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Interfacial strength and debonding mechanism between aerogel-spun carbon nanotube yarn and polyphenylene sulfide

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ABSTRACT

The interfacial bonding properties between the carbon nano-tubes yarn and polyphenylene sulfide are investigated using the micro-bond test. Carbon nano-tubes yarn fabricated by floating catalyst chemical vapor deposition with a high Poisson's ratio of 3.5, and high-performance thermoplastic resin polyphenylene sulfide are used as matrix. In order to improve the tensile strength of the yarn so as to get sufficient data points for the micro-bond test for interfacial bonding strength, a pretreatment that combines drafting and dichloromethane shrinking processes is applied. The pretreated carbon nano-tubes yarn shows a 23% increase in tensile strength (from 117 to 144 MPa) and a 260% increase in initial Young's modulus (from 0.8 to 3.2 GPa). The effective interfacial shear strength is calculated to be 13.1 MPa and analyzed based on fracture mechanism of a mixed failure mode.

1. Introduction

Carbon nano-tubes reinforced thermoplastic composites have attracted increasing attention for their potential applications in many unique end uses owing to their attractive properties [1,2]. Polyphenylene sulfide resin is a high performance thermoplastic matrix in engineering. It is a semi-crystalline polymer with repeated thiophenyl which has high thermal oxidation and chemical resistance [3]. It has advantages of good toughness, low density ($\sim 1.34 \times 10^3$ kg/m^3), high abrasion resistance (friction coefficient of 0.01–0.02) and high chemical and thermal stability comparable to other amorphous high performance engineering resins, such as polyimide, polyarylester and polyetheretherketone [4]. It is inherently fire retardant and maintains good mechanical properties at high temperature (~265 °C) [5]. As a result, fiber reinforced polyphenylene sulfide composites have a great potential in applications of aerospace, chemical engineering, microelectronics, and other industries.

A carbon nano-tubes yarn, as a typical carbon nano-tubes macroscopic assembly, is spun by twisting multi-walled carbon nano-tubes together, and possesses remarkable mechanical, electrical, thermal, and optical properties [6,7]. However, the bonding between carbon nano-tubes yarns and a matrix is critical to realize the potential properties of carbon nano-tubes in composites. Therefore interfacial interaction between yarns of carbon nano-tubes and resins needs to be studied. So far, several methods have been developed to test the interfacial shear strength between fibers and matrices, such as the micro-bond test [8–10], single-fiber fragmentation test [11], push-out and pull-out tests [12–14]. A few studies have also been published to discuss the interfacial shear strength of carbon nano-tubes yarns and resins. Deng et al. have measured the interfacial shear strength between a nano-tubes yarn and epoxy using fragmentation method [15]. Zu and coworkers have investigated the interfacial properties of a carbon nano-tubes fiber and epoxy using micro-droplet tests [16]. In these studies, yarns constituted of carbon nano-tubes are fabricated from carbon nano-tubes arrays with inherently high strength, high modulus and low elongation, suitable for the fragmentation test and the micro-bond test. However, the fabrication process for yarns from arrays is complicated, extremely slow and highly expensive, and thus they are less likely to be used in structural composites. On the contrary, the carbon nano-tubes yarns fabricated by aero-gel spinning method are much less expensive, produced in large quantity and more likely to be used in structural composites in future. Nevertheless, few studies have reported the interfacial bonding between aero-gel spun carbon nano-tubes

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yarns and matrices. One of the reasons for lack of interfacial bonding data for aero-gel spun carbon nano-tubes yarns with matrices is that they are generally too weak to be tested using micro-droplet or any pull-out tests and their failure strains are too large to be tested in the fragmentation test using a single fiber composite. This is because that as-produced aero-gel spun yarns have large variation in yarn diameters, relatively poor nano-tubes alignment, and weak interaction between carbon nano-tubes bundles due to loosely packed yarn structure [17]. To address these problems, a wide variety of treatments have been applied, including polymer impregnation [18], oxygen plasma treatments [19], solvent densification [20], increasing twists [21], cyclic loading [22] and thermal oxidization [23]. Among these methods, solvent densification and cyclic loading are the two simple and effective methods with little damage to the carbon nano-tubes in a yarn. Fan et al. have applied different solvents, such as water, ethanol, and acetone to shrink carbon nano-tubes yarns from several centimeters to 30 μm in diameter [20,24].

In this study, we intend to test interfacial shear strength between an aero-gel spun carbon nano-tubes yarn and polyphenylene sulfide using the micro-droplet test. To improve the tensile strength and modulus of the carbon nano-tubes yarn so as to meet the requirement of the micro-droplet test, dichloromethane was selected to condense the yarn first which was simultaneously stretched by a constant tension for better alignment of carbon nano-tubes in the yarn axial direction. Morphology of the yarns was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). Mechanical properties of the yarns were analyzed by Weibull distribution and *t*-test. The mechanism for the interfacial failure was analyzed.

2. Experimental

2.1. Materials

Pristine multi-walled carbon nano-tubes yarns, directly spun from the *chemical vapor deposition* synthesis zone of a furnace using a liquid source of carbon and an iron nano-catalyst [25], were provided by Suzhou Institute of Nano Tech and Nano Bionics, Chinese Academy of Sciences. Dichloromethane, purchased from Sigma–Aldrich, was used as densification solvent. Thermoplastic polyphenylene sulfide resin (Toray Torelin Co. Ltd, China) with melting temperature of 285 °C and molecular weight of 20,000–100,000 were used to make micro-droplets on carbon nano-tubes yarns.

2.2. Fabrication

The carbon nano-tubes yarn pretreatment was conducted in two steps. As shown in Fig. 1a, under a constant tensile load, the pristine carbon nano-tubes yarn was immersed in dichloromethane for 3 h to fully saturate it, where dichloromethane also functioned as a lubricant agent for carbon nano-tubes re-orientation. Finally, the densified yarn was dried at 50 °C for 5 h to remove residual solvent.

Fig. 1b shows the process of making a carbon nano-tubes yarn/polyphenylene sulfide micro-droplet specimen. Firstly, the yarn with a length of 30 mm was fixed on a copper frame. To make a micro-droplet, polyphenylene sulfide fibers were manually pulled out after melting polyphenylene sulfide chips. A polyphenylene sulfide fiber was then tied on the carbon nano-tubes yarn, and slowly heated to and maintained at 300 °C for 5 min to melt and form a spherical shape in a vacuum oven. The thickness of the polyphenylene sulfide fiber was small enough to get a smooth and uniform micro-droplet with a diameter of about 200 μm.

2.3. Wettability test

To find the best solvent to densify the carbon nano-tubes yarn in the pretreatment, the wettability of the yarn was measured with distilled water, acetone and dichloromethane using static contact angle method [26]. Firstly, the carbon nano-tubes yarns were arranged horizontally and closely parallel to one another to form a film-like plane. Then the contact angles of the carbon nano-tubes yarn and different solvents were measured. Combining Young-Dupre's Equation and Dupre's Equation [27], the static contact angle was calculated using Eq. (1):

$$W_{SL} = \gamma_{LV}(1 + \cos\theta) \tag{1}$$

where W_{SL} is the solid/liquid interfacial energy, γ_{LV} is the liquid surface tension, and θ is the contact angle. The value of W_{SL} indicates the wettability between the carbon nano-tubes yarn and solvent, and a higher wettability makes the solvent more effective to densify the yarn.

In addition, the yarn composed of carbon nano-tubes bundles was highly porous. The typical capillary pressure equation applied to the yarn structure can be expressed as [28]:

$$P = \frac{2\gamma_{LV} * \cos\theta}{\bar{r}} \tag{2}$$

where P is the wicking pressure, $\bar{r}$ is the equivalent radius of the capillary tube, and $\gamma_{LV}\cos\theta$ indicates the adhesive tension between the substrate and the solvent. The voids between nano-tubes bundles can absorb the solvent into the carbon nano-tubes yarn which was densified by surface tension of the liquid during the drying process.

2.4. Characterization

The diameters and morphology of the carbon nano-tubes yarns were evaluated with a polarized light microscope (ECLIPSE LV100POL), transmission electron microscope (JEOLJEM-2100, and 200 kV) and scanning electron microscope (Hitachi TM3000, 5 kV). The mechanical properties of the carbon nano-tubes yarns were tested on a XQ-2 tensile tester (Shanghai Xusai Instrument Co., China) at a crosshead speed of 0.5 mm/min with a gauge length of 10 mm. The Poisson's ratio of the carbon nano-tubes yarns with twist angle of 15° were tested using a tension device under the polarized light microscope.

2.5. Micro-bond test

The interfacial shear strength between yarn and matrix was measured by the micro-bond test [29]. As shown in Fig. 7c, this method pulls a single fiber out of a micro-droplet of polyphenylene sulfide resin to measure the interfacial shear strength between carbon nano-tubes yarn and the matrix, which can be calculated according to Eq. (3) [29]:

$$\tau_i = F_{max}/\pi \tag{3}$$

where F_{max} is the maximum force recorded during the micro-droplet debonding process, D is the fiber diameter, L is the embedded fiber length, πDL is the embedment area, and τ_i is the average interfacial shear strength.

2.6. Statistical analysis

Data were analyzed using *t*-tests to compare the properties before and after the treatment. The confidence interval was set at 95%. Differences among data with a p-value < 0.05 were considered to be statistically significant.