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Effects of thermal histories on interfacial properties of carbon fiber/polyamide 6 composites: Thickness, modulus, adhesion and shear strength

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ABSTRACT

Interface thickness and modulus of carbon fiber (CF) reinforced polyamide 6 (PA 6) composites with different thermal histories are characterized as 331–394 nm and 0.24–0.30 times to fiber modulus, respectively. Transverse fiber bundle (TFB) test is firstly employed for evaluating semi-crystalline PA 6 interfacial adhesion. TFB Failure mechanisms are schematically given. Besides enhanced molecular entangling on fiber surface, increased matrix toughness is also found to have a great effect on improved TFB results. Droplet micro-debonding results show that decreasing cooling rate and increasing annealing temperature both decrease interfacial shear strength (IFSS) though residual PA 6 on carbon fiber surface increases. In the end, the above data are normalized together with some previous measured parameters. It shows that quenching of the CF/PA 6 composites and subsequent annealing are shown to give similar results as slow cooling. Relationships between each other are also discussed.

1. Introduction

In the past three decades, continuous carbon fiber reinforced recyclable thermoplastic mainly focused on high performance polymers such as polyetheretherketone (PEEK), polyethersulfide (PES), polyphenylenesulfide (PPS) and polysulfone (PSU) [1]. Systematically research on engineering PA 6 which has great potential in automotive field under the current background of low-carbon and environment protection is still absent.

Interface, a transit phase between matrix and reinforced fiber, plays an important role in deciding composite properties. The most important two interfacial parameters of thickness and modulus are usually considered having direct influences on load transfer efficiency (LTE) and the ultimate mechanical properties. However, inconsistencies are still exist. For example, thin interface thickness and high interface Young's modulus resulted in efficient stress transfer at the fiber interface using a simple representative volume element (RVE) approach based on the finite element analysis (FEA) [2], while results simulated by Yu et al. [3] indicated that the normal stress increased with the increase of the interface thickness and interfacial shear strength (IFSS) remained unchanged, and the interface modulus had no influence on the stress distributions along the direction to the fiber axis. Kim and Mai [4] also reported that there were inconsistencies on the influence of thickness and modulus on the LTE. It depended on the presence of an elastomeric soft interface or a stiff interface.

Besides interface thickness and modulus, semi-crystalline thermoplastic intrinsic morphological features such as crystal size, nucleus density, crystallinity and transcrystallization also have profound effects on the ultimate properties of carbon fiber reinforced thermoplastic composites. And these features are, in turn, affected by variations of thermal histories [5] which is here defined as the thermal treatment process polymers experience from their molten temperature to their final service temperature. However, inconsistencies also exist for the influences of cooling rate [1,6–10] and annealing treatment [1,6,11,12] on IFSS and LTE mainly for the differences of fiber/polymer systems and processing conditions.

This implies that a systematic study is required to characterize these parameters and clarify the thermal history effects on them and strength of interface and composites, which is essential for the optimization of the fabrication process from the material design point of view as well as for improving macroscopic mechanical performance from the structural design point of view [13,14].

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Local mechanical interfacial characteristics including hardness, stiffness, and modulus were traditionally assessed by nanomechanical techniques based on tip-sample interaction, such as atomic force microscopy (AFM) [15,16], nanoindentation, nanoscratch [17,18], and dynamic modulus mapping [19,20]. Gu et al. [21] presented a dynamic mechanical imaging (DMI) method to extract the whole interface dimension and achieve quantitative analysis on thickness and modulus. However, modulus tested by DMI cannot be directly used both as absolute modulus value due to gap between it and nominal modulus and to compare with moduli of other specimens due to the effect of different surface roughness conditions.

The interfacial properties of certain fiber/matrix systems can be evaluated by micro-mechanical testing techniques or by macro-mechanical testing methods. Micro-mechanical techniques such as fiber fragmentation [6,22,23], fiber pull-out [6,24,25] and micro-debonding [24,26–29] have certain limitations to their use, and have not yet been standardized [30]. Alternatively, macro-mechanical testing methods can be used to indirectly assess fiber/matrix interfacial adhesion, but they require the production of bulk composite laminates, which is time-consuming and costly. Recently, a transverse fiber bundle (TFB) test method has been proposed to assess the fiber/matrix interfacial adhesion without manufacturing composite laminates. Additionally, TFB shows a good consistency with traditional micro-mechanical techniques [31]. It has been widely used to evaluate interfacial adhesion strength in fiber reinforced epoxy composites [31,32] and epoxy composites modified by fillers [30,33,34]. However, application in semi-crystalline thermoplastic matrix composites has not been reported to our best of knowledge.

The aim of the present study is to characterize detailed interfacial parameters and clarify the thermal history effects on them and strength of interface and composites. To this end, we continuously [11] evaluated the interface thickness and modulus using DMI. To realize modulus comparison, we introduced a normalization data processing method. TFB was firstly used in semi-crystalline PA 6 composites to investigate transverse interfacial adhesion behavior. IFSS was evaluated according to micro-debonding test method. A general discussion on normalized parameters was conducted in the end and some interesting results were concluded.

2. Experimental

2.1. Materials

Carbon fiber (T700SC-12K) was purchased from Toray and used as received. Extrusion grade low viscosity PA 6 granules (1013B) were provided by UBE Engineering Plastics. PA 6 powder of 100 mesh was obtained by grinding original granules using a cryogenic shredder with the help of liquid nitrogen. Both two kinds of PA 6 were sufficiently dried before used.

2.2. Interface thickness and modulus characterization

Interface thickness and modulus of carbon fiber reinforced polyamide 6 composites were measured on an in-situ nanomechanical test system (Hysitron Inc., TI-900 TriboIndenter). DMI technology was performed to obtain an image consists of 256×256 modulus values in a selected area of $10\ \mu m \times 10\ \mu m$. A 50 nm radius probe was working in the form of scanning the surface at a constant normal force of 2 μN with a superimposed dynamic force of 1 μN at 200 Hz. Isolated carbon fiber was of more interest since entire interface and more matrix features could be well obtained. Three areas were performed for each thermal history.

2.3. Prepreg manufacturing and microscopic evaluation

In order to prepare qualified TFB specimens, prepregs were used instead of dry fiber bundle. They were fabricated in our laboratory using melt impregnation method with fiber bundles passing through a cross-head impregnation die designed by ourselves. Fiber volume fraction was controlled in the range of 50.0 ± 2.0 percent, thickness was 0.25 ± 0.03 mm and width was 7.00 ± 0.15 mm. POM (Leica DM4000M) was employed to observe polished prepreg cross section for the characterization of fiber distribution and void volume fraction.

2.4. Transverse fiber bundle (TFB) test

A tailored piece of prepreg was fixed between a two-half mold machined according to ASTM D638. After they were placed between two aluminum plates and heated to 80 °C, molten PA 6 was slowly injected into the mold cavities by a single screw extruder. Afterwards, the mold was heated to 240 °C to eliminate prepreg thermal history and cooled with three different nonisothermal cooling procedures: quenching in water (Water), cooling between two aluminum plates (Al), cooling in air (Air). Annealing specimens were obtained by reheating water-quenching specimens and holding them at 130 °C (130), 170 °C (170) and 200 °C (200) for 5 h with vacuum protection, respectively. In the following, they were naturally cooled in air to room temperature.

After each sample was carefully trimmed and polished to ensure the fiber bundle appeared on the surface of the sample, TFB tests were conducted on a universal test machine (WDW-100, Changchun Kexin Co., Ltd.). The cross-head speed was 1 mm/min. More than 5 specimens were tested for each thermal history group. The fracture surfaces were examined by SEM (Apolo 6010) to explore the failure mechanisms.

2.5. Micro-debonding

Micro-debonding specimen was prepared by spraying 100 mesh PA 6 powder on a single carbon fiber fixed on a concave shaped metal frame (Fig. 1). Then the frame was packaged into an aluminum box and kept at 260 °C for 15 min with vacuum protection. Droplets were formed by inherent surface tension of molten polymer. Then PA 6 droplets with different thermal histories were realized by controlling the temperature of the aluminum box similar to the thermal treatments of TFB. Approximately 10–20 valid tests were performed for each thermal history and the IFSS, τ_{app}, can be calculated as follows:

$$\tau_{app} = F/2\pi rl \quad (1)$$

where F is the debonding force, l is the embedded fiber length, and r is the fiber radius.

3. Results and discussion

3.1. Interface thickness and modulus

3.1.1. Thickness

Typical three-color gradient DMI image is presented in Fig. 2(a). The contrast clearly shows that the modulus of the PA 6 matrix (green) is much lower than those of the carbon fiber (blue) and interface (white) adjacent to it, respectively. Through presenting 256 modulus data in a line running cross the fiber center in Fig. 2(a), four feature regions (i.e. fiber center, fiber periphery, interface and PA 6 matrix) can be clearly distinguished (Fig. 2 (b)). The interface modulus is not a constant and displays a