Effect of Molecular Weight and Fiber Diameter on the Interfacial Behavior in Glass Fiber/PP Composites

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ABSTRACT: In this study, the effects of fiber diameter, molecular weight of the matrix polymer, and interfiber spacing in glass fiber-reinforced polypropylene composites were investigated on the interfacial microstructure. The influences of the surface state of the fiber and the heat-treatment condition on the interfacial morphology and the spherulitic formation process in the matrix were also investigated. Consequently, it was found that both the fiber diameter and molecular weight of the polymer significantly influence the thickness of the transcrystalline layer. Also, as the interfiber spacing becomes smaller, the spherulites in the matrix polymer are not seen to be formed between the transcrystalline layers developed on the glass-fiber surface. In addition, the radius of the largest spherulites in the matrix polymer was found to be about the same as the thickness of transcrystalline region and to largely depend on the holding time at the crystallization temperature and cooling condition (or rate). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1191–1197, 1998

INTRODUCTION

The mechanical properties of fiber-reinforced composites are generally known to be greatly affected by such factors as fiber length,[1,2] fiber orientation,[3–5] and the interfacial shear strength[6–9] between the fiber and the matrix. In particular, an evaluation of the interfacial structure and properties is essential for an understanding of the composite properties, as the stress acting on the matrix is transmitted to the fiber across the interface between the fiber and the matrix. Hence, the interfacial bonding strength is controlled mainly by the physical and/or chemical bonding in case of a thermosetting matrix resin.

However, when semicrystalline thermoplastic resins are used as the matrix system, particular interfacial morphological features[10–12] may arise due to the direct influence of the fibers on the crystallization process, i.e., a columnar growth of crystals corresponding to the lateral development of the spherulites, normally referred to as "transcrystallinity," appears along the fiber axis due to the nucleating effect of the fiber, thereby enhancing the interfacial bonding strength between the fiber and the matrix.[13–16]

The work reported here is part of a research project concerned with the elucidation of the relationship between the interfacial microstructure and mechanical properties of glass fiber/thermoplastic resin composites. Hence, this article focused mainly on the effect of the fiber diameter (D_f), molecular weight (MW) of the matrix polymer, and interfiber spacing on the interfacial microstructure in glass fiber (GF)-reinforced polypropylene (PP) composites. In addition, the influence of the surface state of the fiber on the interfacial morphology and the variation of the spherulitic formation process in the matrix phase with different heat treatments were examined.

EXPERIMENTAL

Fiber

The GFs used for this study were supplied by Han Kuk Fiber Glass Co., Ltd., graded as "E-type" with

a density of 2.54 g/cm^3 and three different diameters of D_f = 9.6, 12.1, and 19.5 μm. However, only a grade of fiber of D_f = 12.1 μm was mainly used for the effective analysis and comparison of the data obtained. In addition, carbon fiber of 7.43 μm diameter was also used for reference in the study. The average fiber diameters were estimated from the length and weight of the fiber using the value of the fiber density for the GF and with the aid of a laser for the carbon fiber.

Matrix Polymer

The matrix material used for the preparation of the composites was commercially available isotactic PP, supplied by Korea Petrochemical Ind. Co., Ltd., with three melt-flow indexes (MFI), i.e., MFI = 3.5, 8, and 15. A grade of the polymer of MFI = 15 was mainly used, unless otherwise stated, throughout the study for an effective comparison among the data.

Surface Treatment of the Fiber

The GFs used in this study are classified into three types, designated as "treated," "untreated, moistened," and the "untreated, dried" GFs, according to the condition of surface treatment as follows: The first is obtained by washing the as-received (silane-treated) E-glass fiber in acetone for 30 min, followed by vacuum drying at 80°C for 3 h to remove any spin finish or impurity. The second type corresponds to the one made by allowing the untreated (without the silane-type coupling agent) GF to stand for a long time in the air so as to absorb sufficient (equilibrium) moisture. Finally, the third is obtained by washing the untreated GF in acetone, followed by vacuum drying at 80°C for 24 h to get rid of any moisture or impurity present. Unless otherwise noted, however, the E-glass fiber appearing in the text hereinafter will stand for the first type of GF. In addition, carbon fibers used for reference were of two types: epoxy-treated and untreated.

Specimen Preparation for Optical Observation

A test specimen for observation of the interfacial microstructure (or crystalline structure) of composites using a polarizing optical microscope were prepared according to the following procedure: A small amount of PP was placed onto a cover glass preheated to ca. 220°C on a hot stage, then a single filament of GF was put on the melted PP, and,

finally, another preheated cover glass was placed over the sample and pressed down using a weight of 300 g to ensure complete melting and constant film thickness[17] and subjected to the following heat treatments appropriate for crystallization studies:

Heat-Treatment Condition

The samples thus obtained were heat-treated at a temperature of 220°C, above the melting temperature of PP by ca. 30°C, to ensure complete melting and to remove any thermal history. The melt holding (or annealing) times were varied as 5, 30, 60, and 120 min. The samples held in the melt for a prescribed period were cooled to room temperature of ca. 13°C by three different procedures: "water-supercooling," done by quick immersion into water; "rapid cooling," where the cooling was carried out through use of two sheets of steel plate containing the melt-held samples between them; and "air-cooling," done by standing the sample in the air at ca. 13°C, where a wooden pincette was used to minimize the heat-conduction effect. Among them, in particular, the rapid-cooling method based on the use of steel plates was taken as the standard cooling condition throughout the study in view of the optimum cooling rate.

Besides, several other heat-treatment procedures were employed for the crystallization studies of PP composites in the presence of reinforcing fibers. Typical examples among them will be given in the following: In the first case, the samples held for a given period at 220°C were rapidly cooled to 130°C, corresponding to the crystallization temperature (T_c) of the maximum rate as found by observing the growth of spherulites of PP, where they were again held for different periods of 10, 60, and 120 min, followed by cooling to room temperature by the rapid-cooling procedure. In another case, the melt samples held at 220°C were cooled to the final cooling temperature of 30, 50, 80, or 100°C by the rapid-cooling procedure using the steel plates and held for ca. 5 min at the respective temperatures, followed by rapidly cooling to room temperature.

Optical observations on the samples thus prepared were made using an Olympus microscope (PMG 3) with cross-polarizers in order to investigate the transcrystallinity developed on the fiber surface as well as spherulites in the matrix for PP composites reinforced with GF or carbon fiber, the number of test specimens for a given type of
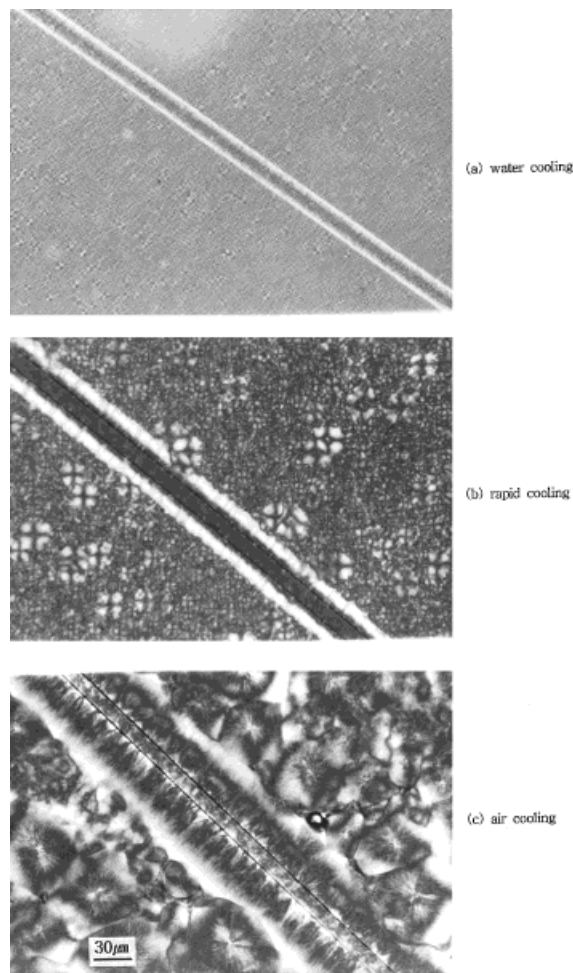
Figure 1 Transcrystallinity and spherulitic morphology of E-glass fiber/PP composites crystallized according to various cooling procedures from the melt held for 30 min at 220°C (MFI = 15).

experimental condition being 5 to 8, as required by the correct evaluation of the results obtained.

RESULTS AND DISCUSSION

From a series of studies on crystallization morphology (both the transcrystalline and spherulitic structures) of the PP composite samples obtained by varying the melt holding time at 220°C, it was found that melt holding of 30 min corresponds to the standard condition to differentiate among the interfacial microstructures of different experimental conditions under the present situation covered. Hence, this value was taken as the standard melt holding time throughout the study.

Figure 1 shows the variation of both the trans-

crystalline and spherulitic growths with the cooling condition (or rate) for PP with surface-treated GFs crystallized upon cooling from the melt held at 220°C for 30 min according to the respective cooling procedures. From this figure, we can easily understand that in case of the water-(super)-cooling condition, the transcrystalline layer is not well developed along the fiber axis as is well known, and even any really distinctive spherulitic growth is hard to discern in the matrix phase, nearly similar to the amorphous state. In contrast, in the case of the air-cooling, both the transcrystallinity and spherulites are well developed in the composites. In addition, the lateral extent (or thickness) of the transcrystalline layer and the size (or radius) of the largest spherulites for the rapid-cooling condition are intermediate between those for the water-cooling and the air-cooling. Hence, rapid cooling was taken as the standard cooling condition, unless otherwise noted. Meanwhile, the reason why the size of the spherulites is the largest for the air-cooling is that the residence time near 130°C, corresponding to the maximum crystallization temperature of PP, is longer compared to other cooling conditions.

Figure 2 represents the variation of the fiber–matrix interfacial morphology with the MFI (or MW) of the polymer in E-glass fiber/PP composites, each sample crystallized from the melt held at 220°C for 30 min by rapid cooling (based on the use of steel plates) to room temperature. For the lowest MW (or highest MFI) polymer studied, it can be seen that the nucleation density along the fiber is high and the lateral extent of the transcrystalline layer is also remarkable.

On the other hand, as the MW of the polymer is increased, the transcrystalline layer becomes less uniform and less pronounced. This behavior can be explained as follows: In the case of the low MW polymer, there are a number of chain ends; accordingly, the probability of an attachment of the polymer molecules onto the fiber surface is increased, thereby rendering the increased nucleation density and transcystalline growth along the fiber.[10] However, this will be more difficult for longer chains because of the inhibiting effect caused by chain entanglements.[10] The same reason can be applied to the size of the spherulites in the matrix phase.

In Figure 3, the optical microphotographs showing the variation of the interfacial microstructure with the fiber diameter in E-glass fiber/PP composites are given, each crystallized by rapid cooling from the melt similarly to the previ-
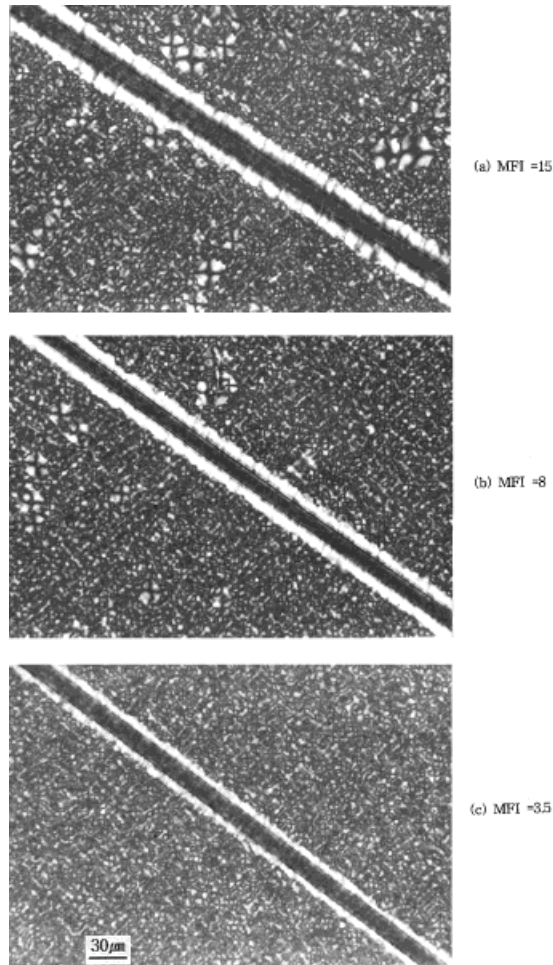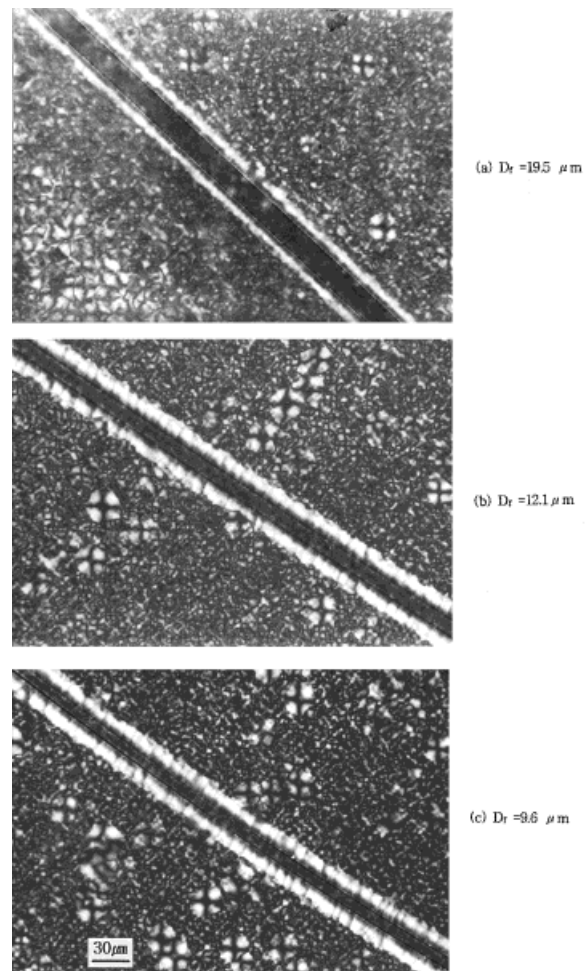
Figure 2 Optical microphotographs showing the variation of the interfacial microstructure with MFI of the polymer for PP with E-glass fibers, crystallized upon rapid cooling from the melt held at 220°C for 30 min.

ous case. From this figure, we can see that as the fiber diameter decreases the thickness of the transcrystalline layer is considerably increased relative to the fiber diameter.[9] A qualitative, although speculative, explanation for this could be made in terms of the surface phenomenon—more specifically, the Laplace equation on the pressure difference between inside and outside the bubble, i.e., if we plausibly assume that the fiber is embedded in the matrix fluid to act as "bubble," such as occurring during the melt fabrication for sample preparation, the pressure within the bubble will be inversely proportional to the fiber diameter, and, hence, the large wetting (or shrinkage) force being exerted to the smaller-diameter fiber by the matrix fluid.

As a result, the tendency of the fiber to nucleate the crystallization of the matrix polymer will be promoted, thus leading to the increased transcrystalline region responsible for a strong interfacial bond. In addition, from the investigation made on the interfacial microstructure of the E-glass fiber/PP composite samples obtained at different final cooling temperatures as described in the Experimental section, although not given here for want of space, it was found that as the final cooling temperature is decreased both the thickness of the transcrystalline region and the radius of the spherulites in the matrix polymer decrease, which is probably because there is not sufficient time for the polymer molecules to crystallize, in particular around 130°C of the maximum crystallization rate, due to the rapid-cooling rate.

As shown in Figure 4, experiments on the interfacial microstructure of E-glass fiber/PP com-

Figure 3 Optical microphotographs showing the variation of the interfacial microstructure with fiber diameter for PP with E-glass fibers, crystallized upon rapid cooling from the melt held at 220°C for 30 min (MFI = 15).
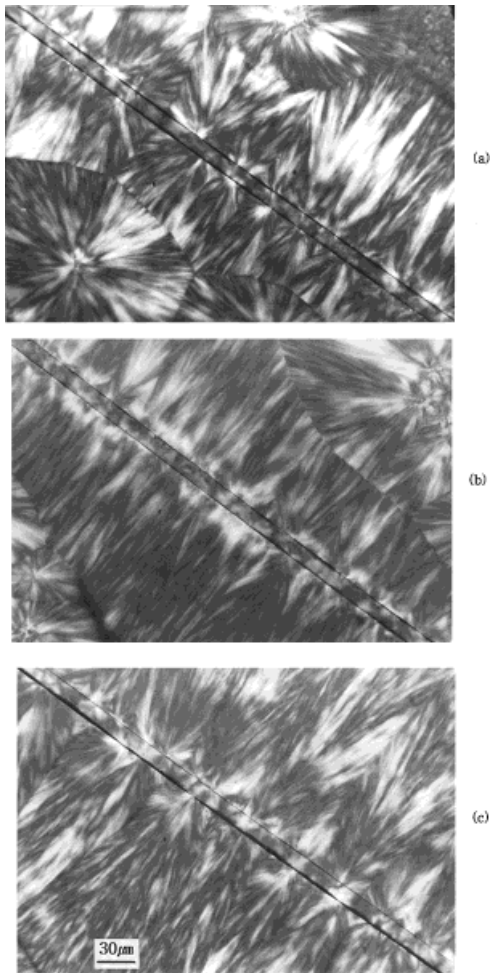
Figure 4 Interfacial microstructure of PP with E-glass fibers: samples held at 220°C for 30 min, rapid-cooled to 130°C, then held again for (a) 10, (b) 60, and (c) 120 min, followed by rapid cooling to room temperature.

posite samples obtained using different holding times of 10, 60, and 120 min were also carried out, according to which as the holding time is increased both the transcrystalline and the spherulitic growth become more pronounced, as may be expected from the previous results.

Optical microphotographs showing the interfacial microstructure of PP with untreated GFs of different drying conditions are given in Figure 5. From this figure, it can be seen that the transcrystallinity is less developed on the GF surface for the moistened fiber than for the dried one. This difference may be attributable to the fact that the critical surface tension of the fiber is decreased due to the absorption of moisture, thus resulting in a decrease in wettability by the liquid, and,

hence, a decrease in the nucleating ability of the fiber.

As follows from the comparison of the results between the treated and the untreated (dried) GFs, the lateral extent of the transcrystalline layer does not seem to differ much in either case. In addition, as evident from the previous results noted, the thickness of the transcrystalline layer is almost the same as the radius of the largest spherulites in the matrix, implying that the GF surface and nuclei surviving in the bulk have almost the same activity.

Figure 6 shows the interfacial microstructure of the PP composite samples based on epoxy-treated and untreated carbon fibers, chosen for reference even though it is not a new result, revealing that any distinctive difference does not
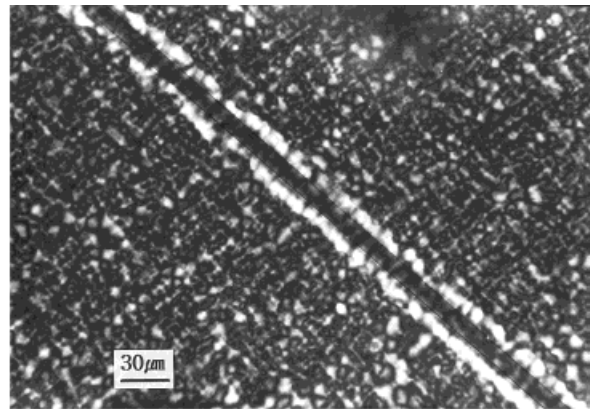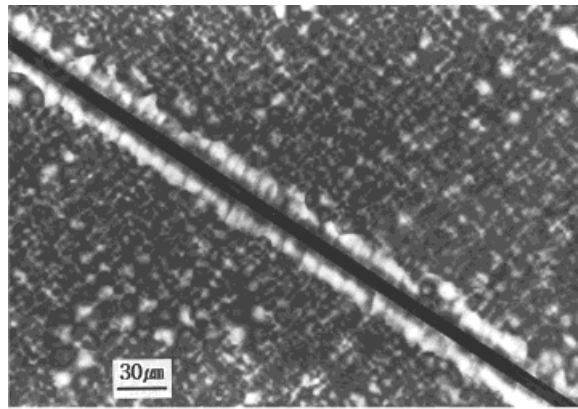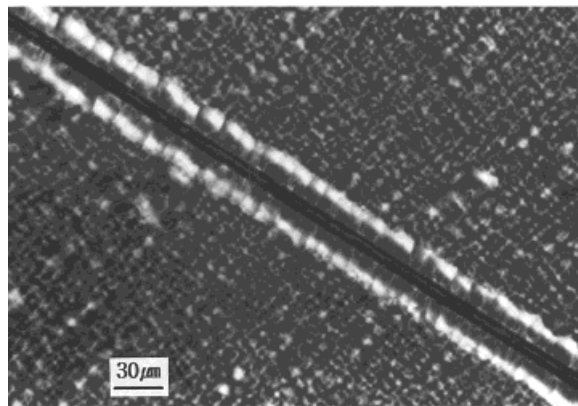

(a)
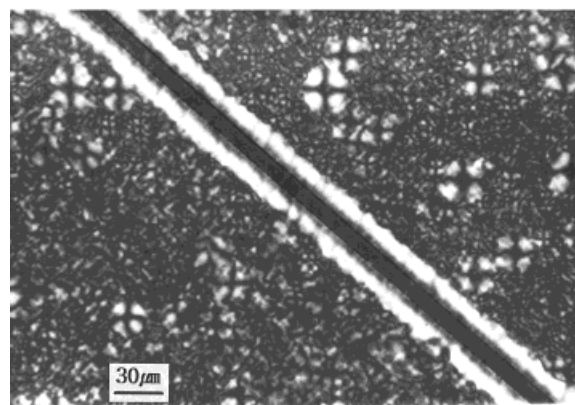
(b)

Figure 5 Interfacial microstructure of PP composites based on untreated GFs: (a) moistened; (b) dried, glass fiber, crystallized upon rapid cooling from 220°C.

(a)

(b)

Figure 6 Interfacial microstructure of PP composites based on (a) untreated and (b) treated carbon fiber, crystallized upon rapid cooling from 220°C.

gesting that nucleation on the fiber dominates the matrix nucleation, i.e., transcrystallinity along the fiber is predominantly formed over the spherulites in the matrix polymer. Therefore, in the case of real composites with a high fiber volume fraction, because the distance between the fibers is short, transcrystallinity in the interphase occurs only and a spherulite polymer cannot form in the space between the fibers as shown in Figure 7.

Consequently, we may expect that the formation of transcrystallinity on fiber surface causes the properties of the fiber surface and the matrix to become more similar, thus yielding the effective wetting of the fibers by the matrix, strong interfacial adhesion, good dispersion of the fibers in the matrix, and, hence, strong mechanical properties

(a)

(b)

(c)
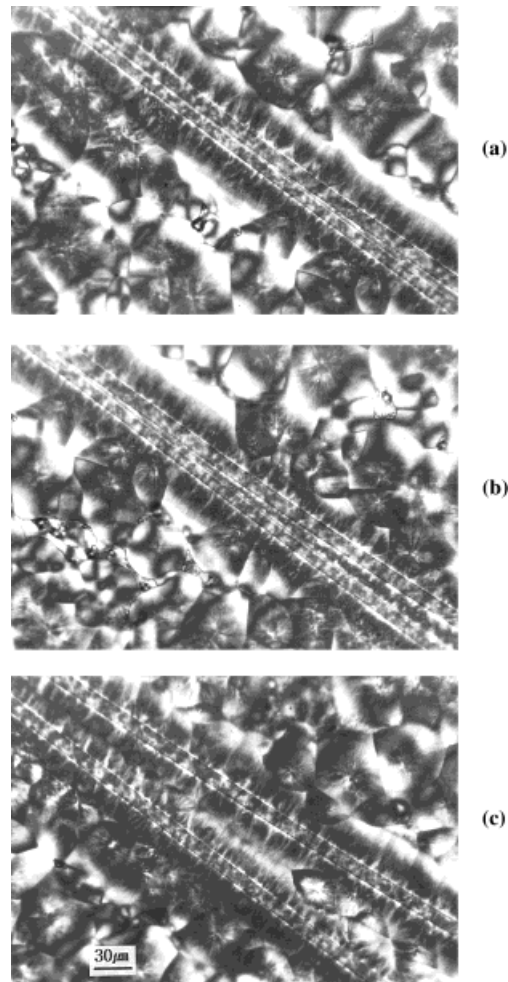
Figure 7 Cross-polar optical microphotographs of E-glass fiber-reinforced PP composites, crystallized from the melt held at 220°C for 30 min by air-cooling to room temperature.

seem to exist between the two cases. When compared to the results for the GF under about the same heat-treatment condition, the case for the carbon fiber was found to have a more pronounced transcrystalline region owing to the effect of the lower fiber diameter, as stated before.

To investigate the interfacial morphology as found in actual E-glass fiber/PP composites, optical microphotographs of composite samples obtained by molding the matrix polymer with a multifiber are given in Figure 7. It can be easily seen that as the interfiber spacing becomes smaller the spherulites in the matrix polymer are not seen to be formed between the transcrystalline layers developed on the GF surface, sug-

of the composites. Although this view has been already confirmed in the case of carbon fiber-reinforced polyethylene composites, work along this line for the PP composite system is still in progress.

CONCLUSION

The findings made from this study can be summarized as follows:

1. The interfacial transcrystalline structure is significantly affected by the fiber diameter of the GF and the molecular weight of the PP.
2. The thickness of the transcrystalline region is almost the same as the radius of the largest spherulites in matrix.
3. The size of the spherulites in the matrix depends largely on both the holding time at the crystallization temperature and the cooling condition (or rate) from the melt to room temperature.
4. The formation of the transcrystalline structure in fiber-reinforced composites based on semicrystalline thermoplastic resins impedes the spherulitic formation and development within the matrix phase.
5. In case of real composites with a high fiber volume fraction, because the distance between fibers is short, transcrystallinity occurs only in the interphase and spherulites cannot form in the space between the fibers.

REFERENCES

1. P. Hancock and R. C. Cuthbertson, *J. Mater. Sci.,* **5,** 765 (1970).
2. D. M. Bigg, *Polym. Compos.,* **6,** 20 (1985).
3. R. T. Curtis, M. G. Bader, and J. E. Bailey, *J. Mater. Sci.,* **13,** 377 (1978).
4. M. Taya and T. W. Chow, *J. Mater. Sci.,* **17,** 2801 (1982).
5. R. K. Mittal and V. B. Gupta, *J. Mater. Sci.,* **17,** 3179 (1982).
6. A. R. Sandi and M. R. Piggott, *J. Mater. Sci.,* **20,** 421 (1985).
7. A. R. Sandi and M. R. Piggott, *J. Mater. Sci.,* **20,** 431 (1985).
8. C. K. Moon, H. H. Cho, and J. O. Lee, *J. Appl. Polym. Sci.,* **44,** 561 (1992).
9. C. K. Moon, J. O. Lee, and H. H. Cho, *J. Appl. Polym. Sci.,* **45,** 443 (1992).
10. M. J. Folkes and S. T. Hardwick, *J. Mater. Sci. Lett.,* **3,** 1071 (1984).
11. F. Kumamaru, T. Oonu, T. Kajiyama, and M. Takayanagi, *Polym. Compos.,* **4,** 325 (1983).
12. J. K. Tan, T. Kitano, and T. Hatakeyama, *J. Mater. Sci.,* **25,** 3380 (1990).
13. Y. C. Lee and R. S. Porter, *Polym. Eng. Sci.,* **26,** 633 (1986).
14. T. Bessell and J. B. Shortall, *J. Mater. Sci.,* **10,** 2035 (1975).
15. C. K. Moon, Y. S. Um, H. H. Cho, J. O. Lee, and T. W. Park, *Polymer (Korea),* **14,** 630 (1990).
16. C. K. Moon, *J. Appl. Polym. Sci.,* **54,** 73 (1994).
17. C. K. Moon and Y. S. Um, *Polymer (Korea),* **15,** 289 (1991).