Effect of Fiber Molecular Weight on the Interfacial Morphology of iPP Fiber/Matrix Single Polymer Composites

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ABSTRACT: Through introducing the iPP fibers having different molecular weights into their supercooled or molten matrices, fiber/matrix single polymer composites of iPP have been prepared, and the obtained interfacial morphologies were studied by means of polarized light microscopy. It was found that the interfacial supramolecular structure was affected by not only the introduction temperature but also the molecular weight of the iPP fibers. At low fiber introduction temperatures, solid iPP fiber induces the growth of α-iPP crystals and results in the formation of pure α-iPP transcrystallization layer in the vicinity of iPP fiber regardless of its molecular weight. At high fiber introduction temperatures, completely molten iPP fiber, with either high or low molecular weight, loses its nucleation ability toward iPP matrix. The interfacial structure induced by incomplete molten iPP fibers is different from fiber to fiber. This has been explained in terms of different relaxation behavior of the fiber, which has been further confirmed by the annealing experiment of the high molecular weight fiber/matrix system at the fiber introduction temperature.

Introduction

Crystallization of isotactic polypropylene (iPP) from the melt has been widely studied for many decades. It is well-known that iPP is a polymorphic material. Except for the reported three crystalline modifications including monoclinic (α), trigonal (*β*), and triclinic (*γ*) forms,[1] also a smectic mesophase has been reported depending on different sample preparation.[2−5] Experimental results indicated that the α-modification is the thermodynamically most stable one, while the *β*-form is thermodynamically metastable and difficult to obtain under normal processing conditions. However, because of its different performance, including lower crystal density, melting temperature, and fusion enthalpy, markedly improved impact strength, and toughness,[6−8] special techniques were developed for generating *β*-iPP.

To prepare samples of *β*-iPP, selective *β*-nucleants are commonly used.[9] Moreover, crystallization of commercial iPP in temperature gradient[10−12] and in sheared[13−15] or strained melt[16] encourages the development of the *β*-phase. Varga et al.[15] reported a simple way for creating shear stress by fiber pulling, which was attested to be efficient in producing samples rich in *β*-modification. Through systematic studies, they found that shearing the melt by fiber pulling yields primary α-row nuclei along the fiber. On the surface of these α-row nuclei a α to *β* growth transition takes place during crystal growth, which leads to the formation of a layer enriched in the *β*-phase along the pulled fiber. In this process, a higher growth rate of the *β*-phase (G_β) than that of α-phase (G_α) is the kinetic requirement for the α*β*-growth transition.[9,15−19] It should be pointed out that the kinetic requirement is only a sufficient condition to ensure the growth of the *β*-crystals. Otherwise, the fast growing α-iPP crystals will embed the generated *β*-nuclei. The understanding of why the α*β*-secondary nucleation occurs on the surface of the in situ formed α-row nuclei remains, however, a central problem. In other words, the mechanism of the α*β*-bifurcation is still not quite clear so far.

In our previous studies, the interfacial structure of the iPP fiber/matrix single polymer composites as a function of the fiber introduction temperature as well as the subsequent crystallization temperature of the matrix was studied by means of optical and electron microscopies.[20−24] It was found that partial melting of the iPP fiber is in favor of the formation of *β*-iPP crystals. In the present study, the influence of fiber molecular weight on the induced interfacial structure was studied, and the results obtained here provide some further clues on the mechanism of the formation of *β*-iPP crystals. The purpose of this paper is to present the detailed experimental results about the effects of fiber molecular weight on the fiber induced interfacial structure of the iPP fiber/matrix single polymer composites. On the basis of the observed polymorphic behaviors, the formation mechanism of the *β*-iPP crystals is discussed.

Experimental Section

The matrix polymer used in this work was commercial grade isotactic polypropylene (iPP), GB-2401, with melt flow index of 2.5 g/10 min, M_w of ~4.4×10^5, and melting temperature of 170 °C, produced by Yanshan Petroleum and Chemical Corp., China. The granular iPP materials were used without any further treatment. Thin iPP films, 40−50 μm in thickness, were prepared by compression-molding the iPP granules at 200 °C.

To elucidate the influence of molecular weight of the iPP fiber on the interfacial structure of the single polymer composites, iPP fibers with different molecular weight (designated as F1−F5) were produced by a homemade melt-spinning device. The spinning temperature was 200−240 °C. The resulting iPP fibers were then subjected to a cold-draw procedure at 110 °C with a draw ratio of 4. To remove the sizing agents on the fibers surface, the fibers were treated for 4 h with refluxing acetone and then dried in a vacuum oven at 40 °C for 24 h. The characteristics of the used fibers are reported in Table 1.

The iPP fiber/matrix homogeneity composites were produced by a procedure as shown in Figure 1. The iPP matrix thin film was first heated to 200 °C for 10 min to erase possible effects of thermal history of the sample on the subsequent crystallization and then moved to a preheated hot plate, where the iPP matrix was kept in the molten or supercooled molten state at the moment of fiber

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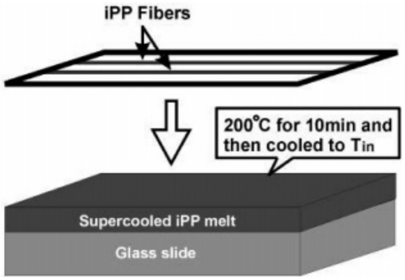

Figure 1. A sketch shows the sample preparation procedure.

Table 1. Characteristics of the Used iPP Fibers

samples	MI (g/10 min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_m (°C)	birefringence
F1	15	42 700	1.94×10^5	4.54	168.2	17.7
F2	25	46 400	1.85×10^5	3.98	166.3	18.7
F3	35	39 000	1.70×10^5	4.35	165.7	17.9
F4	45	36 000	1.20×10^5	3.33	165.1	20.5
F5	55	34 800	1.15×10^5	3.32	163.7	20.7

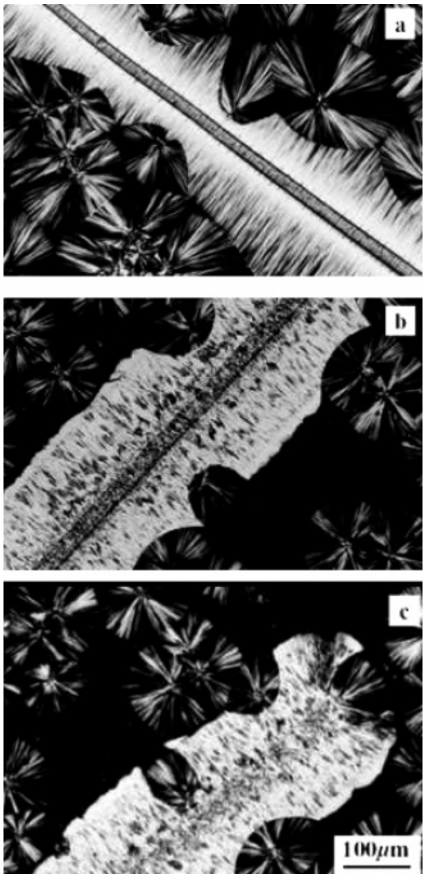

Figure 2. Polarized optical micrographs of iPP fiber/matrix homogeneity composites, which were prepared by introducing the fiber F1 into its single polymer melts at (a) 167, (b) 178, and (c) 185 °C and then cooled to 135 °C for isothermal crystallization.

introduction. As the iPP molten or supercooled molten thin layer reached an equilibrium at the desired temperature, homogeneous iPP fibers tightly fixed on a metal frame (as shown in Figure 1, upper part) were introduced into the iPP matrix at different temperatures. After introduction of the fibers, the prepared iPP fiber/matrix composites were subsequently moved quickly to another hot plate set at 135 °C for isothermal crystallization.

For optical microscopy observation, an Olympus BH-2 optical microscope was used in this study. All optical micrographs presented in this paper were taken under cross-polarized light.

Results

Figure 2 shows the optical micrographs of iPP fiber/matrix homogeneity composites, which were prepared by introducing high molecular weight fiber F1 into supercooled or molten iPP matrix at different temperatures and then isothermal crystallized at 135 °C for 2 h. It can be clearly seen that by introducing the iPP fiber F1 into its homogeneity matrix at 167 °C (Figure 2a) the iPP fiber is not molten and displays distinct boundary in the single polymer composite. Nevertheless, the solid iPP fiber shows strong nucleation ability toward its homogeneity matrix and results in the formation of transcrystallization zone in the matrix. Melting test demonstrates that the transcrystalline layer surrounding the iPP fiber is in its α-form. Moreover, birefringence measurements indicate that the iPP with both transcrystalline structure and spherulitic structure possesses a negative optical character. When the introduction temperature is elevated to 178 °C (ca. 10 °C above the melting temperature of the fiber), as shown in Figure 2b, even though the outline of the iPP fiber can still be clearly identified, the iPP fiber is evidently thicker than that shown in Figure 2a. This indicates the occurrence of swelling of the iPP fiber caused by melting and chain relaxation at present temperature. At the same time, the supermolecular structure of the induced interfacial layer is quite different from that shown in Figure 2a. It is attested that the interfacial layer is now composed of fully crystalline β-iPP with very strong birefringence. When the fiber introduction temperature is set at 185 °C (see Figure 2c), the outline of the fiber is no more recognizable, indicating a more severe melting of iPP fiber at 185 °C. Nevertheless, during the recrystallization process, the molten iPP fiber crystallizes in its β-form and further induces the crystallization of iPP matrix resulting in the formation of β-iPP transcrystalline zone with strong birefrigence. This unambiguously demonstrates the existence of "memory effect", or in other words, some local order of the molecular chains previously included in a crystal lattice of the fiber has been preserved and transforms into crystalline self-nuclei during the cooling process. It is worth noting that there do exist some local regions where the molten iPP fiber recrystallizes in α-form spherulitic structure (see upper-right corner of Figure 2c). This may reflect a complete melting and chain relaxation of iPP fiber. The different melting behavior of the iPP fibers may be associated with different local qualities of the fibers. Anyway, the above results indicate that melting or partial melting of the iPP fiber F1 is in favor of the formation of β-iPP crystals. This is consistent with the results reported in ref 21.

Figure 3 presents the interfacial structures of the F2/matrix iPP homogeneity systems prepared at various temperatures. By introducing the F2 fiber into its supercooled homogeneity matrix at 166 °C (close to its melting point), as shown in Figure 3a, the iPP fiber is not molten on the whole (most likely due to the short time used for fiber introduction). As in the case of F1/matrix system, the interfacial layer is composed mainly of α-transcrystals, even though some fanlike β-crystals dispersed in the α-transcrystalline layer, as indicated by a white arrow, are occasionally observed. If the introduction temperature is elevated to 168 °C, 2 deg over its melting point, the iPP fiber loses its original morphology and cannot be distinguished from the induced column layer (see Figure 3b). Now the interfacial layer is composed of both α- and β-crystals. The fan-shaped β-crystals, as indicated by white arrows, grow obviouly faster than the neighbored α-crystals and stop the growth of its neighbor α-crystals. When fiber introduction temperature is set at 172 °C (see Figure 3c), the iPP fiber becomes very thin and shows weaker birefringence than the surrounded column layer.

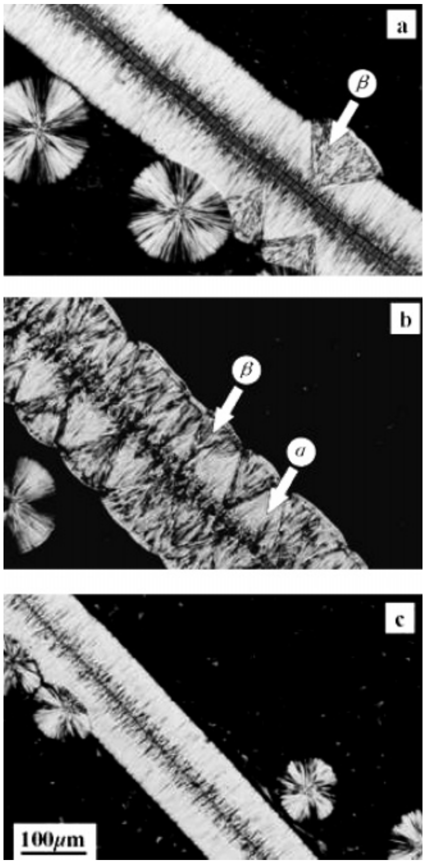

Figure 3. Polarized optical micrographs show the interfacial structures of iPP fiber/matrix homogeneity composites prepared by introducing the fiber F2 into its single polymer melts at (a) 166, (b) 168, and (c) 172 °C and then crystallized at 135 °C isothermally.

This indicates a more severe melting of the iPP fiber with respect to that in Figure 3a,b. Now, the interfacial layer is composed of pure α-crystals. This clearly demonstrates that the melting extent of the fiber plays a very important role in producing *β*-iPP crystals. It should be pointed out that a suitable melting state of iPP fiber for inducing a fully *β*-transcrystalline layer has not been found for the F2/matrix system in the present work.

For the F3/matrix system, the induced crystallization behavior is even different. Figure 4 depicts the interfacial morphologies of F3/matrix composites, which were prepared by introducing the F3 iPP fiber into its supercooled or molten matrix at different temperatures. When the fiber introduction temperature is set at 162 °C, 3 deg lower than its melting temperature, the iPP fiber is kept in the solid state and induces the crystallization of iPP matrix in its α-modification. At its melting temperature, i.e., 165 °C, as shown in Figure 4b, the molten fiber is predominantly surrounded by the α-iPP transcrystals even though the occurrence of partial melting of the iPP fiber as judged from its morphology and thickness. There are a few of fan-shaped *β*-crystals appeared on one side of the iPP fiber, as is indicated by a white arrow labeled with a "*β*". When the fiber introduction temperature is further elevated to 170 °C, the interfacial morphology is shown in Figure 4c,d. It is clear that the iPP fiber melts more completely than that in Figure 4b, and in some place the iPP fiber is even molten out (see Figure 4d). Nevertheless, the induced interfacial layer is still mainly of α-crystals. Only one fan-shaped *β*-crystals has been seen in the lower-right coner of Figure 4c. This is somewhat different from the fibers with higher molecular weight where the melting or partial melting of iPP fiber is in favor of triggering the growth of *β*-crystals.

If the iPP fibers with even lower molecular weight (e.g., F4 and F5) are used, interfacial morphologies with *β*-iPP crystals are hardly observed at any conditions. As shown in Figure 5, the iPP fibers are predominately surrounded by α-iPP crystals at any fiber introduction temperatures.

From the above observations, it is clear that solid iPP fiber induces the growth of pure α-iPP crystals and results in the formation of α-form transcrystallization layer in the vicinity of the iPP fibers. This is associated with the strong surface-induced heterogeneous nucleation and subsequent spatial confined crystal growth. Considering that all of the used iPP fibers have the same α-crystalline modification, homoepitaxial crystallization of iPP matrix on its homogeneity fiber surfaces in the α-form is expected. Completely molten iPP fibers, with either high or low molecular weight, show no nucleation ability toward iPP matrix material at all. With incomplete or partial melting of the iPP fiber, the resultant interfacial structures are quite different from fiber to fiber. Since the iPP matrix material and the sample preparation procedures are all the same for those systems, the different interfacial structures should be resulted from the inherent nature of the used fibers. It is demonstrated that all of the used iPP fibers possess the same α-crystalline modification with similar very high crystallinity (see Figure 6). AFM and SEM characterizations also revealed very smooth surfaces of the used fibers. One can further see from Table 1 that the used fibers have similar orientation as estimated by the birefringence measurement. The only differences between the fibers are the molecular weight and the relating melting index. Taken all those into account, the different interfacial structures should originate from the different molecular weight of the fibers. According to these results, the formation mechanism of the *β*-iPP transcrystals can be discussed as follows.

Discussion

As mentioned in the Introduction, the occurrence of the α*β*-secondary nucleation on the surface of the in situ formed α row nuclei in the fiber pulling experiments rather than growth of α-iPP crystals is a hard understanding problem. In our homogeneity composite systems,[23] it was occasionally observed that the iPP fibers could be broken off by selective melting at temperatures above the melting point of *β*-iPP but below that of α-iPP (see parts a and b of Figure 7). Since the used iPP fibers are originally in their α-form as confirmed by the X-ray diffraction experiments (Figure 6), the break of the iPP fibers unambiguously implies that some local parts of the original α-iPP fibers have transformed into *β*-form through melt recrystallization. This may suggest that the local order and environment of the macromolecular chains just before nucleation taking place are important for *β*-nucleation of iPP. Moreover, the facts obtained in present work—(i) solid or completely molten iPP fibers show similar induced crystallization behavior of the iPP matrix regardless of their molecular weight and (ii) incompletely molten iPP fibers generate different interfacial structure of the composites—indicate that the oriented molecular chains survived during partial melting of the fiber play a very important role in the subsequent recrystallization of the polymer melts.

It is well-known that the melting behavior of macromolecules is quite different from that of the low molecular weight compounds. Because of the long chain character, the molecular chains should experience a "recoiling" or "relaxation" process during melting. The recoiling process may take quite long time depending on melting temperature and the molecular weight. Through studying the effect of melting history on the recrys-

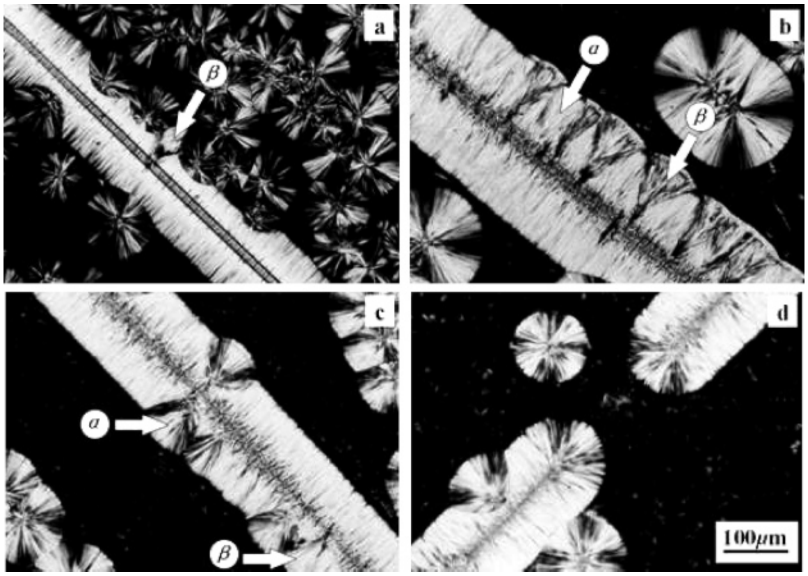

Figure 4. Polarized optical micrographs of iPP fiber/matrix homogeneity composites, which were prepared by introducing the fiber F3 into its single polymer melts at (a) 162, (b) 165, (c) 170, and (d) 172 °C and then cooled to 135 °C for isothermal crystallization.

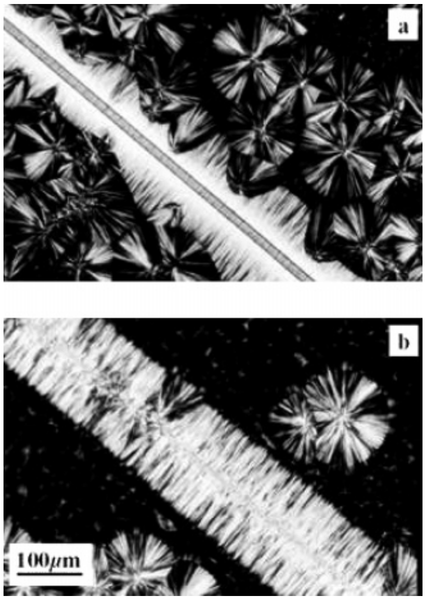

Figure 5. Interfacial structures of iPP fiber/matrix homogeneity composites prepared by introducing the fiber F5 into its single polymer melts at (a) 157 and (b) 165 °C and then cooled to 135 °C for isothermal crystallization.

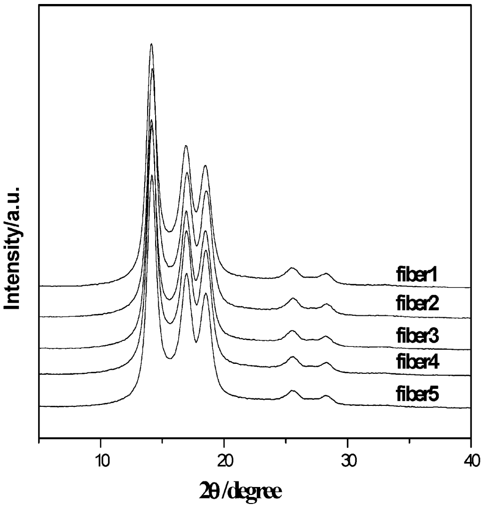

Figure 6. Wide-angle X-ray diffractions of the used iPP fibers.

tallization in detail by optical microscopy, Varga et al.[18] concluded that some local order of the molecular chains previously included in a crystal lattice can be preserved as “prenuclei” or sometime referred to “nucleation precursors”, which are prone to transform into crystalline self-nuclei during recooling and initiate the recrystallization of the polymer melt. This phenomenon is closely related to the sheared polymer melts. Extensive studies on the relaxation and crystallization of sheared polymer melts indicated that metastable oriented structures in sheared polymer melts might resist relaxation upon cessation of shearing and could act as “prenuclei” from which development of fold chain lamellae with the chain axis highly oriented along the shear direction taken place.[24−28] It is worth noting that the “prenuclei” cannot survive forever. They can remain active only for a certain period of time after cessation of shear flow at the temperatures above its melting point. Azzurri and Alfonso have studied the lifetime of shear-induced crystal nucleation precursors in detail.[29,30] They reported that the lifetime of the nucleation precursors is a very sensitive function of both relaxation temperature and molecular weight. Now turn back to our systems, since the fibers are highly oriented, the melting process of the fibers are actually similar to the sheared polymer melts. Considering that the fiber introduction was performed in a quite short time and at temperatures close to or slightly above the nominal melting point of the fibers, a complete recoiling of the molten iPP fiber could hardly be attained before recooling of the samples. In other word, the partial or incomplete molten iPP fiber may exist actually in the form of amorphous domains with oriented or stretched macromolecular segments and/or chains as in the sheared polymer melts. These oriented molecular segments or chains, in turn, serve as nucleation precursors and initiate the crystallization during cooling process. In this case, the formation of the β-iPP crystals is not unexpected on the basis that shear stress is attested to be in favor of the formation of β-crystals as observed in the fiber-pulling experiments.

From the above discussion, it is concluded that the formation of β-crystals is associated with the oriented or stretched macromolecular chains survived during incomplete melting of the highly oriented iPP fiber. Taken this into account, the

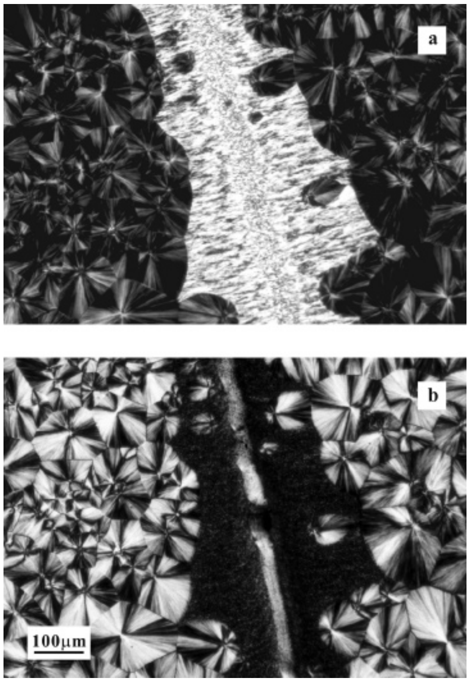

Figure 7. Polarized optical micrographs of an iPP fiber/matrix composite crystallized isothermally at 116 °C for 30 min. The temperature of fiber introduction was 173 °C. (a) As-prepared sample and (b) after melted at 158 °C for 5 min.

interfacial morphological difference of the prepared iPP single polymer composites with iPP fiber being partially molten should be associated with the different relaxation behavior of the used fibers. Indeed, while Alfonso et al.[29,30] reported that relaxation time is proportional to $M^{1.5}$, through study the shear-induced crystallization of iPP with different molecular weight and distribution, Hsiao et al.[28] found that only the molecules having chain length (molecular weight) above a critical value (critical orientation molecular weight M^*) can form oriented and stable nuclei. This clearly indicates that the lower is the molecular weight the faster relaxes the shear-induced molecular orientation. For our case, even though different relaxation behavior of the fibers with different molecular weight is expected, the appearance of transcrystallization layers around the partially molten iPP fibers indicates that abundant nucleation precursors have survived in all of the homogeneity systems during sample preparation. However, varying in the relaxation extent, the surviving nucleation precursors can create different types of nuclei, i.e., the β-iPP nuclei for the high molecular weight system and α-iPP nuclei in rich for the lower molecular weight system. Taking the ease relaxation of the lower molecular weight fibers into account, it may be concluded that the relaxation extent of the originally highly oriented iPP chains plays an important role in generating its β-form crystals. If this hypothesis holds true, a sufficient relaxation of iPP fiber F1 in the F1/matrix system at fiber introduction temperature will reduce its ability in generating β-iPP crystals. Figure 8 shows the optical micrographs of the F1/matrix iPP single polymer composites prepared by introducing the iPP fiber into its single polymer melts at 175 °C, kept at introduction temperature for different time, and subsequently cooled directly to 135 °C for isothermal crystallization. From Figure 8a, it can be clearly seen that, after 5 min annealing at 175 °C, the iPP fiber is more obviously molten as compared with Figure 2b. It induces, however, still the crystallization of iPP melt in its β-form. Increasing the annealing time, e.g. 10 min, not only the total nucleation ability but also the ability in generating β-iPP crystals have decreased obviously (see Figure 8b). By annealing the sample at the fiber introduction temperature for 15 min (Figure 8c), the density of the nuclei formed along the molten fiber becomes sparse. Individual nuclei along the iPP fiber are now recognizable. This implies that less and less nucleation precursors remain active as the elapsing of the annealing time. Moreover, the appearance of fully α-iPP transcrystals indicates undoubtedly that the more relaxed molten iPP fiber has lost its ability in triggering the β-crystallization of iPP. In conclusion, relaxation extent of the originally highly oriented iPP chains is an important parameter for controlling the formation of β-iPP transcrystalline layers. The exact origin of β-nucleation is not quite clear here. But considering that isochiral chains are involved in the β-iPP crystals, one may suggest that microdomains with isochiral chains are probably produced through chains rotation in the viscous melt during relaxation. These isochiral chain aggregates transform into β-iPP nuclei during cooling process and initiate the growth of β-iPP crystals.

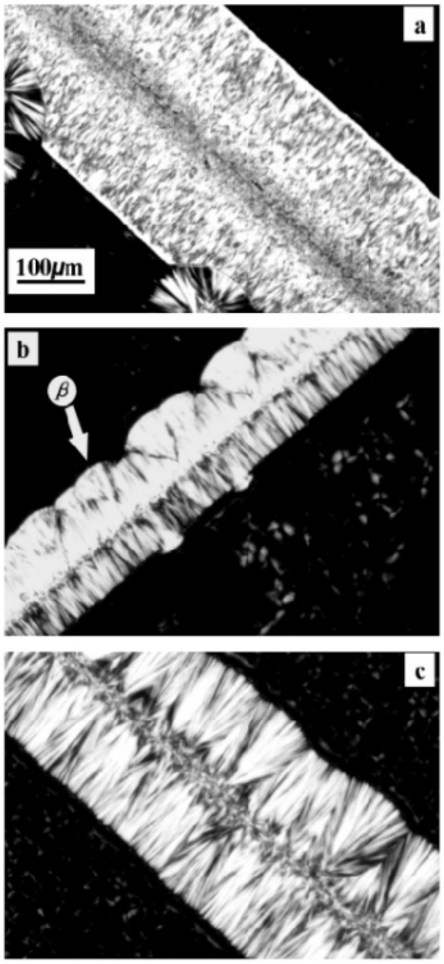

Figure 8. Polarized optical micrographs of iPP fiber/matrix homogeneity composites, which were prepared by introducing the fiber F1 into its single polymer melts at 175 °C, kept at that temperature for (a) 5, (b) 10, and (c) 15 min and then cooled to 135 °C for isothermal crystallization.

It is worth noting that, except for the direct influence of molecular weight on the relaxation process of a polymer, the structure nature of the fiber related on molecular weight may also exert some effects on its relaxation. For example, structural characterzation of iPP fibers demonstrated the existence of fibrillar structures or shish crystals.[31−33] During fiber spinning, a different quantity of the fibrils may be developed depending on the molecular weight of the used material. Ran et al.[31] even postulate that the contituents of the mesophase in iPP fibers include oriented bundles of helical chains with random helical hands or even without helical structure. All of these may also show great influence on the relaxation process of the fiber. Therefore, a detailed study on the induced crystallization behavior of fibers with different cold draw ratio or even without cold drawing is now under way.

Conclusions

The interfacial structures of iPP fiber/matrix single polymer composites with iPP fibers having different molecular weights were studied in detail by optical microscopy. The results show that the solid iPP fiber induces the growth of pure α-iPP crystals and results in the formation of α-form transcrystallization layer in the vicinity of iPP fiber due to the spatial confined crystal growth. Completely molten iPP fibers, with either high or low molecular weight, lose their nucleation ability toward iPP matrix material. The interfacial structure induced by incomplete molten iPP fibers is, however, different from fiber to fiber. For high molecular weight fiber, e.g. F1, the incomplete melting induces the formation of fully β-iPP transcrystalline layers. Decreasing in fiber molecular weight, e.g., when fiber F2 and F3 are used, a mixture of α- and β-crystals in the transcrystallization layers is observed at temperature slightly above their melting points, while fully α-transcrystals are observed interfacial morphology at even higher temperature. With further decrease in molecular weight, mainly α-transcrystals are induced regardless of the fiber introduction temperature. These results indicate that the relaxation extent of the originally highly oriented iPP chains is a key factor for controlling the formation of β-iPP transcrystalline layers. This is further confirmed by the annealing experiment of the high molecular weight fiber/matrix system at fiber introduction temperature.

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References and Notes

(1) Lotz, B.; Wittmann, J. C.; Lovinger, A. J. *Polymer* **1996**, *37*, 4979.
(2) Natta, G.; Peraldo, M.; Corradini, P. *Rend. Accad. Naz. Lincei* **1959**, *26*, 14.
(3) Corradini, P.; Petraccone, V.; De Rosa, C.; Guerra, G. *Macromolecules* **1986**, *19*, 2699.
(4) Liangbin Li, L. B.; de Jeu, W. H. *Macromolecules* **2003**, *36*, 4862.
(5) Poncin-Epaillard, F.; Brosse, J. C.; Falher, T. *Macromolecules* **1997**, *30*, 4415.
(6) Varga, J. *J. Macromol. Sci., Part B: Phys.* **2002**, *41*, 1121.
(7) Karger-Kocsis, J.; Moos, E.; Mudra, I.; Varga, J. *J. Macromol. Sci., Part B: Phys.* **1999**, *38*, 645.
(8) Karger-Kocsis, J. *Polym. Eng. Sci.* **1996**, *36*, 203.
(9) Varga, J. Crystallization, Melting and Supermolecular Structure of Isotactic Polypropylene. In *Polypropylene*: *Structure, Blends and Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; Vol. 1, pp 56−115.
(10) Crissman, J. M. *J. Polym. Sci.* **1969**, *7* (A2), 389.
(11) Fujiwara, Y. *Colloid Polym. Sci.* **1975**, *253*, 273.
(12) Lovinger, A. J.; Chua, J. O.; Gryte, C. C. *J. Polym. Sci., Part B: Polym. Phys.* **1977**, *15*, 641.
(13) Leugering, H. J.; Kirsch, G. *Angew. Makromol. Chem.* **1973**, *33*, 17.
(14) Devaux, E.; Chabert, B. *Polym. Commun.* **1991**, *32*, 464.
(15) Varga, J.; Karger-Kocsis, J. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 657.
(16) Varga, J.; Ehrenstein, G. W. *Polymer* **1996**, *37*, 5959.
(17) Shi, G.; Zhang, X.; Qiu, Z. *Makromol. Chem.* **1992**, *193*, 583.
(18) Varga, J. *J. Mater. Sci.* **1992**, *27*, 2557.
(19) Varga, J.; Fujiwara, Y.; Ille, A. *Periodica Polytech. Chem. Eng.* **1990**, *34*, 255.
(20) Li, H.; Liu, J.; Wang, D.; Yan, S. *Colloid Polym. Sci.* **2003**, *281*, 973.
(21) Li, H.; Jiang, S.; Wang, J.; Wang, D. J.; Yan, S. *Macromolecules* **2003**, *36*, 2802.
(22) Li, H.; Zhang, X.; Kuang, X.; Wang, D J.; Li, L.; Yan, S. *Macromolecules* **2004**, *37*, 2847.
(23) Li, H.; Zhang, X.; Duan, Y.; Wang, D.; Li, L.; Yan, S. *Polymer* **2004**, *45*, 8059.
(24) Eder, G.; Janeschitz-Kriegl, H.; Liedauer, S. *Prog. Polym. Sci.* **1990**, *15*, 629.
(25) Isayev, A. I.; Chan, T. W.; Shimojo, K.; Gmerek, M. *J. Appl. Polym. Sci.* **1995**, *55*, 807.
(26) Somani, R. H.; Hsiao, B. S.; Nogales, A.; Srinivas, S.; Tsou, A. H.; Sics, I.; Baltà−Calleja, F. J.; Ezquerra, T. A. *Macromolecules* **2000**, *33*, 9385.
(27) Somani, R. H.; Hsiao, B. S.; Nogales, A.; Fruitwala, H.; Srinivas, S.; Tsou, A. H. *Macromolecules* **2001**, *34*, 5902.
(28) Nogales, A.; Hsiao, B. S.; Somani, R. H.; Srinivas, S.; Tsou, A. H.; Balta-Calleja, F. J.; Ezquerra, T. A. *Polymer* **2001**, *42*, 5247.
(29) Alfonso, G. C.; Scardigli, P. *Macromol. Symp.* **1997**, *118*, 323.
(30) Azzurri, F.; Alfonso, G. C. *Macromolecules* **2005**, *38*, 1723.
(31) Ran, S. F.; Zong, X. H.; Fang, D. F.; Hsiao, B. S.; Chu, B. *Macromolecules* **2001**, *34*, 2569.
(32) Hautojärvi, J.; Leijala, A. *J. Appl. Polym. Sci.* **1999**, *74*, 1242.
(33) El-maaty, M. I. A.; Olley, R. H.; Bassett, D. C. *J. Mater. Sci.* **1999**, *34*, 1975.

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