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Tensile and interfacial properties of polyacrylonitrile-based carbon fiber after different cryogenic treated condition

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ABSTRACT

Polyacrylonitrile-based carbon fibers are cryogenically conditioned both through a low cooling rate and a quench rate to explore the effects of cryogenic treatments on properties and micro-structures of carbon fibers. The internal structure, tensile properties and surface morphologies of the fiber are investigated. Increase in crystallinity and tighter packing of molecules of the fiber after the cryogenic treatments are observed regardless the cooling rate. After slow cooling cryogenic treatment, the inter-planar distance increases in the fiber axial direction and decreases in the fiber radial direction, resulting in 3% shrinkage of fiber diameter and extension in fiber axial direction. Scanning electron microscopy and atomic force microscopy analysis show slightly wider and deeper rill-like folds and 41% roughness increase for the fiber surfaces, leading to an increase in interfacial shear strength between the fiber and epoxy by 30.2%. In contrast, after sharp cooling cryogenic treatment, no obvious change is detected in inter-planar distance, fiber diameter, surface morphology and interfacial shear strength with epoxy. The bimodal additive Weibull distributions of tensile strengths for the cryogenic treated fibers show an increase of the bimodality parameter α and a decrease in scale parameter σ indicating higher probability of extrinsic defects but no significant mechanical degradation of the fiber after cryogenic treatments.

1. Introduction

Carbon fibers reinforced polymer composites (CFRP) is rapidly developed and applied as typical advanced composites due to its favorable mechanical and physical properties [1,2]. The composites need to withstand large cyclic temperature variations and extremely low temperatures when serve at various extreme conditions such as the lightweight liquid hydrogen (LH_2) fuel tanks for next generation reusable space launched vehicles (RSLVs) [3,4]. Cyclic temperature variations during fueling/refueling cycles cause residue stress and degradation of composites [5,6]. Therefore, considerable attention has been paid to CFRP composites to explore the mechanical property and failure mode at cryogenic temperatures [6–12] or after cryogenic conditioning [5,13,14].

Among most of the studies, micro-cracks and even fracture of the composites was observed due to the residual stresses induced by the large difference in the linear coefficient of thermal expansion (CTE) between the fibers and the matrices [15]. Cryogenic mechanical properties of polymers have been investigated [16,17]. However, these studies showed a common trend of increased strength and stiffness at cryogenic temperature, but no degradation and cracks developed [18,19]. In addition, after cryogenic conditioning, the crystallinity of polymers like polyimide, polyetherimide, polytetrafluoroethylene, polycarbonate, and polyurethane are increased as well [20–22].

Compared with the isotropic polymers, the carbon fibers exhibit an anisotropic feature which leads to different CTE along axial (about −0.1 ~ −0.5 p.p.m°C) and radial (about 7–12 p.p.m°C^{-1})

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directions of the fiber [23,24], indicating that contraction in radial and extension in axial directions will be aroused by cryogenic temperatures while the matrix contracted in all directions. Larger differences in the CTE between the carbon fiber and the matrix generated the thermal stresses and caused corresponding increase in micro-cracking at cryogenic temperatures [25]. Therefore, the carbon fiber properties are critical to reveal the interaction between the fiber and the matrix as well as the mechanism of the property degradation of CFRP by cryogenic temperatures. However, little has been reported about the influence and the mechanisms of cryogenic temperatures on both properties and submicrostructures of carbon fibers.

In this study, a selected polyacrylonitrile (PAN)-based carbon fiber was cryogenically treated either in a high cooling rate or quenched and low cooling rate for comparison. The microstructure was characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The single fiber tensile test was conducted to explore the flaw distribution and mechanical properties. The surface and interfacial properties were investigated by scanning electron microscope (SEM) and the micro-bond test.

2. Experimental

2.1. Material selection and cryo-treatment

The selected carbon fiber T300 (Toray Industries, Japan) were adopted. Before the cryogenic treatment, the samples were cleaned by immersing the fibers into acetone solvent for 30 min, and then washed by distilled water. The cryogenic treatment was carried out using a temperature-programmed control cryogenic chamber (SXL-30, Chemicophysics research institute of CAS, China). The carbon fibers were subjected to cryogenic temperature by two different methods, namely temperature program controlled method (TPCM) and quench method (QM). In TPCM, the fibers were cooled from room temperature down to 77 K at a rate of 2 °C/min and then maintained at that temperature for 12 h. In QM process, the samples were directly put into liquid nitrogen (77 K) environment, which means the treated temperature suddenly decreased from ambient temperature to cryogenic temperature, and then maintained at 77 K for 12 h. The schematic of cryogenic treatment processes under different cooling rates is shown in Fig. 1.

2.2. Microstructural test

Molecular structure changes of the fibers were investigated using XRD (D/Max-2550PC, Japan RIGAKU) technique. Nickel filtered Cu-Ka radiation (k = 1.54 Å) generated at 40 kV and 200 mA was used for the angle (2θ) range from 0 to 60°. Fourier transform infrared spectroscopy (FTIR) (NEXUS-670, Nicolet, America) was used to generate the IR spectra.

2.3. Single fiber tensile test

The fiber tensile properties were measured using a single fiber tensile testing machine (XS(08)XG, Shanghai Xusai Instrument Co., China) at a crosshead speed of 20 mm/min and a gage length of 20 mm at 20 °C and 65% relative humidity. Fiber diameters were measured by a polarized light microscope (ECLIPSE LV100 POL, Nikon) with a digital image capturing system. At least 50 specimens were tested for each sample and the means were reported.

2.4. Surface morphology analysis

The surface morphology of the carbon fibers was investigated using Scanning electron microscope (SEM) machine (Model JSM-5600LV, JEOL, Japan) at a voltage of 15 kV. Surface roughness of the fibers was measured using an atomic force microscope (AFM) on a MultiMode Digital Instrument Nanoscape III set-up in the contact mode under ambient conditions.

2.5. Interfacial property test

The un-treated and cryo-treated carbon fibers were selected from a bundle to prepare the micro-bond samples as described in Ref. [26]. EPOLAM 2008 epoxy resin and EPOLAM 2008-F curing agent (AXSON Technologies Shanghai Co. Ltd.,China) were mixed in a ratio of 5:1. After placing the beads on the fibers, the samples were cured for 3 h at 45 °C. The micro-bond test was carried out using a single fiber tensile testing machine with crosshead speed of 1 mm/min at 20 ± 1 °C and 65% relative humidity. The interfacial shear strength (IFSS) was calculated according to the equations derived from the well-known shear-lag model [27].

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 2 showed the XRD patterns of untreated and cryo-treated carbon fibers, in which Fig. 2(a) and (b) represented equator diffraction and meridian diffraction, respectively. The strongest diffraction peak in equator diffraction pattern is the diffraction peak of (002) crystal face while that in the meridian diffraction is the diffraction peak of (100) crystal face. The calculated results of crystallinity; crystallite size; inter-planar spacing and preferred orientation are shown in Table 1.

A small increase in crystallinity and a decrease in crystallite size were observed for the fibers treated by TPCM process which indicated tighter arrangement of molecules and reduction of amorphous phase. This may be attributed to the hoop stress in the fiber radial direction induced by shrinkage of the fiber and strengthening of bonding forces between molecules when the temperature decreased from RT to 77 K. Moreover, the reduction of micro- and nano-sized pores in the fiber may affect the changes of interlayer spacing [28,29] because the compression stress may force anisotropic expanding and merging of tiny pores leading to looser molecular packing along the fiber axial direction and tighter molecular arrangement in fiber radial direction when the fibers undertake TPCM process.

However, the carbon fiber treated with QM showed an increase of inter-planar spacing in d100 but no obvious change in d002. This showed the difference created by the cooling rate on fiber molecular arrangement. TPCM process applied gradual compression stress to the fiber and thus provided sufficient time for the movement of the molecular chains to accommodate the deformation, resulting in a tighter packing of molecules in fiber radial direction. For the QM process, the fiber was compressed suddenly, permitting no time for the molecules to adjust their arrangement in the fiber radial direction, while molecular disorder was created in axial direction by quenching.

The crystallinity and molecular orientation did not change substantially as diameters for the treated carbon fibers varied after the treatments. It is likely due to the fact that the molecular structure of carbon fibers is not the same as regular polymers. Carbon fibers are composed of turbostratic structure in the core and graphite structure in sheath. These structures are very stiff at low temperatures. In order to increase crystallinity and molecular orientation, carbon fibers often have to be heat treated at temperatures 1700–2000 °C at which carbon fibers are graphitized due to stiffness of the molecular structure. Therefore, at low temperatures, neither crystallinity nor molecular orientation could be