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Micromorphologic feature of the crystallization of isotactic polypropylene after melt-shearing[*]

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Summary

The formation of β-cylindritic micromorphologic structure produced by pulling a Kevlar fiber from an isothermal crystallizing β-nucleated isotactic polypropylene melt (at T_c=133°C) has been studied by using polarized light microscope, phase contrast optical microscope, scanning electron and atomic force microscopes. The micrographs reveal a clearly interfacial shear zone, α-cylindrite, β-cylindrite and β-spherulites near the sheared layer. Some of the point-like β-nuclei was not originated from the surface of the interfacial shear zone. A modified model based upon the theory of shear-induced crystallization can explain the phenomenon of polymorphic structure and the boundary shape near the interface without assuming epitaxial growth.

Introduction

Isotactic polypropylene (iPP) is a polymorphic material with a number of crystal modifications. Three crystalline phases are well known for iPP: α monoclinic phase (1), β hexagonal phase (2,3), and γ orthorhombic phase (4-6). Usually iPP crystallizes in the most thermodynamically stable α-phase from the melt. The birefringence of α-phase spherulites is positive, negative or mixed type depending on the crystallization temperature (7). These spherulites are easily distinguished from β-phase spherulites which revealed a very strong negative birefringence. The metastable β-phase crystallizes from the melt in temperature range of 105-135°C. Several factors favor β-phase crystallization: thermal gradient, shearing or elongation of the melt during crystallization and nucleating agents in the polymer.

The iPP morphology near the sheared layer was most studied by a thermo-optical method only. Leugering et al. (8) first pointed out the fact that shearing of iPP increases the amounts of the β-modification. Dragaun et al. (9) demonstrated that a critical threshold of shear rate has to be exceeded for β-phase crystallization. Varga (10) found that the a and β phases coexist in the transcrystalline-like

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interphase region by selective melting of the β-phase. Varga and Karger-Kocsis (11-13) suggest this transcrystalline-like (or cylindritic) crystallization is induced by self-nucleation of the iPP, which is different from heterogeneous nucleation. Due to the limited resolution of polarized light microscopy (PLM), the micromorphologic feature at the fiber-polymer interface cannot be captured. The authors (14,15) suggested a model to explain the formation of this polymorphic structure by assuming that melt-shearing, caused by fiber pulling, is associated with the formation of α-row nuclei. The surface of the in-situ formed α-row nuclei may induce the nucleation of the β-phase. They believed that auto-epitaxy in iPP may be a possible explanation for the observed α-β bifurcation on the α row-nuclei.

Kobayashi et al. (16) derived a set of equations for the sheared polymer melt. They accounted for the entropy decrease by molecular orientation. In the high temperature region, both rates of nucleation and growth increase rapidly with molecular orientation. Yeh and Hong (17,18) estimated that the tremendous increase of nucleation rates in sheared polyethylene melt can be several orders of magnitude higher than that in the quiescent state if the nucleation is heterogeneous, and the enhancement in homogeneous nucleation is much higher. In a recent paper, Vancso et al. (19) reported the results of atomic force microscopy (AFM) study which aimed at imaging interfacial morphologies. Unfortunately, it is still an open question, whether auto-epitaxy in iPP can fully explain the experimental observations or not. In contrast to previous works of PLM, the aim of this contribution is to clarify the nature of the cylindritic micromorphologic feature at the β-iPP/Kevlar 49 interface. A modified schematic diagram depicting the polymorphic boundary lines is proposed and the origin of β-cylindrite is discussed without the assumption of epitaxial crystallization.

Experimental

The β-iPP resin used in this study was a Daplen BE 50 821c grade, marketed by PCD (Linz, Austria). An Aramid fiber (Kevlar 49, DuPont, USA) was placed in an iPP film between two glasses which resulted in a thickness about 30-50 μm. PLM investigations were carried out in a Leitz Dialux 20 microscope, equipped with a hot stage. The specimens were heated to 200°C and maintained at this molten state for 5 min. The hot stage was then cooled to the crystallization temperature (T_c=133°C) at a rate of 40°C/min. The fiber was manually pulled at T_c and the specimens were allowed to crystallize for 1 hr. These specimens were later etched chemically according to the procedure of Olley and Bassett (20) in order to study the interface morphology by phase contrast optical microscopy (PCLM; Leitz, Wetzlar, Germany), AFM, and scanning electron microscopy (SEM; Jeol 6400). AFM experiments were performed at ambient condition in a tapping mode by using a NanoScope IIIa setup (Digital Instruments). The scanning frequency was 0.6 Hz and all images shown were captured without the use of image filtering.

Results and discussion

The PLM micrographs in Figs. 1a and 1b exhibit the basic features of shear induced cylindritic morphology. When a fiber was pulled in the matrices of β-iPP at T_c, a β-phase cylindritic structure appeared (Fig. 1a). As the temperature was increased from T_c to 156°C, the β-spherulites and the β-cylindritic layer melted and the “saw teeth” α phase nearby the fiber survived, as shown in Fig. 1b. This observation agrees with the previous results from the thermo-optical studies of α-iPP (7-9,11-15). In addition to the cylindrite the sample contains the α- and β-modification crystals in a great density which results in distorted boundary between the α- and β-spherulites. The α-spherulites appear in the sample and generally at a considerable delay.

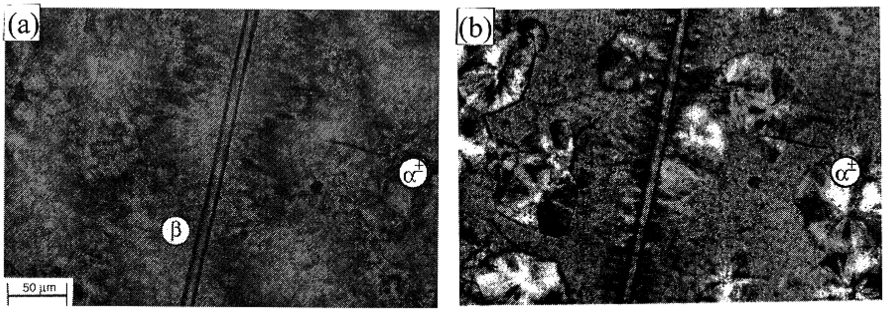

Fig.1 Evidence of β-cylindrite formation for Kevlar 49/β-iPP by PLM (a) $T_c=T_{pull}=133°C$. (b) Morphology after melting the β-phase at 156°C.

Fig. 2 depicts the morphology after chemical etching revealed by PCLM which shows a clearly interfacial shear zone (pre-oriented crystalline zone near the bottom edge), α- and β-cylindritic layers.

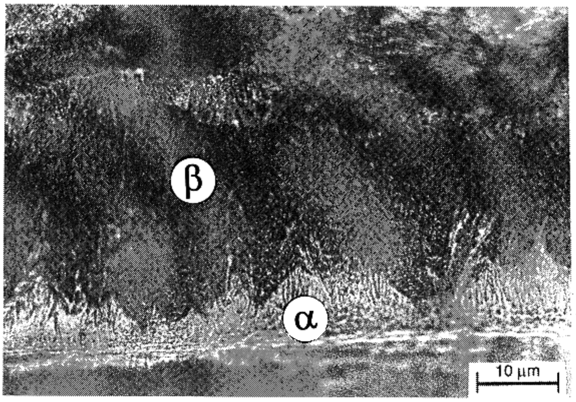

Fig.2 PCLM micrograph of the etched β-iPP/Kevlar 49 specimen formed by pulling a fiber under the condition $T_c=T_{pull}=133°C$.

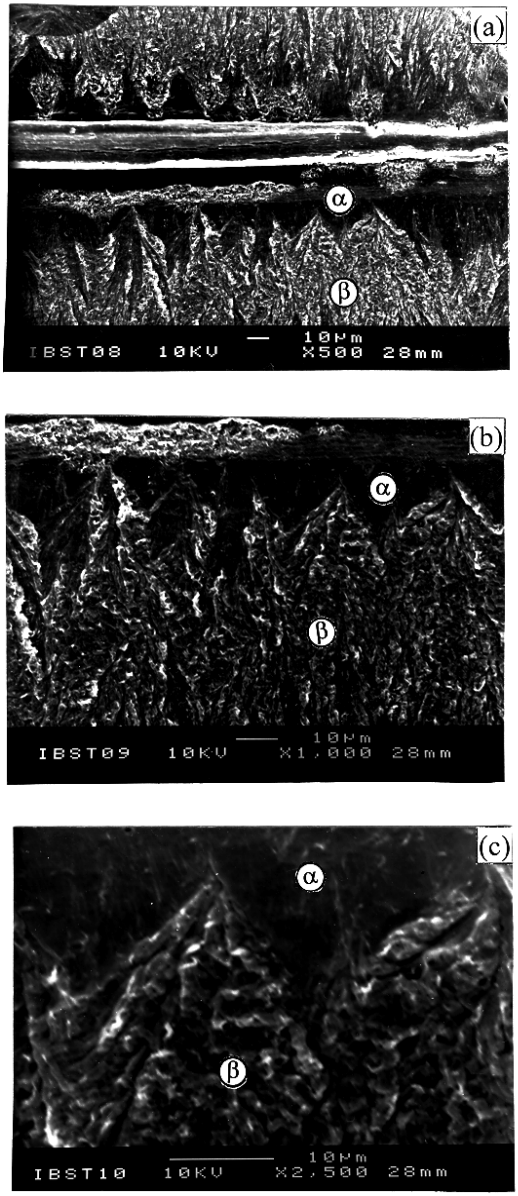

Fig.3 SEM micrographs after chemical etching of β-iPP/Kevlar 49 specimen (a) The α- and β-cylindrites crystallized isothermally at $T_c=T_{pull}=133°C$ with palm shape boundaries are clearly discernible (b) A close-up of α-, β-cylindrites near the bottom side of the fiber. (c) The point-like β-nuclei are not located on the surface of pre-oriented crystalline zone.

The β-cylindritic layer is about a few μm to 10 μm distant from the shear zone containing oriented polymer chains along the fiber length. This micrograph shows the interfacial region near the fiber-melt interface with a magnification significantly higher than the resolution limit of optical microscopy. It yields valuable information regarding the micromorphologic feature of sheared melt in the vicinity of fiber and indicates the impingement lines between the α- and β-cylindritic layers are not completely straight. Some of the boundary lines between the α-cylindrite and β-spherulites (later developed into β-cylindrite) are hyperbolic.

Fig. 3a depicts the micromorphologic feature after chemical etching revealed by SEM which shows α-cylindritic layer, β-cylindritic layer, and a clearly pre-oriented crystalline zone on the bottom side of the pulled fiber. A close-up of the α-cylindrite texture near the bottom side of fiber is shown in Figs. 3b and 3c. The number (or the density) of α-nuclei at 0-10 μm distant from the shear zone is larger compared with the point-like β-nuclei. Thus α cylindrite formation is favored in the close vicinity of the fiber. As shown in the micrographs (Fig. 3), an α-cylindrite with palm shape is formed with a distance of about 20 μm between two point-like β-nuclei which is not located on the surface of pre-oriented crystalline zone. Because of the greater growth rate of the β-phase (G_β) with regard to the α-phase (G_α) (21), the β-spherulites will encompass the α-cylindrite, which thus becomes an inclusion. During the formation of an inclusion, the growing fronts of the β-spherulites meet behind the inclusion forming a straight intrinsic ββ-spherulitic boundary, which leads to the characteristically micromorphologic feature of β-cylindrite. Fig. 4 displays $(40\mu m)^2$ scan: the fiber is located near the bottom margin of the micrograph (the fiber itself is not shown). The basic micromorphologic feature observed in AFM image is similar to the images obtained by SEM: the point-like β-nuclei in the vicinity of fiber are obvious and the β-cylindritic structure can be clearly seen. AFM image showing the point-like β-nuclei indicates the number of α-nuclei are much larger nearby the pulled fiber.

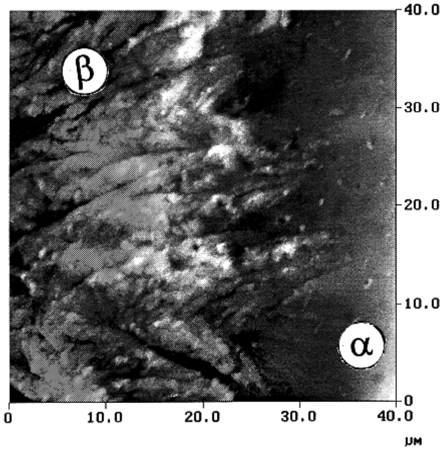

Fig.4 Tapping AFM image of the etched β-iPP with α- and β-cylindrites caused by pulling of a Kevlar 49 fiber under the condition $T_C=T_{pull}=133°C$.

The micromorphologic feature nearby the pulled fiber is shown as being α phase in Fig. 1b. It should be noticed that there are β heterogeneous nuclei in β-iPP melts. By pulling a fiber, the induced α- and β-crystallization near the interface started earlier than for the heterogeneous or homogeneous ones and $N_\alpha > N_\beta$, where N is the number of stable nuclei. An overgrowth of the β-phase was observed for temperatures 100°C $< T_c \leq T_{pull} <$ 140°C, where $G_\beta > G_\alpha$ (21). T_{pull} is the fiber pulling temperature. The earlier stage of formation of the β-cylindritic layer inhibits the growth of β heterogenerous and α homogeneous nuclei. The shear-induced crystallization is located only tens of microns distant from the fiber surface. This is as a result of the strong decrease of shear stress in radial direction of the pulled fiber (22).

Varga quantitatively analyzed the boundary lines developed between cylindrite and spherulite by using mathematical equations (10). He defines “d” as a distance from the surface of the cylindrite to the nucleus of the spherulite. It should be noted that the growth rate of the β phase is about 30% faster than that of the α phase at 133°C when crystallized from the quiescent melts (21), i.e., $G_\beta/G_\alpha \approx 1.3$. The relationship of $G_\beta/G_\alpha > 1$ still exists in sheared melt at 133°C. In sheared iPP melts the pre-oriented crystalline zone is formed first and $N_\alpha > N_\beta$ in the vicinity of pulled fiber. A great number of α nuclei develop into α-cylindrite and the point-like β nuclei grow radially. The boundary lines between α-cylindrite and β-spherulites (later developed into β-cylindrite) are hyperbolic because G_r (= G_β/G_α) >1. Straight-line boundaries may also be formed if β-nuclei are sporadically initiated on the growing a-cylindritic front, i.e., d=0 or d→0. Based on the results of micrographs and the theory of shear-induced crystallization. we propose a modified schematic diagram as shown in Fig. 5 which can explain the phenomena of polymorphic structure and the boundary lines near the pulled fiber without assuming epitaxial growth.

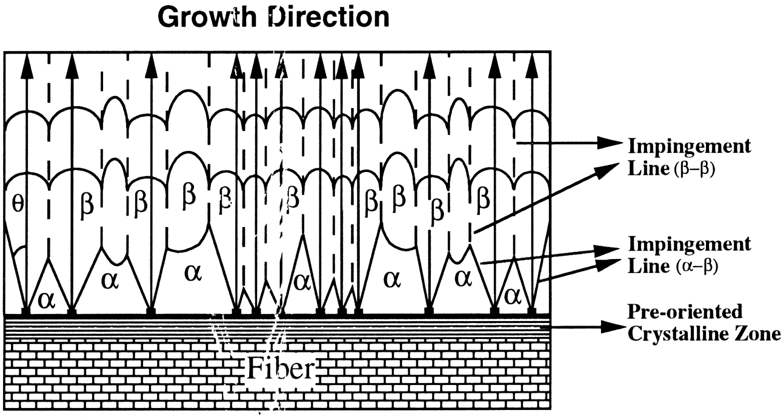

Fig.5 Schematic diagram on the β-cylindritic formation in β-iPP/Kevlar 49 due to melt shearing under the condition of $T_c = T_{pull} = 133$°C.

The experimentally observed shape of boundary differs from that expected from the above model because the density of β-nuclei depends on the applied stress (9), the pulling temperature, and the crystallization temperature.

Conclusion

The results presented here show that the induced α- and β-crystallization near the pulled fiber starts earlier than for the heterogeneous or homogeneous ones and the density of α-nuclei is much higher than that of β-nuclei. The polymorphic structure and the boundary lines of sheared β-iPP melt in the vicinity of pulled fiber can be explained from the theory of stress-induced crystallization and a modified model without assuming epitaxial growth.

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