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Continuous carbon fiber/crosslinkable poly(ether ether ketone) laminated composites with outstanding mechanical properties, robust solvent resistance and excellent thermal stability

Yunhe Zhang[a], Wei Tao[a], Yu Zhang[a], Lin Tang[b], Junwei Gu[b,**], Zhenhua Jiang[a,*]

[a] Key Laboratory of High Performance Plastics (Jilin University), Ministry of Education, College of Chemistry, Jilin University, Changchun, 130012, PR China
[b] MOE Key Laboratory of Material Physics and Chemistry Under Extraordinary Conditions, Shaanxi Key Laboratory of Macromolecular Science and Technology, Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, Shaanxi, 710072, PR China

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ABSTRACT

Continuous carbon fiber (CCF) reinforced polymeric composites have attracted significant attention in the aeronautic and automobile industries. In this study, novel CCF/poly(ether ether ketone) (PEEK) composites with robust solvent resistance, excellent thermal stability and outstanding mechanical properties were successfully fabricated *via* a facile solution impregnation process, mainly ascribed to the introduction of the crosslinkable phenylethynyl pendant to PEEK (PEP-PEEK) with excellent solubility. After the crosslinking reaction, PEP-PEEK presented robust solvent resistance, good thermal stability, and high mechanical properties. The longitudinal tensile strength of the CCF/PEP-PEEK composites significantly improved to 1610 MPa, which was 19 times stronger than the longitudinal tensile strength of PEP-PEEK. In the meantime, the CCF/PEP-PEEK composites also had a higher long-term operating temperature, excellent thermal stability and high heat distortion temperature. This study was performed as part of a larger effort to provide a simple and feasible method for the preparation of high quality continuous fiber reinforced poly(ether ether ketone) composites.

1. Introduction

As typical representatives of advanced composites, carbon fiber-reinforced polymeric composites (CFRPs) have gained attention in sports, the automotive and aerospace industries and military due to their high specific stiffness and strength, robust chemical stability (solvent resistance), good thermal stability, and so on [1,2]. To our knowledge, the present matrix resins used to prepare CFRPs are usually thermosetting resins, such as epoxy resins [3–6], bismaleimide resins [7,8], cyanate ester resins [9,10] and polyimide resins [11–13], due to their good processability and steady mechanical properties in high-temperature environments. However, their low toughness and damage tolerance remain limitations for further applications [14,15].

Recently, continuous fiber reinforced high-performance thermoplastic polymeric composites (CFRTPCs) have gained enormous scientific attention due to their light weight, high mechanical properties, damage tolerance, and so on [16–19]. However, most of these thermoplastic polymers usually suffer from poor and high-cost processability due to their high melting temperature (T_m), melt viscosity, and poor solubility [20,21]. Poly(ether ether ketone) (PEEK), a typical high performance engineering thermoplastic resin, has exceptional mechanical properties, excellent thermo oxidative stability and flame retardancy; relatively excellent thermal stability (T_g of 143 °C, T_m of 343 °C, and decomposing temperature of 580 °C); and outstanding resistance to chemicals and solvents (it is only soluble in 98% sulfuric acid) [22–24]; PEEK has been widely used in many applications, such as in the aerospace, automotive and biomechanics industries [25,26].

As a result, it is extremely difficult to fabricate continuous fiber/PEEK prepregs using pristine PEEK as a matrix [27–29]. To improve the processability of the continuous fiber/PEEK prepregs, much efforts has focused on modifying the existing chemical structure of PEEK. For example, Jian et al. [30] introduced phthalazinone moieties into a PEEK matrix. Hoffmann et al. [31] synthesized a novel PEEK containing phosphorus. However, these PEEKs had poor solvent resistance because of the self-limitation of the polymer structures. Moreover, the operating temperatures of these PEEKs still depended on the T_g of the polymer. Wang et al. [32] prepared carbon fiber reinforced poly(ether ether ketone) matrix composites (CF/PEEK) based on a process of ultrasonic-assisted placement used an in situ consolidation technique. Qureshi et al. [33] tested CF/PEEK rings and skin panels with in situ

* Corresponding author.
** Corresponding author.
E-mail addresses: nwpugjw@163.com (J. Gu), jiangzhenhua@jlu.edu.cn (Z. Jiang).

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consolidations using a hot blast as the heating source and carbon fiber reinforced poly(ether ether ketone) (CF/PEEK) as the prepreg. However, the mechanical properties of these composites were still not satisfactory owing to the limitations of process engineering.

In our present work, a series of crosslinkable poly(ether ether ketone)s with phenylethynylpendant (PEP-PEEK) copolymers were successfully synthesized from 4-phenylethynylhydroquinone (PEP-PH), hydroxyphenol and 4, 4′-difluorobenzophenone *via* an aromatic nucleophilic substitution reaction. Corresponding continuous carbon fiber/PEP-PEEK (CCF/PEP-PEEK) composites were also fabricated by solution impregnation, followed by laminated molding. ^{1}H nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) measurements were performed to analyze and characterize the chemical structure, composition, crosslinking behaviors and thermal properties of the PEP-PEEKs. Furthermore, the hot pressing temperature, forming pressure and fiber content affect the mechanical properties of CCF/PEP-PEEK composites were also investigated.

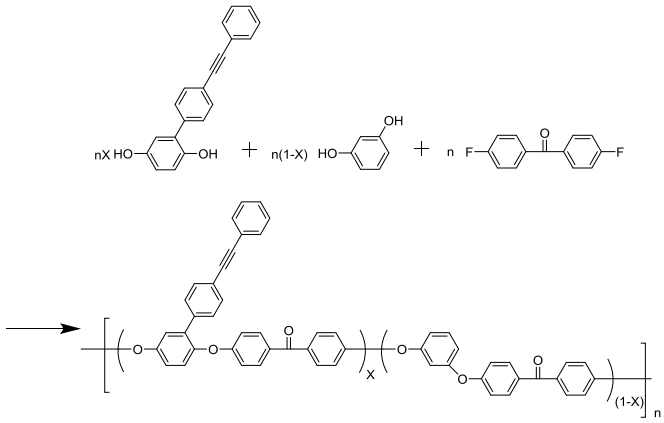
2. Experimental

2.1. Materials

4-Bromoaniline, 1, 4-benzoquinone, copper (I) iodide, resorcinol, and 4, 4-difluorobenzophenone were purchased from Aladdin Shanghai Development Co. Ltd, China. Dichlorobis(triphenyl-phosphine) palladium (II) and phenyl acetylene were purchased from TCI Shanghai Development Co. Ltd, China. Carbon fibers (TR50S 6L) were obtained from Mitsubishi Rayon Co. Ltd, Japan. 4-Phenylethynylphenyl hydroquinone (PEP-PH) was synthesized in our laboratory according to our previous work [34]. And other reagents were commercially obtained and used as received.

2.2. Synthesis of PEP-PEEK copolymers

The synthesis route of PEP-PEEK copolymers is depicted in Scheme 1. A typical process involved a 100 mL three-necked flask equipped with a mechanical stirrer, Dean-Stark trap, nitrogen inlet and condenser, with PEP-PH (1.145 g, 4 mmol), 4, 4-difluorobenzophenone (4.364 g, 20 mmol), resorcinol (1.762 g, 16 mmol), anhydrous potassium carbonate (K_2CO_3, 3.312 g, 24 mmol), toluene (15 mL) and N-methylpyrrolidinone (NMP) (25 mL) added in sequence. The obtained mixtures were vigorously stirred under a nitrogen atmosphere and were maintained at 140 °C for 3 h to remove the resulting water. The reaction temperature increased to 160 °C and was maintained at this temperature for another 5 h to complete the above reaction. The viscous mixture was then poured into 800 mL acidic water. The obtained threadlike polymer was pulverized and washed with hot ethanol and water. A white copolymer was obtained after drying under vacuum at 100 °C for 12 h. Copolymers were prepared by varying the mole ratio of PEP-PH and resorcinol. The copolymers were designated as 20%PEP-PEEK, 30% PEP-PEEK and 40%PEP-PEEK, in which the molar ratios of PEP-PH to resorcinol were 2/8, 3/7 and 4/6, respectively.



Scheme 1. Synthesis of PEP-PEEK (X = 0.2, 0.3, 0.4).

2.3. Preparation of CCF/PEP-PEEK prepregs

CCF/PEP-PEEK prepregs were prepared using a numerically controlled fiber winding machine, and the flow chart is shown in Fig. S1. First, a chloroform solution with 6.5 wt% 30% PEP-PEEK was poured into a resin bath. Then, the CCFs passed the resin bath with a guiding roller and were sufficiently saturated with the resin solution. When the fiber bundles rolled through the glue removing roller, the excess resin solution on the fiber bundle surface was removed. Meanwhile, the fiber bundles were infiltrated with more resin solution under tension. Finally, the fiber bundles were collected by a collecting roller.

2.4. Fabrication of CCF/PEP-PEEK laminated composites

CCF/PEP-PEEK laminated composites were prepared using laminated molding, and the flow chart is shown in Fig. S2. Dried prepregs were clipped and evenly spread into the mold to laminate them using a settling procedure (Fig. S3). After cooling to room temperature and removal from the mold, the laminated composites were precisely cut out by a diamond-tipped precision saw. Different hot pressing temperatures (210, 230, 250 and 270 °C), forming pressures (4, 6, 8, 10 and 12 MPa) and a fiber content of 55 wt% were applied.

2.5. Analysis and characterization

The ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra of the samples were obtained on a Bruker AVANCE NMR spectrometer (^{1}H, 300 MHz) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the an internal reference. The molecular weights of the samples were determined by gel permeation chromatography (GPC) with DMF containing 3 g/L LiCl as the eluent. The molecular weight of the samples was calibrated with a polystyrene standard. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 10 °C/min under nitrogen. Thermal-gravimetric analyses (TGA) of the samples were performed using a PerkinElmer TGA-1 thermo-gravimetric analyzer in the range of 25–800 °C at a heating rate of 10 °C/min under nitrogen. The scanning electron microscope (SEM) morphologies of the samples were analyzed using a JEOLJSM-6700 to observe the fracture morphologies. The tensile properties of the samples were measured on a SHIMADIU AG-I 1KN according to ASTM D790 at a strain rate of 2 mm/min. The flexural properties of the samples were estimated using a three-point bend test method according to the ASTM D790 standard with a crosshead displacement rate of 1 mm/min. The interlaminar shear strength (ILSS) of the samples was measured on a SHIMADIU AG-I 1KN according to the ASTM D2344 standard at a rate of crosshead movement of 1 mm/min. The heat deflection temperature (HDT) of the composite sample (80 mm × 10 mm × 4 mm) was measured on a Ceast HDT Vicat 500 Aloxide instrument at a heating rate of 5 °C/min and load of 1.8 MPa.

3. Results and discussion

3.1. PEP-PEEK copolymers

The obtained PEP-PEEK copolymers were characterized using ^{1}H NMR, GPC and TGA. All of the resonance signals in the ^{1}H NMR spectra of PEP-PEEKs were assigned to the corresponding protons (Fig. S4), which indicated that PEP-PEEK copolymers were successfully synthesized. The PEP-PEEKs copolymers had a high molecular weight and low polydispersity. The average molecular weights of the PEP-PEEK

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