

Effects of Fibers on the Glass Transition Temperature of Polyphenylene Sulfide Composites

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SYNOPSIS

The glass transition temperature (T_g) of polyphenylene sulfide (PPS), and of several commercial and model PPS prepregs with aramid, carbon, and glass fibers was studied by means of differential scanning calorimetry. The T_g of unreinforced PPS was found to range between 83–90°C, depending on source and molecular weight. The T_g of the commercial prepregs was depressed by about 3–5°C from that of the corresponding unfilled PPS, an effect that was ascribed to the plasticization of the PPS by one or more components of the fiber finish (size) that was assumed to have diffused into the PPS polymer. In the case of model prepregs prepared with finish-free reinforcing fibers, an expected increase in T_g was observed. In model prepregs prepared with finished (sized) aramid fibers, the T_g was depressed as in the case of the commercial prepregs. With sized AS-4 carbon fibers, the T_g was increased, but significantly less so than with unsized AS-4 fibers. With sized glass fibers, the same slight increase in T_g was observed as with unsized glass fibers. The increase or decrease of T_g in all cases was a function of the fiber content in the model PPS prepregs.

INTRODUCTION

Fiber-reinforced composites based on crystallizable thermoplastic polymers are an important category of materials whose properties depend on the degree of crystallinity and the crystalline texture of the matrix. The extent and nature of crystallization of any particular thermoplastic polymer is controlled largely by its thermal history. In fiber composites it is reasonable to expect that the reinforcing fibers will have some influence on the crystallization process. It has been reported that in certain cases, the morphology near the fiber surface may be quite different from that which develops in the bulk of the matrix, giving rise to a so-called transcrystalline region or interphase.^{1,2} A particularly striking example of this transcrystalline morphology is shown in Figure 1. While there have been many speculations, there does not appear to be an agreed upon understanding of the factors that control the formation of this dual morphology. It is obvious, however, that

the relative rates of nucleation and spherulite growth at the fiber surface and in the bulk of the polymer will play an important if not controlling role.

Several studies have focused attention on the influence of reinforcing fibers on the crystallization kinetics and the crystalline structure and morphology of thermoplastic polymers. An overview of these studies suggests that one cannot generalize these effects and that each system must be considered individually. Poly(phenylene sulfide), a widely used crystallizable thermoplastic polymer that has received considerable attention, provides a good model material to investigate the influence of a filler material on the crystallization process. While there have been many studies of PPS crystallization,^{3–6,9} only a few reports have dealt with the influence of fibers on the kinetics of the process. Desio and Rebenfeld⁷ recently reported that the crystallization half-times (the inverse of the crystallization rate) under isothermal crystallization conditions of three commercially available PPS prepregs containing carbon, glass, and aramid fibers were significantly lower than the unreinforced PPS. Nadkarni and Jog⁸ reported similar effects in the case of a glass reinforced PPS composite.

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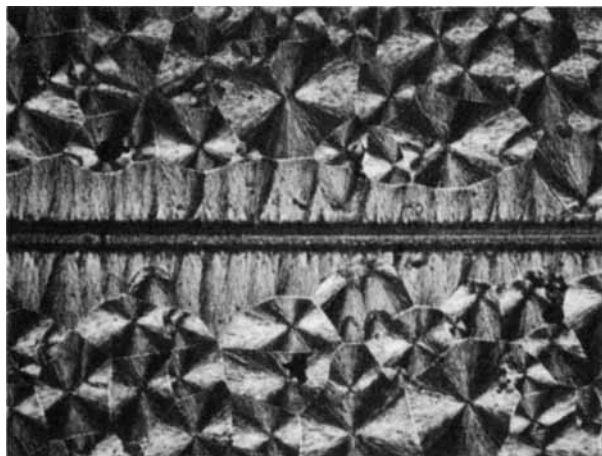


Figure 1 A Kevlar fiber embedded in PPS (Phillips). The presence of a transcrystalline region surrounding the embedded fiber is clearly evident.

Since crystallization rates are related to the glass transition temperature (T_g), our attention has recently been directed at the influence of reinforcing fibers on the T_g of PPS, which is generally reported to be in the region of 85°C. The incorporation of fiber fillers into a polymer matrix would be expected to increase the T_g due to the restrictions on chain mobility from wall effects. Indeed, Ma et al.⁵ reported a 5°C increase in T_g for a carbon fiber-reinforced PPS prepreg. However, systematic studies of the influence of fibers on the T_g of PPS do not seem to have been undertaken, and we wish to report our results that may shed a new light on the many subtle interactions between fibers and thermoplastic matrices in composites.

EXPERIMENTAL METHODS AND MATERIALS

DSC Analysis

The glass transition temperature was determined by differential scanning calorimetry using a Perkin-Elmer DSC-4 System interfaced through an A/D converter to an IBM PS-2/Model 50 computer controlled by Laboratory Microsystems software. Samples for DSC analysis were prepared in appropriate aluminum pans by standard techniques. Prior to each scan for T_g evaluation, the samples were heated above the melt temperature (321–327°C) for 3 min, immediately quenched by immersion into an ice-water bath for 2 min, and dried to ensure that no water was retained. T_g was evaluated by scanning over a temperature range of 25–110°C at a heating

rate of 10°C/min. T_g is reported as the midpoint of the transition region. A typical scan through the T_g range for unreinforced PPS is shown in Figure 2.

PPS Polymer

Studies were performed on PPS polymer from two sources. Phillips Petroleum provided unfilled PPS film (Ryton) and four unidirectional commercial prepreg tapes. Hoechst Celanese provided their PPS material in granular form in four different molecular weight levels (300, 500, 1400, and 3250 melt indices).

Commercial Prepregs

The four unidirectional prepreg tapes provided by Phillips Petroleum were: (1) PPS reinforced with 60% and 66% by weight carbon fiber, (2) PPS reinforced with 70% by weight glass fiber, and (3) PPS reinforced with 55% by weight aramid fiber. The unfilled PPS film and the PPS used in the prepreg tapes were of the same grade.

Model Prepregs

A number of model prepregs were prepared in order to have available sample composites with fibers of known characteristics and over a range of fiber contents. A compression molding procedure was used which involved placing an appropriate quantity of fiber between two sheets of PPS film or between layers of granular PPS in a metal mold, heating to 300°C under pressure at 120 psi for 30 min, and subsequently cooling the mold in ambient air before removal of the composite. A typical fluorocarbon mold release agent (Miller-Stephenson) was applied on all metal surfaces that come in contact with the polymer. The fibers used were an unsized and a sized AS-4 carbon fiber (Hercules Inc.), Kevlar 49 aramid fiber (E.I. du Pont de Nemours & Co.) that was available finish-free (without size) and with a typical spin finish (size), and glass fiber (Owens Corning Fiberglas Corp.) that was provided size free (water sized WS) and with a "PPS compatible" size.

RESULTS AND DISCUSSION

The T_g of the unfilled PPS Ryton film was found to be 88.1°C, while that of the PPS provided by Hoechst Celanese was found to be molecular weight dependent and to range between 83.6 and 90.5°C. Summarized in Table I are the T_g values for the four commercial prepregs. The values shown in Table I

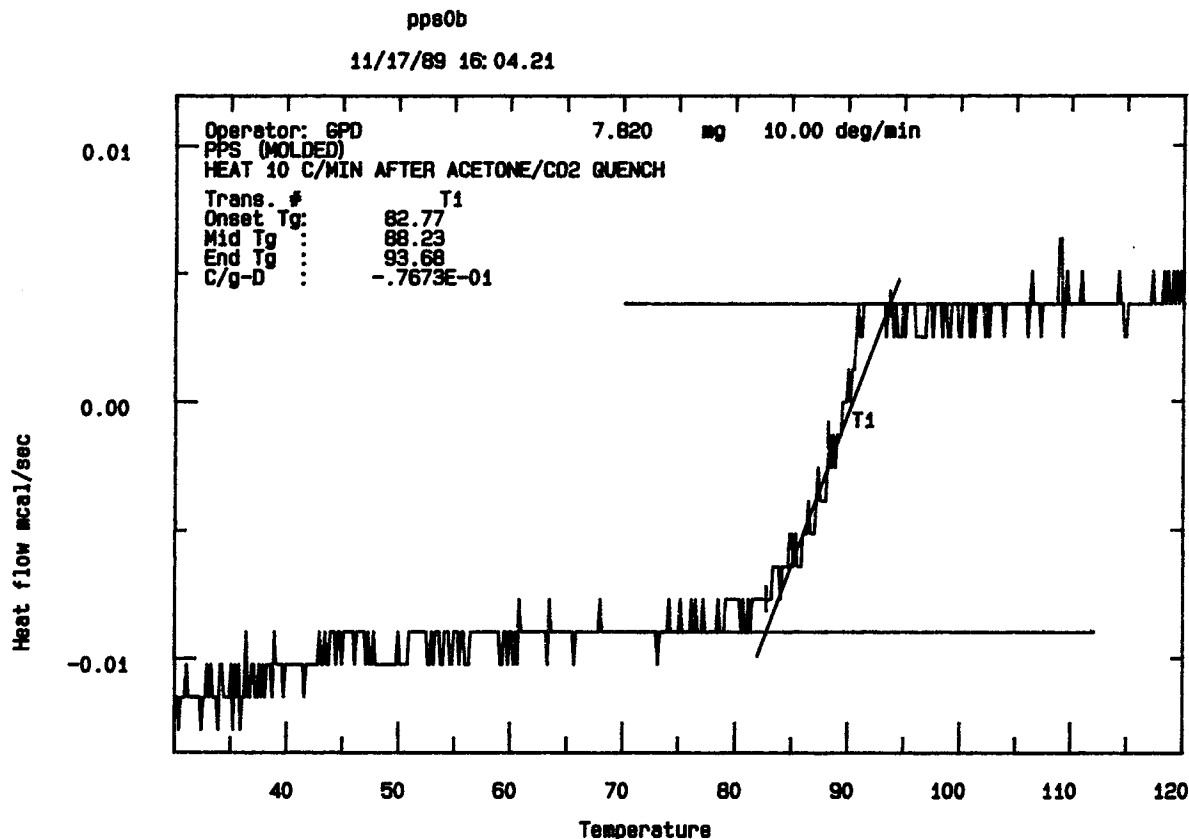


Figure 2 Typical DSC scan for determination of glass transition temperature.

and in the figures are averages of three to five specimens along with the standard deviation. The modest but real decrease in the T_g for the fiber-reinforced prepreps relative to that of the unreinforced PPS is contrary to expectation based on the concept of a wall effect. The T_g depression that we observe is consistent with the enhanced crystallization kinetics reported by Desio and Rebenfeld⁷ for the same materials, but is difficult to interpret mechanistically. We can only suggest that the T_g depression reflects a plasticization of the PPS from some moiety on the fiber surface that dissolves or diffuses into the PPS. It is most probable that this chemical sub-

stance is a component of the fiber finish or sizing agent which is generally applied to fibers as a processing aid or to improve adhesion between the fibers and matrix. Unfortunately, we do not have precise information about the fibers that were used in these commercial prepreps, but we can assume that sizing agents were used in accord with normal practice.

In order to explore this matter further, model PPS prepreps were prepared with the various fibers over a range of fiber contents. The T_g values of the model prepreps prepared with the Ryton PPS film and unsized and sized Kevlar 49 aramid fibers are shown in Figure 3. There is a systematic increase in T_g as a function of fiber content of the model prepreps prepared with the unsized Kevlar, while there is a systematic decrease in T_g of the prepreps prepared with the sized Kevlar. We also observed that prepreps based on Kevlar fibers where the size had been removed by extraction with methanol gave T_g values that were indistinguishable from those of prepreps prepared with the unsized Kevlar. Similar results were obtained with the model Kevlar prepreps prepared with the PPS from Hoechst Celanese as shown in Figure 4. The results with Kevlar certainly con-

Table I T_g of Commercial PPS/Fiber Prepreps

	Fiber Content (wt %)	T_g (°C)
PPS	0	88.1 ± 0.2
PPS/Carbon	60	86.8 ± 0.4
PPS/Carbon	66	86.5 ± 0.6
PPS/Glass	70	85.4 ± 0.3
PPS/Aramid	55	83.1 ± 0.6

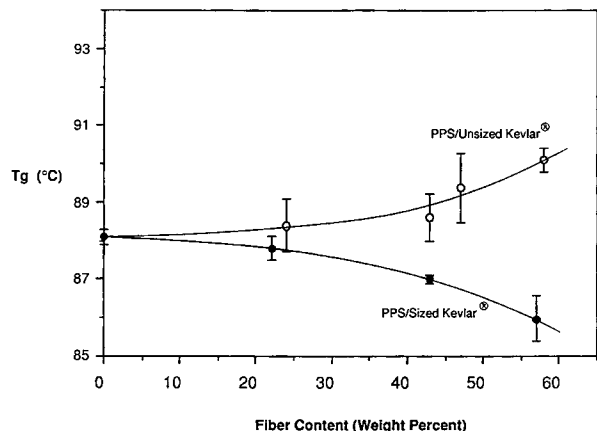


Figure 3 Glass transition temperature as a function of fiber content for PPS (Phillips) reinforced with sized Kevlar and unsized Kevlar aramid fibers.

firm the hypothesis that T_g depression of prepregs can be associated with a plasticization effect from the sizing material.

The model prepregs prepared with the carbon fibers (unsized AS-4 and sized AS-4) also showed an increase in T_g that was related to the fiber content (Fig. 5), but the increase in T_g for the sized carbon fiber prepreg was significantly less than for the unsized system. It would appear that the difference between the two systems is equivalent to a T_g depression attributable to the size.

The results for the model prepregs prepared with the glass fibers are summarized in Figures 6 and 7. With both types of PPS, both the water-sized (WS) and "PPS compatible"-sized fibers showed an increase in T_g that was dependent on the fiber content in the prepreg. Clearly the PPS compatible size used

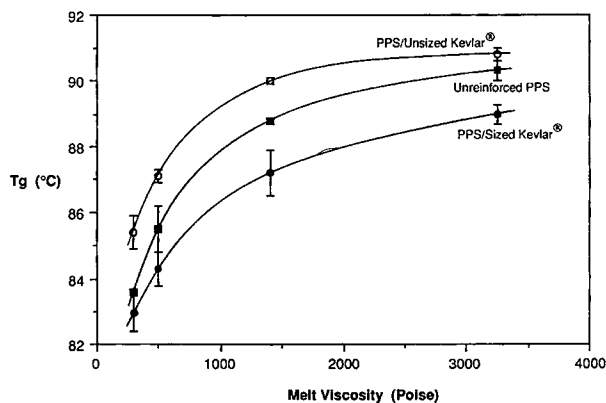


Figure 4 Glass transition temperature as a function of melt viscosity for unreinforced PPS (Hoechst Celanese), and PPS (Hoechst Celanese) reinforced with sized and unsized Kevlar aramid fibers.

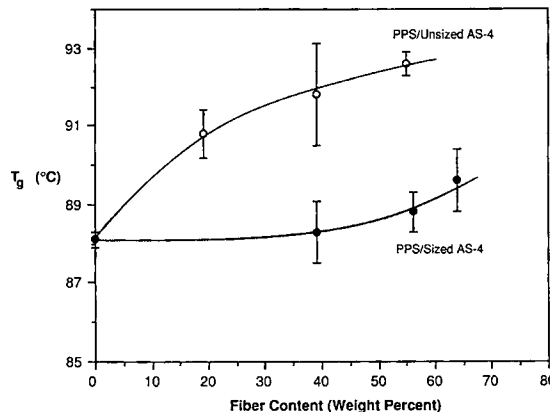


Figure 5 Glass transition temperature as a function of fiber content for PPS (Phillips) reinforced with sized and unsized AS-4 (Hercules) carbon fibers.

with these glass fibers is different from that used with the Kevlar and the carbon fibers in that it did not diffuse into the PPS matrix or at least did not plasticize the PPS to depress the T_g .

The results for the model prepregs are, in general, consistent with the suggestion that the T_g depression in the case of the commercial prepregs is related to a plasticization mechanism arising from a component of the size.

CONCLUSION

We believe that these are the first experimental observations of a T_g depression for a thermoplastic matrix that can be associated with fiber reinforcement. We also believe that these results are ex-

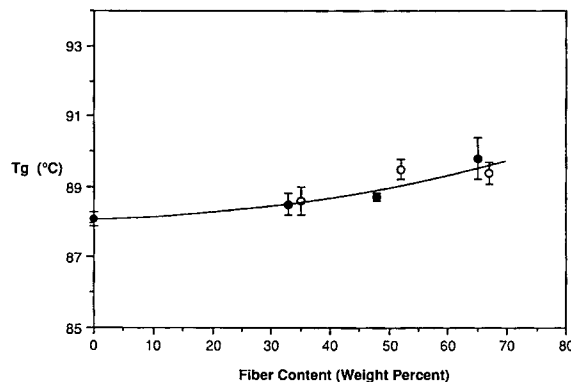


Figure 6 Glass transition temperature as a function of fiber content for PPS (Phillips) reinforced with water-sized (unsized) glass (○), and PPS-compatible-sized glass (●) fibers.

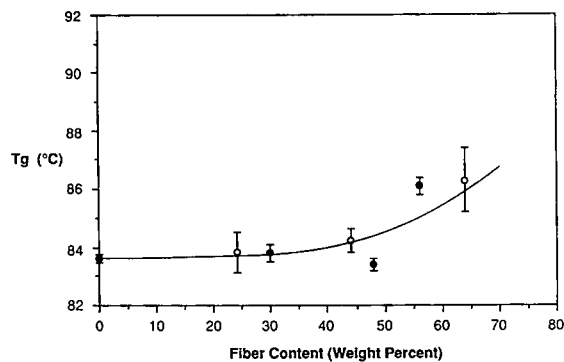


Figure 7 Glass transition temperature as a function of fiber content for 300 melt viscosity PPS (Hoechst Celanese) reinforced with water-sized (unsized) glass (○), and PPS-compatible-sized glass (●) fibers.

tremely significant and that they may point to improved understanding of physicochemical phenomena at fiber/matrix interfaces. It is clear from our data that the T_g depression of PPS prepregs can be associated with the finish on the fiber surface. While the depression is relatively small (in the 3–5°C range), it must be recognized that we measure a T_g for the polymer that is an average value including both plasticized and unplasticized polymer. It is not unreasonable to suggest that the T_g of the PPS polymer at and near the fiber surface may be much lower than the average measured T_g value. Obviously, the relative diffusivities in PPS of the finish and of the various components of the finish would control the spatial distribution of the T_g depression from the fiber surface to the bulk of the matrix. We can only speculate at this point that the T_g depression of the PPS polymer at the fiber surface may be much greater than that indicated by the measured average value.

It may also be appropriate to speculate further on the significance of T_g depression with respect to the mechanism whereby finishes and sizes function. One purpose of sizes on fibers that are to be used as reinforcements in composites is to allow the development of a “perfect” interface, i.e., one without flaws, imperfections, and voids. For example, finishes are usually formulated to allow improved wetting of the fibers by the matrix, although the precise manner by which these finishes function to provide

perfect interfaces is not known. It is conceivable that depressing the T_g of the matrix near the fiber surface by localized plasticization of the thermoplastic polymer may be an operative mechanism whereby the finish achieves its function. A plasticized polymer region near the fiber surface would imply increased segmental mobility and a lower effective viscosity which should permit the formation of an improved and possibly even a “perfect” interface.

While many of our data support these ideas, it must be noted that our data with the water-sized and PPS-compatible-sized glass fibers indicate that the problem is complex and that many mechanisms must contribute to the development of good interfacial properties in fiber-reinforced composites. Our studies of T_g shifts are being extended to include a wider range of fibers and finish formulations, and also other thermoplastic matrices.

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REFERENCES

1. S. Y. Hobbs, *Nature Physical Sci.*, **234**, 12 (1971).
2. Y. Lee and R. S. Porter, *Polym. Eng. Sci.*, **26**, 633 (1986).
3. L. C. Lopez and G. L. Wilkes, *Polymer*, **29**, 106 (1988); and **30**, 882 (1989).
4. S. Z. D. Cheng, Z. Q. Wu, and B. Wunderlich, *Macromolecules*, **20**, 2802 (1987).
5. C. C. M. Ma, J. T. Hu, W. L. Liu, R. S. Liu, H. C. Hsia, and B. Y. Shieh, *Polym. Composites*, **8**, 256 (1987); and Proceedings 31st International SAMPE Symposium, 1986, p. 420.
6. T. W. Johnson and C. L. Ryan, Proceedings 31st International SAMPE Symposium, 1986, p. 1537.
7. G. P. Desio and L. Rebenfeld, *J. Appl. Polym. Sci.*, **39**, 825 (1990).
8. J. P. Jog and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **30**, 997 (1985).
9. A. J. Lovinger, D. D. Davis, and F. J. Padden, Jr., *Polymer*, **26**, 1595 (1985).

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