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Surface modification of carbon fibers by a polyether sulfone emulsion sizing for increased interfacial adhesion with polyether sulfone

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ABSTRACT

Interests on carbon fiber-reinforced thermoplastic composites are growing rapidly, but the challenges with poor interfacial adhesion have slowed their adoption. In this work, a polyether sulfone (PES) emulsion sizing was prepared successfully for increased interfacial adhesion of carbon fiber/PES composites. To obtain a high-quality PES emulsion sizing, the key factor, emulsifier concentration, was studied by dynamic light scattering technique. The results demonstrated that the suitable weight ratio of PES to emulsifier was 8:3, and the resulting PES emulsion sizing had an average particle diameter of 117 nm and Zeta potential of −52.6 mV. After sizing, the surface oxygen-containing functional groups, free energy and wettability of carbon fibers increased significantly, which were advantageous to promote molecular-level contact between carbon fiber and PES. Finally, short beam shear tests were performed to evaluate the interfacial adhesion of carbon fiber/PES composites. The results indicated that PES emulsion sizing played a critical role for the enhanced interfacial adhesion in carbon fiber/PES composites, and a 26% increase of interlaminar shear strength was achieved, because of the improved fiber surface wettability and interfacial compatibility between carbon fiber and PES.

1. Introduction

During the past few decades, carbon fiber-reinforced thermoplastic composites have been an area of active research for both academic and industrial communities, because of their low weight and superior mechanical properties combined with cost-effective processing and recyclability [1]. Unfortunately, although excellent in-plane properties have been achieved from well-designed structures of composites, low interlaminar strength remains a serious issue [2].

Delamination is one of the most significant limiting factors for the reinforcing efficiency of carbon fibers, and mainly results from the weak interfacial adhesion between carbon fibers and matrices. To achieve strong interfacial adhesion in composites, many methods concerning surface treatment of carbon fibers have been performed including electrochemical treatment [3–5], liquid or gaseous oxidation [6–8], chemical grafting [9–11], plasma etching [12–15], high-energy irradiation [16–18], etc. These approaches can enhance the surface roughness and oxygen-containing functional groups of carbon fibers, but most of them are developed for the interfacial modification between carbon fibers and thermosetting polymers because of strong chemical interactions. In the case of thermoplastic composites, it is difficult for the functional groups supplied by thermoplastics to react chemically with the surface oxygen-containing functional groups of carbon fibers, and only limited success has been achieved from increased surface roughness and oxygen-containing functional groups [19]. During manufacturing of carbon fibers, fiber surface treatment is followed immediately by sizing process to obtain polymer coating onto carbon fibers that can promote interfacial adhesion of carbon fibers to matrix polymers. Therefore, new sizings are developed to enhance the interfacial adhesion in carbon fiber composites [20–22]. Sizing determines several key fiber characteristics, such as strand integrity, abrasive resistance, fiber processability and compatibility with matrix polymers. In view of the compatibility between carbon fibers and matrix polymers, the choice of sizing depends on the matrix to achieve the maximum degree of interfacial adhesion [23,24].

Polyether sulfone (PES) is a high-performance thermoplastic polymer with outstanding thermal stability, flexibility and flame resistance, widely used as a matrix for carbon fiber composites [25]. However, challenges with poor interfacial adhesion between carbon fiber and PES have slowed their adoption. Common sizings available for carbon fibers are various epoxy dispersion systems

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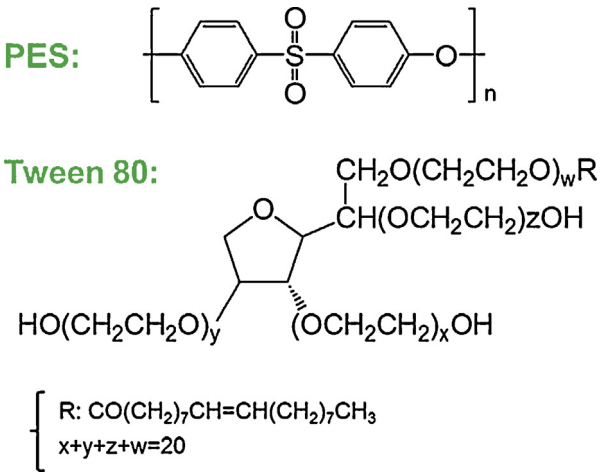

Fig. 1. Chemical structures of PES and Tween 80.

[26,27]. The epoxy sizing, however, is incompatible with PES and its degradation temperature (~250 °C) is obviously lower than the processing temperatures (>300 °C) of PES, which result in poor interfacial adhesion in carbon fiber/PES composites [28]. Yumitori et al. [29] used an amino-terminated PES solution as sizing to increase the interfacial adhesion between PES-sized carbon fibers and PES matrix, whereas the solution sizing had been abandoned in industrial production due to potential risks from organic solvents [30], such as polluting work environment, harming employees' health and eroding equipment. In our previous study [31], an organic solvent-free polyamic acid sizing was synthesized to improve the adhesion of the carbon fiber/PES interface, but the compatibility between the sizing resin and PES was still limited.

To combine the high compatibility of PES solution sizing with PES matrix and the characteristic of aqueous dispersion of PAA sizing, a PES emulsion sizing was prepared for the first time in this study. The emulsion characteristics were characterized by a dynamic light scattering technique to obtain a suitable concentration of emulsifier. The surface properties of PES-sized carbon fibers were analyzed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and a dynamic contact angle test. The interlaminar shear strength of carbon fiber/PES composites was measured with the short beam shear test.

2. Experimental

2.1. Materials

Carbon fibers, T700SC-12000-50C, were purchased from Toray industries, Inc. (Japan). Prior to use, carbon fibers were refluxed in acetone for 48 h to remove (desize) the surface sizing polymer. E2010 PES granules were obtained from BASF (Germany). Other chemicals were purchased from Shanghai Civi Chemical Technology Co., Ltd. (China). Chemical structures of PES and Tween 80 are shown in Fig. 1.

2.2. Preparation of PES emulsion sizing and sizing treatment

A typical procedure for the preparation of PES emulsion sizing is as follows. First, a 5% acetone solution of Tween 80 was added into deionized water, and a high-speed homogenizer was employed to disperse Tween 80 into deionized water with a mixing speed of 10 000 rpm for 30 min. Next, PES granules were dissolved in dimethylformamide (DMF) with a PES content of 25 wt.%, and further the PES solution was added slowly into the above emulsion of Tween 80 with a mixing speed of 10 000 rpm for 60 min.

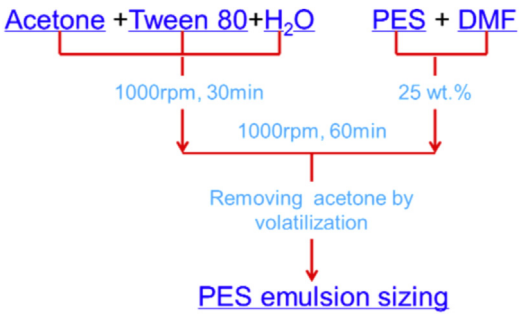

Fig. 2. Schematic for the preparation of PES emulsion sizing.

Finally, the PES emulsion sizing was obtained with the PES content of 1.0 wt.% by stirring for extra 48 h to remove acetone by volatilization, in which the weight ratio of PES to Tween 80 was 8:1 and the DMF concentration was 2.8 wt.%. In addition, PES emulsion sizings containing different weight ratios of PES to Tween 80 (4:1, 8:3 and 2:1) were also prepared by aforementioned procedures. All above steps are illustrated in Fig. 2.

Sizing treatment was carried out by a continuous impregnation process. Desized carbon fibers were pulled through the PES emulsion sizing, and subsequently dried in a hot gas oven at 180 °C. Then, a PES sizing layer was obtained on carbon fiber surface and the sizing content of the sized carbon fibers was 1.29 ± 0.08 wt.% (averaged from eight successful measurements).

2.3. Preparation of carbon fiber/PES composites

E2010 PES granules were dissolved in an acetone/cyclopentanone mixture of 1:2 by volume with PES content of 20 wt.%. Unidirectional prepregs were prepared by continuously dipping carbon fibers into the above PES solution, and then dried at 150 °C in a vacuum oven for 72 h. The carbon fiber/PES composite panels were manufactured by compression molding at 350 °C for 30 min under a pressure of 5 MPa. Finally, the composite panels were cut into specified samples by a diamond saw blade for short beam shear test.

Moreover, the fiber volume fractions of the composites reinforced by desized, as-received, Tween 80 sized and PES sized carbon fibers were 66%, 62%, 61% and 57%, respectively, which were determined according to ASTM D3171.

2.4. General characterizations

Particle size distribution and Zeta potential of the PES emulsion sizing at 25 °C were examined by a Nano ZS90 particle analyzer (Malvern, UK) with 10 samples for every type of sizing. SEM images were obtained on a JSM-6367LV electron microscope (JEOL, Japan) at 10 kV. XPS was performed by an ESCALAB 250XI electron spectrometer (Thermo Scientific, UK) with an Al Kα source.

2.5. Dynamic contact angle test

Dynamic contact angles were detected on a DCAT21 dynamic contact angle meter and tensiometer (Dataphysics, Germany) according to the Wilhelmy plate method at an immersion speed of 0.05 mm/s. The results were averaged from eight successful measurements. Deionized water and diiodomethane were chosen as testing liquids to determine the surface energy (γ), polar component (γ^p) and dispersive component (γ^d) according to Owens–Wendt method [32]. The properties of the probe liquids are listed in Table 1.