



Electrospun-fiber induced transcrystallization of isotactic polypropylene matrix

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ABSTRACT

To reveal the influences of fiber diameter and characteristics on the surface-induced matrix crystallization, four different fibers, i.e. syndiotactic polystyrene (sPS), Nylon 6, and polyhydroxyamide (PHA) and poly(p-phenylene benzobisoxazole) (PBO) fibers, were used to study their nucleating abilities towards isotactic polypropylene (iPP) matrix. Among them, micron-sized PBO fibers were obtained from the supplier, whereas submicron-sized fibers of sPS, Nylon 6 and PHA were prepared by the solution electrospinning process developed in this laboratory. To resolve the observation difficulty due to the fast nucleation rate and crystal growth at high supercooling degrees ($>60\text{ }^{\circ}\text{C}$), a high speed camera was mounted on the polarized optical microscope equipped with a hot stage to successfully snapshot the corresponding processes at various crystallization temperatures (T_c) in the range of $96\text{--}120\text{ }^{\circ}\text{C}$. For all the active fibers, only α -form iPP transcrystallites were observed at the fiber/matrix interface. Two crucial parameters were proposed for characterizing the fiber nucleating ability, i.e. the interfacial free energy difference ($\Delta\sigma$) based on the heterogeneous nucleation from a thermodynamic point of view, and the maximum temperature for transcrystalline layer observed (T_{\max}) based on a kinetic consideration. Values of $\Delta\sigma$ for different fibers were derived on the basis of the tertiary nucleation taking place in the selective “grooves” at the fiber surface. It was found that the nucleating rate of sPS fibers was scaled with the fiber diameter, and $\Delta\sigma$ showed a negligible diameter dependence, but T_{\max} slightly increased with increasing fiber diameter. For all the fibers investigated, an intimate relation between the $\Delta\sigma$ and T_{\max} was derived and used to compare their nucleating abilities.

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1. Introduction

When fibers are introduced in a semicrystalline polymer matrix, under certain circumstances, a highly oriented crystal layer with the chain axis parallel to the fiber axis is observed at the fiber/matrix interface. This distinct morphology is termed the transcrystalline layer (TCL) and is resulting from a profound nucleation density at the fiber interface in comparison with that in the bulk, in which conventional spherulites are developed. TCL exhibits a higher Young's modulus but less ductile behavior than the bulk spherulites [1,2]. Due to the restricted lamellar growth in a direction perpendicular to the fiber surface, anisotropic modulus in the TCL has recently been measured using the nano-scale shear and indentation technique [3]. On the basis of the heterogeneous nucleation theory, the interfacial free energy difference of the crystallizing polymer chains at the fiber surface ($\Delta\sigma_{\text{TCL}}$), and that in the bulk ($\Delta\sigma_{\text{B}}$) are readily determined and compared with each other for predicting the TCL formation from a thermodynamic point

of view. By studying the ultra drawn PE fibers embedded in the PE matrix, Ishida and Bussi [4] proposed that TCL is likely to develop at the fiber surface provided that $\Delta\sigma_{\text{TCL}}$ is lower than $\Delta\sigma_{\text{B}}$. However, several investigations demonstrated that this criterion is merely a sufficient condition, not a necessary one [5,6]. In other words, TCL is also observed for a system with $\Delta\sigma_{\text{TCL}}$ larger than $\Delta\sigma_{\text{B}}$, suggesting that other kinetic factors should be taken into account for the TCL development. Similar with the PE fibers/PE system, Sun *et al.* [7] recently reported that isotactic polypropylene (iPP) fibers could also induce the transcrystallization of iPP matrix at its surface. Thomason and Van Rooyen [8] have carried out a detailed study on the iPP transcrystallization on various fibers and they concluded that TCL formation is relevant with the magnitude of thermal stress at the fiber/matrix interface induced by the mismatch of thermal expansion coefficient between the *solid fiber* and *melt*. In addition to the fiber-pulling [8], temperature gradient is also a practical means to generation TCL at various fiber surfaces [9]. Many mechanisms have been suggested with an attempt to account for the plausible origin for the TCL formation; however, none of them could be successfully applied to all the cases reported. A review article of the recent progress of TCL research provided a good comparison among them [10]. Regarding the TCL effect on the

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interfacial strength, moreover, controversial results obtained from different analytical techniques were often found in various fiber/polymer composites. Basically, two principles are frequently applied for characterizing the interfacial strength; one is based on the stress criterion which is more readily to apply due to its simplicity, the other is based on the fracture energy criterion, which possesses more underlying physics and is independent of the specimen geometry. Using the micro-debonding test, Chen and Hsiao [11] showed that the presence of TCL could increase ca. 40% in the debonding force in the poly-ether-ketone-ketone composites with various fibers such as Kevlar, pitch-based carbon, and PAN-based carbon fibers. However, the matrix crystallinity was varied in the single-fiber composites with TCL (~28%) from that without TCL (0%), suggesting the difference in the mechanical strength for a comparison basis. Using a sophisticated method of asymmetric double cantilever beam test, Cho *et al.* [12] were able to determine the adhesive fracture energy (G_a) between iPP and the surface-modified silicone substrate with the presence of TCL at the interface. They found that the thicker the TCL thickness, the higher the measured G_a due to the variation of failure locus. By means of the micro-bond test, Gati and Wagner [13] reported that the presence of TCL produces little, if any, effect on the measured G_a in the Kevlar 149/poly(caprolactone) single-fiber composites. Based on the conventional single-fiber pull-out test with the introduction of frictional stress at the debonded region, we have shown that the presence of TCL does not promote the level of adhesion in the PTFE fiber/iPP single-fiber composites, whereas the frictional stress at the interface is enhanced when samples are crystallized at high temperatures [14].

Discovered by Iijima in 1991 [15], carbon nanotubes (CNTs) are known as the strongest materials with a Young's modulus of $\sim 10^3$ GPa, and a diameter of ~ 2 nm for single-walled CNTs and ~ 20 nm for multi-walled CNTs. The nano-scale diameter together with a large aspect ratio (~ 1000) makes the CNT-related composites more attractive in the practical applications than the conventional carbon fibers, which possess a diameter of ~ 10 μm . Although development of TCL at the single CNT surface has been occasionally reported using electron microscopy [16], difficulties have been encountered to monitor the evolution of TCL at the CNT surfaces due to its extremely tiny diameter. Zhang *et al.* [17] have used CNT bundles, instead of single CNT, with a diameter of 10 μm to readily nucleate a columnar structure of iPP. An intriguing question is immediately raised: what is the effect of fiber diameter on the crystallizing matrix? Or, does the nucleation ability of fibers depend upon its diameter? To resolve this unexplored issue left to date, in this study a series of syndiotactic polystyrene (sPS) fibers with various diameters in a range from 300 nm to 6 μm are prepared using the electrospinning technique operated at an elevated temperature. Fibers in such a diameter range make it more feasible to trace the crystallization kinetics of TCL, if occurs, under optical microscopy. In addition to electrospun sPS fibers, electrospun Nylon, and polyhydroxyamide (PHA) fibers together with the commercial poly(*p*-phenylene benzobisoxazole) (PBO) fibers are also used to investigate their abilities to induce the nucleation of iPP. PBO fibers are noted for their better tensile strength and modulus than the Kevlar fibers, whereas their nucleation ability towards polypropylene matrix is still unknown yet. Combined with previous findings on other fiber types (Kevlar, carbon, PET and PTFE) [5], nucleation abilities of seven active fibers towards the same batch of iPP are compared and the results will be discussed in terms of $\Delta\sigma$. Although plausible mechanisms for the TCL formation have been offered by various authors in the past, none of them could be applicable to all the reported circumstances. In this paper we shall show that in quiescent crystallization the transient thermal stress, which is associated with the transient temperature

evolution in the fibers, is the driving force to induce the aligned segments of iPP chains adjacent to fibers. These oriented chain segments are parallel with the fiber surface, serving as the nucleation precursors for TCL formation. Since fiber surface consists of many "grooves" (or steps) of various heights, the potential nuclei are most likely to locate in these grooves provided that the groove length is sufficiently larger than the critical lamellar thickness, l^* , to fulfill the tertiary nucleation, which is a less energy process than the secondary nucleation.

2. Experimental

2.1. Materials

The same batch of iPP powder used for our previous TCL studies [5] was applied in this study; it had a viscosity average molecular weight (MW) of 2.8×10^5 g/mol. Commercial PBO fibers with a diameter of 15 μm were supplied by Dow Chemical Co. Electrospinning process developed in this laboratory [18] has been successfully performed to obtain sPS, Nylon, and PHA fibers. To prepare sPS fibers with various diameters, electrospinning of sPS/*ortho*-dichlorobenzene (*o*-DCB) solutions with various concentrations was carried out at a solution temperature of ~ 140 °C. The sPS pellets were provided by Dow Chemical Co. with a weight average MW of 2.0×10^5 g/mol. The as-electrospun sPS fibers possessed a diameter ranging from 0.3 to 6.0 μm . For Nylon fibers, room-temperature electrospinning of 18 wt.% Nylon/formic acid solutions was conducted under the processing conditions of 0.1 mL/h, 15 kV and 7 cm for the tip-to-collector distance. The diameter of electrospun Nylon fibers was 0.37 ± 0.12 μm . The pellets of Nylon 6 were purchased from Polysciences, Inc. and its weight average MW was 3.5×10^4 g/mol. BisAPAF-IC PHA powders kindly provided by Prof. Hsu (NCKU) were synthesized from a low temperature polymerization of 2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (BisAPAF) and isophthaloyl chloride (IC). They were dissolved in the DMAc/THF co-solvent with a volume ratio of 1/9 to form a 20 wt.% solution first, then the homogeneous solution was electrospun at room temperature to prepare PHA fibers with a diameter of 0.33 ± 0.12 μm [19].

2.2. Measurements

The testing fibers were covered with iPP powders and placed in a well-controlled hot stage (Linkam, THMS600) at a temperature of 200 °C for 10 min to homogenize the iPP melts. Then, the samples were cooled at a rate of 100 °C/min to the desired temperature (T_c) for isothermal crystallization. Dry nitrogen was introduced to eliminate the plausible thermal degradation. Crystallization of iPP on the fibers was monitored with a polarized optical microscope (POM, Leica DMLP) equipped with phase contrast lens and two different CCD systems. For the high T_c range above 125 °C, a conventional CCD (Leica, DFC420) with a frame speed of 4 frames/10 s was sufficient to catch the nucleation evolution of iPP at the fiber surface. In contrast, a high speed CCD camera (Redlake, Motion Pro 10000) was used for the low T_c range due to the rapid nucleation and crystal growth of iPP at high supercooling degrees. The number of iPP nuclei at the fiber surface was accounted at selected time, and the nucleation density on fibers was expressed by number of nuclei per unit length of fiber. The sample thickness was controlled to be ca. 20 μm in all cases. At a given T_c , the nucleation rate (I) was determined from the linear slope of the plots of nucleation density versus elapsed time, and the intercept of the time axis provided the induction time (t_i). Experimental details have been reported in our previous paper [5]. Fiber surface was investigated by atomic force microscopy (AFM) in the tapping mode

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