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Adhesion force measured by atomic force microscopy for direct carbon fiber-epoxy interfacial characterization

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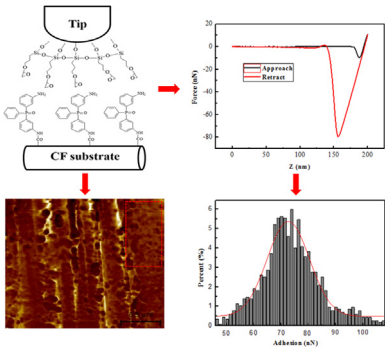
HIGHLIGHTS

- A novel technique to study the interfacial adhesion in carbon fiber/epoxy composite by atomic force microscopy was proposed.
- The adhesion forces between three types of carbon fibers and epoxy functionalized tip were measured.
- Adhesion force results demonstrate the direct effect of surface chemistry of carbon fiber on the interfacial adhesion.
- Adhesion force measurement has excellent correlation with single fiber microbond test on the carbon fiber/epoxy composite.

GRAPHICAL ABSTRACT



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ABSTRACT

Adhesion force measurement by Atomic force microscopy (AFM) is used to investigate the interfacial interaction of the carbon fiber (CF)/epoxy composite for the first time. The epoxy functionalized AFM tip and three types of carbon fibers with different surface chemistry and morphologies were used in this study. Results show that the Bis (3-aminophenyl) phenyl phosphine oxide (BAPPO) modified CF possesses a much larger adhesion force (72.7 nN) than the as-received and de-sized CF (22.5 nN and 17.9 nN, respectively) due to formation of the chemical bonding between the BAPPO modified CF and the epoxy functionalized tip. Single fiber microbond test demonstrates that the interfacial shear strength (IFSS) of BAPPO modified CF/EP composite is 15% and 22% larger than that of as-received and de-sized CF/EP, respectively. This nanoscale manipulation by AFM provides a new avenue to measure the interfacial adhesion between the CF and epoxy at the molecular level.

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1. Introduction

Carbon fiber reinforced epoxy composites have attracted considerable attention from both academia and industry due to their superior specific strength and elastic modulus [1,2]. As known, the mechanical properties of fiber-reinforced composites are not only influenced by the intrinsic characteristics of the fiber and matrix but also depend on the interfacial adhesion between the reinforcing CF and the resin matrix. Excellent interfacial adhesion is essential to ensure efficient load transfer from matrix to fibers, which can reduce stress concentrations and thus improve the overall mechanical properties. So far, various techniques including fiber pull-out [3–5], fiber push-out [6,7], and fiber fragmentation [8–11], have been used to characterize the interfacial adhesion between the fiber and matrix. These techniques can provide a lot of information about interfacial interactions such as the interfacial shear strength (IFSS) and the critical energy release rate, G_{IC}. However, both the sample fabrication and measurement are tedious. Therefore, it is desirable to develop a direct and novel technique to obtain the interfacial adhesion force and understand the adhesion mechanism between fibers and matrix especially at the molecular level.

Atomic force microscopy (AFM) is commonly considered as a powerful tool for imaging the nanoscale topography of materials and recording the mechanical, electrical, piezoelectrical, magnetic and chemical properties of sample surfaces [12–15]. Recently, a kind of novel AFM imaging mode, namely, PeakForce Quantitative Nanomechanical Property Mapping (QNM), was introduced for both the topography imaging with a high resolution and accurate measurement of nanomechanical properties of the substrate including modulus, deformation and dissipation [16]. In addition, this technique allows quantifying adhesion forces between the AFM tip and substrate under different environmental conditions [17]. In such an experiment, the substrate is scanned by a tip mounted on a cantilever spring. When the tip first approaches and then retraces from the substrate, the force between the tip and the substrate is measured by monitoring the deflection of the cantilever.

When the AFM tip is chemically functionalized, the adhesion force obtained can reflect the chemical interaction between specific molecules on the functionalized tip and the target substrate, which has found wide applications in biological fields, surface science and material science [18,19]. For example, D. Alsteens et al. [18] applied AFM with hydrophobic tips for directly measuring the local hydrophobic forces on organic surfaces, and found the nanoscale AFM measurement had an excellent correlation with the macroscale wettability measurements. M.A. Poggi et al. [20] examined the adhesion between thiolated AFM cantilever tips and the single walled carbon nanotube paper using a chemical force microscopy and observed a direct correlation of adhesion force with respect to the thiol terminal group on the AFM cantilever tips ($NH_2 > CH_3 > OH$). Based on the above discussion, it is expected that the adhesion force measurement by AFM can also applied in the fiber-reinforced composite to study the interfacial interaction between the epoxy and CF from the molecular level, which was, however, never reported in the open literatures.

In this paper, the interaction force between carbon fiber and epoxy was measured by using the AFM tip modified with (3-glycidyloxypropyl) trimethoxysilane. Three types of CFs were chosen as the substrate for the adhesion force measurement, and their morphologies, surface chemical composition and surface energy were analyzed by AFM, X-ray photoelectron spectroscopy and dynamics contact angle test, respectively. In addition, a traditional single fiber microbond test was also performed to verify the results obtained from the adhesion force measurement.

2. Experimental work

2.1. Materials

T300 polyacrylonitrile-based carbon fiber was used in this research and their parameters provided by the manufacturer of ToRay Ltd., Japan are listed below: tensile strength: 3.5 GPa, density: 1.8 g/cm^3, and diameter: 6.5 μm. The epoxy resin (E-51) and curing agent (H-256) were provided by Shell Chemical Corporation. (3-Glycidyloxypropyl) trimethoxysilane (98%) and thionyl chloride were purchased from Sigma-Aldrich, USA. Triphenylphosphine oxide (98%) and hydrazine hydrate (98%) were obtained from Aladdin Reagent Corp. (Shanghai, China) and TCI Ltd., Japan, respectively. Pd/C catalytic agent (5%), concentrated sulfuric acid (95–98%) and nitric acid (68%) were provided by Sinopharm Chemical Reagent Co., Ltd., China. All chemical reagents and solvents were used as received and without further purification.

2.2. Preparation of three types of carbon fibers

i) *as-received CF sample*: As known, the as-received T300 carbon fiber was covered by a layer of commercial epoxy sizing agent on its surface.
ii) *de-sized CF sample*: The as-received CF was refluxed in acetone at 70 °C for 48 h to remove the surface sizing agent and other contaminants, and the obtained CF was denoted as 'de-sized CF'.
iii) *BAPPO-CF sample*.

Bis(3-aminophenyl) phenyl phosphine oxide (BAPPO) was synthesized in two steps. At the first step, triphenyl phosphine oxide (13.9 g, 0.05 mol) was stirred in a 250 ml round-bottom flask in a nitrogen atmosphere. Then 96% sulfuric acid (100 ml) was added. When the reactants were dissolved and cooled to −5 °C in an ice/salt bath, a mixed solution of fuming nitric acid (5.2 ml) and sulfuric acid (50 ml) was added dropwise over a period of 2 h. Then, the mixed solution was maintained at room temperature for 8 h followed by adding 1 l of ice into the solution for hydrolysis. When the ice was melted, the mixture was extracted with chloroform and rinsed with sodium bicarbonate aqueous solution until neutral pH. At last, BNPPO with a 70% yield was obtained after removing the solvent and recrystallizing the solid residue from absolute ethanol.

The second step was conducted in a 250 ml round-bottom flask containing the as-prepared BNPPO (14.3 g, 0.04 mol), absolute ethanol (100 ml) and catalytic agent Pt/C (0.5 g). When the reaction temperature reached 80 °C, 80% $N_2H_4 \cdot H_2O$ solution (65 ml) was added dropwise over a period of 1 h. Then, the reaction was maintained at 80 °C for another 24 h. Subsequently, the Pt/C and solvent was removed by filtration and vacuum distillation, respectively. After the recrystallization from 50% ethanol, BAPPO with an 80% yield was finally obtained.

Before the introduction of BAPPO, the de-sized CFs were firstly oxidized in the concentrated nitric acid (HNO_3) at 80 °C for 3 h to obtain the carboxyl functionalized carbon fibers (COOH-CF). The COOH-CF further reacted with a mixture of 100 ml thionyl chloride and 5 ml dimethyl formamide at 80 °C for 48 h to obtain the acyl chloride functionalized carbon fibers (COCl-CF). The BAPPO modified CFs were subsequently prepared by the reaction of COCl-CF with a mixed solution of BAPPO (2.8 g), dimethyl formamide (100 ml) and triethylamine (5 ml) at 120 °C for 24 h. Through the above steps, 3 wt% of BAPPO was introduced onto the de-sized CF surfaces (coded as BAPPO-CF).

2.3. Adhesion force measurement

Adhesion force measurement between CF substrate and epoxy functionalized AFM tip was performed in a commercial Nanoscope VIII MultiMode SPM system (Bruker, Santa Barbara, CA) with Peak Force Tapping mode at room temperature and a relative humidity of 40–60%. Epoxy functionalized AFM tip was obtained by treating the as-received silicon nitride AFM tip (SCANASYST-AIR) with (3-glycidyloxypropyl) trimethoxysilane [21]. Specifically, the as-received AFM tip was first immersed into a standard piranha solution of H_2SO_4/