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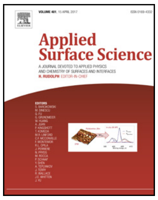

Full Length Article

Optimization of interfacial properties of carbon fiber/epoxy composites via a modified polyacrylate emulsion sizing

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ABSTRACT

The adhesion behavior of epoxy resin to carbon fibers has always been a challenge, on account of the inertness of carbon fibers and the lack of reactive functional groups. In this work, a modified polyacrylate sizing agent was prepared to modify the interface between the carbon fiber and the epoxy matrix. The surface characteristics of carbon fibers were investigated to determine chemical composition, morphology, wettability, interfacial phase analysis and interfacial adhesion. Sized carbon fibers featured improved wettability and a slightly decreased surface roughness due to the coverage of a smooth sizing layer, compared with the unsized ones. Moreover, the content of surface activated carbon atoms increased from 12.65% to 24.70% and the interlaminar shear strength (ILSS) of carbon fiber/epoxy composites raised by 14.2%, indicating a significant improvement of chemical activity and mechanical property. SEM images of the fractured surface of composites further proved that a gradient interfacial structure with increased thicknesses was formed due to the transition role of the sizing. Based on these results, a sizing mechanism consisting of chemical interaction bonding and physical force absorption was proposed, which provides an efficient and feasible method to solve the poor adhesion between carbon fiber and epoxy matrix.

1. Introduction

The interest in using carbon fiber reinforced polymer composites (CFRPs) is growing due to their outstanding strength-to-weight, stiffness-to-weight ratios and low density, compared with conventional materials [1–3]. However, as carbon fibers are brittle and inert, many problems arise during the manufacturing process, such as filament breakage, fluffing and weak cohesive force between fibers and the matrix. In addition, intrinsically poor interfacial adhesion between reinforcing carbon fiber surface and polymer materials causes a reduction in mechanical properties of CFRPs [4–6]. Hence, methods to improve the interfacial adhesion behavior between carbon fiber and polymer attract widespread attention in developing advanced CFRPs [7–9].

Resin and fiber modifications are the main methods to improve the interfacial bonding [4]. Primarily, the alteration in carbon fiber surface can be generally categorized as wet chemical modification, dry modification and multi-scale modification [5–13]. The 'wet' methods include applications of polymer sizing [6], chemical modifications with acids [7] and electrochemical modifications [8]. The 'dry' methods include plasma treatments [9], high-energy irradiation [10] and thermal treatments [11]. A 'Multi-scale' coating for carbon fiber consists of nano-particles/carbon nano-tubes/graphene modifications using techniques such as electrophoretic deposition (EPD) [12] and chemical vapor deposition (CVD) [13].

Compared to the above methods, sizing exhibits obvious advantages in industrial manufacturing for its low-complexity and low-cost. It is crucial in generating excellent interfacial properties because it protects the brittle fibers from damage, provides suitable strand integrity and serves as a coupling agent for the fiber/matrix bond, as well as improving composite processibility. In brief, the interfacial properties of carbon fiber can be feasibly tailored by proper sizing [14].

The efficiency of sizing adhesion at the interface depends upon the simultaneous action of various parameters, mainly upon physical force absorption and chemical interaction. On one hand, due to the structural integrity of an interphase in the composite, a good interfacial bonding ensures an efficient load transfer from the

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matrix to the fiber, which helps to reduce stress concentrations and improve overall mechanical properties [11,12]. On the other hand, the addition of coupling agent along with the sizing materials creates the covalently bonded functional groups at the carbon fiber surface, that are further responsible for chemical interactions with the matrix polymer [13–15]. In simple terms, the mechanism can be summarized to 'one surface and two combinations' [7–16]. Here, the coating formed by the sizing is the 'one surface'. Two combinations, one is H-bonding interaction and Van der Waals interaction between the carbon fiber surface and sizing agent; the other is mainly chemical network tangles of molecular chains between sizing agent and resin matrix.

To a large extent, the sizing agent of carbon fiber can improve the wettability of carbon fibers if the film formers of sizing agents are similar to the matrix resin [16,17]. Previous work in this field mainly focused on epoxy-type sizing agent, because most matrices for CFRPs are epoxy resin [17,18]. At present, commonly used epoxy-oriented film formers in sizing include modified epoxies [18], polyurethanes [19] and polyesters [17]. Among them, as one of low-cost polyesters, modified waterborne polyacrylate (WPA) emulsion have been widely utilized in sizing because of their specific properties, such as good film-forming, environmental friendliness and mechanical properties [20–22]. Furthermore, one promising approach to improve physicochemical properties of WPA emulsion is to adopt a multiphase polymeric system. Due to its complex chemical structure, a multiphase polymeric system will exhibit properties superior to any of their component homopolymers. Therefore, our research adopts organosilicone and fluoropolymer to modify polyacrylate (PA) thanks to their excellent self-cleaning, low surface energy and chemical resistance [23–25].

The objective of this paper is to study the effects of sizing on the interphase region of carbon fiber/epoxy composites and explore the surface chemical composition enrichment, surface morphological changes, interfacial adhesion transition and mechanical property improvements. To achieve this objective, an understanding of the physicochemical variation on carbon fiber surface is needed. Previous research tends to focus on how materials in sizing worked with fiber and matrix on a macro-scale, rather than pay attention to the relationships between interphase microstructure and the properties of the composites [1–22]. Dai et al. [29] investigated the effect of a commercial sizing on the interfacial adhesion of carbon fiber/epoxy composites by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analysis (XPS). Ge et al. [30] synthesized a modified tetraglycidyldiaminodiphenylmethane sizing through phase inversion emulsification method. They analyzed the reasons for increased interfacial strength by Fourier Transform Infrared spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), abrasion resistance, fluffs, and stiffness tests and Interlaminar Shear Strength (ILSS). In our research, the micro-properties of sizing emulsion were simply investigated using the technique of FT-IR, particle size and Zeta potential analysis (DLS), transmission electron microscopy (TEM); besides, the effects of sizing on the structure and performances of composites were systematically investigated by XPS, atomic force microscopy (AFM), scanning electron microscope (SEM), energy disperse spectroscopy (EDS) and the ILSS. Finally, the sizing mechanism of interfacial adhesion between the carbon fibers and epoxy matrix was proposed.

2. Experiments

2.1. Materials

The unsized PAN-based carbon fibers were supplied by the Institute of Coal Chemistry, Chinese Academy of Sciences. Triton X-100 (olyethylene glycol mono(p-1,1,3,3-tetramethyl butyl)phenyl ether), maleic anhydride (MA), glycidyl methacrylate (GMA), 2-ethylhexyl acrylate (EHA), *n*-butyl acrylate (BMA), sulphurous acid (H_2SO_3, 6%), polydimethylsiloxane (PDMS), lauryl mercaptan (TDDM), 2,2,2-Trifluoroethyl Acrylate (E(3F)A), ammonium bicarbonate (NH_4HCO_3), ammonium persulfate ($(NH_4)_2S_2O_8$) were purchased from Aladdin Industrial Corporation. Deionized water was used for all of the emulsion polymerization experiments. The matrix system used consisted of Epoxy 618 and the harder H-256, which were supplied by Yisheng Resin Factory, China.

2.2. Preparation of sizing emulsion

The emulsion polymerization was conducted in a 250 ml three-necked flask, involving a two-step process. The first step was self-emulsifying procedure: prior to the polymerization, the certain stoichiometry of X-100 and MAH were mixed into the flask to polymerize for 20 min at 347 K. Then, GMA and H_2SO_3 were successively added, along with the stirring at 500 rpm, for 1 h. The second step was emulsion polymerization: a certain stoichiometry of EHA, BMA, GMA, PDMS, TDDM and E (3F) A was added to the aforementioned solution for further polymerization. Among them, EHA and BMA performed as film former and TDDM acted as molecular weight regulator. In addition, NH_4HCO_3 was added in order to reduce the pH value of the system. Afterwards, nearly 5% of $(NH_4)_2S_2O_8$ was used as initiator to trigger the radical polymerization. Finally, the mixture reacted for 1 h under mixing speed of 500 rpm at 352 K to obtain the final emulsion. The recipe used in the polymerization is given in Table 1.

2.3. Sizing treatment of carbon fiber and preparation of carbon fiber-reinforced composites panels

The schematic illustration of manufacturing sized carbon fiber and its composites is illustrated in Fig. 1.

2.3.1. Sizing treatment

The process of sizing treatment was performed by a successive impregnation technology. The virgin carbon fibers were pulled through the obtained sizing emulsion, which was kept in a circulating state achieved by a pump to avoid sedimentation. Then the sized fibers were dried instantly in a hot gas oven at 120 °C. Finally, the new sized fibers were collected onto a spool.

2.3.2. Preparation of CFRP panels

The sized carbon fibers were first heated at 150 °C for 15 min in the oven. Then, the compression molding method was employed to prepare carbon fiber/epoxy composites. It was performed as follows: (1) The unidirectional prepreg of carbon fiber/epoxy was cast into a mold. (2) The composite specimens were heated at 120 and 150 °C for 1 h without pressure. (3) The composites were cured in an oven according to a curing step at 180 °C for 2 h and 250 °C for 4 h. After curing process, the mold was cooled to room temperature. Typically, the content of the resin in the composites was kept in the range of 30–40 wt.% and all the samples were 6 mm in width and 2 mm in thickness. As a comparison, the virgin carbon fibers were also prepared in this way.

2.4. Analytical methods

The sizing emulsion was evaluated by FT-IR spectroscopy (BrukerVertex-70) to confirm its reactivity. Subsequently, the average particle size and distributions of sizing were examined by DLS (LS13320, Beckman Coulter Instruments, USA) and TEM (JEM-2100, Hitachi, Japan).

The surface chemical composition of CFs was analyzed by XPS (Thermo Fisher Scientific, USA) with an Al Kα source. After that,