Interfacial Properties of PP/PP Composites

T. Kitayama,[1] S. Utsumi,[2] H. Hamada,[3] T. Nishino,[4] T. Kikutani,[5] H. Ito[5]

[1]*Sumitomo Chemical America, Inc., 335 Madison Avenue, Suite 830, New York, New York 10017*
[2]*Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 5-1 Anegasakikaigan, Ichihara-shi, Chiba 299-0195, Japan*
[3]*Division of Advanced Fibro-Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
[4]*Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan*
[5]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-Okayama 2, Meguro-ku, Tokyo 152-8552, Japan*

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ABSTRACT: All-polypropylene (PP/PP) composites, consisting of homoisotactic PP fibers and a propylene–ethylene random copolymer matrix, were manufactured. The interfacial morphologies and mechanical deformation of the composites were investigated. It was found that a transcrystalline layer was formed in the matrix depending on the molding conditions. This layer is composed of two regions with different morphologies: In one region close (<300 nm) to the fibers, lamellae exist very densely and the *c*-axes of the crystal lattices are oriented along the longitudinal direction of the fiber. In the other region, a little away (>300 nm) from the fiber, a cross-hatched structure was observed. The well-developed transcrystalline layer could be highly elongated, and no debonding was observed at the fiber/matrix interface by the tensile stress in the direction perpendicular to the fiber. It is conceivable that this is the reason for the observed improvement of the transverse tensile properties in the PP/PP composite with a transcrystalline layer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2875–2883, 2003

INTRODUCTION

In recent years, many studies were carried out on various kinds of composites with excellent properties in order to comply with the demands for performance enhancement. It has been pointed out that the characteristics of a composite are not only dominated by the properties of the reinforcement and the matrix resin, but also by those of the interface formed between the two matters.[1,2] Often, the reinforcement and the matrix resin are different, so various coupling agents are utilized to adhere them effectively. The coupling-agent treatment for glass fibers and the oxidation treatment for carbon fibers are typical examples.[3,4] Furthermore, studies on the interfaces of the composites have progressed greatly through recent advances in instrumental analysis techniques.[5,6]

Composites using the same kind of materials for the reinforcement and the matrix resin are very interesting materials because physical deterioration due to interfacial problems is avoided.[7] These composites are also useful from a recycle point of view. Most studies on composites using the same kind of materials are polyethylene (PE)/PE combinations, in which the low-density PE matrix resin is filled with an ultrahigh modulus and strength PE fibers.[8] Although the PE/PE composites show excellent mechanical properties, their use is limited by the low melting point of PE. On the other hand, isotactic polypropylene (PP) has been used in various fields because of its excellent physical properties such as heat resistance. One disadvantage of using PP compared with other reinforcements is that PP possesses a relatively low crystal modulus.[9] This implies that the ultrahigh modulus of PP cannot be obtained intrinsically. However, PP fibers with a moderately high strength (1.04 GPa) and a high elastic modulus (12.7 GPa) have been recently developed through the special drawing of PP fibers.[10] Thus, we are interested in making all-PP composites because of interfacial, thermal, mechanical, economical, and ecological benefits.

A transcrystalline layer has often been observed in the matrix near the incorporated fibers.[11–13] However, many reports gave contradictory results for the reinforcement effects of the transcrystalline layer in the composites. For example, some reported that the transcrystalline layer reduces the interfacial adhesion of all-PE/PE composites,[14,15] but others reported that it improves the tensile properties in the transverse direction and also brings a better adhesion strength to the interface.[16] The transcrystalline layer was also observed for PP composites containing glass fibers.

Correspondence to: H. Hamada (hhamada@ipc.kit.ac.jp).

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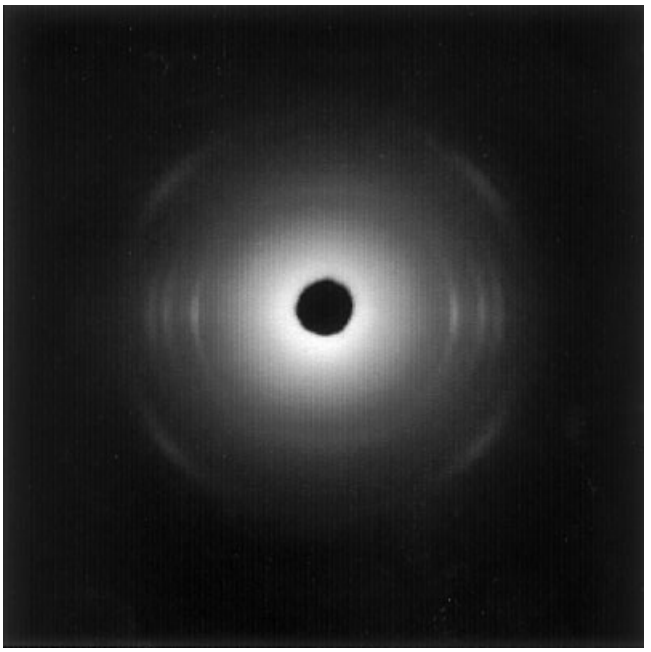

Figure 1 X-ray fiber photograph of the spun and drawn homo-PP fiber.

Again, contradictory results were reported for the PP-based composites.[17–20]

In this study, we made an all-PP/PP composite using a PP–PE random copolymer as the matrix resin and a homo-PP as the fiber. The morphologies and the mechanical reinforcements of the transcrystalline layer formed in the interface were investigated.

EXPERIMENTAL

Materials and specimens preparation

The materials used in this study were a homo-PP (HX100G, Sumitomo Chemical Co., Ltd., Tokyo, Japan) fiber and a propylene–ethylene random copolymer matrix (S131, Sumitomo Chemical Co., Ltd.). The homo-PP (MI = 60) was extruded from a 10-hole spinneret, each with a diameter of 0.6 mm, at 200°C. The throughput rate was controlled at 15 g/min. The PP fiber was spun up to the take-up velocity of 1.0 km/min and continuously taken up to the velocity of 2.0 km/min at room temperature.

Figure 1 shows an X-ray fiber photograph of the drawn fiber. The Ni-filtered CuKα radiation was irradiated, and the diffraction was recorded with a flat camera. The crystallite orientation was not especially high because of a relatively low draw ratio. The difference in the elastic modulus between the longitudinal and transverse directions of the fiber was believed not to be too high.

Figure 2 shows differential scanning calorimetric traces of the fiber and the matrix resin. They were obtained using a differential scanning calorimeter (DSC, 7-Series, Perkin–Elmer Instruments, MA) at the heating rate of 10°C/min. The melting endotherm of the matrix was complete at 153.0°C, prior to any fiber endotherm. The 35°C difference between their melting points enables us to mold all-PP composites.

Figure 3 shows a schematic illustration for the molding process of the composite with a single PP fiber/PP matrix combination. Two 250-μm-thick films were introduced between the female and the male molds and then a single fiber was inserted between them [Fig. 3(a)]. In this study, the molding temperatures (T_{mold}) of 150, 160, and 163°C were chosen. They are the temperatures far below, just below, and at the melting point of the incorporated fiber, respectively. The molds were preheated at the temperatures of each T_{mold} and then closed [Fig. 3(b)]. After holding for 1 min at 1.9 MPa, the resultant PP/PP composite was cooled from each T_{mold} to 25°C for 3 min [Fig. 3(c)]. During processing, the molding temperature, T_{mold}, is one of the most important factors to maximize the adhesion and to keep the original fiber shape. The single-PP fiber/PP composites molded at different temperatures were obtained to investigate the formation of the transcrystalline layer in the surface of the incorporated fiber.

Observation of micromorphologies

The observations of the interfacial morphologies of the all-PP composites were conducted by polarized optical microscopy (PLM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). In the PLM (Axiophot, Carl Zeiss, Jena, Germany) observation, a cross section of the PP/PP composite sliced into 10 μm was set on a microscope stage. The stage could be combined with a stretching device es-

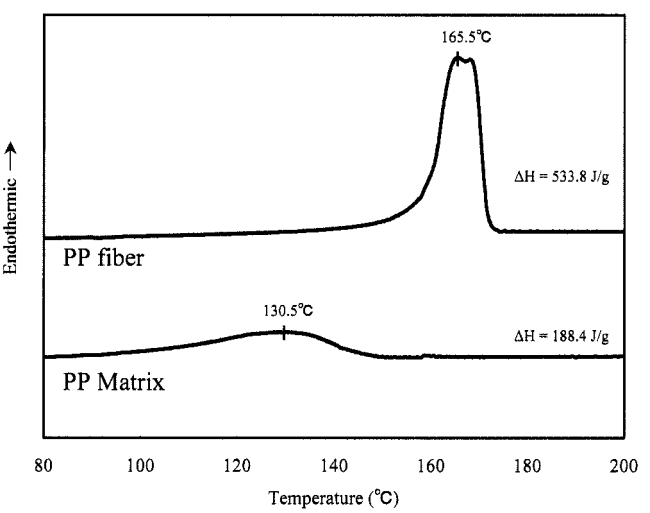

Figure 2 Differential scanning calorimetric traces of the homo-PP fiber and the PP–PE copolymer matrix resin.

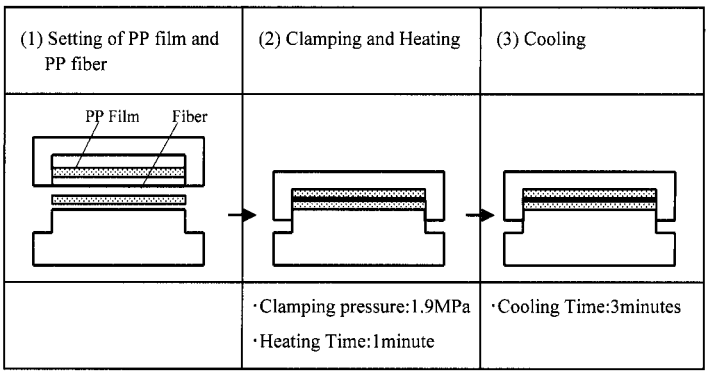

Figure 3 Schematic illustration for the molding process of the single PP fiber/PP matrix composite.

pecially designed for stretching of the cross section. The *in situ* PLM observation was performed during a tensile test. An atomic force microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) was also used for the observations. The probe tip, made of Si3N4 (the spring constant of 0.032 N/m), was scanned in a 50-μm-square range across the interface of the PP/PP composite with a constant force mode. In the TEM (H8000, Hitachi High-Technologies, Tokyo, Japan, acceleration voltage = 200 kV) observation, the microtomed cross section was stained with RuO4 in order to observe the lamellae at the fiber/matrix interface.

Longitudinal and transverse properties

To confirm the longitudinal and transverse tensile properties, a PP/PP composite with a volume fraction (*Vf*) of 7% was molded. Figure 4 shows a schematic drawing of the stacking sequence on the PP/PP composite. A T_{mold} of 163°C was chosen.

Tensile tests at the longitudinal and transverse directions were carried out using a tensile test machine (Instron Universal Testing Machine 4466 Series, Instron Corp., MA) at room temperature. A test specimen for the tensile test was cut from a molded sample using a metallic mold. Figure 5 shows the specimen geometry. The test speed was 1 mm/min and the spun length was 40 mm.

An experimental value of the tensile modulus was compared with a theoretical value, which was calculated from the law of the mixture. This law takes the tensile modulus of the PP fiber and PP matrix into consideration, respectively. When the coefficients between the experimental and theoretical values in the longitudinal and transverse directions are α_0 and α_{90}, respectively, the tensile modulus in the longitudinal

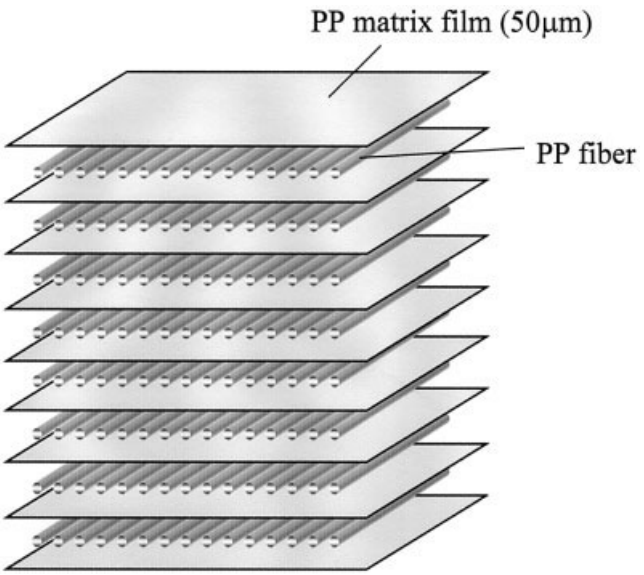

Figure 4 Schematic drawing of stacking sequence on PP/PP composite at *Vf* = 7 vol %.

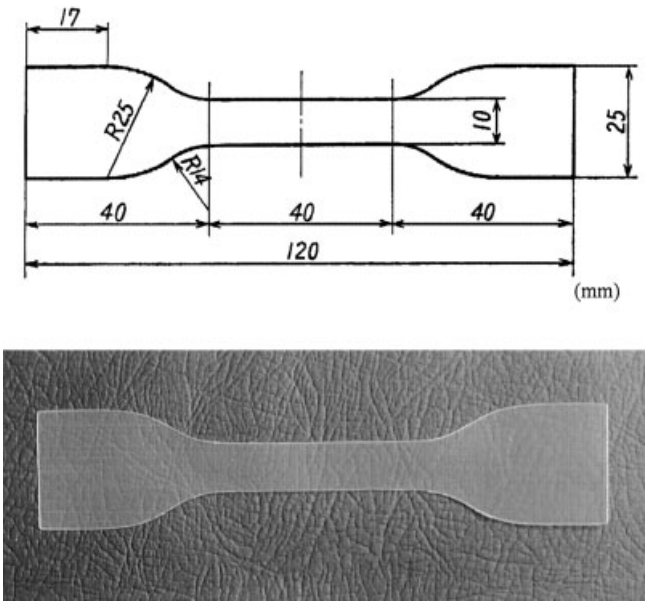

Figure 5 Specimen geometry for tensile test.

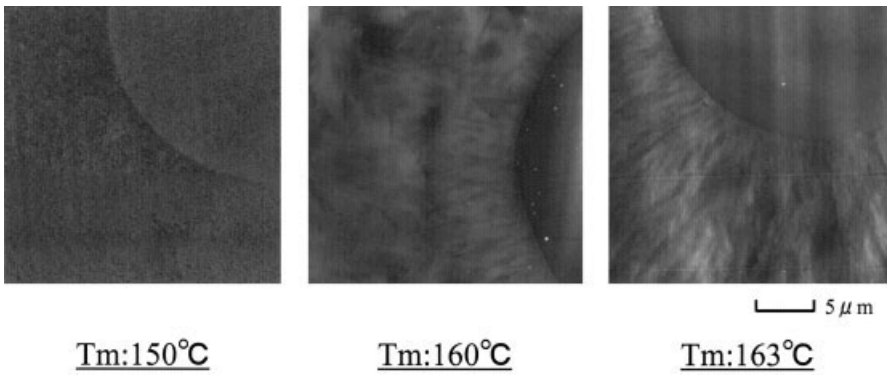

Figure 6 Atomic force micrographs of the cross sections of PP/PP composites molded at 150, 160, and 163°C.

(E_{0exp}) and transverse directions (E_{90exp}) can be expressed by

$$E_{0exp} = \alpha_0 \{Vf\, E_f + (1 - Vf)E_m\}$$

$$E_{90exp} = \alpha_{90} \frac{E_f E_m}{(1 - Vf)E_f + Vf\, E_m}$$

where E_f and E_m represent the tensile modulus of the PP fiber and the PP matrix, respectively, and Vf is the fiber volume fraction.

RESULTS AND DISCUSSION

Observations of transcrystalline layer near the fiber surface

Figure 6 shows AFM images of the cross sections of PP/PP composites molded at 150, 160, and 163°C. The matrix resin was melted at T_{mold} = 150°C. However, the fiber surface was believed not to be melted completely. Accordingly, a small transcrystalline layer was formed at the fiber surface for the composite molded at 150°C. On the other hand, the transcrystalline layers were well developed for the composite molded at 163°C. It was considered to be due to the melting of the fiber surface to some extent.

However, the fiber diameter before and after molding was hardly changed, which indicates that the fiber melted very slightly in these conditions. Table I shows the tensile test results of the original PP fiber heat-treated for 15 min using an oven (FC-62D; Toyo Seisakusho Co. Ltd., Chiba, Japan), which corresponds to the time for the actual molding conditions. The results indicate that the tensile properties of the heat-treated fiber were changed by the heat treatments. Notice that the tensile properties of each fiber after heat treatment at the temperatures of 150, 160, and 163°C were almost all the same. Furthermore, shown in Figure 7 are the data from X-ray photographs of the original fiber and the heat-treated fibers. The same crystallite orientation was observed. This means that the fiber melted very slightly in these conditions.

TABLE I
Tensile Properties of PP Fiber

	Tensile strength (MPa)	Tensile modulus (GPa)
Original	291.1	3.48
150°C	318.4	2.35
160°C	301.1	2.28
163°C	313.1	2.26

In composites comprising the PP matrix resin filled with Kevlar fiber or carbon fiber, the matrix resin must be held for a relatively long period (typically 6 h) near the crystallization temperature to form a transcrystalline layer.[21] These are in contrast to the case of PP/PP composites in this study where a transcrystalline layer can be formed during cooling at a rate similar to that applied for the ordinary molding processing (the rates of cooling are 42–46°C/min).

Next, we conducted TEM observations of the transcrystalline layers. Figure 8 shows a TEM photograph of the matrix near the fiber of the single-fiber PP/PP matrix composite molded at 150°C. The arrow indicates the longitudinal direction along the fiber.

Figure 9 shows a TEM photograph of the cross section across the matrix and the fiber for the same specimen as in Figure 8. The observed direction is perpendicular to that in Figure 8. The lamellae appeared bright under the RuO_4 staining conditions. The thickness of each bright region is about 10 nm, which agrees well with the lamella thickness conventionally reported.[22] In Figure 9, the lamellae are dispersed randomly irrespective of the existence of the fiber surface, and a spherulitic structure was observed. On the contrary, in Figure 8, the regular lamellae with their axes perpendicular to the fiber surface were observed in the regions very close to the fiber surface. This proves that even the composite molded at 150°C has some small transcrystalline layer from the TEM observation.

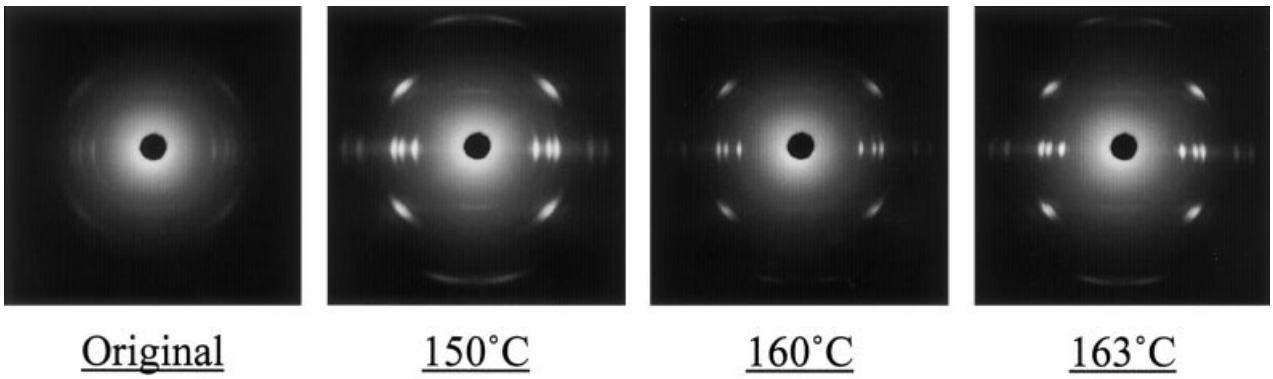

Figure 7 X-ray fiber photograph of the heat-treated homo-PP fiber.

Figure 10 shows a TEM photograph of the matrix along the fiber of the PP/PP composite molded at 163°C. The densely packed lamellae with their axes perpendicular to the fiber surface were clearly observed in the region within 300 nm from the fiber surface. This reveals that the PP chains are arranged parallel to the fiber direction. In the region apart from the fiber surface (>300 nm), the lamellae laying parallel to the fiber surface were also observed. These are considered to construct a cross-hatched structure, and the parallel lamellae would be daughters. Dean et al. carried out X-ray diffraction experiments on the PP transcrystalline layer formed on the surfaces of Kevlar fiber. It was reported that the transcrystalline layer was composed of cross-hatched lamellae with curved daughter lamellae.[23,24] Their observation would correspond to the whole layer because the diameter of the incident X-ray beam is at least several micrometers.

Figure 11 shows a TEM photograph of the cross section around the single fiber of the PP/PP composite molded at 163°C. The lamellae parallel to the fiber surface were observed in the region apart from the fiber surface (>300 nm), but no significant structure was observed near the fiber surface. The former is considered to correspond to the daughter lamellae as in Figure 10, and the latter indicates that the *c*-axes of the chains in the transcrystalline layer are parallel to the fiber direction, that is, so-called edge-on lamellae[25] were developed.

A schematic illustration of the lamellae orientation near the fiber surface, based on the above observations, is shown in Figure 12. In the transcrystalline layer close to the fiber surface, the lamellae lay perpendicular to the fiber direction. These are well developed with a high crystallinity. In the region a little away from the fiber surface, a cross-hatched structure, composed of the parent lamellae (whose *c*-axes are parallel to the fiber surface) and the daughter lamellae (whose *c*-axes are perpendicular both to the fiber surface and the parent lamellae), was observed. It is an

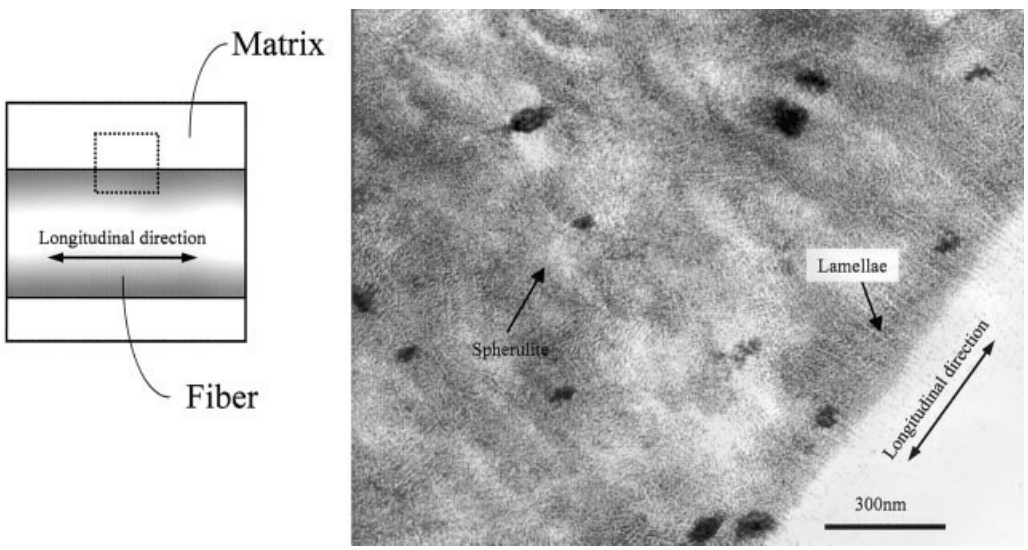

Figure 8 Transmission electron micrograph of the matrix near the fiber of the single-fiber PP/PP matrix composite molded at 150°C. The arrow indicates the longitudinal direction along the fiber.

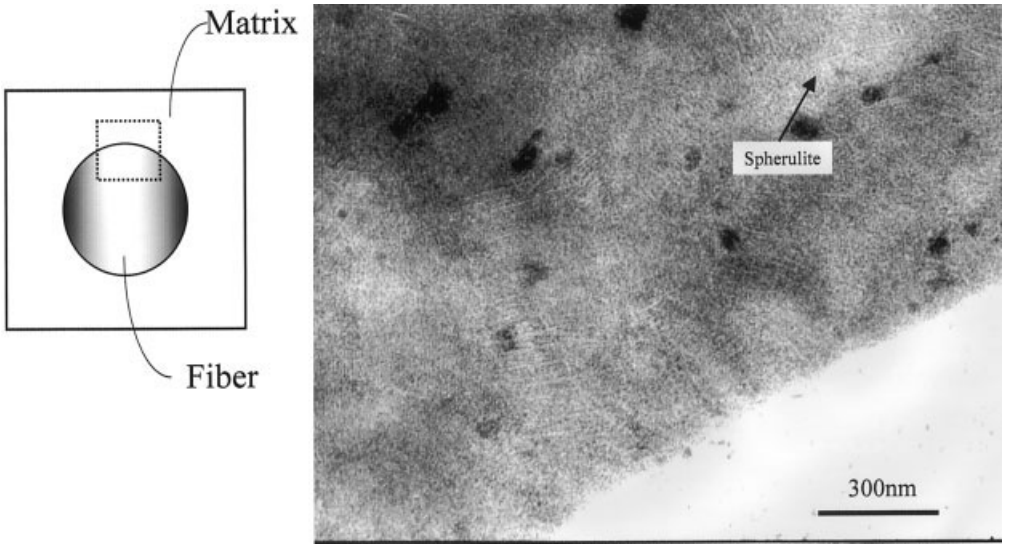

Figure 9 Transmission electron micrograph of the cross section across the matrix and the fiber for the same specimen as in

interesting phenomenon that, in spite of the use of poorly oriented fibers, the *c*-axes in the transcrystalline layer were well oriented along the fiber. Sadovsky and Wagner evaluated the mechanical properties of the PP transcrystalline layer formed on the surface of the carbon fiber by using Vickers and Knoop microindentation and observed a strongly anisotropic Young's modulus.[26]

Tensile behavior of transcrystalline layer

Figure 13 shows polarized optical micrographs of the cross section around the single fiber of the PP/PP composites before and after the tensile tests. In the sample molded at 150°C, which has less of a transcrystalline layer, void formation was observed at the interface between the fiber and the matrix resin after the tensile test. The same phenomena were also observed for the sample molded at 160°C. In the sample molded at 163°C, where a well-developed transcrystalline layer could be observed, the interface was not destroyed and the transcrystalline layer was stretched along the tensile direction. This shows that the adhesion at the interface was much improved for the sample molded at 163°C. The good adhesion would be due to the presence of a well-developed transcrystalline layer, in which the dense lamellae were grown from the fiber surface. Hata et al.[27] investigated the

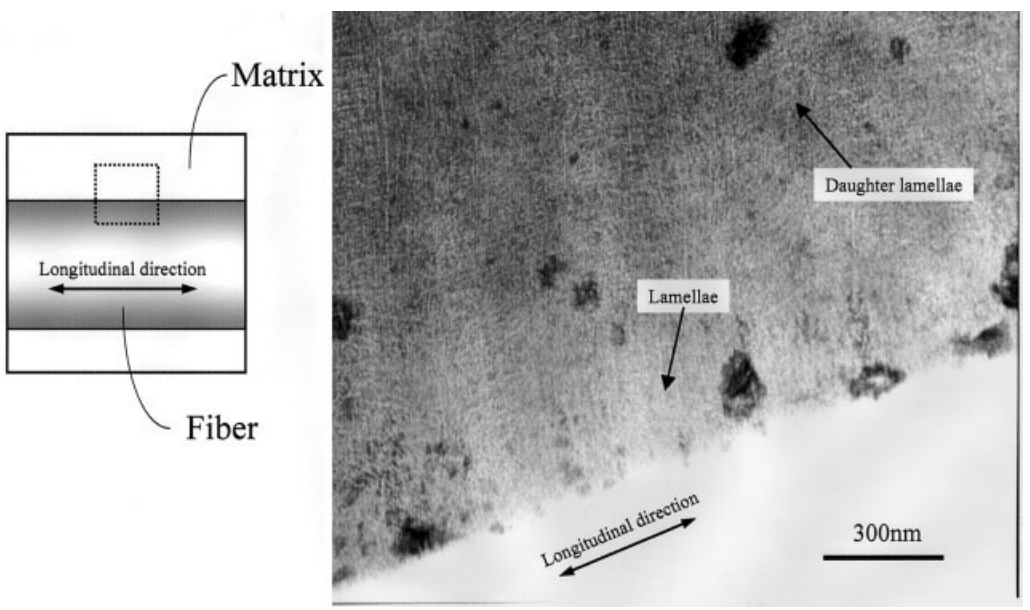

Figure 10 Transmission electron micrograph of the matrix along the fiber of the PP/PP composite molded at 163°C.

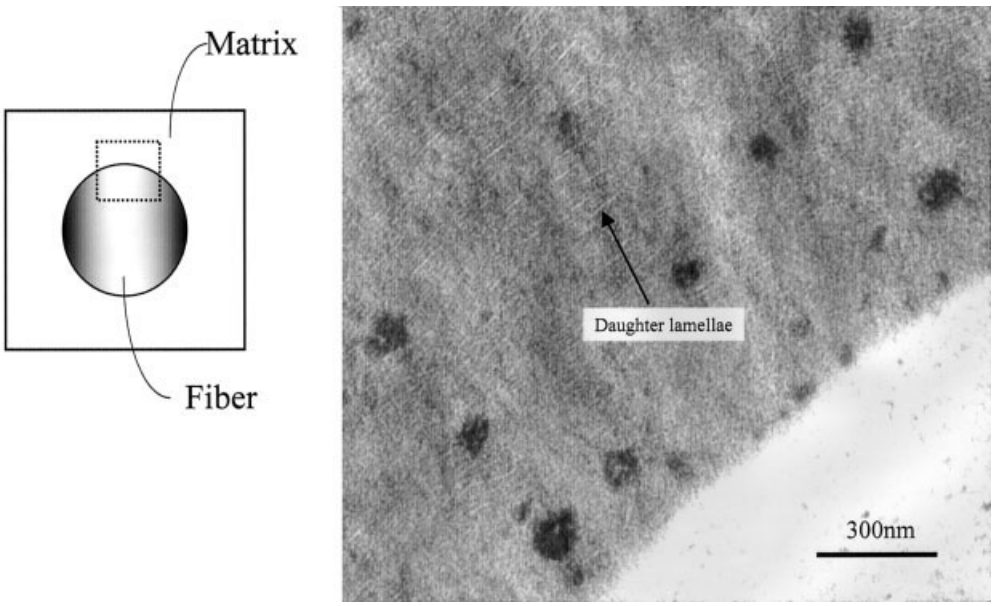

Figure 11 Transmission electron micrograph of the cross section around the single fiber of the PP/PP composite molded at 163°C.

macroscopic mechanical properties of the transcrystalline layers of PP with about a 300-μm thickness. The transcrystalline film could be stretched up to 800%. This elongation at break is very high compared with that for the conventional PP film with spherulites.[28] Thus, a highly stretched matrix resin in Figure 13 is considered to be the specific property of the transcrystalline layer.

Figure 14 shows SEM photographs of the fibers after the tensile tests. In these cases, the PP/PP composites were stretched to the break in the transverse direction. Even after the tensile tests, the surface of the fiber was as smooth as that of the original fiber in the sample molded at 150°C. This indicates that interfacial debonding occurred. On the other hand, the adhesion residue of the matrix resin was found on the fiber surface in the sample molded at 163°C. This demonstrates that the transcrystalline layers improve the tensile properties of the PP/PP composites in the direction perpendicular to the fiber.

Longitudinal and transverse properties

To confirm the behavior of a PP/PP composite produced at the temperature of 163°C, the tensile test was carried out. Table II shows the tensile strength, tensile modulus, and coefficient, which was calculated from the law of mixture, in the 0° and 90° directions. From this result, in the longitudinal direction, the coefficient α_0 was 0.79, which was lower than 1. On the other

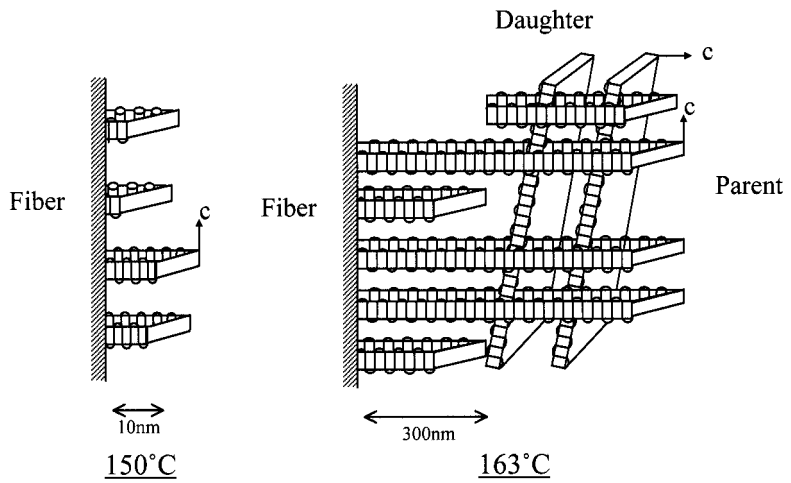

Figure 12 Schematic illustration of the lamellae orientation near the fiber surface.

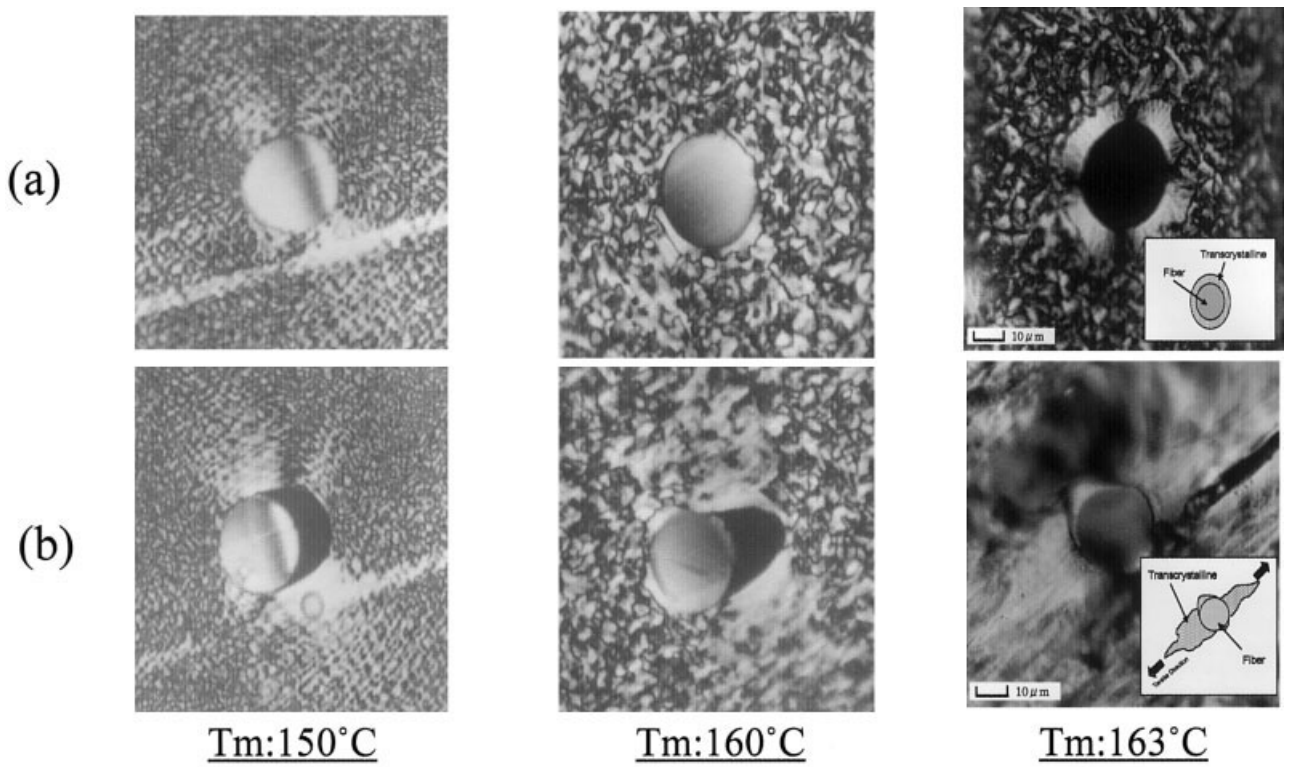

Figure 13 Polarized optical micrographs of the cross section around the single fiber of the PP/PP composites molded at different T_{molds}, before and after the tensile tests.

hand, in the transverse direction, the coefficient α_{90} was 1.03, which was near about 1. This means that the transcrystalline layers improve the tensile properties of the PP/PP composites in the direction perpendicular to the fiber. Furthermore, these results agreed with the results reported by Teishev and Marom.[16]

CONCLUSIONS

The PP/PP model composites were manufactured by utilizing the melting point difference between the homo-PP fiber and the propylene–ethylene random copolymer matrix, and the interfacial morphologies and the mechanical property were investigated. A cross-hatched structure was observed in the region a little away from the fiber. However, transcrystalline layers were developed in the vicinity of the fiber (>300 nm), where extremely dense lamellae were grown in the direction perpendicular to the fiber surface. It was found that the *c*-axes of the PP crystal are oriented in the longitudinal direction of the fiber in the transcrystalline layer. These transcrystalline layers could be highly stretched under the tensile stress without debonding at the fiber/matrix interface. This is considered to be attributed to the high adhesion strength of the composite in the direction perpendicular to the fiber axis in all-PP/PP composites. The transcrystalline layers will be expected to be more developed from

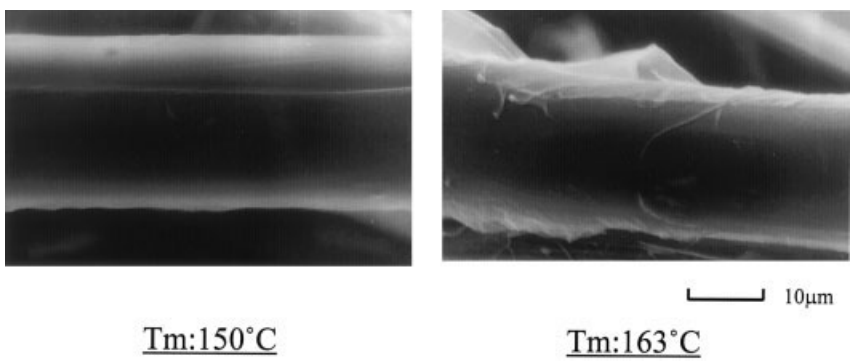

Figure 14 SEM photographs of the PP/PP composite after tensile test.

TABLE II
Tensile Properties of PP/PP Composites

	Tensile strength (MPa)	Tensile modulus (GPa)	Coefficient α
0°	42.45	0.498	0.79
90°	13.75	0.419	1.03

the more highly oriented PP fiber. The effect of the fiber structure on the morphologies and the properties will be reported in the future.

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