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# Crystallization behavior of polyphenylene sulfide (PPS) and PPS/carbon fiber composites: Effect of cure

**Kwang Hee Lee[1,*], Min Park[1], Young Chu Kim[2], and Chul Rim Choe[2]**

[1]High Performance Polymer Laboratory, Korea Institute of Science and Technology,
P.O. Box 131, Cheongryang, Seoul, Korea
[2]Polymer Materials Laboratory, Korea Institute of Science and Technology, Korea

## Summary

The effect of cure on the crystallization rates of polyphenylene sulfide (PPS) and PPS/carbon fiber composites has been studied by differential scanning calorimetry (DSC). The crystallization rate of PPS increased with increasing degree of cure. The carbon fiber acted as a nucleating agent to enhance the crystallization rate of PPS. The fully cured PPS seemed to be saturated with nucleating sites formed through the cure reaction. Therefore, the presence of carbon fibers gave little effect on the crystallization rate of the fully cured PPS.

## Introduction

Polyphenylene sulfide (PPS) is a specialty engineering plastic recognized for its unique combination of properties, including thermal stability and chemical resistance (1-3). An important characteristic of PPS is its ability to undergo change when heated in the presence of oxygen (4-6). The change generally represents alterations in properties and characteristics as a result of increasing molecular weight, and has been described in terms of "curing". Two most important reactions involved in this curing are cross linking and chain extension (6).

The change of molecular structure resulting from the cure reaction inevitably influences the crystallization behavior of PPS. Much has been studied on the crystallization kinetics of PPS by several groups (7-17). However, there are few articles that deal with the curing effect. In this work, an effort has been made to understand the effect of degree of cure on the crystallization behavior of PPS and PPS/carbon fiber composites.

## Experimental

The PPS used in this study was Ryton V-1 in the form of off-white neat powder from Phillips Petroleum Company. Molecular weight was estimated to be about 18,000 from the intrinsic viscosity measurement using Mark-Houwink equation parameters reported by Stacy (18).

The carbon fibers (Torayca T300) were supplied by Toray in the form of rovings. The fiber diameter is about 8 μm. The sizing present on the surface of the fibers has a thickness of 0.1 ~ 0.2 μm, and consists of an epoxy prepolymer. These fibers were refluxed in dichloromethane for 5 days to remove the sizing as well as impurities. After refluxing with deionized water for 12 hours, the fibers were dried at 120 °C for 48 hours.

The fibers were chopped into short-length filaments in an electrical grinding mill. They were compounded with PPS using a Brabender twin screw extruder operating at 320 °C. The fiber content in composites was 25 % by weight. Prior to compounding, the materials were dried in a vacuum oven at 150 °C for 6 hours. The strand leaving the

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[*] Corresponding author

extruder was directly quenched in a water-bath, pelletized, and dried in an oven at 80 °C for two days. The pellets were ground and sieved with a series of standard meshes to prepare powder samples. Neat PPS sample was also prepared in the same method to obtain control data.

Isothermal curing behavior was investigated by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-4 calorimeter. A 10 mg powder specimen was rapidly heated to a predefined cure temperature between 210 and 250 °C and then cure exotherm was measured. The environment was dry air.

Crystallization behavior was studied by dynamic DSC. Samples were heated to 320 °C and kept for 10 min to erase previous thermal history, and then crystallized at a constant cooling rate of 10 °C/min in pure nitrogen.

## Results and discussion

*Figure 1* shows the normalized isothermal DSC thermograms of PPS at various cure temperatures. It is noted that the higher the cure temperature, the greater the heat of cure. This trend can be explained in view of the permeability of oxygen into PPS particles. It is well known that the permeability is a product of solubility and diffusivity. Since the sorption of incompressible light gases such as oxygen and nitrogen is almost independent of the temperature in the range of our consideration (19), the permeability of oxygen into PPS particles depends on temperature mainly through the diffusivity term. It should be pointed out that there may exist a critical crosslinking density near surface over which diffusion of sorbed oxygen molecules becomes practically difficult. The heat of cure would be proportional to the amount of oxygen diffused into PPS particles before the critical crosslinking density is reached. Therefore, the increase of overall heat of cure is attributed to the increased permeability through the diffusivity term with increasing cure temperature. In addition, the increase of amorphous fraction resulting from partial melting near the melting point of PPS (285 °C) would provide more opportunities for cure reaction in amorphous region.

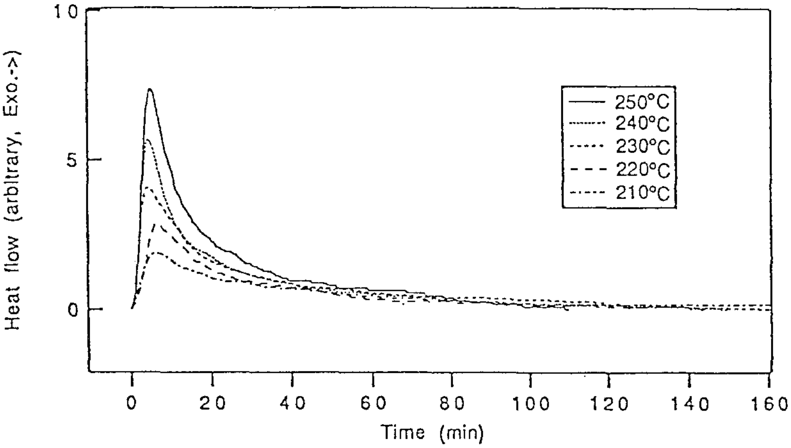


Fig.1 Normalized DSC thermograms showing isothermal cure behavior of PPS at different temperatures.

*Figure 2* shows the effect of cure temperature on the heat of cure for unfilled, unsized carbon fiber reinforced, and sized carbon fiber reinforced PPS. The heat of cure of the unsized carbon fiber reinforced PPS is almost equal to that of the unfilled PPS. On the other hand, the heat of cure of the sized carbon fiber reinforced PPS is much greater than that of the unfilled PPS. When considering the only difference between the sized and the unsized carbon fiber is whether a sizing exists on the fiber surface or not, it is deducted that the sizing should have an influence on the cure behavior of PPS. The epoxy prepolymer used as the sizing is thermally degraded at cure temperatures as shown in *Fig. 3*. Since the cure reaction of PPS proceeds *via.* the radical mechanism (5), the unstable degradation products such as free radical may initiate and/or accelerate the cure reaction near the fiber surface, resulting in an increased heat of cure. Although the reaction mechanism has not been verified, the epoxy sizing must have taken some part in chemical reactions at elevated temperatures to increase the amount of cure of PPS.

The effect of cure on the crystallization of PPS can be seen in *Fig. 4*, where 'half cured' means that the curing process is half complete. It is clearly that the curing significantly enhances the crystallization rate of PPS. The molecular junctions resulting from intensive crosslinking in the amorphous region can act as a nucleating agent (7). *Figure 5* shows polarized optical micrographs of the cured PPS samples crystallized at 240 °C after remelting at 320 °C for 10 min. It is noted in the figure that the number of nuclei

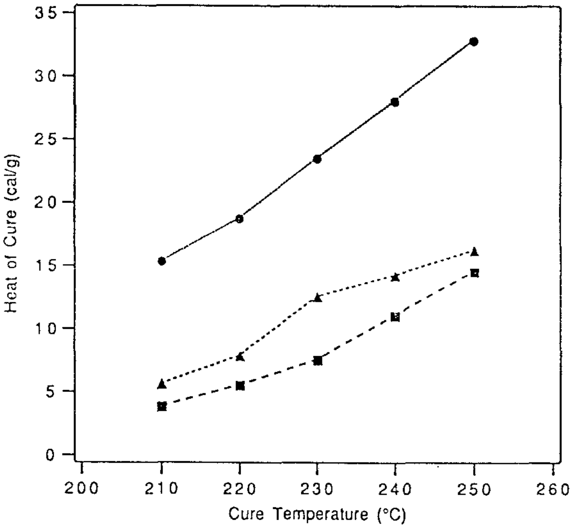


Fig.2 Effect of cure temperature on the heat of cure for unfilled(■), unsized carbon fiber reinforced(▲), and sized carbon fiber reinforced(●) PPS.

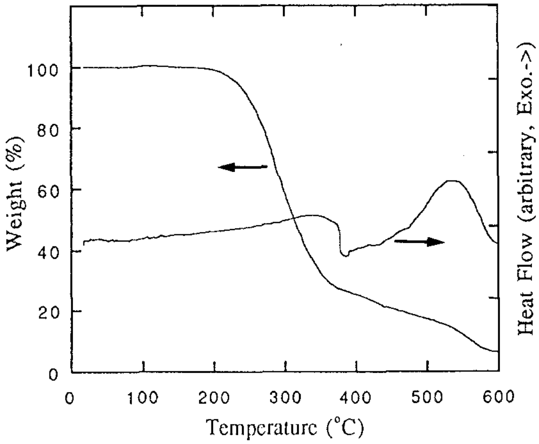


Fig.3 TG/DTA thermograms of the sizing material extracted from the carbon fiber, measured in static air at a heating rate of 10 °C/min.

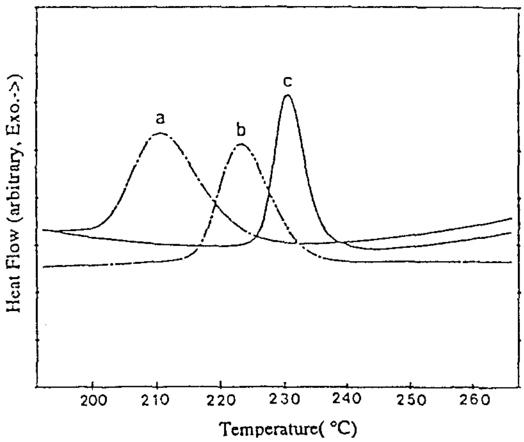
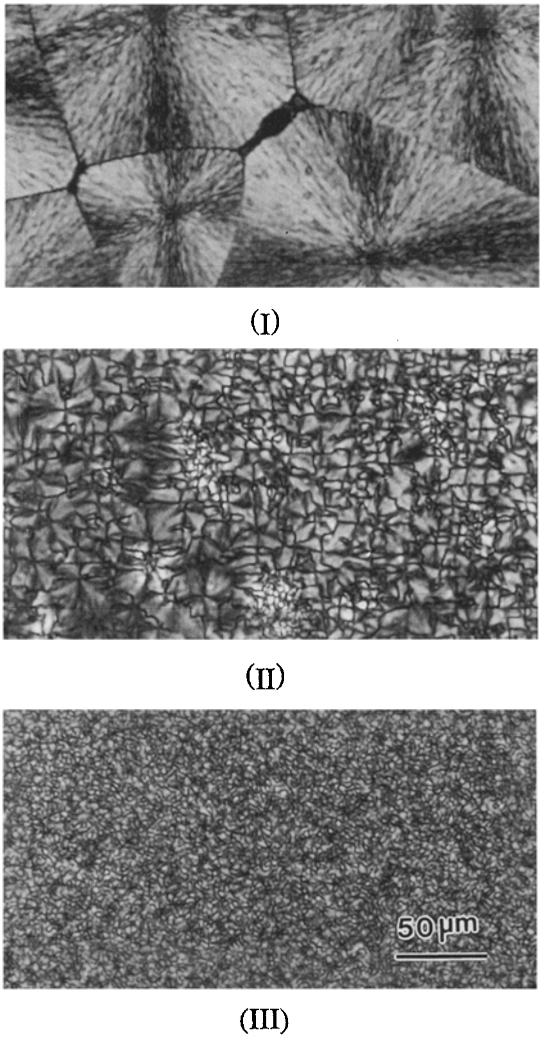


Fig.4 Dynamic DSC thermograms of cured PPS samples measured at a cooling rate of 10 °C/min. (cure temp.: 250 °C)

Degree of cure:
(a) uncured,
(b) half cured,
(c) fully cured.


(I)

(II)

(III)

Fig.5 Polarized optical micrographs of cured PPS samples crystallized at 240 °C after remelting at 320 °C for 10 min.

Cure temp. : 250 °C,
Degree of cure:
(I) uncured,
(II) half cured,
(III) fully cured.

highly increases with the degree of cure. Although the diffusion of polymer chains would be restricted with increasing degree of cure, a large increase in the number of nuclei can enhance the overall crystallization rate. It should be also considered that the change of molecular structure by chemical reactions such as chain scission, chain extension, and crosslinking has an influence on the crystallization rate of PPS.

*Figure 6* shows the effect of cure on the crystallization behavior of the sized carbon fiber reinforced PPS. At lower cure temperatures below *ca.* 230 °C, the crystallization rate increases with increasing degree of cure (*Fig. 6-(I)* ). This trend can be understood in the same manner for the unfilled PPS. As the cure temperature increases, the cure effect becomes complicated. Severe curing reaction at the interface between carbon fibers and PPS, involving the degradation of the sizing, would reduce the nucleating ability of the carbon fibers. At higher cure temperature, the interface effect on the crystallization rate becomes more important. Therefore, the crystallization rate of the fully cured sample is slower than that of the half cured sample as shown in *Fig. 6-(II)*.

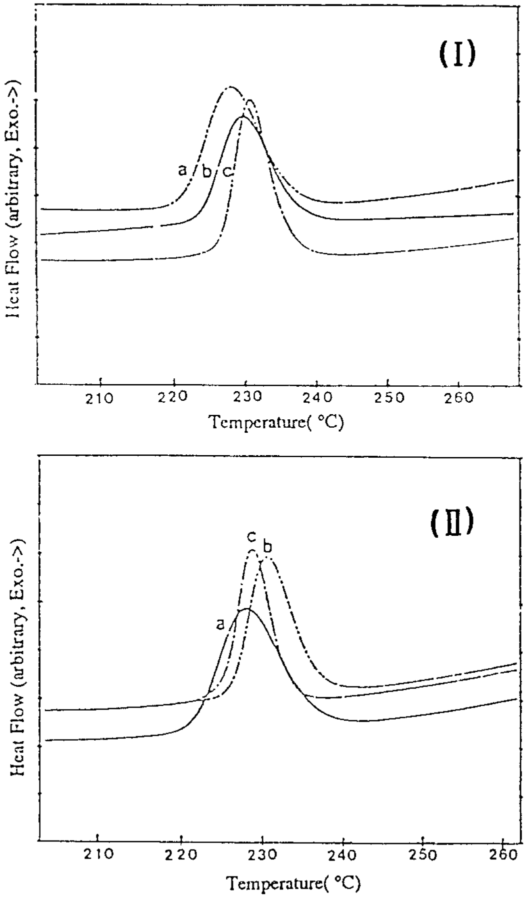


Fig.6 Dynamic DSC thermograms for sized carbon fiber reinforced PPS samples measured at a cooling rate of 10 °C/min.

Cure temp.:
(I) 220 °C,
(II) 250 °C.

Degree of Cure:
(a) uncured,
(b) half cured, (c) fully cured.

*Figure 7* shows comparisons of the crystallization rates between the unfilled PPS and the sized carbon fiber reinforced PPS for two different curing conditions. The crystallization rate of the uncured samples highly depends on the presence of carbon fibers as illustrated in *Fig. 7-(I)*. This behavior results from a strong nucleation ability of the fibers. However, the crystallization rate of the fully cured samples does not show a substantial difference (*Fig. 7-(II)* ). The fully cured PPS would be saturated with nucleating sites formed through the intensive cure reaction. The fiber effect on the crystallization rates is, therefore, less important. The crystallization rate might be affected not only by the reduced nucleation ability of the carbon fibers but also by the molecular structure changes due to the cure reaction.

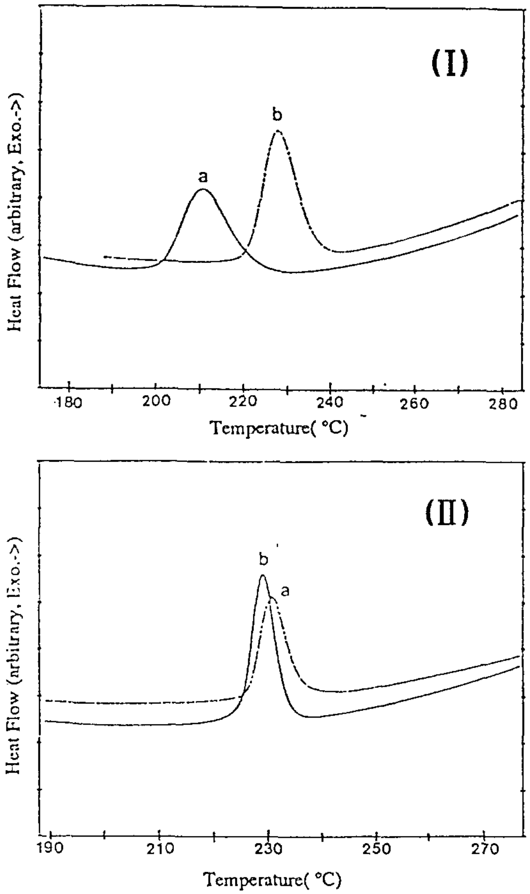


Fig.7 Comparison of crystallization rates between PPS (a) and sized carbon fiber reinforced PPS (b). (cure temp.: 250 °C).

Degree of cure:
(I) uncured,
(II) fully cured.

## Conclusion

The overall heat of cure of PPS increased with increasing cure temperature. The epoxy sizing coated on carbon fibers influenced the curing behavior of PPS in some way, and the overall heat of cure of the sized carbon fiber reinforced PPS was shown to be much greater than that of the unfilled PPS. The rate of crystallization of PPS increased with the degree of cure. The carbon fiber acted as a nucleating agent to enhance the crystallization rate of PPS. The fully cured PPS seemed to be saturated with nucleating sites formed through an intensive cure reaction. Therefore, the presence of carbon fibers gave little effect on the crystallization rate of the fully cured PPS.

The interpretation of the crystallization behavior of PPS and PPS/carbon fiber composites is much complicated since the curing influences it in multiple aspects. Accordingly, some speculations in this work need more detailed studies and the results will be reported in the next papers.

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