

The Effect of Interfacial Microstructure on the Interfacial Strength of Glass Fiber/Polypropylene Resin Composites

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SYNOPSIS

In this study, a new method to form resin droplets on fibers has been developed, and samples for the single fiber pull-out test were prepared using this method. The effects of microstructure of polypropylene (PP) resin and the microstructure of interface between the glass fiber and PP resin on the interfacial strength have been investigated. In addition, the influence of the microstructure of the interface on the interfacial strength of glass fiber-reinforced PP composites have been discussed. It has been found that in the pull-out test, the transcrystallinity formed at the interface between the glass fiber and PP resin improved the interfacial strength when no spherulites developed in the PP matrix. On the other hand, it has been found that when the spherulites were well developed in the PP matrix, the transcrystallinity formed at the interface reduced the interfacial strength. Finally, rapid cooling has been shown to improve the interfacial strength between the fiber and resin in the crystalline polymer matrix composites. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

To date, thermosetting resins such as epoxy and unsaturated polyester resins have been used extensively in continuous fiber-reinforced composites because of their high strength and good thermal resistance. Recently, however, increasing interest is being shown to thermoplastic resins because of their economic and mechanical advantages, such as ease of fabrication, reproducibility, indefinite shelf life of the "prepreg," greater toughness, etc. Moreover, due to the development of advanced engineering thermoplastics with their excellent thermal resistance and mechanical properties (e.g., polyimide, polyphenylenesulfide, polysulfone, PEEK, etc.), there is a growing demand for fiber reinforced thermoplastic composites.

The interfacial properties of fiber-reinforced composites strongly influence the performance of composite materials.¹⁻⁵ Consequently, measuring the interfacial shear strength between the fiber and the resin has become one of the more fundamental ways to evaluate the mechanical properties of short fiber-reinforced composites.⁶ If the interfacial shear

strength is too low, then the mechanical properties of the composites are controlled mainly by an interface that has low shear strength; hence, the performance of the reinforced fiber will not be reflected, even when using a high-strength fiber. On the other hand, if the interfacial shear strength is too high, the fracture toughness of composites could be reduced due to the poor resistance against crack propagation.^{7,8} Therefore, it is necessary for the interfacial shear strength of the fiber-reinforced composite to be controlled to optimize the performance of composites. In principle, the interfacial bonding strength between the fiber and matrix can be controlled by using suitable coupling agents in conjunction with surface modification of the fiber, such as chemical oxidation,⁹ plasma etching,^{10,11} etc. In addition, the correct evaluation of the interfacial shear strength for a particular composite system will be of great help when trying to optimize the performance of composites. Thus, an evaluation of interfacial structure and properties is essential for understanding composite properties, because the stresses acting on the matrix is transmitted to the fiber across the interface between fiber and matrix. In the case of a thermosetting matrix resin, the interfacial shear strength is controlled primarily by physical and/or chemical bonding. In contrast, when

semicrystalline thermoplastic resins are used as the matrix, particular interfacial morphological features may arise along the interface due to the direct influence of the fibers on the crystallization process. This feature is a columnar growth of crystals corresponding to the lateral development of the spherulites, normally called "transcrystallinity."¹²⁻¹⁵ This transcrystallinity is produced along the fiber axis due to the nucleating effect of fiber, thereby enhancing the interfacial bond strength between fiber and matrix. However, some researchers have shown that transcrystallinity can increase¹⁵⁻¹⁷ or decrease^{18,19} the interfacial shear strength.

In a previous study performed on the glass fiber/polypropylene composites system,²⁰ it has been found that factors such as fiber diameter, molecular weight of the matrix polymer, and heat-treatment conditions can influence the interfacial microstructure and mechanical properties of the composite.

In the present study, a new method to make the single fiber pull-out test specimen for the measurement of the interfacial shear strength in glass fiber/thermoplastic resin system is introduced. Furthermore, the influence of variations in the interfacial microstructure that comes from different heat-treatment conditions on the interfacial shear strength of PP with glass fiber is investigated.

EXPERIMENTAL

Materials

The materials used in this study are as follows. The fiber, supplied by Han Kuk Fiber Glass Co., Ltd., Korea, was E-glass, and had the following properties: density, 2.54 g/cm^3 , diameter, $19.5 \text{ }\mu\text{m}$, and tensile strength, $166 \pm 0.41 \text{ GPa}$. The mean fiber diameter has been estimated from the measurement of the length and weight of the fiber with the aid of the known fiber density. The tensile strength was measured using a tensile tester equipped with a load cell with a 200 g capacity. The crosshead speed was 2 mm/min, and the gauge length of the sample was 20 mm. The average value was determined by testing about 100 samples.

The as-received fibers were coated by the manufacturer with a silane coupling agent. These fibers were washed in acetone for 1 h to remove any foreign materials and vacuum dried at 80°C for 3 h. The matrix resin was a commercially available isotactic PP (melt flow index = 15), supplied by Korea Petrochemical Ind. Co., Ltd., and had a density of 0.90 g/cm^3 and melting temperature of 163°C . In this

work, the formation condition for all specimens was to hold samples at 220°C for 1 h, then using various cooling rates down to the room temperature.

Forming Resin Droplets on Glass Fibers

Of the methods available for measuring the interfacial shear strength between the fiber and matrix, the single fiber pull-out test method based on forming resin droplets on a fiber surface appears to be one of the more useful methods in terms of sample preparation: the microbond method developed by Miller et al.²¹ and the solution microbond method proposed by the author et al.,²² respectively, for the thermosetting and thermoplastic resins. However, in this study, there were problems in controlling the size and spacing of resin droplets on a single fiber using the latter method, for it consists of forming resin droplets on the fiber surface by dissolving polymer molecules in a suitable organic solvent. Other researchers have reported tying polymer thread²³ or placing polymer threads of the trouser form on the fiber to form a resin droplet via melting, but these methods are extremely difficult for fibers with small diameters to form a number of resin droplets at a time and to control the size and spacing of resin droplets on a single fiber. Hence, the author has developed a new method for forming resin droplets on glass fibers to overcome these difficulties as follows. As illustrated in Figure 1, the fibers are first aligned parallel to each other and fixed on the frame made of 3 mm diameter steel wires. Then the polymer threads ($20\text{--}30 \text{ }\mu\text{m}$ diameter) are placed across on the fiber and heated in an electric furnace above (220°C), the melting point of the polymer to form resin droplets on the fibers via surface tension.

Measurement of Interfacial Strength

The single fiber pull-out tests^{21,22} for measuring the interfacial strength between the fiber and matrix

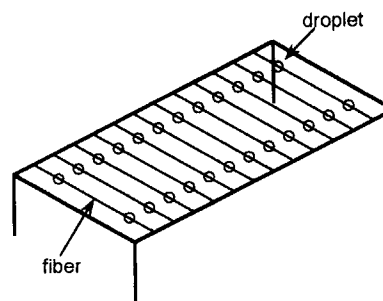


Figure 1 Schematic representation for the formation of resin droplets on fibers for the pull-out test.

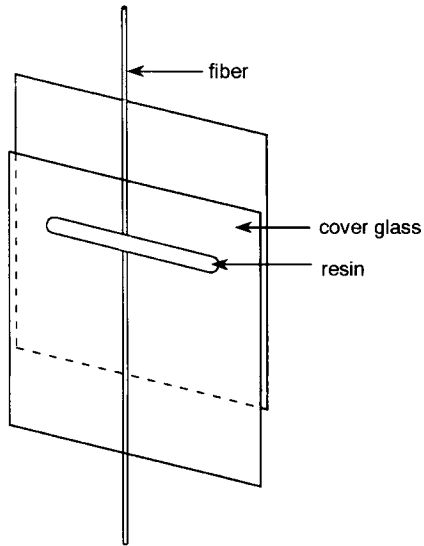


Figure 2 Schematic diagram for embedding of fiber in a resin strip between two cover glasses for microscopic observation and the pull-out test.

were carried out on samples obtained by the new method. The number of test specimens was 40–50 for each experimental condition.

From a previous study,²⁰ the cooling rate from the melt to room temperature has been found to affect significantly the crystallization behavior and, hence, the microstructure of both the fiber–matrix interface and the matrix phase. The conventional pull-out test method, however, can give the data for the interfacial strength, but it is difficult, by this method, to confirm visually the variation in interfacial microstructure arising from different cooling rates. Hence, the author devised a convenient way to prepare the pull-out test specimen, which makes it possible not only to evaluate the interfacial strength, but also to observe the interfacial microstructure via an optical microscope.

This method is based on using two cover glasses as shown in Figure 2, where a PP strip (50–200 μm) and a single glass fiber located across the strip are

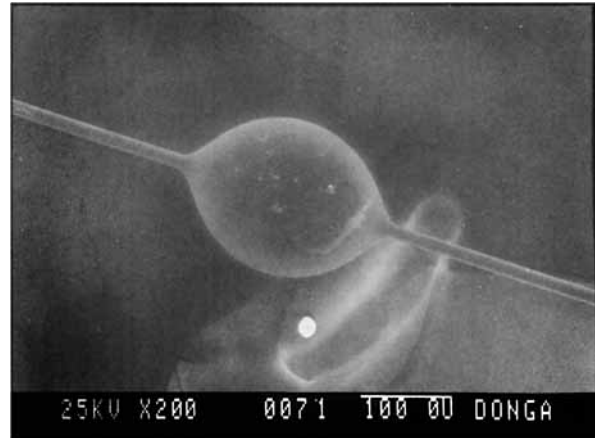


Figure 3 Typical PP resin droplet on a glass fiber.

placed on one cover glass, and the other cover glass is placed on top of the setup and pressed down using a weight of 300 g to ensure complete melt and constant thickness. Then, this pressure is maintained at 220°C for 1 h, and cooled down to room temperature (ca. 13°C) by three different cooling procedures to give samples for the pull-out test. The three procedures are, in the order of increasing cooling rate: (1) “furnace cooling,” made by opening the door of a furnace slightly; (2) “air cooling,” made by the samples standing in air of ca. 13°C; and (3) “ice water cooling,” based on using ice water. The pull-out tests on samples that were cooled using the three conditions were carried out using a tensile tester equipped with a load cell of 200 g at a cross-head speed of 2 mm/min and free length of 5 mm. The pull-out samples were of two types, one due to resin droplets and the other using cover glasses.

Tensile Test

Tensile tests were carried out on PP sheets and glass fiber/PP composites obtained from the furnace and ice water cooling procedure. These different cooling procedures were used in order to investigate the ef-

Table I Interfacial Strength of E-Glass Fiber/PP Resin Droplets with Various Holding Time at 220°C, Cooled in Air from the Melt to Room Temperature

Holding Time at 220°C	0.5 h	1 h	2 h	4 h
τ_d (MPa)				
(std. dev.)	10.60 \pm 2.27	11.39 \pm 2.08	11.30 \pm 2.18	11.39 \pm 2.28

Table II Interfacial Strength of E-Glass Fiber/PP Resin Droplets with Various Cooling Procedures from the Melt Held at 220°C for 1 h

Cooling Procedures	Furnace Cooling	Air Cooling	Ice Water Cooling
τ_d (MPa) (std. dev.)	6.54 ± 1.39	11.39 ± 2.08	13.97 ± 2.27

fect of the crystallization condition (mainly cooling rate) on the microstructure of matrix and interface and, hence, the mechanical properties of the resulting composites.

Tensile test specimens for PP sheets were prepared in a vacuum oven at 220°C and 1.0 MPa for 1 h. The compressed sheets (ca. 0.5 mm thick) were then cooled to room temperature by fast (ice water) or slow (furnace) cooling.

Rectangular strips with shape of dumbbells (10 by 100 mm) for the two cooling rates of the samples were trimmed by a paper cutter and tensile tested using an Instron testing machine having a 25 mm extensometer, and using a crosshead speed of 10 mm/min. In addition, PP composite sheets containing unidirectional glass fibers were also prepared in a vacuum oven. PP composite sheets was made as follows. First, glass fiber tows were arranged unidirectionally on a rectangular frame, and then fixed at both ends of the tows. After this, they were interleaved with upper and bottom side of the arranged fiber tows previously made amorphous PP sheets (0.2 mm thick) and compression molded at 220°C and 1.0 MPa for 1 h in vacuum oven to remove any voids.

Transverse tensile test specimens were made by the lamination of PP composite sheets at 220°C and 1.5 MPa for 1 h in a hot press.

Microscopic Observations

In order to compare the interfacial microstructure of the glass fiber/PP resin in samples crystallized by different cooling procedures, microscopic obser-

vations were carried out on the pull-out test specimens based on using cover glasses prior to the test, and, to investigate the interfacial morphology (transcrystallinity) as found in actual composites, microscopic observation samples were obtained by molding PP with multiglass fiber. This was the same molding method as for the pull-out test specimens that used cover glasses. In addition, to estimate the adequacy of the shape of the resin droplets formed on a single fiber according to the new method mentioned above, SEM microphotographs of the tensile fracture surfaces were taken on the glass fiber/PP composite samples crystallized by the furnace cooling and ice water cooling procedures.

RESULT AND DISCUSSION

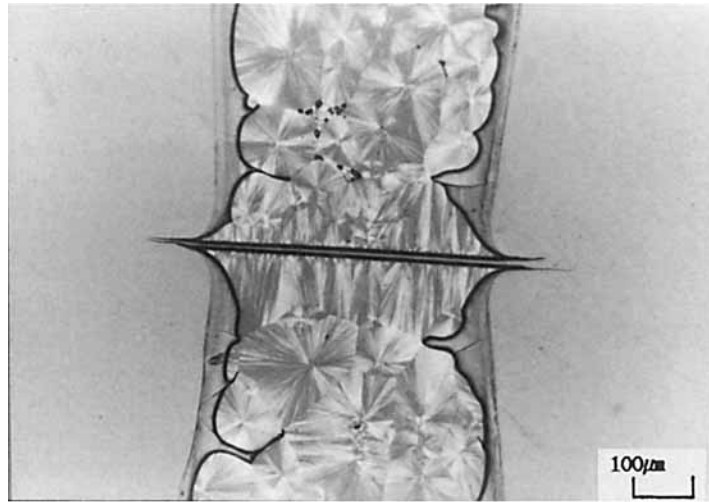
New Method of Resin Droplet Formation

Figure 3 shows a Scanning Electron Microscope (SEM) photograph of a PP resin droplet formed by using the new method on a glass fiber. As shown in the photograph, the droplet shape was symmetric around the fiber axis. The glass fibers were arranged unidirectionally and fixed in a specially designed fixture. The melted organic thread formed droplets on the glass fiber by the surface tension of the resin. Furthermore, the size of resin droplets can be controlled by adjusting the diameter of polymer thread and the distance between the arranged fibers.

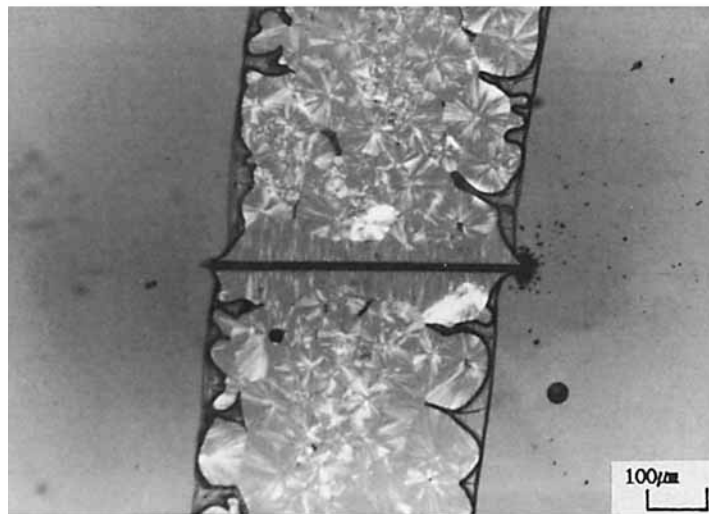
Table I shows the interfacial shear strengths (IFS) for various holding times at 220°C, cooled in air from the melt to room temperature. For the

Table III Interfacial Strength of E-Glass Fiber/PP Resin Strip with Various Cooling Procedures from the Melt Held at 220°C for 1 h

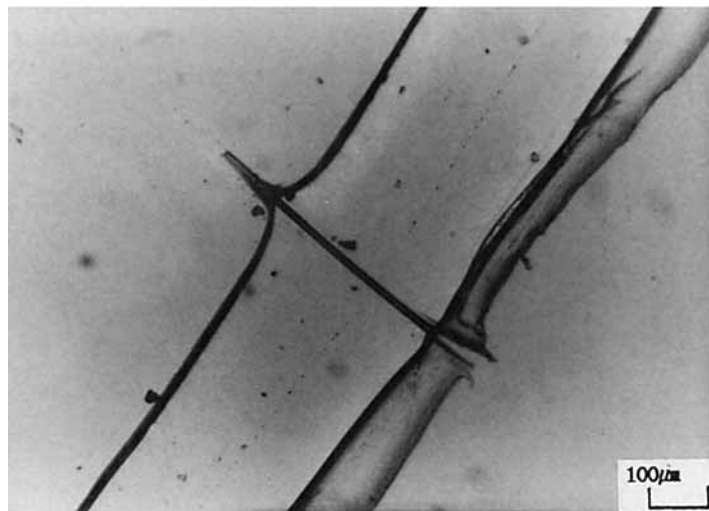
Cooling Procedures	Furnace Cooling	Air Cooling	Ice Water Cooling
τ_d (MPa) (std. dev.)	4.16 ± 1.19	6.04 ± 1.49	9.71 ± 2.08



(a)



(b)



(c)

Figure 4 Interfacial microstructures of PP an embedded glass fiber, crystallized via various cooling procedures from the melt to room temperature. (a) Furnace cooling; (b) air cooling; (c) ice water cooling.

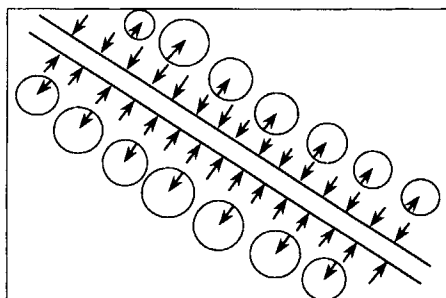


Figure 5 Schematic illustration of the working forces around the fiber.

specimen with 30 min holding time, the IFS was lower, whereas the IFS was almost constant in case of holding more longer than 1 h.

Interfacial Strength

Table II shows the IFS for various cooling procedures after forming a resin droplet on the glass fiber. Fast cooling rates yielded high the IFS. The highest values of the IFS was first, ice water cooling, second, air cooling, and finally, furnace cooling.

Table III showed the IFS of specimens using cover glasses via the same condition as Table II. Although the general trend was the same as in Table II, the values were lower than those in Table II for the same conditions. This difference is probably because of specimens of different shape. That is, the pull-out specimens in Table II were resin droplets, whereas the pull-out specimens in Table III were resin flat with about 0.1 mm thickness, thus leaving insufficient resin at the contact portion of cover glass when samples were formed.

Figure 4 shows photographs of polarized-light microscopy after the pull-out test. Changes can be seen in the microstructure caused by the various cooling procedures. In the specimens of the furnace and air cooling, the transcrystallinity in the interphase and the spherulites in matrix were well developed, but in ice water cooling, both the trans-

crystallinity and the spherulites were not seen, and matrix was almost amorphous. In the matrix, the spherulite size for furnace cooling was larger than that of air cooling.

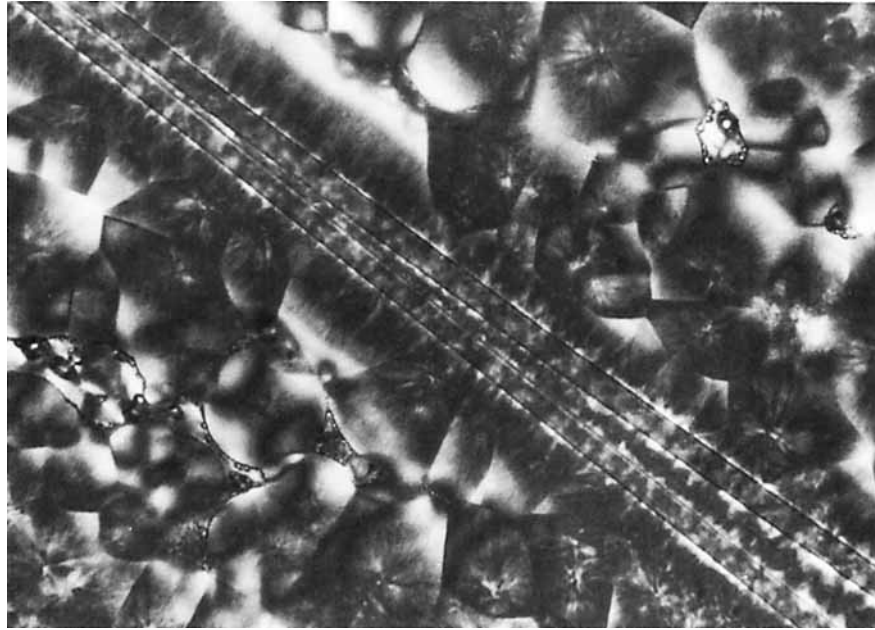
Comparing Tables II and III with Figure 4, the interfacial microstructure of the fiber and the matrix have a great influence on the IFS. For carbon fiber/HDPE composites,²⁴ transcrystallinity that formed in the interphase improved the IFS. On the other hand, in this work, the IFS decreased as the amount of transcrystallinity increased. This is probably because of the different microstructure in the matrix. In case of the carbon fiber/HDPE specimen,²⁴ transcrystallinity was formed in the interphase, whereas spherulites did not form significantly in the matrix. In this work, however, spherulites were formed well in the matrix resin (refer to Fig. 4).

The IFS measured in the pull-out test is considered to be based on the physic-chemical bonding force and the frictional forces between fiber and matrix.²⁵ Because this physic-chemical adhesion is constant for the same surface treatment and matrix resin, the change in the IFS is related to the size of the frictional force. Because multiplying the contraction force by the frictional coefficient makes the frictional force, and for the same two materials the friction coefficient is constant, the IFS is only dependent upon the contraction force affecting on the interphase. Therefore, the contraction force that is formed in the interface can be expected to be related intimately with the developing condition of the spherulites in the matrix resin.

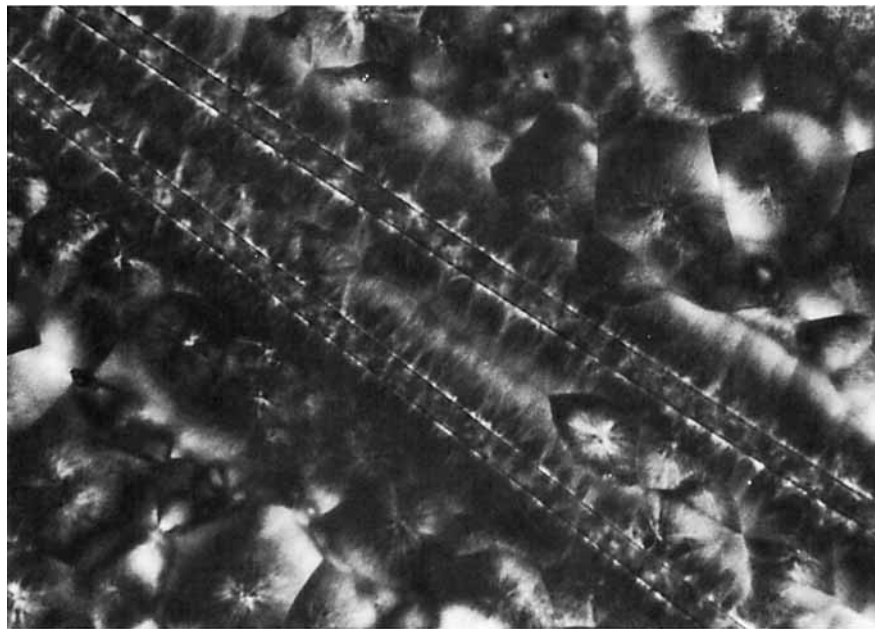
When the polymer was cooled down from the melt, more contraction occurred in the crystallinity portion than in the amorphous portion. Therefore, in the absence of the developing spherulites, the well-formed transcrystallinity in the fiber/resin interface increased the IFS. On the other hand, as shown in the Figures 4(a) and (b), and Tables II and III, the well-formed transcrystallinity with many well-developed spherulites in the matrix decreased the IFS. This decrease in the IFS is due to the fol-

Table IV Tensile Properties of PP Resin Sheet with Different Cooling Procedures from the Melt Held at 220°C for 1 h

Cooling Procedures	Furnace Cooling	Ice Water Cooling
σ (MPa) (std. dev.)	30.91 \pm 1.49	26.55 \pm 2.67
ϵ (%) (std. dev.)	18.1 \pm 5.3	408 \pm 117



(a)



(b)

Figure 6 Crosspolar optical microphotographs of PP around E-glass fibers, crystallized from the melt held at 220°C for 1 h by air cooling to room temperature.

lowing reason shown in Figure 5. In the interlayer, two contractional forces for the transcrystallinity in the fiber and spherulites in the matrix resin com-

pensated for each other through opposing forces, the total contracting forces on the fibers became weak, thus decreasing the IFS.

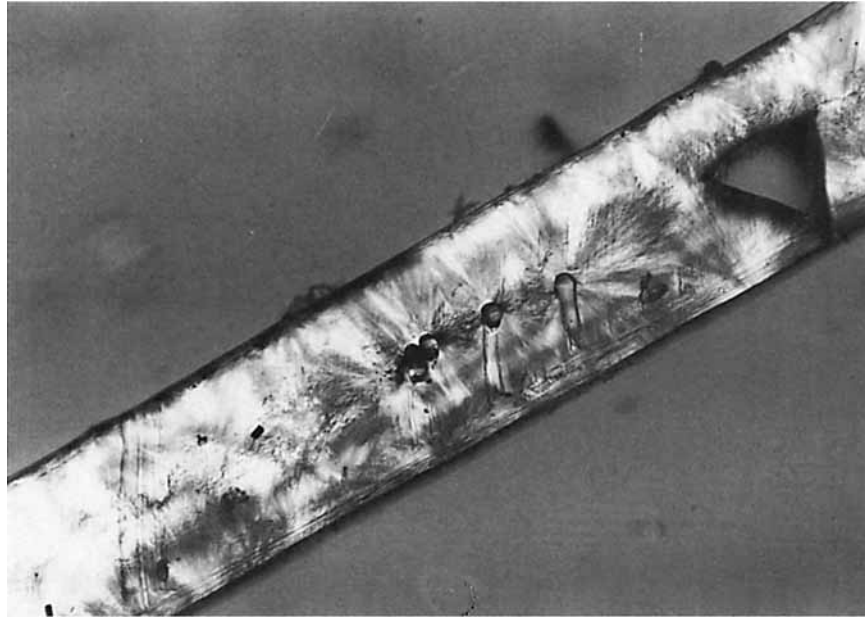


Figure 7 Crosspolar optical microphotograph of the transcristallinities around fibers (air cooling).

In Tables II and III, the reason for the higher IFS for ice water cooling compared with the furnace or air cooling is the same reason as described before. In addition, the reason for the higher IFS for the air cooling than the furnace cooling is that the size of spherulites in the furnace cooling is larger than for the air cooling condition. Therefore, because the compensating force in the interfaces became larger, the contraction forces working on the fibers is small.

Finally, forming transcristallinity in the interface does not always improve the IFS, and the IFS is considered to be related intimately to the developing condition of spherulites in the matrix resin. If many spherulites did not form in advance in the matrix, the transcristallinity in the interface formed by the nucleating effect of the fiber, which must improve the IFS. However, in the polymer matrices with rapid crystallinity can also result in the opposite result, because of both the transcristallinity and spherulites in the interface and matrix can be formed simultaneously.

The Tensile Test

Table IV shows the results of tensile tests for the furnace and ice water cooling condition during formation of PP sheet. The tensile strength for the ice water cooling exhibited lower than for the furnace cooling, whereas the extension ratio was much higher than for the furnace cooling.

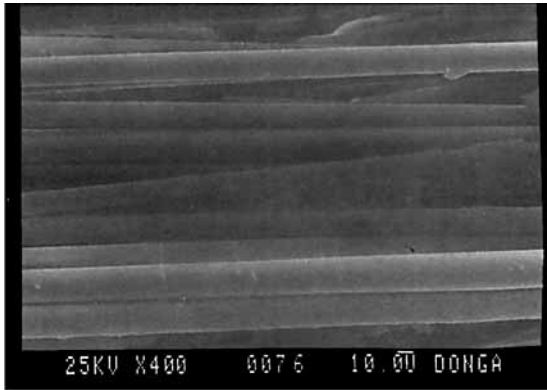
Microscopic Observation

Figure 6 shows a crosspolar optical microphotograph of the transcristallinity of the between fibers. It can be seen that as the interfiber spacing became smaller, the spherulites in the resin matrix did not seem to form between the transcristallinity layers that developed on the glass fiber surface, suggesting that nucleation on the fiber dominates the matrix nucleation, i.e., transcristallinity along the fiber is predominantly formed over the spherulites in resin.

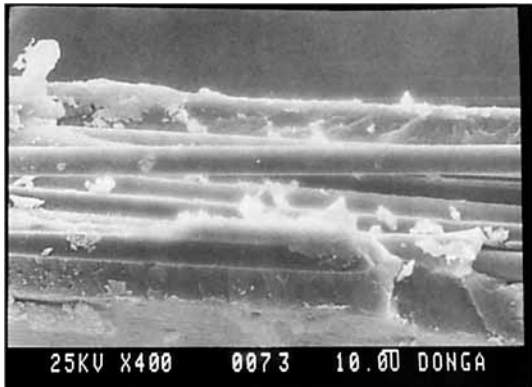
In the pull-out test, transcristallinity in the interface and the condition of developing spherulites in the matrix affect on the IFS. However, in the case of composites with a high fiber volume fraction, because the distance between fibers are short and transcristallinity in the interphase occurs only, spherulites cannot form in the place between fibers as shown in Figure 6(a). Therefore, the decrease in the IFS due to the spherulites is not expected to occur in the composite system.

Figure 7 shows a crosspolar optical microphotograph of the transcristallinities around the fiber. It can be predicted that, as contractional forces due to the formation of the transcristallinity around the fibers compensate each other by opposing forces, the total contracting forces on the fibers become weak. Thus, the decrease of the IFS is based on the same reason as in the pull-out test result.

Figure 8 shows the SEM microphotographs of the fractured surface of an unidirectional glass fiber/



(a)



(b)

Figure 8 SEM microphotographs showing the fracture surface of E-glass fiber/PP composites. (a) Furnace cooling; (b) ice water cooling.

PP resin composites. The fiber volume fractions were 20.1 (a) and 20.8 vol % (b), and transverse tensile strengths were 14.99 (a) and 15.68 MPa (b), respectively. The fiber surface looks clean in the furnace cooling case, whereas some of resin seems to be adhered to the fiber surface in the ice water cooling case. This difference shows that ice water cooling condition gives higher IFS than does furnace cooling.

To summarize, in the glass fiber/PP resin composites, the transcrystallinity formation results in a decrease in the IFS. In the pull-out test, the transcrystallinity formation at the interface can improve the IFS, whereas in the composites with high fiber volume fraction, transcrystallinity may reduce the IFS. Also, in the case of short fiber-reinforced com-

posites with smaller fiber fraction, the IFS can be weak due to the spherulites development in the matrix around the fiber [refer to Fig. 6(b)]. Therefore, to improve the IFS in the crystalline polymer matrix resin, the rapid cooling procedure is required when making composites.

CONCLUSION

The conclusions drawn from this study on a new method to make the single fiber pull-out test specimen for the measurement of the interfacial shear strength in glass fiber/thermoplastic resin system and the influence of variations in the interfacial microstructure that comes from different heat-treatment conditions on the interfacial shear strength of PP with glass fiber are as follows.

1. A newly proposed method for forming resin droplets on fiber based on the surface tension effects of the molten liquid has been found to be useful when measuring the interfacial strength between a reinforcing fiber and a thermoplastic resin.
2. The interfacial strength was largely affected by the microstructure of the interphase.
3. The effect of the transcrystallinity developed at the fiber-matrix interface on the interfacial shear strength seemed to depend on the state of the spherulitic growth in the matrix resin.
4. When crystallizable thermoplastic resins are used as matrices in fiber-reinforced composites, the melt cooling rate in molding has proved to be one of the most important factors in controlling physical properties of the final product. This is because it will affect the microstructures of both the fiber-matrix interface and matrix phase, the interfacial shear strength, and, hence, mechanical properties of PP sheets and glass fiber/PP resin composites.

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