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Original Research

Effect of TiO_2@SiO_2 nanoparticles on the mechanical and UV-resistance properties of polyphenylene sulfide fibers

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Abstract

In order to avoid the inherent photo-catalysis and aggregation of TiO_2 in PPS, TiO_2 nanoparticles were coated with SiO_2 layers, which were chosen as the UV absorbent to improve the UV stability of polyphenylene sulfide (PPS) fiber. The PPS–TiO_2@SiO_2 nanocomposites fibers were prepared via melt spinning, and the nanocomposites fibers displayed different crystallization behaviors on variation of the diameters of TiO_2@SiO_2 nanoparticles, as confirmed by Differential Scanning Calorimetry (DSC). The spinnability, breaking strength and UV-resistance properties of PPS nanocomposites fibers, as measured by homemade melt spinning machine, Xenon-lamp Weather Resistance Test Chamber and Yarn Tensile Tester, manifested the dependence on the diameters. The addition of nanoparticles with the diameter of 25 nm improved the spinnability and the mechanical performance of PPS most, which is attributed to the heterogeneous nucleation effect of nanoparticles. The UV-resistance properties of the PPS nanocomposites were improved by the addition of TiO_2@SiO_2 nanoparticles. After aging for 180 h, PPS nanocomposites fiber still maintained a high strength.

Keywords: Polyphenylene sulfide; TiO_2@SiO_2; Mechanical performance; UV-resistance; Filament

1. Introduction

In last decades, nanomaterial/polymer nanocomposites have attracted considerable attention [1–4]. Most of nanoparticles are used for mechanical reinforcement, as well as the flame resistance, thermal stability, electrical properties enhancement [5–8].

PPS fiber, a kind of high-performance fiber, has excellent heat resistance, corrosion resistance and flame resistance. However, due to the poor UV-resistance properties the breaking strength of PPS seriously degrade as exposed to sunlight [9]. In recent years, organic ultraviolet light stabilizers [10–14] and inorganic nanomaterials [15–19] were populated into polymer matrix to improve the UV stability of polymer. Organic ultraviolet light absorbents have been employed for stabilization of polymers for a long time. But they are easy to consumed and migrate from polymer. Moreover, the initial boiling temperature of organic UV absorbents is too low ($< 300\ ^{\circ}C$) to populated into PPS fiber. TiO_2, as a notable inorganic UV absorbers, have been widely used to stabilize polymers [20–24] due to their remarkable UV absorb performance and environmentally friendly nature. In previous studies, the PPS fiber containing TiO_2 has been intensively attempted to improve the UV stability of PPS fiber. When the content of TiO_2 was 1.5 wt%, the breaking strength retention of PPS composites fiber after UV degradation increased [25]. However, the breaking strength of PPS/TiO_2 nanocomposites fiber and the residual breaking strength were still too low because of the inherent photo-catalysis and aggregation of TiO_2 in PPS matrix. In order to solve these disadvantages, TiO_2 was coated with SiO_2 layer [26–29]. It shows that Rhodamine B was not photodegraded by TiO_2@SiO_2. The photocatalytic activity of TiO_2 is suppressed by the amorphous SiO_2 layer [27]. Moreover, the amorphous SiO_2 layer was able to reduce the hardness of

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rutile TiO_2, which was a good strategy to reduce the abrasion of the spinning components in the industrial production process.

In this work, PPS–TiO_2@SiO_2 nanocomposites fibers containing different sizes of TiO_2@SiO_2 were prepared. The non-isothermal crystallization behavior of PPS nanocomposites were determined by DSC. The effect of the dimension of TiO_2@SiO_2 on the structure and properties of PPS nanocomposites fibers were characterized by electron microscopy, thermal and mechanical analyses. The stability of PPS–TiO_2@SiO_2 fibers under the simulated sunlight was studied by the Xenon-lamp Weather Resistance Test Chamber.

2. Experimental

2.1. Materials

Fortron® linear PPS resins in the pellet forms (0309P4) were supplied by Ticona Polymers, a business of Celanese Chemicals. Three variations of TiO_2@SiO_2 (the diameter of TiO_2 are 25 nm, 60 nm and 100–200 nm, respectively.) were purchased from Jingruiz Co. China. Spinning oil (emulsion, DELION F-7422) were supplied by Takemoto Oil & Fat Co., Ltd. The surface of TiO_2@SiO_2 were modified by γ-(2,3-epoxypropoxy) propytrimethoxysilane.

2.2. Preparation of PPS–TiO_2@SiO_2 nanocomposites

Nanocomposites of PPS–TiO_2@SiO_2 were prepared by mixing TiO_2@SiO_2 nanoparticles into the PPS matrix using the twin-screw extruder at 295 °C. In this way, PPS nanocomposite samples contained 1.5 wt% of three variations of TiO_2@SiO_2, respectively. The neat PPS were also prepared under the same melt-blended conditions.

2.3. Spinning of nanocomposites

The nanocomposites fibers containing 1.5 wt% TiO_2@SiO_2 were prepared from home-made Melt spinning machine using a spinning nozzle with 36 spinnerets of 0.4-mm diameter each under the following conditions: the spinning temperature of 320–325 °C, the throughput of 1.2*30 cm^3/min, and the spinning speed of 600 m min^{-1}. In this way the pre-oriented isotropic fibers were prepared and drawn with the draw ratio of 4.3. The prepared nanocomposites fibers were labeled PPS resins, PPS–TiO_2@SiO_2-25 nm, PPS–TiO_2@SiO_2-60 nm, PPS–TiO_2@SiO_2-100 nm. The average fineness of PPS nanocomposites fibers were 3.91–4.07 dtex.

2.4. Photo-oxidative aging of nanocomposites fiber

The nanocomposites fibers were aged in the Xenon-lamp Weather Resistance Test Chamber for 20 h, 100 h, 180 h, respectively. The ambient temperature was 60 ± 3 °C, and the humidity was 60 ± 5%.

2.5. Characterization

2.5.1. Scanning electron microscope (SEM)

SEM images were taken by S-4800 FE-SEM. Both the cross-sectional area of PPS nanocomposites were undrawn yarn (cross-cut in liquid nitrogen). For the investigation, cross-cutfibers were placed vertically on an aluminum stage. Then all the samples gold sputtered before imaging.

2.5.2. X-ray diffraction (XRD)

Crystallinity of the fiber samples were carried out by a Rigaku D/max-2550 PC XRD over the range, 5–60°(2θ), using Cu Kα radiation ($\lambda = 0.15405$ nm). The fiber samples were cut into power before measuring.

2.5.3. Differential Scanning Calorimetry (DSC)

Non-isothermal crystallization behavior of nanocomposites resins and crystallinity of PPS nanocomposites fiber were carried out using a Netzsch 204F1 Differential Scanning Calorimeter. The crystallinities of nanocomposites fibers were examined. All DSC were performed under nitrogen atmosphere and the weights of sample were between 5 and 10 mg. The crystallinities (X_c) of the fiber samples were calculated from the following formula:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\varphi_i \Delta H_m^0} \quad (1)$$

where ΔH_m is the enthalpy of fusion; ΔH_{cc} is the enthalpy of cold crystallization, and φ_i is the mass fraction of PPS matrix. The value of ΔH_m^0 is the enthalpy of fusion for 100% crystallinity of PPS, which is 80.45 J/g [30].

2.5.4. Mechanical properties measurement

The mechanical properties and denier of the nanocomposites fibers were determined with XQ-1A tensile strength tester and XD-1 denieroscope at ambient temperature. The measuring length and deformation rate were 10 mm and 10 mm min^{-1} respectively. Twenty fibers of each sample were measured and the average values were reported. Because the oiling agent lost during the aging, the tensile strength of multifilament was unreliable. Thus, all the samples for tensile strength measurement were monofilament.

3. Result and discussion

3.1. Dispersion of TiO_2@SiO_2 inside PPS nanocomposites fibers

SEM images of cross-section of PPS composites fibers are shown in Fig. 1. After coated by SiO_2 layer, the dimensions of TiO_2 increased. TiO_2@SiO_2 was uniformly dispersed in the PPS fiber owing to the low polarity of TiO_2@SiO_2 and the increase interaction between PPS molecules and epoxy group. The good interfacial compatibility and homogeneous dispersion of TiO_2@SiO_2 in PPS matrix was the major effect factor of the spinnability, structure and mechanical property of PPS fiber. However, the oversize of TiO_2@SiO_2 (as shown in