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Interfacial crystallization and mechanical property of isotactic polypropylene based single-polymer composites

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ABSTRACT

Isotactic polypropylene (iPP) based single-polymer composites (SPCs) were prepared by introducing iPP fibers into the molten or supercooled homogeneous iPP matrix. The influences of fiber introduction temperature (T_i) on the resultant morphology of transcrystallinity (TC) and mechanical properties of SPCs were investigated via a polarized optical microscopy (POM) and a universal tensile test machine. The effects of interfacial crystallization on mechanical properties were also studied. The tensile strength of SPCs was observed to increase firstly and to reach a maximum value at $T_i = 160$ °C, and then to decrease with further increasing the T_i. Wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and POM were employed to understand the mechanical enhancement mechanism. It is found that the enhanced tensile strength of SPCs was strongly dependent on the synergistic effects of TC, high orientation degree of iPP fibers and good adhesion between the iPP fiber and the matrix.

1. Introduction

In the past few decades, isotactic polypropylene (iPP) has been the major polymeric construction materials in the light of its impressive consumption. One outstanding advantage is its excellent comprehensive properties, including easy processing, low manufacturing cost and so on [1]. Unfortunately, the intrinsic low mechanical strength of iPP limits its further applications. Hence, considerable efforts have been made in order to further improve its mechanical properties. One of the most common methods is by embedding various fibers (carbon, clays, glass, etc.) in the iPP matrix to produce composites [2–5]. However, two main problems must be avoided if the heterogeneous fibers are added in the thermoplastic matrix. The first is the interfacial residual stress due to different thermal expansion between heterogeneous fibers and polymer matrix [4]. The second is the weak interfacial adhesion owing to the incompatibility among the heterogeneous components [6]. The interfacial interaction between fiber and matrix is a crucial prerequisite for determining the mechanical property [7]. Among the various methods (including the increased specific surface area of fibers, improved chemical activity of fiber surfaces, and matched compatibility) to enhance the interfacial interaction in the iPP/fibers composites [8–14], interfacial crystallization such as transcrystallinity (TC) [15] is regarded as an efficient and economical approach [16]. Moreover, TC around the fiber, possessing better load transfer ability than amorphous layers, is believed to be of crucial significance to improve the interfacial interaction between matrix and fibers [17,18].

On the other hand, in light of recyclability, the presence of heterogeneous additives or inclusions, such as glass fibers, clays and magnetic nanoparticles, is an inevitable obstacle for polymer based composites. Hence, the composite systems with the matrix and the fiber being from the same polymer are preferable candidates. In other words, these systems mean mono-component composites or single-polymer composites (SPCs). The concept of SPCs is not new, which was proposed for the first time by Capiati and Porter four decades ago [19]. Such self-reinforced systems have specific economic and ecological advantages. This can be understood as follows: 1) desired mechanical property can be achieved as a result of the occurrence of TC and good interfacial adhesion for

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the semicrystalline polymer matrix; 2) SPCs show undoubtedly advantages in terms of recyclability. Hence, up to now, many preparation methods of iPP based SPCs have been proposed [20–22] and summarized in the recent literature [23–25]. However, although the influences of crystallization temperature, fiber introduction temperature, fiber molecular weight, and matrix molecular mass on the interfacial morphology of iPP based SPCs have been investigated [26–29], the effect of interfacial features on the mechanical properties of SPCs has been rarely reported up to date.

In this paper, iPP fiber was introduced into iPP film to prepare iPP based SPCs. The interfacial features of SPCs and their tensile strength as a function of introduction temperature were investigated. The underlying origin for the improved tensile strength of SPCs is discussed based on the results of polarized optical microscopy (POM), scanning electron microscope (SEM), wide-angle X-ray diffraction (WAXD).

2. Experimental

2.1. Materials

The iPP (T30S) employed in this work was a commercial grade iPP, provided by Dushanzi Petroleum Chemical Co. Ltd, China. Its melt flow index (*MFI*) and weight-average molecular weight (M_w) were 3.0 g/10 min (230 °C, 21.6 N) and 39.93 × 10^4 g/mol, respectively.

2.2. Melt spinning

The iPP fibers used in this work were melt spun by using a mini co-rotating twin-screw extruder (SJSZ-10A, Wuhan Ruiming plastic and mechanical Co. Ltd) with a length-to-diameter ratio (L/D) of 16 and a die diameter of 3.0 mm. The temperature of both barrel and die was 200 °C. The spun fibers were air-cooled and taken up by a winder. To obtain the finest fibers, the screw speed and the take-up speed were maintained at 1 rpm and 30 m/min, respectively. In the case of the highest take-up speed, it produces a fiber with a draw ratio (area of extruder die vs. section area of iPP fiber) of 100. The average diameter of the as-prepared iPP fibers was ca. 30 um. The iPP fibers were first rinsed several times in acetone with the aid of ultrasonication, then cleaned with deionized water, and finally dried in a vacuum oven at 40 °C for 5 h. The melting behaviors of iPP fibers and granules were obtained by differential scanning calorimeter (DSC) method, which are shown in Fig. S1 in Supplementary data. Compared with iPP granules, iPP fibers have a higher melting point, which provides a prerequisite for the SPCs preparation. At the same time, molecular orientation, crystal modification and tensile strength of iPP fiber were also investigated, which are shown in Fig. S2, S3 and S4 in Supplementary data.

2.3. SPCs preparation

Firstly, iPP thin film as matrix was prepared by compression-molding at 200 °C with a pressure of 10 MPa. The resultant iPP thin film was subsequently heated in a well-controlled hot stage (Linkam, THMS600) at 200 °C and maintained for 10 min to remove any possible thermal history effects. Then, the iPP thin film was cooled at a rate of 30 °C/min to the preset temperature (viz., introduction temperature, T_i), where the film was maintained in the molten or supercooled molten state. Once the molten or supercooled molten iPP thin film reached an equilibrium at T_i, the iPP fiber supported by a metal frame was introduced into the film (iPP matrix). Subsequently, the sample was cooled quickly to the isothermal crystallization temperature (T_c, 134 °C) at a rate of 30 °C/min, at which the isothermal crystallization of SPCs was allowed for 10 min. The iPP fiber quality content, viz., volume content (C) of SPC is calculated as 0.59% (C was estimated as the fractional area occupied by iPP fiber in the entire tensile sample). The thermal history of SPCs preparation was shown in Fig. 1. For comparison, the pure iPP film without fiber introduction was also prepared with the same thermal history as that of SPCs. According to the melting behavior of iPP fibers (shown by Fig. S1 in Supplementary data), the iPP fiber introduction temperature (T_i) used in this study was selected as 145, 160, 165, 168, 172, and 175 °C, respectively. In a convenient manner, the SPCs prepared at different T_i were labeled as SPC-X and the iPP fibers experienced the same thermal history as that of SPCs were labeled as F-X, where X represents T_i. For example, "SPC-145" denotes a sample prepared at $T_i = 145$ °C, while "F-145" denotes the fiber experienced the same thermal history as that in SPC-145.

2.4. Characterizations

Polarized Fourier Transform Infrared Spectroscopy (FTIR) spectrometer equipped with a hot stage (Linkam, THMS600) under a flowing nitrogen atmosphere was employed to analyze the relationship between molecular orientation and T_i. Before measurements, the iPP fiber was tightly fixed on a metal frame between two parallel ZnSe plates. The iPP fiber was first heated to T_i and held for 2 min, then cooled quickly to T_c (134 °C) at a rate of 30 °C/min. At 134 °C, the isothermal crystallization of iPP fiber was also allowed for 10 min. Finally, the molecular orientation of iPP fiber was qualitatively investigated by the FTIR equipped with a polarizer (NICOLET 6700). The resolution was set as 2 cm^{-1} with an accumulation of 32 scans. The scanned wavenumber range was from 400 to 4000 cm^{-1}.

Tensile strength of SPCs was determined by a universal tensile test machine (UTM2203, Shenzhen Suns Technology Stock Co., Ltd, China) with a load cell of 100 N and under a crosshead speed of 0.5 mm/min at room temperature. The mean and standard deviation were reported based on at least ten samples. Before test, the samples after isothermal crystallization were quenched immediately into a mixed ice/water solution to preserve the crystalline morphology. The SPCs were cut into rectangular geometry (10 × 2 × 0.06 mm^3) for mechanical test.

To observe the interfacial crystallization of SPCs, an Olympus BX51 POM equipped with a hot stage (Linkam, THMS600) was used in this study. The pictures were taken automatically to record the evolution of interfacial morphology at a regular time interval. Furthermore, the morphology of tensile fractured zone of SPCs was also observed by POM.

To characterize the crystalline structure of SPCs, two-

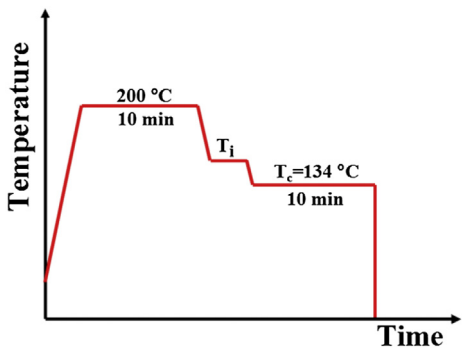

Fig. 1. Schematic of thermal history as a function of time. T_i represents the iPP fiber introduction temperature (i.e.,145, 160, 165, 168, 172, and 175 °C).