Composites Part A 112 (2018) 337–345

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

Improved wettability and interfacial adhesion in carbon fibre/epoxy composites via an aqueous epoxy sizing agent

Fuyao Liu[a], Zhuo Shi[b], Yubing Dong[a,*]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China
[b] Zhejiang Dayang Biotech Group Co., Ltd, Hangzhou, Zhejiang 311616, China

ARTICLE INFO

Keywords:
A. Carbon fibres
A. Polymer-matrix composites (PMCs)
B. Interface/interphase
B. Wettability

ABSTRACT

In this paper, a modified epoxy emulsifier (MEE) was synthesised for preparing an aqueous epoxy sizing agent, which was used to reinforce interfacial adhesion of carbon fibre (CF)/epoxy composites. The sizing agent was evenly wrapped on the fibre surface with tiny particles, as well as increased the surface roughness of fibres; meanwhile, the activated carbon atoms on the surface of sized CF were further increased, as confirmed via SEM, AFM and XPS. The contact angle (CA) of fibres was observed via drop-on-fibre system. The results showed that the wettability of CF was significantly improved and the CA of CF was reduced by approximately 23°. According to the single-fibre fragmentation test, the interfacial shear strength of sized CF/EP composites increased by 70%–76%. The improvement of interfacial adhesion could be mainly attributed to the generation of chemical interaction bonds and the interface mechanical interlock of CF and the epoxy matrix.

1. Introduction

Carbon fibre reinforced polymer (CFRP) composites are widely used in aerospace, civil construction, lightweight automotive, sports goods and others due to their excellent mechanical properties [1–3]. The performance of CFRP is dependent to the interfacial adhesion of the fibres and the matrix resin; however, the CF surface is chemically inert because of crystallised graphitic basal planes that cause poor interfacial stress being transferred from the matrix to fibres, subsequently decreasing overall performance of CFRP and limiting its application [4,5]. Recently, various methods and techniques have been employed to improve interfacial adhesion between the matrix and fibres, such as chemical grafting [6–9], direct growth of CNT/SWCNT [10–13] and spraying solutions containing GO/VGCF on CF [14–17]; nevertheless, all these treatment approaches are not conducive for mass industrial production due to complex fabrication processes.

Solution-type sizing agents are being widely studied because of increasing environmental protection requirements. Luo et al. [18] employed aqueous sizing solutions consisting of commercial isocyanate-modified epoxy and KH560 to ameliorate the compatibility of LCF/PA6 composites, whose outstanding mechanical properties have been showed at a sizing concentration of 22 wt%. Ge et al. [19] synthesised modified epoxy resin with EP (F-51) and diethanolamine; the sizing agents, which were composed of water-soluble modified EP and poly (alkylene glycol allyl glycidyl ether) (AEPH), was used to treated CF, and the ILSS of the sized CF composites was highly enhanced. Furthermore, Yuan et al. [20] prepared a PES emulsion sizing solution to treat CFs and significantly increased the free energy and wettability of the treated CFs.

In this present study, bifunctional group EP (E-51), triethylenetetramine and butyl glycidyl ether were employed to synthesise a modified epoxy emulsifier (MEE), which was used to emulsify and cure epoxy resin. A new environmentally friendly aqueous epoxy sizing, composed of MEE, E-51/F-51 and deionised water, was prepared to improve the wettability of CF and interfacial adhesion of CF/EP composites.

Various test methods have been adopted to explore the influence of the sizing agent on the CF and its composites. Moreover, further research on the surface wettability of the CF after sizing has been done based on the Drop-on-Fibre Systems [21], which measures the contact angle of the droplet with the fibre, aqueous epoxy was loaded on single carbon fibre, and the influence of loaded droplet volume for contact angles was investigated, which provides a good reference for similar evaluations; meanwhile, interfacial shear strength (IFSS) of CF/EP composites has been analysed by using single-fibre fragmentation test (SFFT) [22].

---

[*] Corresponding author.
E-mail address: dyb19831120@zstu.edu.cn (Y. Dong).

https://doi.org/10.1016/j.compositesa.2018.06.026
Received 19 April 2018; Received in revised form 7 June 2018; Accepted 19 June 2018

2. Experiment

2.1. Materials

The commercial CFs T300B with a nominal diameter of 7 µm that were used in the present study were supplied by Toray industries, Inc. (Japan). Bisphenol A epoxy resin 618 (E-51) [epoxy value (EV) = 0.48–0.54, viscosity = 10000–25000 Pa·s/25 °C] was purchased from Hangzhou Wuhui Port Adhesive Co., Ltd. (China), and Bisphenol F epoxy resin NPEF-164X (F-51) [EV = 0.48–0.54, viscosity = 7–11 Pa·s/25 °C] were purchased from Dalian liansheng trading Co., Ltd. (China). Triethylenetetramine (TETA) and butyl glycidyl ether (BGE) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. (China).

2.2. Preparation of the modified epoxy emulsifier

Primary and secondary amines contain active hydrogen atoms; thus, they easily undergo nucleophilic addition reactions with epoxy groups. In order to prevent secondary amines from participating in competitive reaction at low temperatures, a proton-accepting aliphatic ether was used as a solvent. In this work, a slight excess of polyamine TETA was reacted with E-51 resin and aliphatic ether was used to cap the molecular chain, afterwards, the modified resin was dissolved in deionised water after neutralisation by acid.

The synthesis procedure was as follows: Appropriate amounts of TETA (22.8 g) and solvent propylene glycol methyl ether (PM, 14 g) were added to a three-necked flask equipped with a mechanical stirrer and heated to 65 °C in a water bath, and calculated amounts of solvent PM (24 g) and E-51 (27 g) were dripped into the flask through the constant pressure funnel within 1.5 h. Excess TETA was removed by distillation under reduced pressure after reaction for 2.5 h. Upon reaching 75 °C, BGE (23.5 g) was transferred into the flask within 1 h and the solution was kept under continuous stirring for 1.5 h. Thereafter, we decreased the temperature to 60 °C and added a small amount acetic acid (20 g) with constant stirring for 30 min, and then the PM and free acetic acid were removed by distillation under reduced pressure. Finally, 100 g deionised water was dripped into the three-necked flask and stirred for 30 min to obtain the modified epoxy emulsifier (MEE, solid content is 40%) as shown in Fig. 1(a).

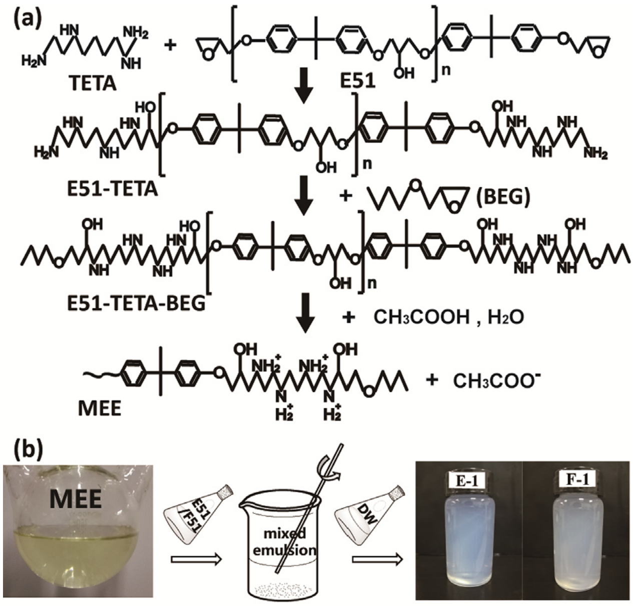

Fig. 1. Reaction route of the MEE (a) and preparation of sizing agents E-1 and F-1 (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Preparation of sizing agent and sizing treatment of CF

The MEE was used to emulsify the EP. The MEE was mixed with E-51 at a mass ratio of 5.2:3 and with F-51 at a mass ratio of 7:3, and the mixtures were kept under constant stirring for 10 min to obtain MEE emulsion. A total of 2 wt% MEE emulsion was dissolved in deionised water under high-speed stirring for 2 h, and finally the MEE emulsion sizing was derived; moreover, the sizing agents containing E51 and F51 were named E-1 and F-1, respectively. All above reaction steps are shown in Fig. 1(b).

CF T300B, whose sizing agent was removed by ultrasound in acetone solution before the sizing treatment, was immersed in a homemade aqueous sizing agent for 5 min and was pulled out at speed of 1 mm/s, and then successively dried in a vacuum oven at 120 °C for 2 h. E-1-sized and F-1-sized CFs were obtained.

2.4. Characterisations

The size and distribution of the particles were analysed by using a Zetasizer Nano S size and molecular weight analyser (Malvern, UK). Nicolet 5700 Fourier Transform Infrared Spectrometer (FTIR, Thermo Electron, USA)in the wave number range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} was used to examined the changes in the functional groups of the modified resins. Surface roughness of the treated CF was analysed using a PSIA XE-100E atomic force microscope (AFM). Surface microstructure was characterised by using a Carl Zeiss SMT Pte vltra55 SEM at 3 kV. The chemical structures of CF were evaluated by using K-Alpha X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA) with a monochromated 150 W Al Kα radiation (hv = 1486.6 eV).

2.5. Fibre contact angle measurements

The contact angle is an important parameter to characterise the wettability of the fibre; a small contact angle means easy spreading of the droplets on the fibre surface, which then indicates enhanced fibre wettability. However, the existing techniques for measuring the plane contact angle are inaccurate when applied to fibres. Therefore, Carroll [21] and Yamaki [23] proposed a droplet profiling method wherein the contact angle is obtained by microscopically observing the morphology of the droplets hanging on the fibres, and the contact angle of the droplets and the fibre is obtained using the Young-Laplace equation and elliptical integral calculation. [24]. Fig. 2(a) illustrates the geometrical simulation of the droplet.

According to Fig. 2(a), the following integral formula is obtained by using the integral calculation:

$$-\frac{d_z}{d_x} = \frac{x^2 + \alpha hr}{[(h^2 - x^2)(x^2 - \alpha^2 r^2)]^{\frac{1}{2}}} \tag{1}$$

$$\alpha = \frac{h\cos\theta - r}{h - r\cos\theta} = \frac{n\cos\theta - 1}{n - \cos\theta} \tag{2}$$

When $\theta = 0$, $\alpha = 1$ and the length $L = 2\,|z(x = r)|$, then the equation is given in the following expression: $\overline{L} = 2[\alpha F(\varphi, k) + nE(\varphi, k)]$, where:

$$\overline{L} = \frac{L}{r},\ n = \frac{h}{r},\ \varphi = \frac{\pi}{2} - arctan\frac{2r}{L},\ k = \sqrt{1 - \left(\frac{2h}{L}\right)^2} \tag{3}$$

and $F\ (\varphi, k)$, $E\ (\varphi, k)$ are the Legendre's standard incomplete elliptical integrals of the first and second kinds, respectively, which are gained from the elliptical integration table. Therefore, the contact angle θ, which is a function of r, h and L may thus be calculated using the following formula:

$$\theta(r, h, L) = arccos\frac{2F(\varphi, k) + n[\overline{L} - 2nE(\varphi, k)]}{2nF(\varphi, k) + [\overline{L} - 2nE(\varphi, k)]} \tag{4}$$

In a typical contact angle measurement, the fibres were tightened on