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Epoxy laminated composites reinforced with polyethyleneimine functionalized carbon fiber fabric: Mechanical and thermal properties

Shusheng Chen, Jiachun Feng *

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

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ABSTRACT

Epoxy (EP) laminated composites reinforced with polyethyleneimine (PEI) functionalized carbon fiber fabric (CFF), which were prepared by pre-depositing polydopamine on the surface of pristine CFF and then further grafting with PEI, were fabricated and their mechanical and thermal properties were investigated in detail. The flexural strength and flexural modulus of PEI-functionalized CFF/EP composites were 32% and 31% greater than that of as-received CFF/EP composites. The interlaminar shear strength and thermal expansion coefficient of PEI-functionalized CFF/EP composites were 55 ± 2 MPa and 48.9 ppm/°C, improved by 34% and 16.8% compared with the as-received CFF/EP composites. Microstructure and thermal analyses revealed that the PEI-functionalization of CFF enhanced interfacial adhesion due to the increase of interfacial crosslinking density, which causes by the curing reaction between EP and PEI. The PEI-functionalized CFF/EP composites achieve a combination of excellent in-plane and out-of-plane properties, thereby holding enormous potential in many application fields.

1. Introduction

The demand of lightweight materials, such as for structural applications, has become an increasingly important issue in recent years due to growing attention on energy conservation and environmental protection [1]. Carbon fiber reinforced epoxy (EP) composites are ideal lightweight materials because of their high strength-to-weight ratio, excellent heat resistance and good chemical resistance. In general, high-performance carbon fiber composites are fabricated with unidirectional or woven carbon fiber fabrics (CFF) as reinforcement, the properties of which outperform that of the random short carbon fiber reinforced composites to a great extent. Due to the unique fiber architectures in laminated composites, the fiber fabrics dominate the in-plane properties that are typically high enough, while the resin matrices and interfaces dominate the out-of-plane properties (e.g., interlaminar shear strength and coefficient of thermal expansion) that are much lower than in-plane properties, restricting their uses in some structural applications [2]. Hence, significantly improving the through-thickness properties of laminated composites, is great important and remains a hot issue for both academy and industry.

In the recent decades, many works have been devoted to improving the through-thickness properties of laminated composites. The most effective approach is increasing the wetting and thus bonding between carbon fibers and matrix by fiber surface treatments, which includes dry and wet oxidation methods [3,4], plasma treatment [5,6], and polymeric coating after the oxidation treatment [7,8]. It has been shown, for example, that in unidirectional carbon fiber/EP composites increasing fiber–matrix adhesion could improve the interlaminar shear strengths [9], the tensile and flexural strengths [10], the longitudinal compressive strength [11], and the mode I and mode II fracture toughness [12]. However, the conventional surface treatments with oxidation procedure, which removes weak outer layers and increases surface active groups of the fibers, would damage the mechanical properties of fibers to some extent and consequently sacrifice the in-plane mechanical properties of laminated composites [13]. Therefore, searching for new efficient approaches for surface functionalization of CFF to prepare laminated composites with balanced improved in-plane and out-of-plane mechanical properties, is highly desirable.

Recently, dopamine, which can self-polymerize under mild reaction conditions and form polydopamine (PDA) film onto almost all types of substrates [14], has drawn great attention due to its amazing chemistry properties. In addition, under oxidizing conditions, the catechols of PDA coating can react with thiols and amines via Michael addition or Schiff base reactions [15], which enables dopamine to serve as a surface functionalization agents. For instance, Wang et al. immobilized silver nanoparticles on the surface of polyethylene terephthalate fibers after modifying fibers

* Corresponding author. Tel.: +86 (21) 6564 3735; fax: +86 (21) 6564 0293.
E-mail address: jcfeng@fudan.edu.cn (J. Feng).

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with PDA [16]. Fu et al. introduced dopamine as a modifier for the surface treatment of ramie fiber [17]. In our previous work, we developed a universal functionalization method of short carbon fibers using dopamine as a robust platform and both hydrophilic and oleophilic surfaces of carbon fibers could be easily achieved. This strategy could pre-activate the fiber surfaces without damaging their mechanical properties, which opens up the possibility of further functionalization [18].

Considering that amine groups of amines can react with the epoxy groups of EP, functionalizing carbon fiber with amine-containing polymers should be able to form a good bridge between carbon fiber and EP matrix. As reported, polyethyleneimine (PEI), rich in amine and imine groups, can react with both PDA [19] and epoxy [20]. Therefore, PEI may be a good candidate for further functionalizing PDA-coated CFF to effectively improve the interfacial properties in the CFF/EP composites. In the present work, we develop a facile two-step route to functionalize CFF with PEI, which was accomplished by grafting PEI onto CFF after pre-deposition of PDA, and prepare PEI-functionalized CFF/EP laminated composites. The macro-performance and morphology evaluation of PEI-functionalized CFF/EP composites indicated that this simple strategy is efficient and PEI is able to form a high interfacial crosslinking density as well as form "cross-bridges" to connect the neighboring laminas, which leads to remarkable improved mechanical and thermal properties in PEI-functionalized CFF/EP composites.

2. Experimental details

2.1. Materials

Turkey A49 unidirectional carbon fiber fabrics (CFF) (T700 12 K) with a filament count of 12 K and fiber areal weight 200 g/m^2 were produced by Tianniao High Technology Co. (Jiangsu, China). According to the supplier, there is no coating on the surface of as-received CFF. E51 epoxy resin (EP), whose viscosity and epoxide value are ~2500 mPa S (40 °C) and 0.48–0.54 eq/100 g, was purchased from Bluestar Wuxi Petrochemical Co. Ltd. (Jiangsu, China). Polyethyleneimine (PEI) with molecular weight of 600 (PEI1) and 10,000 (PEI2), hydroxyphenethylamine hydrochloride (dopamine, 98%), tris(hydroxy-methyl)aminomethane (TRIS, 99%), isophorone diamine (IPDA) and solvents were purchased from Aladdin Reagent Corp. (Shanghai, China). All chemicals and solvents were used as received and without further purification.

2.2. Surface functionalization of CFF

The as-received CFF (AR-CFF) were cut into pieces of 110 mm × 150 mm, followed by depositing PDA on their surfaces as our previous work [18]. The resulting CFF were denoted as PCFF. Subsequently, PCFF were immersed in a buffer solution of PEI1 or PEI2 (5 g/L) for 24 h. The buffer solution was prepared with 10 mM TRIS and its pH was adjusted to 8.5 with 1 M hydrochloric acid, monitored by a pH meter. After a predetermined reaction time, the obtained CFF were rinsed thoroughly with deionized water and dried in a vacuum oven at 50 °C for 24 h, which were denoted as PEI1-PCFF and PEI2-PCFF.

2.3. Fabrication of CFF/EP laminated composites

The vacuum assisted resin transfer molding technique was adopted to fabricate PEI-PCFF/EP laminated composites with 8-ply fabrics. The mass ratio of the epoxy resin vs. the curing agent IPDA was set at 100:21. After the infiltration of epoxy, the composites were cured at 80 °C for 2 h and further cured at 120 °C for 1 h. The vacuum of 0.1 MPa was maintained during the cure procedure. Following the similar procedure, AR-CFF/EP and PCFF/EP composites were prepared as references.

2.4. Characterization

Scanning electron microscopy (SEM, TESCAN 5136 MM) was applied to observe the surface morphologies of CFF as well as the fracture surfaces of composites at an operating voltage of 20 kV. All samples were aurum sputter coated for improving electrical conductivity before SEM observation. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet spectrometer. Thermogravimetric analysis (TGA) was carried out under air atmosphere with a Perkin Elmer Thermal Analyzer from 50 to 800 °C at a heating rate of 20 °C/min. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra^{DLD}) was used to determine the chemical composition of CFF with a monochromatized Al Kα X-ray source (1486.6 eV photons), at a current of 10 mA and a voltage of 15 kV.

Mechanical properties were measured at 23 °C and ~40% relative humidity using a SANS CMT-4102 universal testing machine (Shenzhen, China). To evaluate strengthening/toughening effects of the PEI treatment on the composites, the three-point flexural test (with specimen dimensions of 80 mm × 12 mm × 2 mm) was carried out on specimens with span-to-thickness ratio of 32 at a crosshead speed of 2 mm/min in accordance with GB/T1449-2005. To evaluate toughening effect of the PEI treatment on interlaminar shear strength (ILSS), short-beam shear strength were measured with a span distance of 10 mm and a crosshead speed of 1 mm/min, according to JC/T773-2010. The dimensions of specimens is 20 mm × 10 mm × 2 mm. At least five tests were performed for each sample, from which mean values and standard deviations were derived.

Thermal expansion coefficient (CTE) of composites was characterized by a thermomechanical analyzer (TMA, Mettler-Toledo TMA/SDTS841e) from 50 to 200 °C in nitrogen (N_2) at a heating rate of 5 °C/min. Dynamic mechanical analysis (DMA, Mettler-Toledo DMA/SDTA861e) were conducted to measure the storage modulus and glass transition temperature (T_g) of composites. The specimen dimensions for DMA measurement were 60 mm × 5.0 mm × 2.0 mm. The testing was performed in three-point bending mode at multi-frequencies of 1, 5, 10, 30 and 50 Hz with a heating rate of 2 °C/min between 50 and 200 °C. Differential scanning calorimetry (DSC) (Mettler-Toledo 821e Thermal Analysis System) was used to investigate the curing process of different EP systems at a heating rate of 10 °C/min from 0 to 250 °C under nitrogen atmosphere. The mass ratios of EP/IPDA, EP/PEI1, EP/PEI2, EP/IPDA/PEI1 and EP/IPDA/PEI2 for DSC investigation were set at 100/21, 100/10, 100/9, 100/21/1 and 100/21/0.9, respectively.

3. Results and discussion

3.1. Surface characterization of CFF

The surface topographies of the CFF were observed using SEM. As shown in Fig. 1a, the AR-CFF displays ridges and striations along the axis on the surface. After deposition of PDA, the surface grooves become invisible and granules of coated PDA were uniformly distributed on the surface of PCFF (Fig. 1b). This result is consistent with several previous reports [21,22]. By contrast, Fig. 1c and d shows that the fiber grooves and PDA grains can be hardly seen on the surface of PEI-PCFF, implying that PEI layer were covered on the PCFF.

The surface functionalization of the CFF was supported by the FTIR spectroscopic analyses. For all CFF samples, there are some characteristic absorptions at 1625 and 3422 cm^{-1}, attributed to aromatic C=C and O—H stretching vibration, respectively