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Stepwise growth of melamine-based dendrimers onto carbon fibers and the effects on interfacial properties of epoxy composites

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ABSTRACT

A practical method for growing generation 1–3 melamine-based dendrimers onto carbon fibers (CFs) surface was proposed. The microstructures and interfacial properties of CFs before and after modification were investigated. X-ray photoelectron spectroscopy (XPS) confirmed the successful growth of different generation dendrimers. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images showed that melamine-based dendrimers grafting enhanced surface roughness, and this effect was more pronounced with increasing generation. The results of dynamic contact angle (DCA) demonstrated that the surface energy and the wettability of the grafted CFs were increased with generation. After generation 3 dendrimers grafting, the interfacial shear strength (IFSS) and impact strength of CF/epoxy composites were enhanced by 61.8% and 39.9%, respectively. The tensile strength of the composites were enhanced as the generation increased. Moreover, the reinforcing and toughening mechanisms were also discussed.

1. Introduction

CFs reinforced epoxy resin composites have demonstrated wide potential applications such as in aerospace, marine and automobile industries over the past few decades on account of their excellent mechanical properties [1–4]. However, the major challenge to obtain high mechanical performance CFs composites comes from the weak interfacial adhesion between CFs and epoxy matrix owing to the smooth and inert surface of CFs combined with low surface free energy [5,6]. One means to obviate this limitation is to increase the fiber/matrix adhesion to tailor the surface for resin compatibility [7,8]. The increased interfacial adhesion can be achieved via physical and/or chemical modification of the CF surface with different coupling agents aiming to increase the chemical interaction, mechanical interlocking and wettability with the matrix [9–12]. In general, grafting amine-containing coupling agents are in some regards ideally suited for this task, as amine groups can react with epoxy groups and result in good bridge formation between CFs and epoxy matrix, which can improve the interfacial properties of composites significantly. D.W. Jiang et al. reported that the growth of amino-POSS on CFs surface gives an increase of 22.9% for the ILSS of the composites [13]. The branched polyethyleneimine with a higher density of amine and imine groups have been used to functionalize CFs by L.C. Ma et al. and the ILSS increase by 47.5% compared with the untreated CF composites [14]. These studies also concluded that the content of amino groups on CFs surface plays an important role in the enhancement of interfacial properties. Therefore, the coupling agents with rich amino groups are desired. Besides grafting the nano materials and polymers, the attachment of dendrimers onto CFs surface may result in higher densities of desired functional groups which can be used for that purpose. The amine concentration on the CFs surface can be increased by the growth of amine containing surface-bound dendrimers, and thus supply more opportunities to form chemical bonds between fibers and matrix.

Amine dendrimers which inherit highly branched dendritic structure and high density of nitrogen atoms, could be a good candidate to functionalize CFs and improve interfacial properties of CF/epoxy composites. In the past few years, two kinds of amine dendrimers have been introduced onto the surface of materials,

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namely acrylate-based amine and melamine-based dendrimers [15]. Acrylate-based EDA dendrimer (PAMAM) has been immobilized onto the pores of a immobilized liquid membrane by A. S. Kovvali et al. [16]. In recent years, PAMAM has been used to modify the CFs surface as the coupling agent and significantly improves the interfacial properties of composites due to the sufficient chemical bonding [17]. However, the cost of commercial PAMAM is relative high and the residual ethylenediamine in synthesis process of PAMAM is difficult to remove which can affect the interfacial properties of the composites and restrict their application. Analogous to PAMAM, melamine-based dendrimers are triazines linked by diamines which were first reported by Simanek et al. Compared with PAMAM, the synthesis of melamine-based dendrimers has obvious price advantage and offers ease of y purification, since all the reagents may be readily washed in the end. Recently, they have been grafted onto the mesoporous materials such as MCM-41 and SBA-15 to enhance loading of the support for high-throughput synthesis applications [18,19]. However, to the best of our knowledge, the growth of melamine-based dendrimers onto CFs surface has not been reported so far.

In this study, we represent a stepwise growth of melamine-based dendrimers onto CFs surface, together with investigating the interfacial properties of the CFs reinforced composites. This dendritic compound contains a mixture of primary, secondary and tertiary amines groups. Thus, they are interesting from the perspective that they provide a range of active sites to react with epoxy resin and form “cross-bridges” to connect the CFs and epoxy matrix. In addition, the highly branched structures of the dendrimers are expected to enhance the mechanical-lock between the CFs and the epoxy matrix, which help to further enhance the interfacial properties of the CF/epoxy resin composites. Moreover, the thermal stepwise reactivity of the substitution of cyanuric chloride makes the process is much easier to handle with temperature and environmental friendly compared to that of other dendrimers and offers a promising technology to functionalize CF.

2. Materials and methods

2.1. Materials

PAN-based CFs (diameter 6–7 μm and density 1.76 g cm^{-3}) were purchased from Sino steel Jilin Carbon Co., China. P-Phenylenediamine was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Cyanuric chloride and diisopropylethylamine (DIPEA) was received from Aladdin Co. All other chemicals (acetone, methanol, ethanol, tetrahydrofuran (THF) and isopropanol) obtained from Tianjin Bodi Organic Chemicals Co. Ltd were reagent grade.

2.2. Surface modification of CF

An experimentally derived rule states that mono-, di- and trisubstitution reactions of cyanuric chloride occur at 0 °C, 25 °C and >60 °C, respectively [20]. This thermal stepwise reactivity is used to initially couple the cyanuric chloride via reaction with the hydroxyl groups of CFs at a relatively low temperature. The remaining chlorine groups on the coupled triazine are subsequently substituted by amines at higher reaction temperatures (>60 °C). Moreover, using DIPEA as proton scavenger can result in the high surface chlorine concentration [21]. An overall reaction scheme is shown in Fig. 1.

CFs were firstly extracted by Soxhlet with acetone to remove the polymer sizing and pollutants on the surface of CF (denoted as untreated CF) [22]. Subsequently, the CFs were oxidized in $AgNO_3$/$K_2S_2O_8$ solution at 343 K for 1 h to obtain the carboxyl functionalized CF (CF—COOH) [23]. In order to reduce carboxyl groups to hydroxyl groups, the CF-COOH was submersed in $LiAlH_4$-THF saturated solution, and allowed to react under reflux for 2 h. The obtained fibers (CF—OH) provide the reactive sites of homogeneously hydroxyl groups for further functionality with cyanuric chloride.

After being washed with ethanol and dried, the CF-OH was introduced in a round bottom flask containing THF. Next, DIPEA and cyanuric chloride were dissolved in the reaction mixture. The solution was heated under nitrogen atmosphere at 273 K for 24 h. After reaction, the CF was rinsed three times in THF and two rinsing steps in ethanol, followed by drying in a vacuum oven. The obtained fiber denoted as CF-CC. The CF-CC was then added to a solution of isopropanol. P-Phenylenediamine and DIPEA were added and the solution stirred at 343 K for 24 h to obtain CF-G1. After the reaction, the fibers were washed several times with isopropanol and ethanol to remove the side products such as absorbed triazines and amines on the CFs. Repeating the procedure led to product CF-G2 and CF-G3.

2.3. Characterization

XPS(ESCALAB 220i-XL, VG, UK)was applied to analyze the chemical changes on surface of the CF. The XPS peak version 4.1 software was used for data analysis.

The surface morphologies and the fractured surfaces of the untreated and functionalized CFs were observed by SEM (Quanta 200FEG, Hitachi Instrument, Inc. Japan). The surface roughness (Ra) of CFs was observed by AFM (NT-MDT Co., Moscow, Russia).

Dynamic contact angle meter and tensiometer (DCAT21, Data Physics Instruments, Germany) were used to analyze the surface energy of CF. Deionized water ($\gamma^d = 21.8$ mN m^{-1}, $\gamma = 72.8$ mN m^{-1}) and diiodomethane ($\gamma^d = 50.8$ mN m^{-1}, $\gamma = 50.8$ mN m^{-1}, 99% purity, Alfa Aesar, USA) were used as test liquids. The surface energy (γ_f), its dispersion component (γ_f^d) and polar component (γ_f^p) of CF can be calculated by solving the following equation:

$$\gamma_l(1+\cos\theta) = 2\left(\gamma_l^p\gamma_f^p\right)^{1/2} + 2\left(\gamma_l^d\gamma_f^d\right)^{1/2} \tag{1}$$

$$\gamma_f = \gamma_f^p + \gamma_f^d \tag{2}$$

where, γ_l, γ_l^d and γ_l^p are the liquid surface energy, its dispersion component and polar component, respectively.

The tensile strength of CFs were tested on a universal testing machine (5500R, Instron, USA) according to ASTM D3379-75. A gauge length of 200 mm and cross-head speed of 10 mm min^{-1} were used for all samples. The results of each sample were obtained from the average value of 50 specimens and analyzed using Weibull statistical methods.

The interfacial shear strength (IFSS) was adopted to quantify the interfacial property between CF and matrix resin by the interfacial evaluation equipment (Tohei Sangyo Co.Ltd., Japan). Epoxy resin (E-51) and curing agent (H-256) were mixed in 100:32 mass ratio to prepare microdroplets. The values of IFSS were calculated according to the following equation, which was averaged from the 50 valid data for each sample:

$$IFSS = \frac{F}{\pi dl}$$

Where F is the maximum load recorded, d is the carbon fiber diameter, and l is the embedded length.

Impact tests were carried out on a drop weight impact test system (9250HV, Instron, USA). The specimen dimensions were