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Effects of silanization and silica enrichment of carbon fibers on interfacial properties of methylphenylsilicone resin composites

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ABSTRACT

Effects of silane and silica enrichment of carbon fibers (CFs) on interfacial properties of methylphenylsilicone resin (MPSR) composites were investigated. CFs were oxidized, grafted with 3-aminopropyltriethoxysilane (APS) and then modified with silica nanoparticles prepared by the sol-gel polymerization of tetraethoxysilane (TEOS). Chemical structures of CFs were characterized by confirming the successful grafting. Scanning electron microscopy (SEM) showed a uniform distribution of silica nanoparticles on the CFs surface. The interlaminar shear strength (ILSS) and impact toughness of silanized CF (CF-Siloxane) composites were 12.05% and 7.46% higher than those of untreated composites. However, ILSS and impact toughness of the hybrid fiber (CF/Si) composites obtained from the hydrolysis of different concentrations TEOS improved significantly, especially for grafting silica enrichment with the TEOS concentration of 0.05 mol/L (CF/Si0.05), increasing 45.64% in ILSS and 29.59% in impact properties. Moreover, the hydrothermal aging resistance was also improved greatly. Meanwhile, functionalization processes did not decrease fiber tensile strength.

1. Introduction

Carbon fiber (CF) reinforced polymer (CFRP) composites with the low cost-to-performance as well as high strength-to-weight ratio are increasingly being employed in a wide variety of high-performance structural applications such as the automotive, marine and aerospace industries [1–4]. The performance of CFRP is influenced not only by the intrinsic characteristics of the fibers and matrix resin, but also by the quality of the fiber-matrix interface [5,6]. Good fiber-matrix interfacial properties help to reduce stress concentration by transmitting stress from matrix resin to CFs efficiently, and thus enhance overall mechanical performance. In the past decade, various techniques based on the enhancement of interfacial adhesion between CFs and matrix resin have been proposed such as physical coating treatments [7–10] and chemical grafting methods [11–13].

Methylphenylsilicone resin (MPSR) has been used widely in many engineering fields because of its relatively low price, dielectric properties, ease of handling, thermal and weather resistance [14–16]. MPSR has been one of the more promising materials for polymer matrix resin in composites. However, MPSR exhibits weak interfacial properties with untreated CF owing to the non-polar, low energy and chemically inert surface of CFs [17,18]. As the applications of CF reinforced MPSR composites are becoming more and more important, CF surface modification is required for changing the wettability and chemical interactions between CFs and MPSR.

Functional nanoparticles grafted onto the CFs surface can enhance the wettability, nanoscale roughness or chemical bonding for an improved interfacial strength between CFs and MPSR [19]. Noteworthy, silica nanoparticles with their structural flexibility, thermal and excellent mechanical performance have become a research hot spot [20,21]. The high density silanol groups onto silica surface are beneficial to generate strong interfacial interactions with matrix resin. Recently, silica nanoparticles serving as novel coupling agents have been used to enhance polymer-filler interaction, and thus increase mechanical and thermal properties of polymer composites [22–24]. Several researches have demonstrated the ability of silica nanoparticles coated onto the surface of CFs or incorporated into the polymer resin system to enhance interfacial strength between CFs and matrix resin significantly [21,25–27]. However, there has been no related report on surface modification of CFs with 3-aminopropyltriethoxysilane (APS) functionalization and silica nanoparticles using the hydrolysis of

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tetraethoxysilane (TEOS) for enhancing the interfacial properties of CF/MPSR composites. As a coupling agent, APS has the unique bifunctional structures with both amine and ethoxyl groups which can act as the bridge between CFs and matrix resin to enhance mechanical properties of composites [28]. Moreover, APS molecules could be readily used as starting sites for the growth of silica nanoparticles on the surface of CFs in TEOS aqueous solution.

In this work, we developed an easy and effective method for the introduction of silane and silica enrichment onto CFs surface, and studied the effects of fiber surface treatment on the interfacial properties of CF/MPSR composites. Surface chemical elements and functional groups of CFs before and after modification were measured by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Surface topographies of different CFs were observed by SEM. Following the preparation of CF/MPSR composites using the compression molding method, the properties of composites were investigated. The mechanical properties of CF/MPSR composites were evaluated by ILSS and impact tests. Fractured surface morphologies of composites were studied by SEM.

2. Materials and methods

2.1. Materials

CFs (3 K, tensile strength of 3500 MPa, average diameter of 7 μm and density of 1.76 g cm^{-3}) were purchased from Toray Industries, Inc. Hydroxyl-terminated MPSR was obtained from ShangHai Chemicals Co. APS was obtained from Nanjing Shuguang Chemical Group Co. Ltd. N, N'-Dicyclohexyl carbodiimide (DCC) and 4-Dimethylaminopyridine (DMAP) were provided from Shanghai Prolong Biochemical Co. Ltd. TEOS was received from Aladdin Co. All other chemicals (acetone, toluene, concentrated nitric acid, distilled water, ammonia, tetrahydrofuran, absolute ethanol) obtained from Tianjin Bodi Organic Chemicals Co. Ltd. were reagent-grade. Tetrahydrofuran was distilled for purification before using.

2.2. Surface functionalization of silane and silica enrichment onto CFs

2.2.1. Desizing, oxidation, and silanization treatment of CFs

In order to remove polymer sizing and pollutants, the as-received CFs were firstly washed with acetone solution in Soxhlet extractor for 24 h (denoted as Untreated CF). Then, Untreated CF was oxidized in concentrated HNO_3 at 80 °C for 4 h, and washed with deionized water until the pH was 7 to obtain CF-COOH. To create starting sites for the growth of silica nanoparticles on the fiber surface, carboxyl groups of CF-COOH are needed to react with amino groups of APS for introducing -$Si(OEt)_3$ groups onto the fiber surface. The CF-COOH (100 mg) was reacted with the mixture solution of DCC (100 mg), DMAP (10 mg), APS (3 mL), and THF (100 mL) at 60 °C by stirring under nitrogen atmosphere for 24 h. When completed, the products were washed in excess anhydrous THF under sonication to remove unreacted APS and dried. The APS modified CF were obtained and denoted as CF-Siloxane.

2.2.2. Preparation of surface hydroxylated silica nanoparticles onto CFs

The introduction of silica nanoparticles onto CFs was fabricated by the hydrolysis of TEOS. Briefly, CF-Siloxane was dispersed into an alcohol-water mixed solution of ethanol (82 mL) and distilled water (3.4 mL) and stirred together by a magnetic stirrer for 30 min. Then, ammonia solution (5.6 mL) used as a catalyst was added and stirred vigorously for 10 min. Subsequently, the quantitative TEOS was quickly added into the reaction solution with TEOS concentrations of 0.01, 0.03, 0.05, 0.07, 0.1 and 0.2 mol/L, and allowed to react at room temperature for 15 h. During the preparation process, the silica nanoparticles were covalently bonded via the reaction of Si-OH groups to the CF-Siloxane surface. Finally, the obtained fibers were washed many times with deionized water and absolute ethanol each and dried. The hybrid fibers obtained from different concentrations of TEOS polymerization were denoted as CF/Si0.01, CF/Si0.03, CF/Si0.05, CF/Si0.07, CF/Si0.1 and CF/Si0.2. The whole functionalization processes are schemed in Fig. 1.

2.3. Preparation of CF/MPSR composites

The detailed preparation description of the fiber prepreg is as follows: firstly, CFs were twined around and fastened on to a metal frame with 35 circles. Then, the wrapped fibers were immersed into the MPSR solution for 30 min, and then the fibers were rubbed slightly until MPSR was saturated fully into CFs, and thus the prepreg fibers were obtained. The compression molding method was employed for the preparation of CF/MPSR composites. Typically, CF/MPSR composites were prepared by heating the mold at 120 °C and 150 °C for 1 h without pressure, 180 °C for 2 h under 20 MPa, followed by post curing at 250 °C for 4 h with a pressure of 20 MPa. The fiber contents of Untreated CF, CF-Siloxane, CF/Si0.01, CF/Si0.03, CF/Si0.05, CF/Si0.07, CF/Si0.1 and CF/Si0.2 composites were controlled at about 70 ± 1.5 mass%. The samples dimensions with 20 mm in length, 6 mm in width and 2 mm in thickness were used for ILSS testing, and the samples dimensions were 55 mm × 6 mm × 2 mm for impact testing.

2.4. Characterization techniques

Functional groups of CFs surface before and after modification were characterized by FTIR spectrophotometer (Nicolet, Nexus670, USA). The different CFs were dried for 1 h under vacuum at 60 °C before surface analysis, and a very thin KBr layer using the pelletizer was used for FT-IR data collection by scanning the specimens for 32 times in the wavenumber range of 500–4000 cm^{-1} with the resolution of 2 cm^{-1}.

XPS (ESCALAB 220i-XL, VG, UK) was carried out to detect surface elements of CFs using a monochromated Al Ka source (1486.6 eV) at a base pressure of 2×10^{-9} mbar. The XPS Peak version 4.1 program was used for data analysis.

SEM (Quanta 200FEG, Hitachi Instrument, Inc. Japan) was applied to study the surface structures of CFs with and without modification. All the samples were coated with a thin conductive gold layer by sputtering before SEM observation in order to capture a stable and clear image.

Tensile strength (TS) of a single filaments was performed on a universal testing machine (5569, Instron, USA) according to ASTM D3379-75. The monofilament was adhered to a rectangular piece of paper with a rectangular hole in the middle of the paper. The two long sides of the paper were cut prior to the tensile strength testing. A gauge length is 20 mm and the cross-head speed is 10 mm/min for all the fiber samples. The average value of at least 60 specimens measurements for each fiber type was obtained. Weibull statistical method was employed for analysis of the testing results.

The ILSS of CF/MPSR composites was tested on a universal testing machine (WD-1, Changchun, China) by using a three-point short-beam bending test method with a cross-head speed of 2 mm/min according to ASTM D2344. All the samples dimensions were 20 mm × 6 mm × 2 mm for ILSS testing. The ILSS values were obtained based on the following equation:

$$ILSS = \frac{3P_b}{4bh} \quad (1)$$