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Effect of Matrix Molecular Mass on the Crystallization of β-Form Isotactic Polypropylene around an Oriented Polypropylene Fiber

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Introduction

The β-form of isotactic polypropylene (iPP) is a technologically useful material. In this context, pathways to produce this material have been intensively studied for at least two decades. One method, developed by Varga, is to selectively nucleate β-iPP on preexisting α-iPP row nuclei.[1−5] This method utilizes the different temperature dependences of crystal growth rates of α- and β-iPP, there being a narrow temperature window, 100−140 °C, in which the growth of the β-phase is faster than that of the α-phase.[1,6] It is required then only to provide the β-form nuclei in this regime, for β-form growth to outstrip that of α and become the predominant phase. A simple procedure for growing β material is to embed existing, oriented α-iPP fibers into an iPP melt and then lower the temperature into the temperature region which favors β-form growth.[7−9] With this method, it has been shown that the oriented fibers must be partially melted, by insertion into the existing melt at temperatures above 170 °C, in order to successfully nucleate β-crystallization at a lower temperature.[8] Nothing has been reported on the β-nucleation process for PP β-crystallization induced by oriented fibers. In the work reported here, we explore the role of matrix iPP on this process and, on the basis of these results, suggest a role of the matrix polymer in the nucleation process.

Experimental Section

Matrix polymers, PP-A and PP-B, of lower and higher molecular mass, respectively, are used in this study. Their molecular weights, melt flow index (MFI), and melting temperatures are given in Table 1. iPP fibers were spun at 200−240 °C, using a homemade melt-spinning device. The resulting iPP fibers were then cold-drawn at 110 °C to different draw ratios. To remove the sizing agents on the fiber surfaces, the fibers were treated for 4 h with refluxing acetone and then dried in a vacuum oven at 40 °C for 24 h. Three kinds of fibers, designated as F1, F2-5, and F2-8, with molecular characteristics reported in Table 2, were used in this study. The onset melting (T_{onset}) and complete melting (T_{m}) temperatures of the fibers embedded in the matrix were measured by optical observation with the T_{onset} representing the point when the birefringence of the fiber surface begins to disappear, while the T_{m} corresponding to the point when the birefringence of the fiber disappeared.

The iPP fiber/matrix composites were produced by a procedure whose detailed description can be found in ref 7. 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. As the molten iPP thin layer reached an equilibrium state at the desired temperature, iPP fibers tightly fixed on a metal frame 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 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

A. Basic Result. The basic result of this investigation is that the matrix molecular weight has a significant effect on whether the fiber introduced into the melt will produce a α- or β-product. Figure 1a is an optical micrograph of an iPP F1/PP-A composite prepared by introducing the iPP fiber F1 into the molten PP-A matrix at 180 °C and subsequently isothermally crystallizing at 138 °C for 2 h. According to the strong birefringence and the results of previous studies, the columnar structures shown here are β-cylindrites. Selective melting further confirms that the interface structures correspond to β-crystals, as found in the previous research.[7,10] The experimental results are quite different when F1 is introduced to matrix PP-B under the same conditions, as shown in Figure 1b. Now the interface morphology consists mainly of α-crystals, with only very few fan-shaped regions of β-form (indicated by the arrows). For PP-B, even though F1 undergoes a transition from the solid, oriented state to a totally relaxed state as the fiber introduction temperature is increased, the formation of pure β-cylindrites around the fibers never occurred. Considering that the molecular weight shows no significant effect on the bulk crystallization of the samples at 138 °C (see Figure S1 in the Supporting Information), this set of experiments has shown that while F1 fiber efficiently induces β-crystallization of PP-A, the partially molten F1 fibers cannot nucleate profuse β-crystallization in the higher molecular mass PP-B.

B. Ancillary Experiments. *1. Ability of PP-B To Crystallize into the **β**-Form.* A possible explanation of the inability of the higher molecular weight PP-B to induce β-form crystallization around F1 fibers might be that this polymer can never crystallize into the β-form under a thermal history similar to that used for the melt-introduced fiber experiment. That this is not the case is demonstrated by an experiment in which NT-A β-nucleant was added to a film of PP-B and crystallization was carried out using the same thermal treatment as that used for Figure 1b. In this case, the film crystallized as β-spherulites

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Table 1. Characteristics of the iPP Matrices

samples	MFI (g/10 min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_m (°C)
PP-A	15	42 700	1.94×10^5	4.54	166.9
PP-B	0.5	98 800	4.46×10^5	4.52	166.7

Table 2. Characteristics of the iPP Fibers

samples	MFI (g/10 min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	draw ratio	T_{onset} (°C)[a]	T_m (°C)[a]
F1	15	42 700	1.94×10^5	4.54	4	178	180
F2-5	25	46 400	1.85×10^5	3.98	5	174	179
F2-8	25	46 400	1.85×10^5	3.98	8	180	185

[a] Observed during optical microscopy observation.

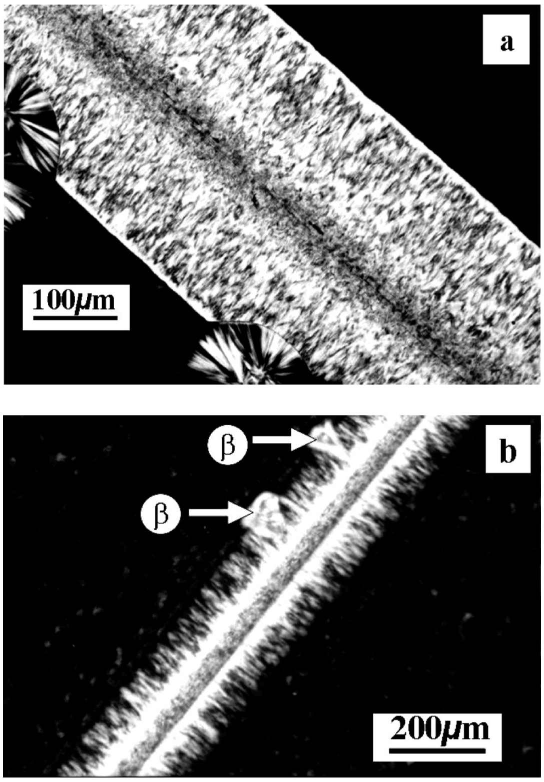

Figure 1. Optical micrographs of the iPP fiber/matrix composites prepared by introducing iPP fiber F1 into molten iPP matrix (a) PP-A and (b) PP-B at 180 °C and subsequently isothermally crystallized at 138 °C for 2 h.

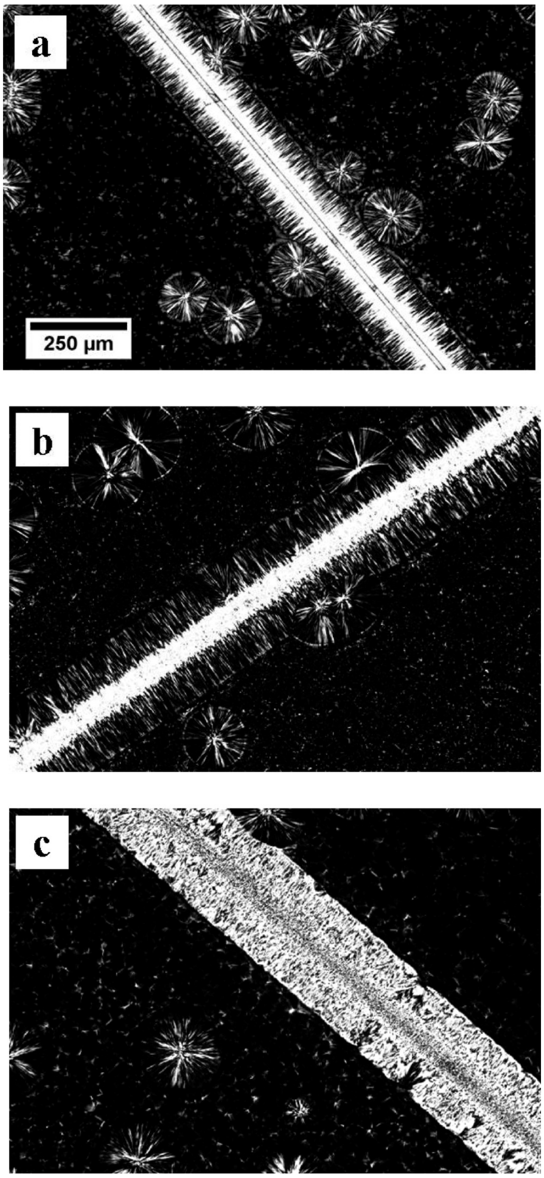

Figure 2. Optical micrographs of iPP fiber/matrix composites prepared by introducing iPP fiber into molten matrix PP-B and subsequently isothermally crystallizing at 138 °C for 2 h: (a) introducing F2-5 at 173 °C; (b) introducing F2-5 at 175 °C; (c) introducing F2-8 at 182 °C.

(not shown here, but viewable as Figure S2 of Supporting Information), which has been identified by a selective melting experiment.

2. *Effect of Fiber Orientation on β-Formation in PP-B.* As the introduced iPP fiber is predominantly responsible for the formation of oriented chain bundles which subsequently decide the crystal modification, the effect of fiber draw ratio on the crystallization of the fiber—PP-B system was examined. Fibers F2-5 and F2-8 were used here. These fibers, of the same iPP, had draw ratios of 5 and 8, respectively. The onset and complete (disappearance of the birefringence) melting temperatures of fiber F2-5 are 174 and 179 °C, respectively; for fiber F2-8, these are 180 and 185 °C. In a first experiment, both of the fibers were introduced into molten PP-B at 173 °C, a condition under which neither fiber melts. In these cases only α-transcrystallization appeared around the fibers after crystallization at 138 °C. The morphology can be seen in Figure 2a. This result agrees with previous studies, in which it was concluded that matrix molecular chains will crystallize homoepitaxially on solid fiber and form α-transcrystallization, regardless of any change of molecular characters of the fiber. The phenomena become more interesting when F2-5 and F2-8 are introduced at temperatures just above their melting onset temperatures into molten PP-B, ensuring that the fibers are in a state of partial melting. F2-5 always induces α-transcrystallization after crystallization at 138 °C, following fiber introduction within the temperature range from 175 to 180 °C, as shown in Figure 2b. But when fiber F2-8 is introduced into PP-B at 182 °C and crystallized isothermally at 138 °C for 2 h, the result is β-transcrystallization around the partially molten fiber, as seen in Figure 2c. These results show that molecular chains in PP-B are able to form the β-phase under the condition of introducing fibers of sufficiently high draw ratio.

3. *Effect of Crystallization Temperature on β-Formation in PP-B.* Changing the draw ratio of fibers is one approach of controlling the preordered state and consequently affecting

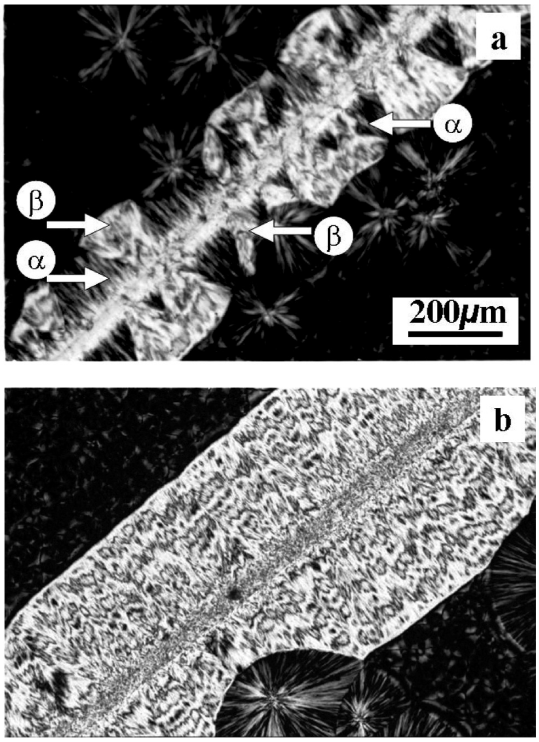

Figure 3. Optical micrographs of iPP fiber/matrix composites prepared by introducing fiber F2-5 into molten matrix PP-B at 175 °C and subsequently isothermally crystallizing at (a) 135 °C and (b) 133 °C for 2 h.

the crystallization kinetics. Another approach is to change the degree of undercooling during fiber-induced crystallization. Here, we introduce F2-5 into PP-B at the same temperature but crystallize isothermally at different temperatures. Figure 3 demonstrates how the isothermal crystallization temperature affects the interface morphology. Figure 3a is an optical micrograph of the composite which was prepared by introducing F2-5 into PP-B at 175 °C and isothermally crystallizing at 135 °C. Here the morphology consists of some fan-shaped β-iPP regions randomly dispersed in the α-transcrystallization layers, and these fan-shaped β-iPP crystals grow clearly faster than do the α-iPP transcrystallization layers. When the crystallization temperature is decreased further to 133 °C, β-iPP-rich cylindrites are produced, and the transcrystallization layers consist of alternatively arranged bright and dark bands, indicating the formation of β-banded transcrystalline structure with strong negative birefringence, as seen in Figure 3b. Decreasing the crystallization temperature from 138 to 133 °C has made a dramatic difference in the ability to induce β-form crystallization.

Discussion

We have seen above that the ability to induce β-crystallization is severely constrained by the values of several parameters: molecular weight of the matrix, degree of orientation of the fiber, degree of relaxation of the oriented fiber, and the temperature of crystallization. In this discussion, we will attempt to understand these constraints.

We first note that even though fiber F-1, introduced at 180 °C, cannot induce β-crystallization of PP-B at 138 °C, crystallization of PP-B into the β-form is induced easily at 138 °C by a heterogeneous nucleating agent. Thus, the problem of using fiber F-1 (vis-à-vis a nucleating agent) is in the nucleation, not in its growth. Since matrices PP-A and PP-B behave differently in β-nucleation after fiber introduction, this strongly indicates that the matrix chains participate in the nucleation process. We have also seen that some degree of relaxation of the molecules of the fiber is necessary to permit β-phase nucleation.[8] Finally, we saw that undercooling of the system must be greater than a critical value for the process to succeed.

On the basis of the above, we suggest a phenomenological hypothesis for the nucleation of the β-phase. The hypothesis is that the necessary condition for the formation of a β-nucleus requires the participation of matrix chains with oriented chains from the partially relaxed fiber surface. The participation of the matrix chains requires their diffusion into the oriented chains of the fiber. Some degree of relaxation of the molecules at the surface of the fiber is necessary for the penetration of the matrix chains, but the orientation must be maintained above some critical level. Lacking such relaxation and interdiffusion, the solid fiber surface will act as a substrate for homoepitaxy of the α-phase. The interpenetration of matrix molecules into the somewhat relaxed oriented molecules in the fiber is qualitatively consistent with all the results of this work. That the lower molecular mass polymer should perform better than the higher molecular mass material reflects the significantly higher diffusivity of the shorter chains. Since the diffusivity is inversely proportional to the square of the molecular mass,[11,12] the diffusivity of matrix PP-A should be more than 5 times greater than that of PP-B. Thus, PP-A can more easily penetrate into the partially relaxed fiber molecules before the latter have lost significant orientation. Therefore, the required chain interpenetration and relaxation for β-nucleation could be easily realized in the lower molecular weight matrix. This concept of the simultaneous requirements of effective interpenetration and maintenance of molecular orientation is the chief outcome of this work.

Also requiring discussion are two other aspects: the roles of fiber draw ratio and of crystallization temperature. The present results are too sketchy to provide more than suggestive concepts, as outlined below.

Empirically, for successful β-phase nucleation, the fiber introduction temperature is restricted to a narrow range above the melting onset temperature. For high draw ratio fibers, the melting temperature is relatively high, leading to an elevated fiber induction temperature for partial melting, relative to fibers of lower draw ratio. This higher introduction temperature enhances the diffusivity of the matrix molecules into the molten fiber (relative to that for lower draw ratio fibers). This is likely the principal effect. There may also be an effect of the higher draw ratio enhancing the relaxation time compared with more poorly oriented fibers. This effect could allow more time for matrix molecules to penetrate the fibers before orientation is lost, enhancing the ability for β-nucleation. Local stresses caused by the heat treatment of the cold-drawn fiber with fixed ends could also play an important role in the β-nucleation.

While the chain interpenetration occurs immediately after fiber insertion, the nucleation occurs at the crystallization temperature. Therefore, the crystallization temperature also affects the nucleation and crystal growth processes. A faster nucleation at lower temperature prevents further relaxation of the molten fiber molecules, which is in favor of β-PP crystallization. The growth rate of the β-phase is also important for the formation of β-iPP. Even though the temperature range for a faster growth of β-phase relative to the α-phase falls into 100−140 °C region (see ref 6), the growth rate difference between the α- and β-PP crystals is very small close to 140 °C. It increases remarkably at lower temperature, e.g. 133 °C, leading to more efficient conversion to the β-form.

Conclusions

Comparing the effects of two different molecular mass matrixes on the induction of β-iPP around α-iPP fibers, it is found that the lower molecular mass i-PP is more efficient. By raising the fiber draw ratio or lowering the crystallization temperature, the higher molecular mass matrix becomes also efficient in inducing the β-form. These results suggest that (1) the matrix iPP is involved in the β-nucleation process and (2) matrix chains must interdiffuse with oriented chains of partially molten fiber to generate β-iPP nuclei. Still needed is a satisfactory molecular model for the β-nucleation.

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Supporting Information Available: Optical micrographs of bulk crystallized PP-A, PP-B, and β-nucleant induced crystallization of PP-B at 138 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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