Highly efficient load transfer in polypropylene/vapor grown carbon fiber nanocomposites

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ABSTRACT

The alignment of fillers and the filler–matrix interfacial adhesion are crucial factors for improving the mechanical properties of nanocomposites. This study focuses on these effects in the melt-spun vapor grown carbon fibers and polypropylene (VGCFs/PP) composite fibers. By using different draw ratio, the alignment of VGCFs and the interfacial crystalline structure in the as-spun fibers can be easily controlled. Tensile testing showed that remarkable enhancements in tensile strength and modulus were achieved at high draw ratio. Topographic analysis of the fractured surfaces indicated that the enhancements were directly related to the strong interfacial adhesion and effective stress-transferring effect during the tensile test. Further analysis showed that the strong interfacial adhesion might be the result of stretching-induced transcrystalline structure. Our study sets a good example to realize a remarkable reinforcement in semicrystalline polymer composites by controlling the interfacial adhesion and filler alignment in a simple but efficient way.

1. Introduction

Nanocomposites have drawn many attentions from scientists and engineers in recent decades, due to their excellent physical and chemical properties [1–3]. Many works have been done, particularly in the field of nanofillers reinforced composites. Usually, one-dimensional nanofillers with large length-diameter ratio, high specific strength and modulus are incorporated in polymers as reinforcing agents [4–6]. Considerable experiments and theoretical investigations show that remarkable improvement in mechanical properties can be achieved with relatively less mass fraction of nanofillers than that of the conventional fillers [7–9]. It has been generally recognized that in order to realize a satisfying reinforcement of the one-dimensional nanofillers three crucial conditions have to be achieved: (1) the homogenous dispersion of nanofillers; (2) the good interfacial adhesion between matrix and nanofillers; (3) the well alignment of nanofillers in certain direction.

Carbon nanotubes (CNTs) possessing superior strength and stiffness are thereby considered as ideal reinforcing fillers for polymers. However, the expensive price and the difficulty in dispersion inhibit their extensive application as reinforcement. Vapor grown carbon fibers (VGCFs), which are fabricated through the decomposition of hydrocarbons over metal catalysts at high temperature with annular carbon layers arranged like a tree ring structure, are more economical than CNTs [10–12]. With a high aspect ratio

and nano-sized diameter ranging from 50 to 200 nm, it processes excellent mechanical, thermal and electrical properties [13,14]. The relatively low cost and easy availability (the simplicity of the growth process) of VGCFs make them ideal substitute for CNTs as reinforcing agent. VGCFs/polymer composites reported in literatures have shown increased mechanical properties through improving interfacial adhesion or/and filler alignment [15,16]. However, the efforts made in strengthening the interfacial adhesion between VGCFs and matrix usually involve chemical modifications which always need complicated preparation procedures with long preparing period [17,18]. Thus, developing a simple but effective physical method to prepare polymer/VGCF composites with high performance remains a great challenge.

Many heterogeneous fillers were reported as good nucleating agents for polymer crystallization and in recent years, the interfacial crystallization on filler surfaces is reported an effective and economical physical way to enhance interfacial adhesion between semicrystalline polymer matrixes and fillers [19–21]. Flow field widely existing in common polymer processing significantly affects the orientation of polymer chains and fillers, and the crystalline morphology, as well as the ultimate mechanical properties of polymer composites [22,23]. Therefore, the effects of the fillers and flow on the crystallization and mechanical properties have gained much attention from researchers. The aligned anisotropic fillers under shear acted as nuclei stabilizer, providing surface where the polymer lamella can epitaxial grow and the induced oriented structure is helpful to the mechanical enhancement of the polymer composites [24,25]. In polymer/VGCF nanocomposites,

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VGCF was also reported a good nucleating agent for polymer crystallization [26,27]. Therefore, in this study, one of our goals is to control the interfacial adhesion by producing different interfacial crystalline structures under extensional flow.

In the present study, a simple but widely used fiber spinning technology is exploited to prepare polypropylene/VGCF composite fibers. We attempt to control the alignment of VGCFs and the interfacial adhesion in the as-spun fibers by adopting different draw ratios and focus on the mechanical properties of the composite fibers and the load-transferring effect between the matrix and VGCF during the tensile deformation. More importantly, the relationship between the stretching-induced interfacial crystalline structures and interfacial adhesion is also discussed.

2. Experimental section

2.1. Materials

Polypropylene (PP) used as polymer matrix was supplied by Dushanzi Petroleum Chemical Incorporation (Xinjiang, China), with $M_w = 39.9 \times 10^4$ g/mol and $M_w/M_n = 4.6$. The vapor grown carbon fiber with a density of 2.0 g/cm^3 was provided by Showa Denko KK, Japan and its diameter and length are about 80–150 nm and 10–20 μm respectively.

2.2. Sample preparation

The Polypropylene and VGCF composites were prepared by melt blending process in different composition (0.5, 1, 2 wt.%, denoted as 0.5CPP, 1CPP, 2CPP hereafter) by using a TSSJ-25 co-rotating twin-screw extruder with the barrel temperature of 170–200 °C, and the screw speed was 120 rpm. The pure PP was also processed in the same situation as the control group. All the obtained materials were pelletized into granules. And after dried for 12 h in a vacuum oven, the granules were melt spun into monofilaments at 200 °C by using a capillary rheometer (Rosand RH70, Malvern, Bohlin Instruments) with a die diameter of 1.0 mm and length-to-diameter ratio of 16. All the extruded composite fibers were air-cooled and collected under tension by a windup spool. By adjusting the take-up speed, fibers with different draw ratio were prepared. The draw ratio, defined as the section area of the capillary die versus that of the fibers, is about 20 for 20 m/min take-up speed and 200 for 150 m/min take-up speed, in which the former speed is served as the low draw ratio (LDR) and the latter one as the high draw ratio (HDR) respectively. The typical diameter is 70 μm and 240 μm for the fibers obtained at high and low draw ratio. The as-spun fibers were labeled according to the mass percent of VGCF and the draw ratio in a terse manner; for example, 2CPP-L and 2CPP-H represent the PP/VGCF composite fibers with 2 wt.% VGCFs prepared at low and high draw ratio, respectively. In the same way, pure PP fibers fabricated at LDR and HDR are marked as PP-L and PP-H.

2.3. Characterizations and measurements

The tensile tests were carried out on an Instron 5567 universal testing machine with a 100 N load cell with a crosshead speed of 50 mm/min at room temperature (23 ± 2 °C). The gauge length was 10 mm and all the values were calculated as the average of at least five specimens for each composition.

Raman spectrum measurement was conduct on a micro-Raman spectrometer (Renishaw) equipped wtih a Leica microscope. The laser with 514.5 nm was excited by 136 M He+ resource. The laser power is 1.7 mW and the laser spot is 2 μm in diameter. To estimate the orientation of the VGCFs in composite fibers, the measurement was made when fiber was at 0° and 90° to the polarized laser light. So, the direction of the E-vector of the polarized laser light was parallel and perpendicular to the fiber axis.

The 2D-WAXS measurements were carried out by using micro X-ray source (Incoatec, GmbH). Bruker Hi-star detector was used. The radiation wavelength is 0.154 nm. The samples were placed with the orientation (stretching direction) perpendicular to the beams. The backgrounds of all the 2D-WAXS patterns had been subtracted, which allowed a qualitative comparison between various samples. Azimuthal scans (0–360°) of 2D-WAXS were made for the (040) plane of PP at the step of 1°. The orientation degree of crystal plane could be estimated by calculating the orientation parameter f from formula (1) and (2) [28]:

$$f = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \tag{1}$$

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi \, d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi \, d\phi} \tag{2}$$

where ϕ is the angle between the normal direction of a given (hkl) crystal plane and the drawing flow direction, and $I(\phi)$ is the scattering intensity at ϕ.

The fractured surface and the interfacial crystalline structure of the composite fibers were observed by an FEI Inspect F scanning electron microscope (SEM) instrument at an acceleration voltage of 20KV. For characterizing the crystallization structure of the fibers, the melt-spun fibers were etched for 2 h in a solution containing 1.3 wt.% potassium permanganate (KMnO$_4$), 32.9 wt.% concentrated sulfuric acid (H$_2$SO$_4$) and 65.8 wt.% concentrated phosphoric acid (H$_3$PO$_4$), according to the procedure proposed by Olley and Bassett [29] and then the surface was coated with a layer of gold.

A Leica DMIP polarizing light microscope (PLM) equipped with a Linkam THMS 600 hot-stage was used to observe the crystallization morphologies of the composite fibers. The composite fiber of about 0.5 cm in length placed between two microscope glass slices was heated to 180 °C with the heating rate of 50 °C/min, maintained for 2 min and then cooled down to 80 °C at the cooling rate of 5 °C/min. The crystallization morphology of the sample was recorded by taking photographs with a digital camera at a constant time intervals.

3. Results and discussion

3.1. Mechanical properties of PP/VGCF composite fibers

The typical stress–strain curves of PP/VGCF composite fibers fabricated at different draw ratios are presented in Fig. 1a and b; the modulus and tensile strength (strength at break) of the composite fibers versus the VGCF contents are shown in Fig. 1c. For the LDR fibers, the tensile strength and modulus of pure PP samples are improved from the 78 ± 2 MPa to 84 ± 7 MPa (8% increment) and 0.81 ± 0.02 GPa to 1.11 ± 0.02 GPa (39% increment) respectively with VGCF content increasing from 0.5 wt.% to 2 wt.%. The increase in the strength and modulus of the fibers are very limited under low draw ratio, namely, the enhancement of VGCFs for the PP fibers is unconspicuous at low draw ratio.

However, one can easily find that the remarkable improvement of tensile properties of composite fibers is achieved by adopting high draw ratio. The tensile strength and modulus of the fibers are gradually increased with the increasing VGCF content (in Fig. 1c). The tensile strength and modulus of composite fibers are improved from 154 ± 7 MPa to 245 ± 11 MPa (59% increment) and 1.13 ± 0.04 GPa to 2.21 ± 0.10 GPa (96% increment) with the VGCF content variation from 0 wt.% to 2 wt.% respectively.