Improving interfacial and mechanical properties of T800 carbon fiber reinforced itaconic acid-based epoxy resin composites by introducing cellulose nanomaterials onto the surface of fibers

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Abstract

In this work, four different cellulose nanomaterials (A-NFC, T-NFC, T-NCC and C-NCC) were introduced onto the surface of T800HBs by a simple dip-coating method. The as-treated T800HB (denoted as T800HB-A-NFC, T800HB-T-NFC, T800HB-T-NCC and T800HB-C-NCC, respectively) were then used to reinforce a new biomass-derived epoxy from itcaonic acid (EIA). The interfacial and mechanical properties as well as dynamic mechanical properties of the as-prepared NCC and NFC-coated T800HB/EIA composites were compared with those of T800HB/EIA composites. The results showed that the introduction of NFC and NCC onto the surface of T800HB can significantly improve the interfacial and mechanical properties as well as heat resistance of the NCC and NFC-coated T800HB CF/EIA composites. However, the degree of the improvement between NFC and NCC is quite significant due to their different aspect ratio. The NFC with a higher aspect ratio than NCC, so NFC performs better in improving the interfacial and mechanical properties of composites than NCC.

Keywords: T800 carbon fibers, itaconic acid-based epoxy resin（EIA）, cellulose nanomaterials, interfacial properties

1 Introduction

Carbon fibers reinforced epoxy resins composites (CF/EP) have been widely used in many structural applications such as aerospace, automotive and civil engineering to replace traditional metal materials because of their superior mechanical properties and good corrosion and fatigue resistance [1-5]. However, the epoxy resins used for the CF/EP composites are usually from petroleum. The increasing worldwide shortage in petroleum cause alternative epoxy from biomass receiving increasing attention [6-9]. Recently, a new biomass-derived epoxy itconic acid (EIA) with a high epoxy value and low viscosity has been developed [9]. It was reported that the EIA has a higher tensile and bending properties compared with the traditional EP such as E51, thus the EIA is a potential alternative to traditional petroleum-based EP in the following decades.

The mechanical properties of CF/EP composites are not only determined by carbon fibers (CF) and EP matrix but also the interphase between the two phases [10]. Usually, there are two main methods to improve the interfacial properties of CF/EP composites. One is treating the surface of CF fibers by fibers sizing and coating [11,12], chemical oxidation [13], plasma irradiation [14]. The other is adding nano-fillers such as graphene [15], carbon nanotubes [16], halloysite nanotubes [17] and cellulose nanomaterials [18] onto the surface of CF. Cellulose nanomaterials ~~i~~ncluding nanocrystalline cellulose (NCC) and nanofibrillated cellulose (NFC) are a promising reinforcement in composites because of their high aspect ratio, excessive mechanical properties and the renewable sources such as natural plants or bacteria.[18]. Introducing the cellulose nanomaterials onto the surface of CF could transfer the stress from EP to CF in the interphase of CF/EP composites, improving the interfacial and mechanical properties of the composites.

In this work, four different cellulose nanomaterials (A-NFC, T-NFC, T-NCC and C-NCC) were introduced onto the surface of T800HBs by simply dip-coating the commercial T800HB with a water suspension of cellulose nanomaterials, the as-treated fibers were denoted as T800HB-A-NFC, T800HB-T-NFC, T800HB-T-NCC and T800HB-C-NCC, respectively.. Then, the four coated T800HB reinforced EIA composites (denoted as T800HB-A-NFC/EIA, T800HB-T-NFC/EIA, T800HB-T-NCC/EIA and T800HB-C-NCC/EIA, respectively) were manufactured, and their interfacial and mechanical properties as well as dynamic mechanical properties were comparatively investigated.

2 Experimental

2.1 Materials

The CFs used in this work were T800HB from Toray Company. The EIA was provided by Ningbo Institute of Material Technology and Engineering. The NFC and NCC were Anionic-NFC, TEMPO-NFC, TEMPO-NCC and Cationic-NCC from Tianjin Haojia Cellulose Company (denoted as A-NFC, T-NFC, T-NCC, C-NCC), respectively. The size parameters of the NFC and NCC are listed in Table 1. The hardener was amino hardener prepared in our lab.

Table. 1 The size parameters of the NFC and NCC

Materials	Average length/nm	Diameter/nm	Aspect ratio
A-NFC	~5500	20-50	500-1000
T-NFC	~5000		
T-NCC	~220	4~10	20-70
C-NCC	~260		

2.2 Fabrication of T800CF/EIA composites

First, the commercial T800HB were dip-coated by using the water suspension with 0.33 wt% of A-NFC, T-NFC, T-NCC and C-NCC, respectively. Then, the coated T800HB (denoted as T800HB-A-NFC, T800HB-T-NFC, T800HB-T-NCC and T800HB-C-NCC, respectively) were dried and used as reinforcement to fabricate the EIA-based composites as followings. The EIA resin was mixed with the hardener at 1:1 chemical equivalent ratio under stirring at 80℃for 15 min. Then, the coated T800HB were impregnated with the above resin and were composited in the mold which was preheating in 80℃. The curing system of the these composites were 120℃/3 h +150℃/2 h. The as-obtained T800 reinforced EIA composites were marked as T800HB-A-NFC/EIA, T800HB-T-NFC/EIA, T800HB-C-NCC/EIA and T800HB-C-NCC/EIA, respectively.

2.3 Characterizations

All the NFC and NCC were studied by dynamic light scattering as well as scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) to characterize the size and the functional groups, respectively. The surface of treated T800HB and untreated T800HB were characterized by scanning electron microscopy (SEM).

The interlaminar shear strength (ILSS), transverse fiber bundle test (TFBT) and flexural properties of the composites were tested on a universal testing machine (INSTRON-1121) based on the standard test methods (JC/T773-2010, DIN EN ISO 527-3 and GB/T 3356-1999 respectively). . The composites were made as 60mm×6mm×2mm for DMTA test, which was performed on aQ800 universal TA with the heating rate of 5 °C/min from 40°C to 220°C, .the amplitude of 9.0μm, and the sweep frequency of 1Hz. The fracture of composites were characterized through SEM (SUPER 55) to confirm the interfacial properties between CFs and matrix.

3 Results and discussion

3.1 Mechanical properties of the composites

The ILSS results of the cellulose nanomaterials-coated T800HB/EIA composites were shown in the Fig. 5, which indicated that introducing NFC and NCC onto the surface of T800HB could enhance the interfacial adhesion between T800 and EIA. As shown in Fig. 5, the ILSS of the composites coated with A-NFC, T-NFC, T-NCC and C-NCC increased to 101.5 MPa (14.6%), 100.8 MPa (13.9%), 95.5 MPa (8.0%) and 94.6 MPa (7.0%) compared to T800HB/EIA (88.5 MPa), respectively. It can be seen that the coating effect of NFCon the improvement in interfacial properties of T800HB/EIA composites is better than that of NCC because of the higher aspect ratio of NFC (500-1000).

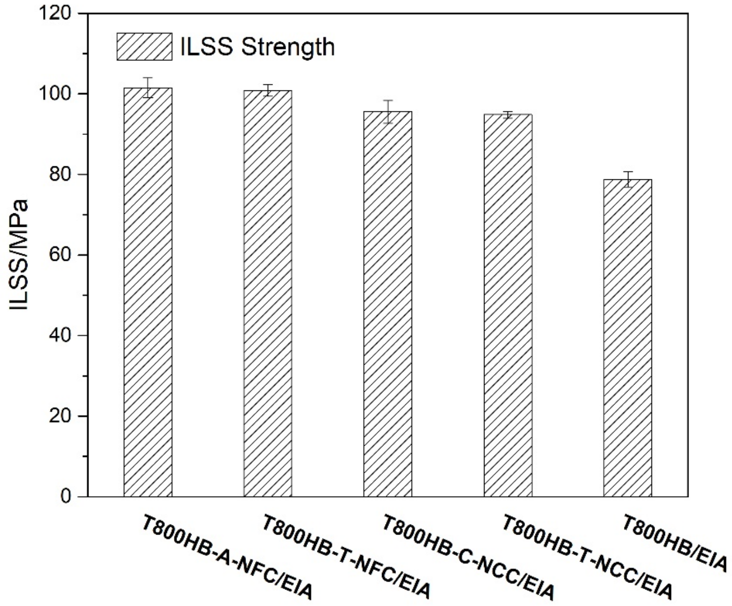

Fig. 1 ILSS of NFC and NCC coated T800HB/EIA composites

The results of transverse fiber bundle test (TFBT) were shown in Fig. 2 which indicated composites coated cellulose nanomaterials performed in a much higher level compared to untreated composites. Similarly,the composite coated with NFC exhibits a much better TFBT result than the one coated with NCC. The reason is that the cellulose nanomaterials can form a high strong interface layer between carbon fibers and matrix so that the broken of composites became difficult. And the high aspect ratio of NFC caused more physical and chemical contact area which made the TFBT strength of the composite coated with NFC was better than that of the one coated with NCC.

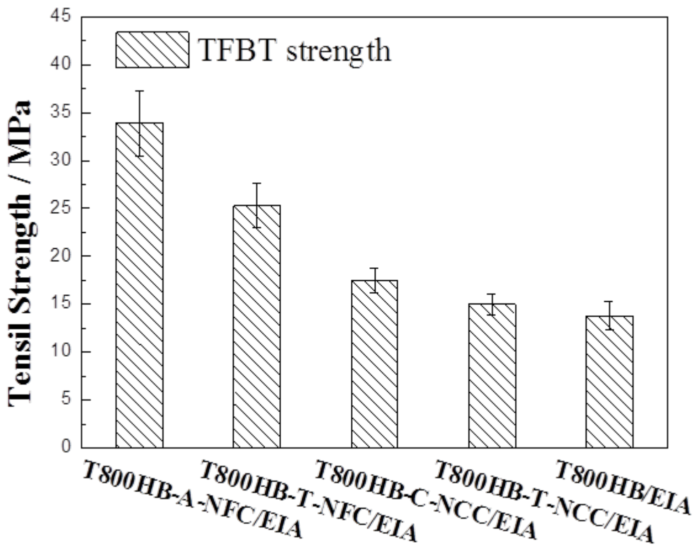

Fig. 2 TFBT strength of NFC and NCC coated T800HB/EIA composites

The results of flexural properties of treated and untreated T800HB/EIA composites were shown in Fig. 3. All the NFC and NCC coated T800HB/EIA composites showed enhanced flexural strength and modulus, but the degree of enhancement was quite significant due to the different aspect ratio and the function groups between NFC and NCC. T800HB-A-NFC/EIA performed the best, and the flexural properties of T800HB-T-NCC/EIA increased a little compared to T800HB/EIA.

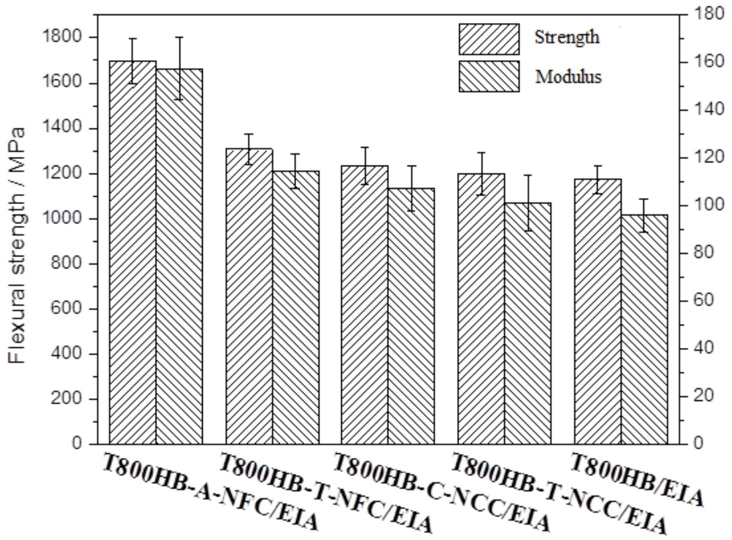

Fig. 3 Flexural strength and modulus of NFC and NCC coated T800HB/EIA composites

It was concluded the enhancement of interface were determined by aspect ratio instead of different functional groups. High aspect ratio improved the contact surface among the interphase, carbon fibers and matrix. What's more, forming interface layer helped transform the stress from matrix to fibers and avoid the concentration of stress which improved the mechanical properties of T800HB/EIA composites greatly.

3.3 DMTA results of composites

The dynamic mechanical properties of treated and untreated composites are shown in Fig. 4 and Fig.5. The storage modulus of the composites coated NFC markedly improved compared to T800HB/EIA, while the composites coated NCC hardly changed. In addition, as shown in Fig. 5, Tg of the composites coated with NFC and NCC were increased, indicating that the exist of NFC and NCC would improve the heat resistance of T800HB/EIA composites. Parameter C and B are often used to evaluate the interfacial adhesion of CFRPs, which can be calculated by the following equations

$$\mathrm{C} = \frac{(E_g'/E_r')_c}{(E_g'/E_r')_m}$$

where E_g' is the storage modulus of glassy state, and E_r' is the storage modulus of rubbery state. Subscript *c* refers to composites and *m* is for matrix.

$$\tan\delta_c^0 = (1 - BV_f)\tan\delta_m$$

where Tan δ is indicated in the loss, and V_f is the volume of fibers, subscript *c* refers to composites and *m* is for matrix. All the parameter B and C for the composites are listed in Table 2.

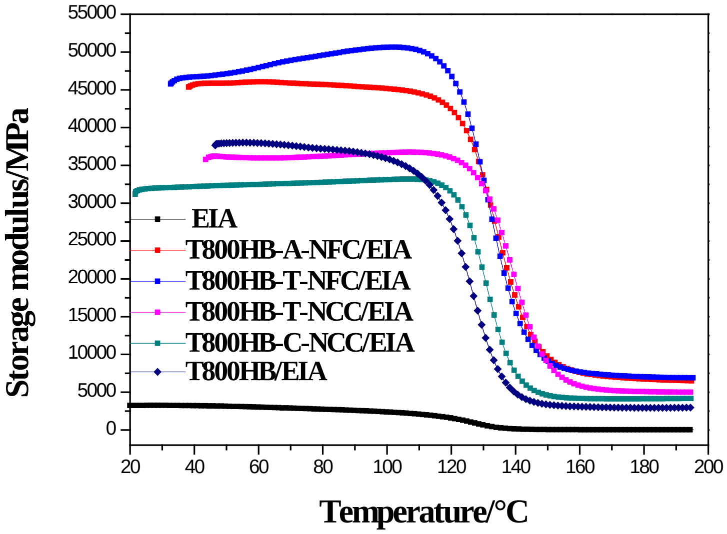

Fig. 4 Storage modulus of NFC and NCC coated T800HB/EIA composites

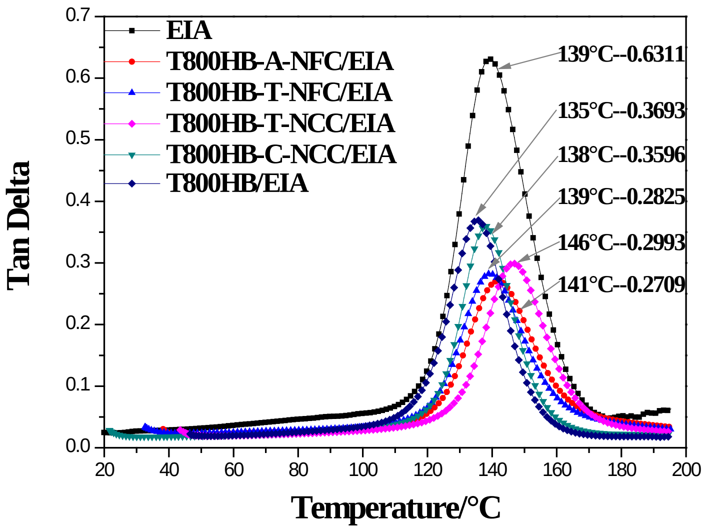

Fig. 5 Tan δ of NFC and NCC coated T800HB/EIA composites

As shown in Table. 2, the C value of NFC and NCC coated composites were all lower than that of T800HB/EIA, and the C value for the NFC-coated composites is lower than that of NCC-coated composites. NFC showed better. While the B value of treated composites were higher than that of T800/EIA, and NFC-coated composites showed much higher B than NCC-coated composites. Usually, the smaller the C and the higher the B, the better the interfacial adhesion. So it was concluded that coating NFC and NCC actually enhanced interfacial properties of the

T800HB/EIA composites as well as improving their heat resistance. Besides, adding NFC were more benefit to improve the interfacial properties of the composites compared to adding NCC.

Table. 2 DMTA parameters of EIA cast and composites reinforced by NFC and NCC deposited carbon fibers

Reinforcement	E_g'/MPa	E_r'/MPa	Tan δ	C	B
Neat EIA Cast	3205	21.07	0.6311	-	-
T800HB-A-NFC/EIA	45874	7006	0.2709	0.0431	0.951
T800HB-T-NFC/EIA	46698	7237	0.2825	0.0424	0.921
T800HB-T-NCC/EIA	36108	5216	0.2993	0.0455	0.876
T800HB-C-NCC/EIA	32186	4105	0.3596	0.0516	0.717
T800HB/EIA	37897	2899	0.3693	0.0859	0.691

3.4 SEM of longitudinal splited composites

The morphology of the longitudinal splited composites were observed by SEM, as shown in Fig. 10. It can be seen that, EIA resin covered NCC and NFC-coated T800HB closely, and the de-bonding between matrix and fibers was easily observed in the untreated T800HB/EIA, indicating the better adhesion between the NCC and NFC-coated T800HB and EIA matrix.

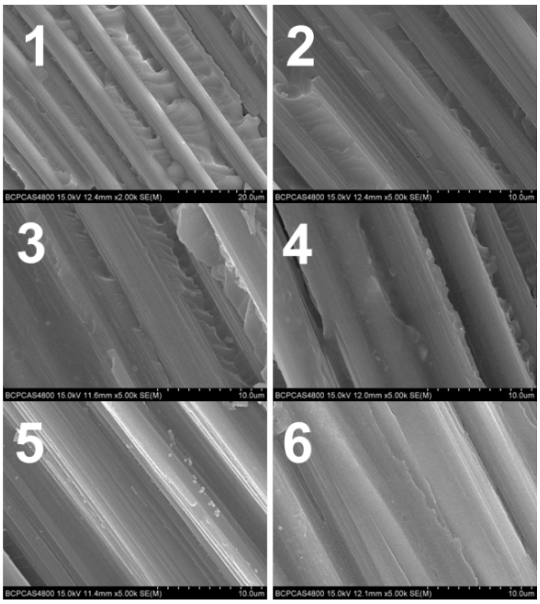

Fig. 6 SEM images of longitudinal splited composites

1,2: T800HB/EIA; 3: T800HB-T-NCC/EIA ; 4: T800HB-C-NCC/EIA; 5: 800HB-T-NFC/EIA; 6: T800HB-A-NFC/EIA

4 Conclusions

In this work, the NCC and NFC coated T800HB reinforced EIA composites (T800HB/EIA) has been prepared. The interfacial and mechanical properties as well as dynamic mechanical properties of the composites were characterized. It was concluded that the introduction of NFC and NCC onto the surface of T800HB can significantly improve the interfacial and mechanical properties of the NCC and NFC-coated T800HB/EIA composites. However, the degree of the improvement is quite significant due to the different aspect ratio. The NFC with a higher aspect ratio than NCC, so NFC performs better in improving the interfacial and mechanical properties of composites than NCC.

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Reference

[1] Yao L, Li M, Wu Q, et al. Comparison of sizing effect of T700 grade carbon fiber on interfacial properties of fiber/BMI and fiber/epoxy[J]. Applied Surface Science, 2012, 263(48):326–333.

[2] Yu B, Jiang Z, Tang X Z, et al. Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating[J]. Composites Science & Technology, 2014, 99(4):131–140.

[3] Dai Zhishuang, Zhang Baoyan, Shi Fenghui, et al. Chemical interaction between carbon fibers and surface sizing[J]. Journal of Applied Polymer Science, 2012, 124(3):2127-2132.

[4] Liu Jianye, Ge Heyi, Chen Juan, et al. The preparation of emulsion type sizing agent for carbon fiber and the properties of carbon fiber/vinyl ester resin composites[J]. Journal of Applied Polymer Science, 2012, 124(1):864-872.

[5] Wu Qing, Li Min, Gu Yizhuo, et al. Reaction of carbon fiber sizing and its influence on the interphase region of composites[J]. Journal of Applied Polymer Science, 2015, 132(18).

[6] Cao L, Liu X, Na H, et al. How a bio-based epoxy monomer enhanced the properties of diglycidyl ether of bisphenol A (DGEBA)/graphene composites [J]. Journal of Materials Chemistry A, 2013, 1(16): 5081-5088.

[7] Li C, Liu X, Zhu J, et al. Synthesis, Characterization of a Rosin-based Epoxy Monomer and its Comparison with a Petroleum-based Counterpart [J]. Journal of Macromolecular Science Part a-Pure and Applied Chemistry, 2013, 50(3): 321-329.

[8] Rao B S, Palanisamy A. Synthesis of bio based low temperature curable liquid epoxy, benzoxazine monomer system from cardanol: Thermal and viscoelastic properties [J]. European Polymer Journal, 2013, 49:2365-2376.

[9] Ma S q, Liu X q, Jiang Y h, et al. Bio-based epoxy resin from itaconic acid and its thermosets cured with anhydride and comonomers [J]. Green Chemistry, 2013, 15(1): 245-254.

[10] Sharma M, Gao S, Mäder E, et al. Carbon fiber surfaces and composite interphases[J]. Composites Science & Technology, 2014, 102(4):35-50.

[11] Wang Y, Liu H, Cheng H, et al. Interface engineering of fiber-reinforced all-oxide

composites fabricated by the sol–gel method with fugitive pyrolytic carbon coatings[J]. Composites Part B Engineering, 2015, 75:86–94.
[12] Zhang Y, Zhao J, Jia Y, et al. An analytical solution on interface debonding for large diameter carbon nanotube-reinforced composite with functionally graded variation interphase[J]. Composite Structures, 2013, 104(5):261–269.
[13] Chen Z K, Xiong X. Microstructure, mechanical properties and oxidation behavior of carbon fiber reinforced PyC/C-TaC/PyC layered-structure ceramic matrix composites prepared by chemical vapor infiltration[J]. Materials Chemistry and Physics, 2013, 141:613-619.
[14] Scher P, Thomas M, Borris J, et al. Strengthening fibre/matrix interphase by fiber surface modification and nanoparticle incorporation into the matrix[J]. Composites Science & Technology, 2013, 74(4):60–66.
[15] Tang L C, Wan Y J, Yan D, et al. The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites[J]. Carbon, 2013, 60(14):16-27.
[16] Gojny F H, Wichmann M H G, Fiedler B, et al. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study[J]. Composites Science & Technology, 2005, 65(15–16):2300-2313.
[17] Liu M, Guo B, Du M, et al. Properties of halloysite nanotube epoxy resin hybrids and the interfacial reactions in the systems[J]. Nanotechnology, 2007, 18(45):455703.
[18] Moon R J, Martini A, Nairn J, et al. Cellulose nanomaterials review: structure, properties and nanocomposites. [J]. Cheminform, 2011, 42(42):3941-3994.