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Tuning interfacial strength of silicone resin composites by varying the grafting density of octamaleamic acid-POSS modified onto carbon fiber

Chunxu Zhang, Guangshun Wu*, Hua Jiang

School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

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ABSTRACT

Octamaleamic acid-polyhedral oligomeric silsesquioxanes (OMA-POSS) were chemically modified onto the surface of carbon fibers (CFs) by a facile and high efficient two-step method. CF was grafted with hydroxyl groups via aryl diazonium reaction, and then covalently functionalized with OMA-POSS. The grafting density could be tuned through the concentration of OMA-POSS. Fiber surface structures were characterized by confirming the covalent bonding nature between OMA-POSS and CF. OMA-POSS was scattered on CF surface uniformly, and fiber polarity and roughness increased with the increased grafting density of OMA-POSS. Interfacial shear strength (IFSS) and interlaminar shear strength (ILSS) of the modified CFs composites enhanced as the grafting density grew, which could be ascribed to OMA-POSS interface with providing different degrees of chemical bonding and mechanical interlocking. Moreover, the hydrothermal aging resistance of composites is highly dependent on the amounts of the introduced OMA-POSS. The storage modulus and the glass transition temperature could increase by 8 GPa and 14 °C based on dynamic mechanical analysis testing. In addition, the interfacial reinforcing mechanisms have been also analyzed, and surface modification maintained fiber tensile strength.

1. Introduction

Carbon fibers (CFs) have become ideal reinforcements of matrix resin composites because of their favorable strength-to-weight and stiffness-to-weight ratios [1–3]. The interface between CF and matrix governs the stress transfer efficiency, and plays an important role in determining mechanical properties of composites [4]. Composites interfacial strength is closely related to interfacial microstructures and chemical interactions. However, the desired microstructures and interfacial bonding could not be obtained owing to the low surface energy and smooth graphitic surface of CFs without surface treatment [5]. With the objective of improving microstructures and interfacial strength of carbon fiber-matrix interface, many surface modifications have been developed for enhancing fiber surface roughness, functional polar groups, and surface energy [6–10].

In-situ modification of CFs with macromolecules becomes a novel and useful method, which could significantly improve the interfacial properties of composites by enhancing fiber surface roughness for mechanical interlock, chemical bonding or wettability of fiber-matrix interface. Gao et al. [11] grafted hyperbranched polyglycerol onto carbon fibers by anionic ring-opening polymerization method, and found that interfacial strength of modified composites was remarkably improved. Yang et al. [12] building nanoporous metal-organic frameworks “armor” on fibers for enhancing interfacial strength of high-performance composite materials. Recently, the hierarchical reinforcements (e.g., graphene oxide (GO)/CF reinforcements, carbon nanotubes (CNT)/CF reinforcements) by chemically grafting nano-scale molecules have stimulated more and more interest [13–15]. The introduced nano-scale reinforcements can change interfacial microstructures obviously and provide sufficient chemical bonding or mechanical interlocking for improving interfacial strength.

Noteworthy, polyhedral oligomeric silsesquioxane (POSS), a kind of novel organic-inorganic nanohybrids, has a special cage-shaped three-dimensional structure (Si−O), which is surrounded by external eight organic substituents [16,17]. Compared to other nanoparticles mentioned above, POSS has good solubility in many organic/inorganic solvents, and can be more compatible with matrix resin. However, external different functional groups of POSS cages can be usually used as reaction sites for further creating the chemical bonds between the reinforcements and matrix resin. Very recently, polyhedral oligomeric silsesquioxane (POSS)/CF hierarchical reinforcements by chemically bonding POSS on fiber surface based on its unique specific age-like nanostructure and good mechanical properties have been proposed by many researchers to increase interfacial strength of composites

* Corresponding author.
E-mail address: wugs_hit1@163.com (G. Wu).

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[18–20]. Several coupling agents, like poly(amidoamine) [21], spiralphosphodicholor [22], carbon nanotube [23], have been introduced to bridge POSS and CF. Composites interfacial strength has a varying degrees of increase. However, the used agents are too expensive or the modification processes are too complicated and time-consuming. In addition, vigorous oxidation process by strong acid treatment could create some defects and surface flaws, which damaged inevitably fiber tensile strength. Hence, direct grafting of POSS onto fiber surface without using expensive bridging agents and acid modification is necessary and competitive.

OMA-POSS cages are selected as the interfacial reinforcements in this study. The reason to establish OMA-POSS is that it possesses external eight polar carboxyl groups. OMA-POSS not only can be grafted onto fiber surface by the reaction between one carboxyl group and phenol group of CF for enhancing surface roughness and polarity, but also create covalent bonding with matrix resin. That is to say, OMA-POSS grafting can provide sufficient covalent bonding and mechanical interlocking into fiber-matrix interface, which helps to enhance interfacial adhesion of composites. Compared with macromolecules, every OMA-POSS molecule possesses eight polar carboxyl groups which provide POSS molecules with high reactivity and compatibility, and OMA-POSS cages with the similar structure and same composition of basic resin can help to improve the wettability and compatibility between CFs and MPSR. POSS is the smallest known silica particle with the overall diameter of 1.5–3 nm. Hence, the numerous and uniform OMA-POSS particles with a size of several nanometers on the surfaces of CFs effectively enhance the fiber surface roughness especially on a nano-scale, and can significantly increase mechanical interlocking. Moreover, OMA-POSS cages have critical dimensions that are much smaller than macromolecules. This arrangement of OMA-POSS modified CFs has the advantage of a complex, hierarchical structure because of the bonds between matrix resin and CFs in addition to the smaller-scale bonds between OMA-POSS and matrix resin. Additionally, OMA-POSS cages with superior thermal stability can fully protect the interface of carbon fiber composites from hydrothermal aging penetration in harsh environment with high humidity.

In the paper, we developed a facile and high efficient two-step method to bond OMA-POSS onto the fiber surface. Phenol groups have been directly grafted onto untreated fiber surface by aryl diazonium reaction in water without the usage of acid oxidation, and then directly introduced OMA-POSS onto the fiber surface by chemical bonding. By optimizing the grafting parameters, a controlled, ordered and active microstructure could be realized at the interface, and systematically investigated effects of the grafting density onto fiber microstructures, composites interfacial strength, the hydrothermal aging resistance as well as the dynamic mechanical properties.

2. Experimental

2.1. Materials

CF (3k; diameter, ~7 μm; tensile strength, about 3500 MPa) was purchased from Toray Industries, Inc. OMA-POSS (CA0298; appearance, white to off-white solid; molecular weight, 1657.89) and MPSR (molecular weight, 2400) were received by Hybrid Plastics Co., Inc and ShangHai Chemicals Co., respectively. Isoamyl nitrite, 4-aminophenophenol, 4-Dimethylaminopyridine (DMAP), deionized water, dimethyl sulfoxide (DMSO), N,N′-Dicyclohexyl carbodiimide (DCC), N,N-Dimethylformamide (DMF), and ethanol (C_2H_6O) were purchased from Tianjin Bodi Organic Chemicals Co. Ltd.

2.2. Facile functionalization of OMA-POSS with different grafting density onto CF surface

OMA-POSS/CF hierarchical reinforcements (CF-POSS) were prepared via a facile and high efficient two-step method: fiber surface grafting of phenol groups by aryl diazonium reaction and chemically grafting OMA-POSS onto fiber surface.

In a typical procedure, the as-received CF (Sized CF) was firstly treated with supercritical acetone/water at 360 °C for 30 min to remove polymer sizing agents (Untreated CF). Subsequently, Untreated CF and 4-aminopheno-phenol were added into the mixed solution of 0.5 mL isopentyl nitrite and 50 mL deionized water at 80 °C by mechanical stirring for 12 h, and then washed in excess DMF and deionized water respectively under sonication until the solution was colorless aiming to remove unreacted aniline derivative (CF-OH). To get OMA-POSS/CF hierarchical reinforcements, the quantitative OMA-POSS was first dissolved in DMSO (50 mL) by sonication for 60 min to obtain different concentrations of OMA-POSS solution (0.1, 0.3, 0.5, 0.7 and 1.0 mol/L). Then, the appropriate amount of CF-OH, DCC (100 mg) and DMAP (10 mg) as catalysts was quickly added in OMA-POSS solution and reacted under magnetic stirring at 50 °C for 12 h. During the grafting process, OMA-POSS was covalently bonded onto CF-OH surface by the reaction between carboxyl groups of OMA-POSS and hydroxyl groups onto fiber surface. After functionalization, the obtained CFs were washed several times with DMF as well as acetone each and dried. The hierarchical reinforcements prepared by different concentrations of OMA-POSS solution were designed as CF-POSS0.1, CF-POSS0.3, CF-POSS0.5, CF-POSS0.7 and CF-POSS1.0. Molecular structure of OMA-POSS and the preparation of OMA-POSS/CF hierarchical reinforcements by two steps were illustrated in Figs. 1 and 2, respectively.

2.3. Fabrication of CF/MPSR composites

CF/MPSR composite laminates have been preparation with the unidirectional fiber prepreg via the compression molding method. Different CFs (Untreated CF, CF-OH, CF-POSS0.1, CF-POSS0.3, CF-POSS0.5, CF-POSS0.7 and CF-POSS1.0) were first wrapped around a metal frame with 35 circles and added into the grooves of mold. Then, MPSR was degassed with a vacuum pump until no bubbles came out of matrix resin, and was injected into the mold aiming to fully make MPSR resin saturate into CF. After that, the mold was put into the thermo-compressor for curing CF/MPSR composites, and the composites were cured at 120 and 150 °C for 1 h, and then 200 °C for 2 h under 20 MPa, followed by post curing at 250 °C for 4 h with the constant pressure. After curing, the mold was cooled naturally to room temperature maintaining the constant pressure with 20 MPa. CF/MPSR composite laminates with similar thickness values of 2 mm, and the laminates dimensions were 20 mm × 6 mm suiting for interfacial property and anti-hydrothermal aging behaviors testing. In addition, fiber contents of laminates were controlled at about ~70 mass%.

2.4. Characterization techniques

Surface chemical structures of CFs before and after modification were characterized based on Fourier transform infrared spectroscopy

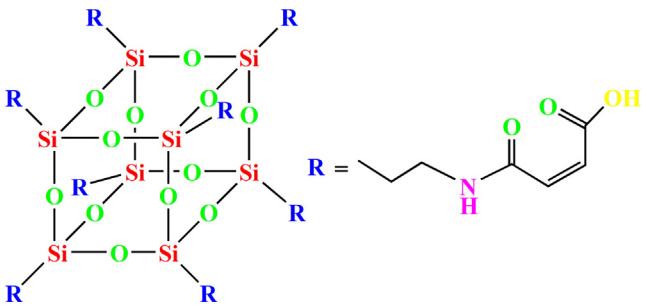

Fig. 1. Molecular structure of OMA-POSS. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)