Interfacial shearing strength and reinforcing mechanisms of an epoxy composite reinforced using a carbon nanotube/carbon fiber hybrid

Fu-Hua Zhang · Rong-Guo Wang · Xiao-Dong He · Chao Wang · Li-Ning Ren

Abstract The performance of a composite material system depends critically on the interfacial characteristics of the reinforcement and the matrix material. In this study, the interfacial shearing strength (IFSS) of a composite with an epoxy matrix and a novel carbon nanotube/carbon fiber (CNT/CF) multi-scale reinforcement was determined by single fiber-microdroplet tensile test, and the interfacial reinforcing mechanisms of the composite were discussed. Results show that the IFSS of the epoxy composite reinforced by CNT/CF is as high as 106.55 MPa, which is 150% higher than that of the as-received T300 fiber composite. And the main interfacial reinforcing mechanisms of this novel composite could be interpreted as chemical bonding, Van der Waals binding, mechanical interlocking, and surface wetting.

Introduction

Carbon nanotube/carbon fiber (CNT/CF) multi-scale reinforcement, which is synthesized by grafting CNTs onto the CFs [1, 2] or growing CNTs through chemical vapor deposition (CVD) directly onto a CF surface [3, 4], shows the potential use for high-performance composite materials. The performance of a composite material system depends critically on the interfacial characteristics of the reinforcement and the matrix material [5]. It has been found that the interfacial strength between CFs and the matrix in a polymeric composite could be greatly improved by growing CNTs onto the surfaces of CFs [4]. In respect of the multi-scale reinforcement obtained by grafting CNTs onto the CFs, there exist chemical bonds between CNTs and CFs, as well as between CNTs and the polymer matrix. Chemical bonding [6] and the intimate contact between the CNTs and the polymer matrix have been suggested as responsible for the high interfacial shear stress. A strong interface of the traditional CF-reinforced polymer composite can also be achieved by forming chemical bonds between CFs and the matrix through fiber surface treatments [7, 8].

Although CNT/polymer composites and CNT/CF multi-scale reinforcement have been the topics of several recent studies, the interfacial bonding properties and reinforcing mechanisms of the epoxy composite in which CNT/CF synthesized by grafting CNTs onto the CFs is used as mechanical reinforcement have not been studied detail. The interfacial properties of polymer composites reinforced by traditional fiber are usually studied by single fiber model composites test [9, 10]. In this study, a single CNT/CF filament-reinforced epoxy microdroplet tensile test was carried out to investigate the interfacial shearing strength (IFSS) of the novel composite, and the interfacial reinforcing mechanisms of the composite were discussed from the view of chemical bonding, Van der Waals binding, mechanical interlocking, and surface wetting.

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Experiment

Sample preparation

In order to prepare the CNT/CF multi-scale reinforcement, the CNTs functionalized with hexamethylene diamine were grafted onto the fiber surface treated by acid and SOCl$_2$ through nucleophilic substitution reaction between amine groups at the end caps of CNTs and acyl chloride groups on the fiber surface [1].

During the preparation of the resin system, epoxy AG-80 and p-diaminodiphenylsulfone were mixed in the ratio of 3:1 and the viscosity of the mixture was regulated by acetone. Single filament approximately 100 mm in length was carefully separated from the fiber tow with a needle and the end of the fiber was taped to parallel sides of a specially designed fiber fixer (as shown in Fig. 1) by using double-sided tape. Then resin microdroplets were applied to the fiber using a syringe and a needle. A drop of the prepared resin was made to flow to the needle tip and allowed to contact with a fiber. After retraction of the needle tip, some of the resin formed spindle-like microdroplets around the fiber under surface tension forces. Then the microdroplets were allowed to cure at 120 °C for 4 h. As-received T300, T300 rinsed by acetone, T300 treated by thionyl chloride, and CNT/CF multi-scale reinforcement [1] were selected to prepare single fiber-microdroplet tensile test samples for comparison. The percentage of surface elements of T300 and CNT/CF was analyzed by X-ray photoelectric spectra (XPS).

IFSS test

Composite interfacial evaluation equipment (MODEL HM410) was employed to determine the IFSS of single fiber-microdroplet composites. The microdroplets with a diameter of about 60 μm were selected and a loading rate of 0.05 μm/s was applied to obtain the interfacial debonding load. The IFSS is an average of at least 100 measurements which can be calculated as the following Eq. 1:

$$\text{IFSS} = \frac{F}{\pi D_f L_e}, \tag{1}$$
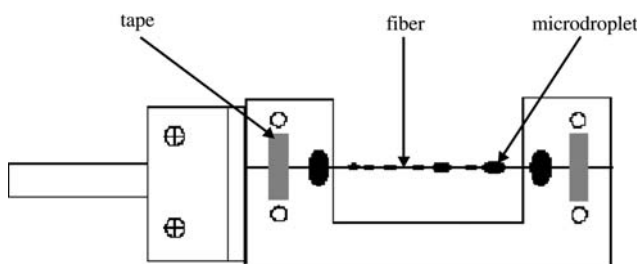
Fig. 1 Sketch of single fiber-microdroplet sample preparation

Table 1 The IFSS of four single fiber-microdroplet composites

Filament	IFSS (MPa)	Increase (%)
As-received T300	42.62	–
T300 rinsed by acetone	18.37	−56.90
T300 treated by thionyl chloride	56.19	31.84
CNT/CF	106.55	150

where F is the maximum load, D_f the diameter of the single fiber, and L_e is the diameter of the microdroplet.

Results and discussion

IFSS

The IFSS of four kinds of single fiber-microdroplet composites with the same resin system is listed in Table 1.

As listed in Table 1, the IFSS of the as-received T300 composite is 42.62 MPa, whereas the IFSS for the T300 rinsed by acetone composite is 18.37 MPa, which is 56.90% less than that of the former. This is because the polymer layer on fibers, which is used to protect CFs during its processing and improve its adhesion property [11], could be removed after rinsed by acetone, resulting in the decrease in the wettability of the fiber surface. The IFSS of the thionyl chloride-treated T300 fiber composite is 56.19 MPa, which is increased by 31.84% compared to that of the as-received T300 fiber composite. The reason may be that the introduction of carboxyl and hydroxyl on CFs after thionyl chloride treatment can improve the wettability of the fiber surface. It should be noted that owing to the incorporation of CNTs, the IFSS of the CNT/CF composite is as high as 106.55 MPa, which is 150% higher than that of the as-received T300 fiber composite.

The fracture surfaces of the composites reinforced using T300 fibers and CNT/CF are shown in Fig. 2a, b. There is almost no CF pull out observed in CNT/CF composite, whereas it is serious in T300 fiber composite. It therefore confirms that the CNTs on CF surfaces helped in improving the interface between the fibers and the matrix. The shear delamination of the hybrid composite is thus reduced and is reflected in their improved interfacial properties.

Interfacial reinforcing mechanisms

Chemical bonding

Load transfer ability could be effectively improved by chemical bonding between the fiber and the matrix. There are chemical bonds connecting CNTs and the CF together, which make the CF like a branched fiber. The
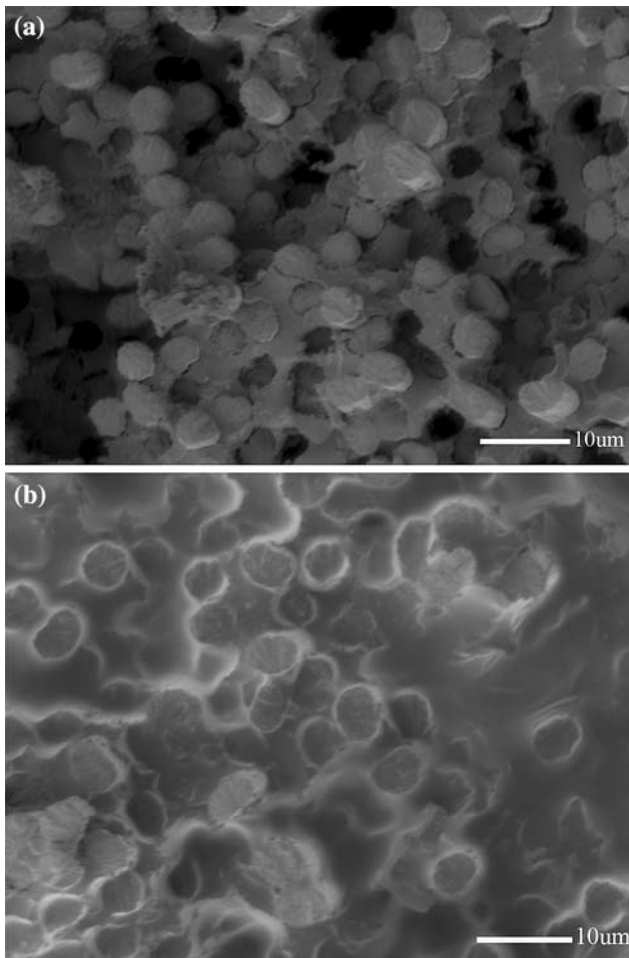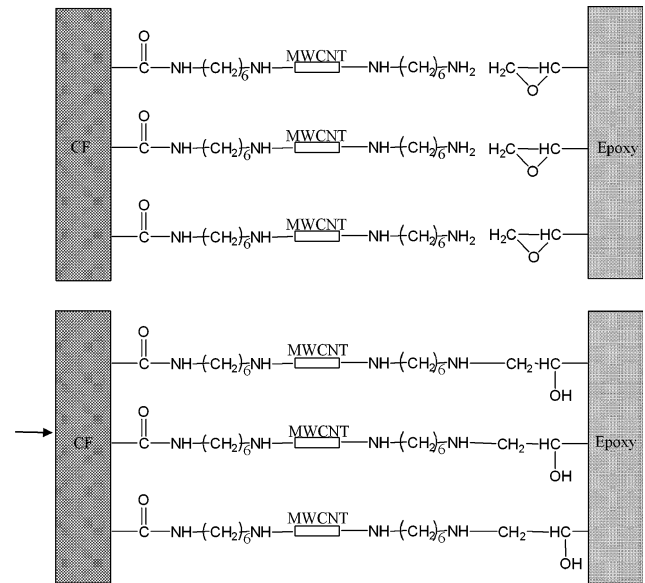
Fig. 2 SEM photos of the fracture surfaces of **a** T300 fiber composite and **b** CNT/CF composite

Fig. 3 Sketch of CNT/CF composite interfacial chemical reaction

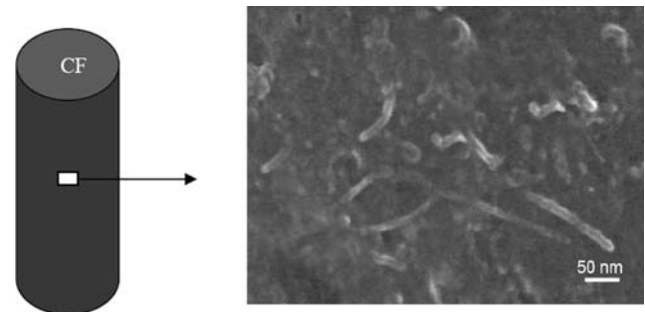**Fig. 4** Representative area of the CNT/CF multi-scale reinforcement [1]

chemical reactions at the composite interface are shown in Fig. 3. One end of the CNT and the epoxy matrix could react through amino and epoxy groups, respectively. Meanwhile, previous study on the CNT/polymer composites indicates that there are chemical bonds between CNTs and polymer [12]. And the IFSS and load transfer ability can be enhanced by over an order of magnitude with the formation of crosslinks between CNT and the matrix involving <1% of the nanotube carbon atoms [13]. Therefore, it indicates that the high interfacial shear stress could be ascribed, to a large extent, to the chemical bonding at the composite interface.

Van der Waals binding

Due to the exceptionally high specific area of CNTs, the Van der Waals interaction which depends primarily on the contact area at the composite interface cannot be negligible. The representative area of the CNT/CF multi-scale reinforcement (265 nm in width and 417 nm in length) is shown in Fig. 4. The content of CNTs on the multi-scale reinforcement is 1.2 wt% [1]. The total length of CNTs measured in the selected area is 800 nm. The radius of the T300 fiber is 3500 nm and the density is 1.76 g/cm^3, and those of CNT are 8 nm and 1.40 g/cm^3, respectively. The specific surface area of the T300 fiber is calculated as 0.4564 m^2/g, and 0.6193 m^2/g for the CNT/CF multi-scale reinforcement, which is 36.23% lager than that of the T300 fiber. Thus, the incorporation of the CNTs at the composite interface can increase the specific surface area of the reinforcement filler significantly, which results in the improvement of Van der Waals interaction at the composite interface.

Mechanical interlocking

The mechanical interlocking between the reinforcement and the matrix induced by fiber surface roughness could
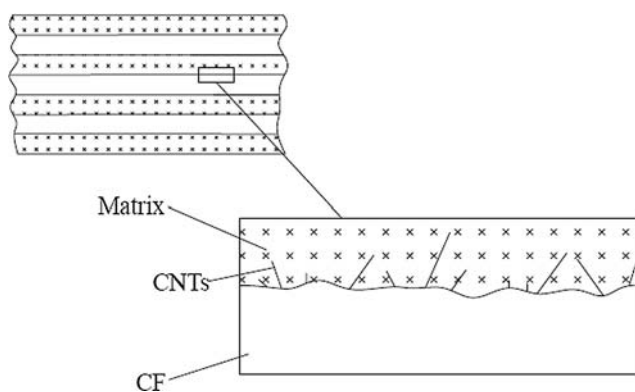
Fig. 5 Sketch of CNT/CF microdroplet composite interfacial structure

restrict the movement of the different phase of materials at the composite interface reciprocally. But this could be difficult for traditional CF-reinforced polymer due to the glazed and inert surface of CFs. The CNT/CF microdroplet composite interfacial structure is illustrated in Fig. 5. The CNTs "nails" on the CF surfaces extend into the polymer matrix and lead to micromechanical interlocking effect at the interface regions, which improve the load transfer ability efficiently. Meanwhile, the amino groups on the end of the "nails" could react with the epoxy matrix during curing process, leading to their connection through chemical bonds. Thus, the incorporation of CNTs offers potential for selective reinforcement, where nanoscale reinforcement can be included in matrix-rich interlaminar regions to improve through-thickness properties of polymer composite and stiffen the fiber/matrix interface [4].

Surface wetting

Sufficiently good adhesion between fibers and matrix is essential for the successful usage of fiber composite. However, resins do not easily wet CFs, due to the relatively inert and non-polar fiber surface [14]. This could be improved by fiber surface treatments [15, 16]. The XPS results of the surface elements percentage of T300 and CNT/CF multi-scale reinforcement are listed in Table 2.

Table 2 shows that compared with those of the as-received T300 fiber, the content of oxygen on CNT/CF surface increases from 16.63 to 21.49%, and the content of

Table 2 The percentage of surface elements of T300 and CNT/CF (%)

Filament	C	O	N	Cl
As-received T300	79.62	16.63	3.40	0.35
CNT/CF	72.58	21.49	4.12	1.82

nitrogen and chlorine increases from 3.40 to 4.12% and 0.35 to 1.82%, respectively. Therefore the contents of polarity functional groups on CNT/CF surface are increased. A sequent of surface treatments on CFs [1] populated the fiber surfaces with active chemical groups such as hydroxyls, carboxyls, and carbonyls, which improved the surface wettability of CFs, and in turn maximized the degree of intimate molecular contact.

Conclusions

Single fiber-microdroplet tensile test indicates that the IFSS of a composite with an epoxy matrix and a novel CNT/CF multi-scale reinforcement is as high as 106.55 MPa, which is 150% higher than that of the as-received T300 fiber composite. The main interfacial reinforcing mechanisms of this novel composite could be interpreted as chemical bonding, Van der Waals binding, mechanical interlocking, and surface wetting.

References

1. He XD, Zhang FH, Wang RG et al (2007) Carbon 45(13):2559
2. Abdelghani L, Alexandre V, Gérard N et al (2008) Mater Lett 62(3):394
3. Li WZ, Wang DZ, Yang SX et al (2001) Chem Phys Lett 335(3):141
4. Thostenson ET, Li WZ, Wang DZ et al (2002) J Appl Phys 91(9):6034
5. Kin L, Sean L (2001) Appl Phys Lett 79(25):4225
6. Wagner HD, Lourie O, Feldman Y et al (1998) Appl Phys Lett 72(2):188
7. Shanahan MER, Bourgès-Monnier C (1996) Int J Adhes Adhes 16:129
8. Yunmitori S, Nakanishit Y (1996) Composites Part A 27A:1059
9. Lei ZK, Qiu W, Kang YL et al (2008) Composites Part A 39:113
10. Eichhorn SJ, Young RJ (2004) Compos Sci Technol 64:767
11. Shao YL, Wang BX (2002) Acta Materiae Compositae Sinica 19(4):29
12. Jia ZJ, Wang ZY, Xu CL et al (1999) Mater Sci Eng A 271(2):395
13. Frankland SJV, Caglar A, Brenner DW et al (2002) J Phys Chem B 106(12):3046
14. Walsh PJ (2001) Constituent Mater 21:35
15. Rashkovan IA, Korabel'nikov YG (1997) Compo Sci Technol 57:1017
16. Menendez JA, Menendez EM, Iglesias MJ (1999) Carbon 37(7):1115