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Orientation in high-density polyethylene/inorganic whisker composite fibers as studied via polarized Fourier transform infrared spectroscopy

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ABSTRACT

In this article, a quantitative measurement of orientation functions for both the polymer matrix and the filler has been carried out, for the first time, in high-density polyethylene (HDPE)/inorganic whisker (SMCW) composite fibers, with aid of polarized Fourier transform infrared (FTIR) spectroscopy. A highly oriented structure was observed in the as-spun fibers, and the orientation functions of both polyethylene and the whisker decreased with the increase of whisker content. During tensile deformation of the fibers, the orientation functions were continuously enhanced as increasing of the strain for the matrix and the filler. However, a fast increase of orientation was found for pure polyethylene fiber and composite fibers with less whisker content, and a slow increase for composite fibers with higher whisker content. Very interestingly, a formation of hybrid shish-kebab structure with whisker acting as shish and polyethylene lamellae as kebab was observed in the as-spun fiber with low loading of whisker (less than 10 wt.%), resulting in a strong interfacial interaction between polyethylene and whisker. As a result, the highest tensile strength was observed in this sample even it had a lower orientation compared with that of pure HDPE. For the composite fiber with 10 and 20 wt.% whisker, no obvious formation of hybrid shish-kebab was observed, resulting in a poor interfacial interaction and subsequently, lower tensile strength. That result indicates that the tensile strength of the fibers depends not only on the orientations of the polyethylene and the whisker, more importantly, on the interfacial interaction between matrix and the filler. The change of orientations of the composite fibers by adding whisker and the formation of hybrid shish-kebab structure were discussed based on rheological measurement.

1. Introduction

Polymer composites have been attracted a great attention due to their academic and industrial importance. It is well-established that the composites exhibit unusual and valuable mechanical, thermal and other special properties when compared with pure polymers [1–5]. Many properties especially the mechanical properties of a composite depend on the natural characteristics and the orientations of both the matrix and the filler [6–8], as well as the interface interaction [9]. For a composite with fixed matrix and filler, the control of the orientations of the two components and the interface interaction will be the first consideration to obtain high performance polymer composite. To determine the orientation function (order parameter) of the polymer matrix, polarized Fourier transform infrared (FTIR) spectroscopy is one of the most frequently tools besides other techniques such as two dimensional X-ray diffraction/scattering (2D-WAXS and SAXS), birefringence, Raman depolarization and sonic techniques [10–15]. However, the determining of ordered parameter of the filler in the composite is always a difficult work. It is usually analyzed by TEM, but hard to be quantitatively calculated [16–20]. In the process of deformation, both the matrix and the filler will undergo further orientation, one needs to know the change of orientations for both the polymer and the filler, for better understanding of the reinforcing mechanism. To the best of our knowledge, the quantitatively determining the change of orientation for both the polymer and the filler in composites during tensile deformation is seldom documented [19,21].

As for the interface interplay, good adhesion leads to efficient stress transfer between the polymer matrix and the dispersed filler in a composite, which helps the material absorb energy and improve the mechanical properties [22–24]. Many works have been focused on the importance of the chemistry used to modify the surface of the fillers and improving the adhesion between the filler and the matrix using coupling agents. On the other hand, some fillers have nucleating effect and polymers can crystallize on them, resulting in improved interface interaction. Transcrystallization, for example, can improve the interfacial adhesion effectively and economically. Thus it is of particular interest to study such surface-induced crystallization [25–27]. Additionally, hybrid shish-

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kebab (HSK) structure, in which the filler (carbon nanotube or whisker) acts as shish and induces polymer (PE or nylon 6) crystal lamellae (kebab) periodically decorating on its surface and aligning approximately perpendicular to its long axis, has been recently reported, and shows great potential to enhance the interfacial interaction for polymer composites [28–37].

Whiskers are fiber-shaped single crystals. They have large length/diameter ratio and the diameter is much larger than carbon nanotubes (CNTs) but much smaller than common fibers. Whiskers could reinforce thermoplastics more effectively for they have much higher specific strength. A lot of works have been focused on the preparation of various polymer/inorganic whiskers composites [38–41]. Recently, organic whiskers such as cellulose whisker and chitin whisker become a fascinating research field, mainly due to their intriguing mechanical properties, widely availability and biodegradability [42–44]. Therefore, whiskers are considered to be an attractive alternative to short glass or carbon fibers for reinforcing thermoplastics and have attracted considerable interests of scientists and engineers. In our previous work, a new type of SiO_2–MgO–CaO whisker (SMCW) and HDPE composites were prepared and the crystal morphology was investigated. A hybrid shish-kebab (HSK) structure has been observed in the injection molded bar of PE/SMCW composites. In this HSK structure, SMCW acted as shish and induced PE crystal lamellae (kebab) periodically decorating on its surface and aligning approximately perpendicular to its long axis under the function of shear [36,37].

In this work, we will quantitatively analyze the orientation of the matrix and the rod-like filler in the high-density polyethylene (HDPE)/inorganic whisker (SMCW) composite fiber, focusing on the orientation and interface debonding in the composite fibers with different compositions under tensile deformation. Due to the scientific importance and technical significance, we also pay attention to the possible formation of hybrid shish-kebab structure in the fibers. The contributions of the orientations of the matrix and the filler, the composition and the interface interplay to the tensile strength, are included. For this reason, firstly the composites with different compositions of whisker were prepared by co-rotating twin-screw extruder, and then the fibers were obtained via melt spinning from a capillary rheometer. The orientations of HDPE and whisker in the as-spun and stretched fibers were investigated mainly with aid of polarized FTIR. The crystalline and phase morphology, especially the interface debonding of the fibers, were examined by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

High-density polyethylene (HDPE) ($Mw = 1.2 \times 10^5$ g/mol), supplied by Fushun Petrochemical Corp., had an MFI of 20 g/10 min and a density of 0.96 g/cm^3. The whisker with a density of 3.0 g/cm^3 was produced in Mianyang Guangda Company (Sichuan, China), which obtained mainly from tremolite and had pairs of chains of silica tetrahedra linked together extend infinitely in one direction within the crystal [45]. Its diameter ranged from 0.2 to 2 μm (mainly from 0.2 to 0.5 μm), and its length was in the range of 5–50 μm. Silicohydride (KH-550), supplied by Chenguang Research Institute of Chemical Industry (Chengdu, China), was used as the coupling agent for SMCW treatment.

2.2. Modification of SMCW and preparation of the samples

The SMCW was treated with 10 wt.% KH-550 solution for 8 min in a high-speed mixer, the exposed in air and dried, which was introduced in our previous work [46].

HDPE and treated SMCW with various compositions were melt blended using a TSSJ-25 co-rotating twin-screw extruder with a barrel temperature of 150–200 °C and a screw speed of 110 rpm. After pelleting and drying, the composite fibers (monofilaments) with a diameter of about 50 μm were melt-spun from a capillary rheometer at 190 °C with a take-up speed of 6 m/min. The as-spun fibers were labeled according to the weight content of whisker. For example, 5WPE represented the composite fiber with 5 wt.% whisker.

2.3. Characterizations and measurements

2.3.1. Fourier transform infrared (FTIR)

The orientation of the composite fibers during stretching was monitored by a Thermo Nicolet FTIR spectrometer with an MCT detector coupled with a mini-stretcher at ambient temperature. The schematic diagram of the experimental setup could be seen elsewhere [47]. An adjustable aperture was used to obtain desired micro-sampling size. Thus, the sampling size was constant (200 μm) along the fiber axis and equal to the transient diameter of the stretched fiber in the transverse direction. During measurements the fibers were stretched step by step at a rate of 2 mm/min along the filament axis. The strain ε, defined as $\varepsilon = (l - l_0)/l_0$ (l, l_0 was the transient and initial length, respectively), was precisely measured by the extension of a preprinted inkmark on the fibers. At each strain, polarized infrared spectra (by rotating a ZnSe polarizer), parallel and perpendicular to the fiber axis, respectively, were collected with a resolution of 4 cm^{-1} and total 64 scans were added. Note that the micro-sampling position was the same for each strain, which was realized by moving the sample stage under a CCD view system of the IR microscope. The orientation functions of the as-prepared fibers were also obtained. The orientation function f and structural absorbance A of a desired absorption band were deduced using following relations [48]:

$$f = [(R-1)/(R+2)]/\left[(3\cos^2\alpha - 1)/2\right] \quad (1)$$

$$R = A_{\parallel}/A_{\perp} \quad (2)$$

where $A_{\parallel}$, $A_{\perp}$ was the parallel and perpendicular absorbance, respectively, and α was the angle between the dipole moment vector and the local chain axis. Typical FTIR spectra in machine (S_M) and transverse (S_T) directions for both pure HDPE and the composite were shown in Fig. 1. To determine the orientation function of HDPE, some characteristic bands were examined. The peaks 730,

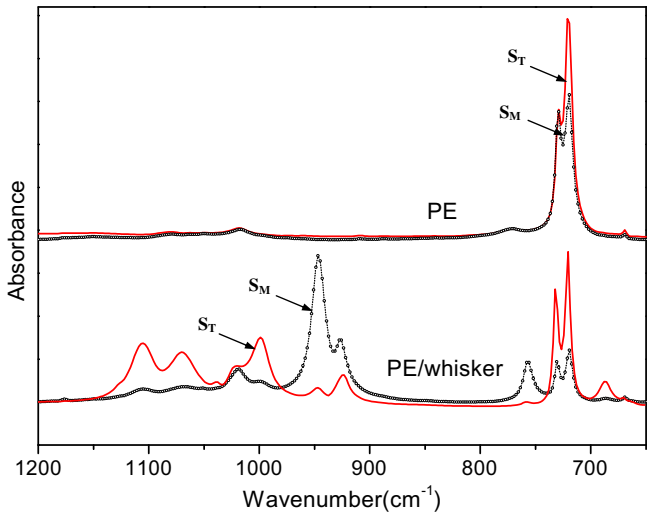

Fig. 1. Polarized FTIR spectra of both PE and the composite in machine (S_M) and transverse (S_T) directions.