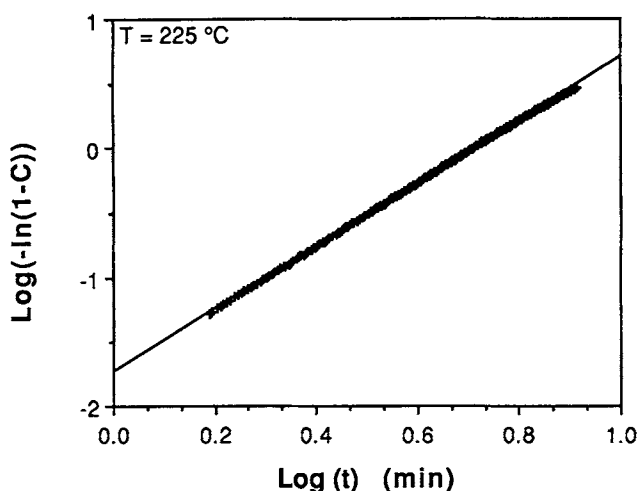Fig. 1.   Typical crystallization exotherm.

Fig. 2. Avrami plot for unfilled PPS.

The overall bulk crystallization kinetics was analyzed using the Avrami equation[5]

$$C = 1 - e^{-Kt^n},$$ (2)

where C = volume fraction of crystals at time t, K = Avrami rate constant, and n = the Avrami exponent, indicative of the type of crystallization process occurring during nucleation and growth. The volume fraction of crystals, C, at any time t can be found by measuring the partial area under the crystallization exotherm as a function of time:

$$C = \frac{\int_0^t (dH/dt)\,dt}{\int_0^\infty (dH/dt)\,dt}$$ (3)

The parameters in eq. (2) can be determined by plotting the double logarithm of that equation,

$$\log[-\ln(1 - C)] = \log K + n \log t$$ (4)

A plot of $\log[-\ln(1 - C)]$ vs. $\log t$ should be linear with slope n and intercept $\log K$. A typical Avrami plot for unfilled PPS is shown in Figure 2.

An important quantity used to describe crystallization kinetics is the crystallization half-time. The crystallization half-time, $t_{1/2}$, is defined as the time at which the extent of crystallization is 50% complete. This can be found by monitoring C as a function of t as shown in Figure 3. The maximum crystallization rate for a particular system occurs at the temperature at which the crystallization half-time is a minimum. To determine the temperature of the maximum crystallization rate, the crystallization half-time can be monitored as a function of the isothermal crystallization temperature.
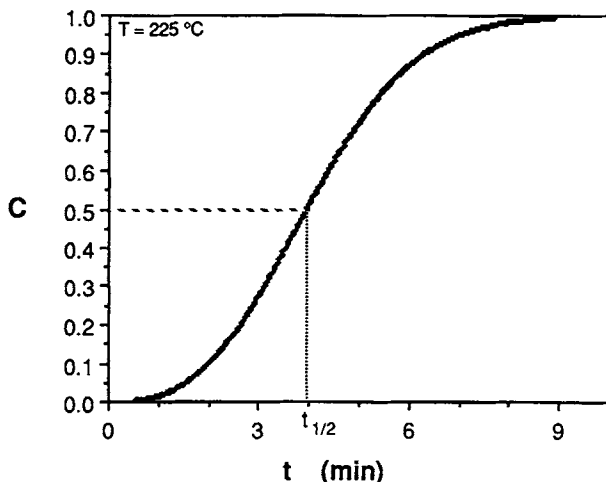
Fig. 3. Volume fraction of crystals as a function of time for unfilled PPS.

EXPERIMENTAL

Crystallization studies were performed on four different samples: unfilled PPS film (Ryton), and three unidirectional prepreg tapes provided by Phillips Petroleum. The three prepreg tapes were: (1) AC 40-66, PPS reinforced with 66% by weight carbon fiber, (2) AG 40-70, PPS reinforced with 70% by weight glass fiber; and (3) AA 40-55, PPS reinforced with 55% by weight Kevlar aramid fiber. The PPS film and the PPS used in the prepreg tapes were of the same grade. For each of the systems studied, the samples were heated to 330°C at a rate of 10°C/min and held there for 10 min before quenching at a rate of 320°C/min to the desired isothermal crystallization temperature. The only exception to this procedure was one series of an unfilled PPS sample which was heated to 350°C, held for 10 min, and then quenched at a rate of 160°C/min to the isothermal crystallization temperature. This was done to simulate the conditions used by Jog and Nadkarni,[1] and the results confirmed that the conditions we used did not yield radically different results.

For the data obtained between the glass transition temperature and the maximum crystallization temperature, amorphous samples were heated at a rate of 200°C/min to the desired temperature and the crystallization process was monitored as a function of time. The DSC scans were collected on a Perkin-Elmer DSC-4 and analyzed with Laboratory Microsystems software and software created in-house.

RESULTS AND DISCUSSION

As discussed above, we used an Avrami analysis to determine the crystallization rate constant K and exponent n for each of the four systems. Typical Avrami plots are shown in Figures 2, 4, 5, and 6. For three of the systems the data fall on a straight line as predicted by eq. (4). For the PPS/aramid system the data deviate from a linear relationship; however, we used the best fit line through the data so that a comparison could be made with the other three systems. This point will be discussed later on.
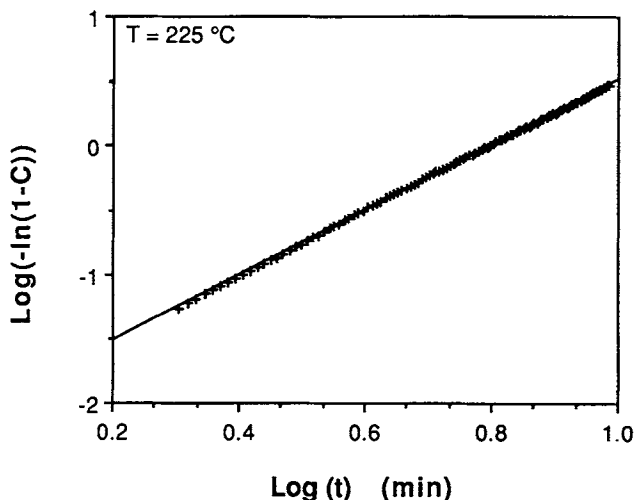
Fig. 4. Avrami plot for PPS/glass fiber system.

The Avrami exponents and rate constants are summarized in Table I for the four systems at four different isothermal crystallization temperatures, 225, 230, 235, and 240°C. As can be sen from Table I, the value of the Avrami exponent n lies between 2 and 3. According to Mandelkern,[6] this range represents 2-dimensional linear crystal growth with heterogeneous nucleation. One must be careful, though, when interpreting Avrami exponents, because other explanations of growth and nucleation are possible. For example, a value of $n = 2.5$ can be interpreted as described above or as 3-dimensional diffusion-controlled crystal growth with homogeneous nucleation.[6,7]

Since the values of n are not equal for all systems, a direct comparison of the rate constants is not possible because the units of the rate constant are dependent on the value of n. Therefore, an alternate means is needed to
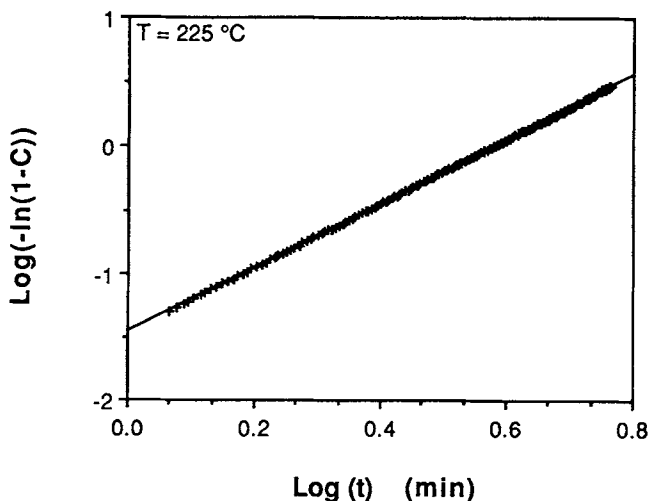

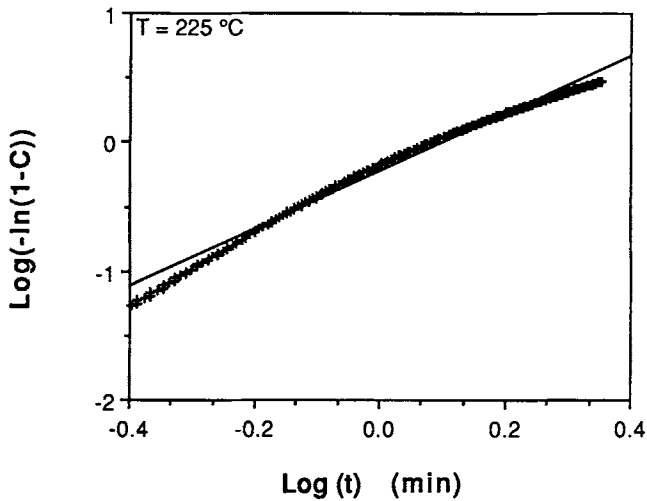
Fig. 5. Avrami plot for PPS/carbon fiber system.

Fig. 6.   Avrami plot for PPS/aramid fiber system.

compare crystallization rates which will have the same units and account for both the nucleation and growth rate of the crystals. Such a quantity is the crystallization half-time. The crystallization half-time is a processing related variable in that it is the time necessary for completion of 50% of the crystallization process.

The crystallization half-time as function of isothermal crystallization temperature is shown in Figure 7. Crystallization half-time increases with increasing isothermal crystallization temperature for all of the systems studied, which is expected for a semicrystalline polymer crystallizing from the melt. Aramid fibers dramatically decrease the crystallization half-time, especially at the higher crystallization temperatures. Carbon fibers also decrease the crystallization half-time, but not to the same extent as the aramid fibers. Our results for the glass filled system show that there is a decrease in crystallization half-time at the higher crystallization temperatures. These observations with respect to glass-filled PPS are consistent with those of Jog and Nadkarni.[1]

To establish whether the area of contact between the fibers and the PPS controls the crystallization kinetics, fiber diameters were measured microscopically and fiber surface areas were calculated for each of the systems. The results are summarized in Table II. We would expect the system with the highest area of contact, PPS/carbon, to nucleate the most crystals and thereby have the lowest crystallization half-time. Our data indicate that the PPS/aramid system, which has a lower surface area per milligram PPS than the PPS/carbon system, has the most dramatic effect on the crystallization half-time. Clearly the area of contact does not provide a sufficient explanation for the trends we see in the data. Similarly, the volume fraction of fibers in each of the samples, 54% for the aramid system, 56% for the glass system, and 59% for the carbon system are not sufficiently different to provide an explanation for the trends in the data. It is apparent from this work, as well as the work of others, that the physical and chemical nature of the fiber surface must in some way influence the rate of the polymer crystallization process.

TABLE I
Influence of Fibers on Crystallization Kinetics of PPS[a]

Sample	225°C		230°C		235°C		240°C	
	n	$K \text{ (s)}^{-n}$	n	$K \text{ (s)}^{-n}$	n	$K \text{ (s)}^{-n}$	n	$K \text{ (s)}^{-n}$
PPS	2.7	3.16	2.7	0.81	2.7	0.75	2.5	0.55
PPS/glass	2.4	14.70	2.3	13.70	2.1	10.20	2.1	5.23
PPS/carbon	2.5	12.90	2.4	8.46	2.3	6.66	2.2	2.54
PPS/aramid	2.2	606.00	2.3	239.00	2.5	35.90	2.6	2.61

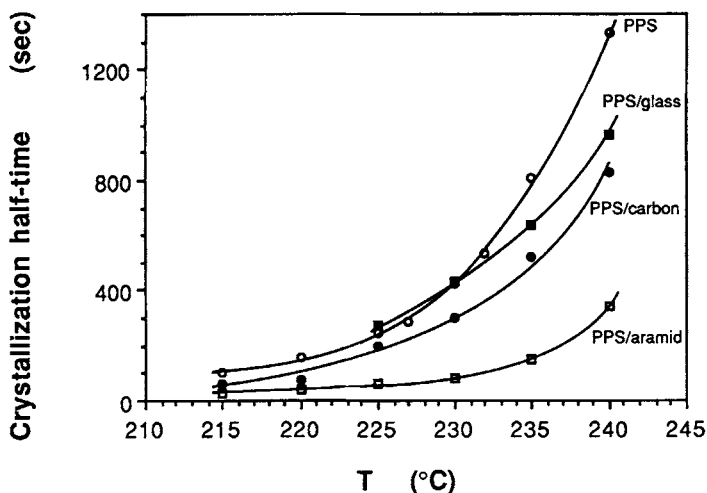[a] Note: All K values have been multiplied by 10^7.

Fig. 7. Crystallization half-time as a function of isothermal crystallization temperature.

Another quantity of interest is the degree of crystallization, X. The heat of crystallization for 100% crystalline PPS, 19 cal/g, was extrapolated from the data of Brady[8] and was used in the determination of the degree of crystallinity according to eq. (1). The degree of crystallinity for the four systems is shown in Figures 8 and 9. For three of the four systems the degree of crystallinity increases systematically with increasing crystallization temperature, as might be expected and as is shown by the data in Figure 8. Furthermore, both the carbon and glass fiber-reinforced PPS systems have a lower degree of crystallinity than the unfilled PPS system at all crystallization temperatures. Jog and Nadkarni[1] also report a lower degree of crystallinity for a glass-filled system than for unfilled PPS. For the PPS/aramid system we observe anomalous behavior in that there is a minimum in the degree of crystallinity. Figure 9 shows an expanded plot of the degree of crystallinity as a function of temperature for the PPS/aramid system, where the plotted points are averages of five different DSC scans and the error bars for each point are the standard deviation of the data. It appears that this minimum in the degree of crystallinity is real. It should be pointed out that the degree of crystallinity in this work is based on the heat of crystallization. Somewhat different values would be obtained if the degree of crystallinity were based

TABLE II
Interfacial Area of Contact[a]

Sample	Fiber diameter (μm)	Fiber density (g/cm^3)	Area of contact (cm^2/mg PPS)
PPS/glass	13.7	2.5	2.73
PPS/aramid	11.7	1.44	2.89
PPS/carbon	7.4	1.8	5.88

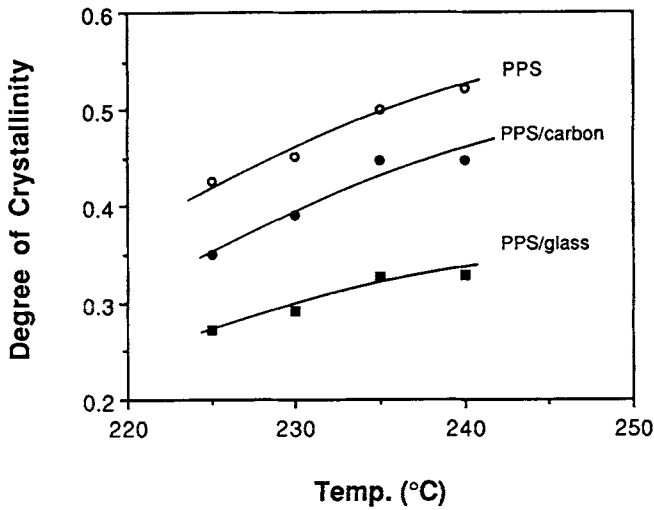[a] $\rho_{PPS} = 1.36$ g/cm^3.

Fig. 8.   Degree of crystallinity versus temperature for unfilled PPS and fiber filled PPS systems.
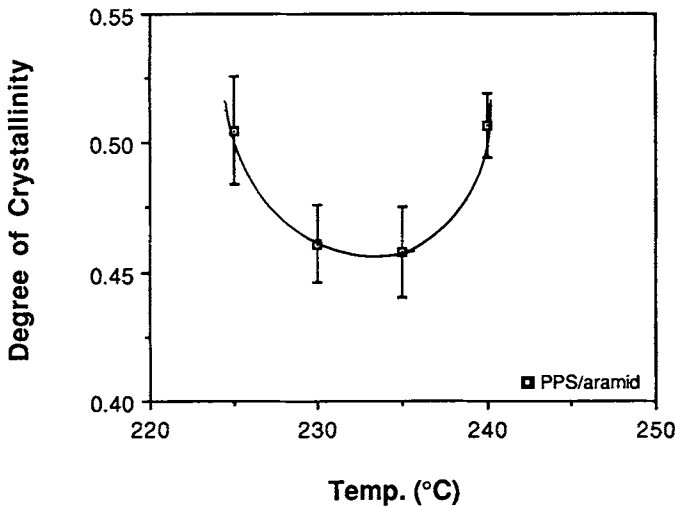

Fig. 9.   Degree of crystallinity versus temperature for PPS/aramid fiber system.

upon the heat of fusion, which could be obtained from subsequent heating scans. There is no reason to believe, however, that this would change the relative rankings of the four composite systems or eliminate the degree of crystallinity minimum in the PPS/aramid composite. Nevertheless, this aspect will be investigated in future studies.

For each of the systems studied we have also undertaken some DSC measurements of crystallization rates in the range 110–125°C. In this temperature range, crystallization rate increases with increasing temperature. Combining these data with the data in the temperature range 225–240°C obtained on cooling from the melt allows us to determine the temperature at which the crystallization rate is a maximum. By plotting the natural logarithm of the
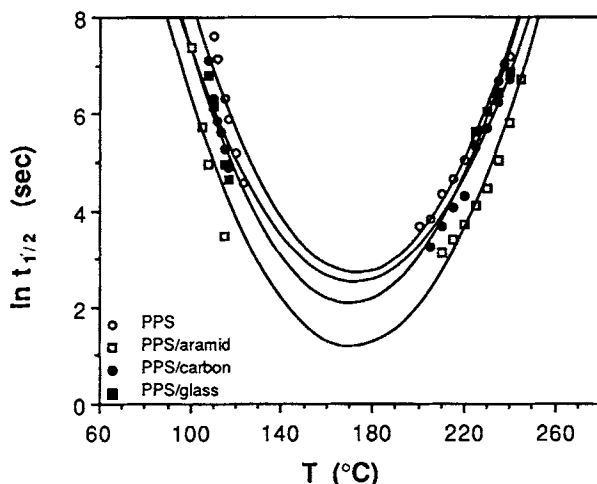
Fig. 10. Crystallization half-time versus temperature for unfilled and fiber filled PPS.

crystallization half-time as a function of temperature and fitting a second order polynomial to the data, the temperature at which the minimum of the crystallization half-time occurs can be found. The data points and the best fit polynomial are plotted in Figure 10; the second-order polynomials for each of the systems are given below:

$$\ln t_{1/2} = 1.0596 \times 10^{-3}T^2 - 0.36726T + 30.416 \quad \text{(PPS)} \tag{5}$$

$$\ln t_{1/2} = 1.0230 \times 10^{-3}T^2 - 0.35086T + 27.155 \quad \text{(PPS/aramid)} \tag{6}$$

$$\ln t_{1/2} = 9.3256 \times 10^{-4}T^2 - 0.32148T + 26.121 \quad \text{(PPS/carbon)} \tag{7}$$

$$\ln t_{1/2} = 1.0699 \times 10^{-3}T^2 - 0.36467T + 29.045 \quad \text{(PPS/glass)} \tag{8}$$

The minimum crystallization half-time, corresponding to the maximum crystallization rate, occurs at 173°C for the PPS film, 171°C for the PPS/aramid system, 172°C for the PPS/carbon system, and 170°C for the PPS/glass system. The results for the PPS film and the PPS/glass system are in good agreement with the data of Jog and Nadkarni[1] and of Lopez and Wilkes.[2]

One of the more interesting and intriguing results from this study is the behavior of the PPS/aramid system. As noted above, the crystallization half-time was the lowest for this system at each of the temperatures studied, and the degree of crystallinity passed through a minimum as a function of temperature. Furthermore, it is necessary to reexamine the Avrami plot for the PPS/aramid system which did not exhibit a linear relationship. As shown in Figure 6, the data would be fitted better with two linear regions, suggesting two different crystallization processes. Speculation at this point is focused on the fact that this system is one in which transcrystallinity frequently occurs near the fiber surface. Transcrystallinity is the development of an interphase near the fiber surface that exhibits a different crystal morphology from that of

the bulk polymer. The morphological aspects of the PPS/aramid system and other PPS/fiber systems are under investigation and will be reported later. However, at this point we wish to suggest that the two crystallization processes may be associated with bulk polymer crystallization and crystallization of the transcrystalline region.

References

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