



Polymorphic structures phase diagram of shear-induced isotactic polypropylene/carbon fiber cylindrites

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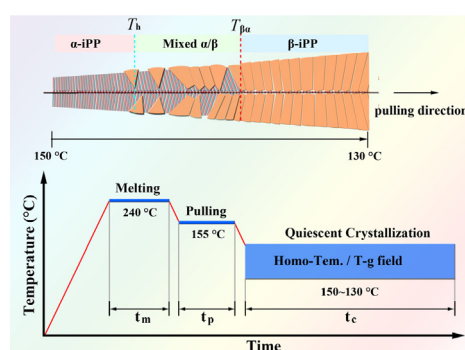
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HIGHLIGHTS

- The crystallization temperature–pulling rate dependent phase diagram of polymorphs in iPP/CF cylindrite was achieved.
- The temperature gradient technique was used to survey the structural transitions arisen from temperature variation.
- The well-defined β -form interface was established readily, which is benefit to load transfer between CF and iPP matrix.

GRAPHICAL ABSTRACT



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ABSTRACT

Depending on the thermal and mechanical conditions of pulling fiber in the supercooled melts of isotactic polypropylene (iPP), three kinds of cylindrite with variable polymorphic structure could be achieved, i.e., pure α -cylindrite, mixed α/β cylindrite, and β -rich cylindrite. However, precisely assessing the synergic action of thermal and mechanical factors on polymorphic structure of cylindrite is still challenging. Thanks to the great convenience of temperature gradient (T - g) technique in surveying structural transitions arisen from temperature variation, a crystallization temperature (T_c)-pulling rate (R_{pull}) dependent phase diagram of polymorphs in iPP/carbon fiber (CF) cylindrite was achieved readily through adopting different R_{pull} s. It was intriguing to suggest that (1) the temperature regime of mixed α/β cylindrite became narrower and narrower as increasing R_{pull} , implying a sudden transition from β -polymorph to α -polymorph upon intensive shearing; and (2) the upper threshold temperature that allowing generation of β fan-shaped domain was independent on R_{pull} , around 145 °C. Moreover, the structural difference between mixed α/β cylindrite and β -rich cylindrite was revealed in detail by scanning electron microscopy. An approximately regular nucleation line of β -form appeared in β -rich cylindrite, due to prevailing α -to- β bifurcation arisen from the edge-on α -lamellae. Whereas, occasional α/β bifurcation was found among a tremendous number of α -lamellae within the mixed α/β regime. Constructing the polymorphs phase diagram is of significance in manipulation of interfacial crystallization entities and fabrication of fiber-reinforced semi-crystalline polymers with high performances.

Brief abstract: In this study, the combined effect of crystallization temperature (T_c) and pulling rate (R_{pull}) on the polymorphic structure of shear-induced cylindrite in isotactic polypropylene (iPP)/carbon fiber (CF) composite was well ascertained by using the T - g field technique. It was found that reducing T_c or improving R_{pull} might induce the transformations of polymorphism from pure α -cylindrite to mixed α/β cylindrite up to β -rich cylindrite. A crystallization temperature (T_c)-pulling rate (R_{pull}) dependent phase diagram of polymorphs in iPP/CF cylindrite was achieved readily. It was intriguing to suggest that (1) the temperature regime of mixed α/β

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cylindrite became narrower and narrower as increasing R_{pull} , implying a sudden transition from β -polymorph to α -polymorph upon intensive shearing; and (2) the upper threshold temperature that allowing generation of β fan-shaped domain was independent on R_{pull} , around 145 °C. The findings of this study are meaningful for construction of appropriate interfacially-crystallized structure, which could efficiently induce interfacial enhancement in polymer/fiber composites.

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1. Introduction

Isotactic polypropylene (iPP) is one of the most widely used polyolefins due to its versatile properties and relatively low manufacturing cost [1–3]. It is well known that iPP exhibits characteristic of polymorphism, mainly including monoclinic α -form, hexagonal β -form, and orthorhombic γ -form [4–6]. Among them, the α -iPP crystal is a thermodynamically stable phase and forms most frequently under general processing conditions. It possesses relatively good mechanical strength but poor impact toughness. In comparison, the β -iPP crystal has higher toughness and ductility than its α -counterpart [6,7]. However, the β -iPP crystal is a thermodynamically metastable phase and hardly obtained upon common conditions. According to literature, there are several methods frequently used to generate β -modification iPP, such as thermal gradient [8,9], shearing [10–12], and special nucleating agents [13,14]. In particularly, the strategy of shear-induced β -iPP has received enormous attention from both of academia and manufacture, due to shearing field exists in most of the polymer processing.

By considering the validity and operability, a fiber pulling technique was frequently adopted to simulate shear field [15,16]. Shear stress was produced at the vicinity of the fiber surface when pulling this monofilament in the supercooled melt of iPP by manual manner or motor device. Since extended macromolecular chains aligned parallel to the pulling direction, the active energy of nucleation decreased substantially, which could lead to dense nuclei sites. Then the subsequent crystallization evolved into a columnar hybrid entity, in which the monofilament fiber acted as the central line and it was encapsulated round by the sheath of iPP crystals. Interestingly, the β -polymorph of iPP could be introduced into such hybrid crystallization entity via the fiber pulling performed upon appropriate operation conditions [17,18]. Varga et al. [10,17] first experimentally revealed that the β -form sectors originated from the α -row nuclei layer via a transition mechanism of α/β bifurcation occurred in α -lamellae. According to its crystallographic feature, they suggested that the columnar β -form entity should be termed “ β -cylindrite” rather than “ β -transcrystallinity” [19]. The latter terminology means that heterogeneous nucleation of β -form directly on the surface of fiber.

A number of works were devoted to describe the principles of constructing β -cylindrite, using the fiber pulling technique, with taking into accounts of various factors like fiber type, pulling temperature (T_{pull}), crystallization temperature (T_c), pulling rate (R_{pull}), shear duration and shear stress. Several types of fiber including glass fiber (GF) [20,21], carbon fiber (CF) [22], poly(ethylene terephthalate) fiber [23] and vectra fiber [12] have been utilized to trigger β -cylindrite successfully. A comparison in the formation kinetics of β -cylindrite between different fibers indicated that the polymorphism of cylindrite is independent on the quality of fibers used. The role of operation temperatures (T_{pull} and T_c) on the formation of β -cylindrite was well demonstrated by Karger-Kocsis et al. [10], whom proposed a kinetics prerequisite that clarifying the temperature interval favorable for β -modification as $T_{\alpha\beta} < T_c \approx T_{\text{pull}} < T_{\beta\alpha}$, where $T_{\alpha\beta} \approx 100$ °C and $T_{\beta\alpha} \approx 140$ °C, referring to the onset of α -to- β transition and β -to- α transition, respectively. This rule involving operation temperatures offers good convenience in estimating the influences of mechanical conditions on the polymorphism of iPP cylindrite.

In the relevant literatures [20,24,25], T_c and T_{pull} were invariant once their values were determined. The influence of shear on the interfacial

morphology and crystal modification at the interface of iPP/glass fiber composite has been ascertained through increasing the fiber-pulling speed [20]. It was proved that higher amplitude of interfacial shear facilitates a higher level of iPP chain orientation in the interfacial layer which is the key point to dominate the resultant crystal modifications. Chen et al. [24] investigated the shear-induced dendritic β -iPP in thin film, which was carried out by scratching supercooled iPP melt with a sharp scalpel at a constant rate. It was concluded that increasing shear flow temperature from 130 to 190 °C led to a decrease in both number density of flow-induced edge-on α -iPP lamellae and subsequent β -iPP crystals. They suggested that the transition from α -iPP edge-on to dendritic β -iPP flat-on lamellae occurred only occasionally. The results obtained by Qin et al. [25] also indicated that higher fiber pulling speed is crucial to promote the generation of β -cylindrite. Moreover, a quantitative evaluation of interfacial shear stress distinctly approved that the threshold for triggering β -modification, 0.042 MPa, is prominently larger than that of α -modification, 0.017 MPa [27]. It is in accordance with the demand of orientation window, i.e., high orientation and ordering levels of the iPP chains in the molten state should be satisfied [28].

As mentioned above, the polymorphic nature of fiber-pulling-induced cylindrite is strongly dependent on both of thermal and mechanical conditions. Although the kinetics prerequisite of $T_{\alpha\beta} < T_c \approx T_{\text{pull}} < T_{\beta\alpha}$ and the demand for orientation window address the appropriate conditions from the viewpoint of operation temperature and shear amplitude, respectively, the synergy of thermal and mechanical factors on adjusting the polymorphic structure of cylindrite was commonly ignored in the past. The amount of operation temperatures chosen was very limited in those studies that inspected the change of crystalline morphology upon different R_{pull} s [17,26,29]. A convenient and effective method is highly desired to utilize a series of temperatures on tailoring the polymorphic structure of iPP/fiber cylindrite. The temperature gradient (T - g) hot stage is a high-efficiency tool to follow particular structural/morphological transformations which sensitive to temperature variation. It has been used in kinds of studies includes the crystallization of semicrystalline polymer [30,31], the construction of surface gradient structure for realizing functionalities [32–34], the phase morphology of polymer blend [35–37], the microphase separation of block copolymer [38,39], etc. Meanwhile, the T - g field with continuous temperature variation allows observing the structural evolution in a same sample, which can minimize the external disturbances. Moreover, compared to the homo-temperature field, the T - g field greatly reduces the number of samples which makes the research easier and more comprehensive.

Crystallization temperature and fiber-pulling rate are two crucial thermo-mechanical factors for dominating the resultant polymorphs in cylindrite. The main aim of our present study is to ascertain the synergistic action of T_c and R_{pull} on the polymorphic structure of iPP/CF cylindrites by using the T - g field technique, which offers a continuous T_c regime from 150 °C to 130 °C. Although a series of discrete R_{pull} s were chosen, for certain single R_{pull} the evolution of polymorphic structure within the whole T_c regime could be acquired through only once experiment. In order to demonstrate the synergistic affect straightforwardly, a T_c - R_{pull} dependent phase diagram of polymorphic structure was established, which might offer new insights into the control rules of the polymorphism in cylindrite. It has been proposed recently that the interfacial crystallization between semi-crystalline polymer and

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