Electronic Supplementary Information

Chemically and uniformly grafting carbon nanotubes onto carbon fibers by poly-(amidoamine) for enhancing interfacial strength in carbon fiber composites

Qingyu Peng[a], Xiaodong He[a], Yibin Li[a,*], Chao Wang[a], Rongguo Wang[a], Pingan Hu[b], Yongda Yan[c] and Thirumany Sritharan[d]

[a] Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, P. R. China

[b] Research Centre for Micro/Nanotechnology, Harbin Institute of Technology, Harbin 150080, P. R. China

[c] Center for Precision Engineering, Harbin Institute of Technology, Harbin 150080, P. R. China

[d]College of Engineering, Nanyang Technological University N1.3-B1, 70 Nanyang Drive, Singapore 637457

[*] Corresponding author: Tel/Fax: +86-45186402326. E-mail address: liyibin@hit.edu.cn (Y. B. Li)

Materials

The multi-walled carbon nanotube (Chengdu Organic Chemicals Co. Ltd) used has the length of 10-20 μm. Carbon fiber used is T300B-3000-40B (Toray Industries, Inc.). The amino is provided with Poly-(amidoamine) (PAMAM, Aldrich Inc.) dendrimers (Generation 0) with ethylenediamine core and amino surface groups, as shown in Fig.S1. The coupling agent used is N-[(dimethylamino)-1H-1, 2, 3-triazolo [4,5,6] pyridin-1-ylmethylene]-N- methylmethanaminium hexafluorophosphate N-oxide(HATU, GL Biochem Ltd) All other chemicals were purchased from Tianjin Bodi Organic Chemicals Co. Ltd.

CNT-CF hierachical reinforcement preparation

The MWCNTs were refluxed in a 3:1 (by volume) mixture of concentrated nitric and sulfuric acid for 2h at 80 ^{o}C to introduce carboxylic groups, then washed several times with de-ionized water until the pH value of the wash water was 7, followed by drying in a vacuum furnace. The carbon fibers were desized in acetone at 60 ^{o}C for 48 h and then oxidized in concentrated nitric acid at 100 ^{o}C for 2 h. Subsequently, the carbon fibers were taken out and washed several times with de-ionized water until the pH value of the wash water was 7, followed by drying in a vacuum furnace. 3×10^{-5} mol PAMAM and a small amount of HATU were added into 30ml dry dimethylformamide (DMF) and dissolute with ultrasonic for several minutes. The carboxyl-functionalized carbon fibers were immersed into the DMF solution at room temperature for 4 h in order to complete the amine-functionalization. After that, the amine-functionalized carbon fibers was washed with de-ionized water and dried under vacuum. Then, the amine-functionalized carbon fibers were immersed into the suspension of oxidized 50mg CNTs and some HATU in 30ml DMF at room temperature for 4 h. The obtained fibers were rinsed in DMF.

Characterization

CNT/CF reinforcement characterization

The surface morphologies of CNT/CF reinforcement were observed by field emission scanning electron microscope (FESEM, model S-4300, Hitachi, Japan). The chemical reactions were confirmed by X-ray photoelectron spectroscope (XPS, Model K-Alpha, Thermofisher Scienticfic Company, US) using a monochromated Al Kα source and a pass energy of 50 eV at a base pressure of 1×10^{-8} mbar.

The interfacial shear strength evaluation

The interfacial shear strength (IFSS) was chosen to quantify the interfacial property between CFs and resin matrix. The interfacial evaluation equipment (MODEL HM410, Japan) was employed to determine the interfacial shear strength of composites by micro-bond test. The sketch of single fiber-micro-bond test is shown in Fig. S2. Single 60 mm-in-length filament was carefully separated from the fiber tow. The fiber ends were mounted in trestle, as shown in Fig. S2. The EPON 618, 650 type Low Molecular Polyamide and Di-n-butyl phthalate (DBP) were mixed at the weight ratio of 100:60:7. Then the mixture was dropped onto carbon fiber to form microdroplets. The microdroplets were cured at 30°C for 24 h and 60°C for 12 h.

The trestle together with fiber was moved at a cross head displacement rate of 0.05μm/s. Under the optical microscopy, a microdroplet was chosen and de-bonded by fixture where the de-bonding load F could be recorded. The IFSS was calculated as :

$$\tau = \frac{F_{\max}}{\pi d_f Le} \qquad (1)$$

where τ – interfacial shear strength, $F_{\max}$ – maximum tensile force, d_f – diameter of the examined fiber, Le – the length of the fiber part embedded in the matrix.

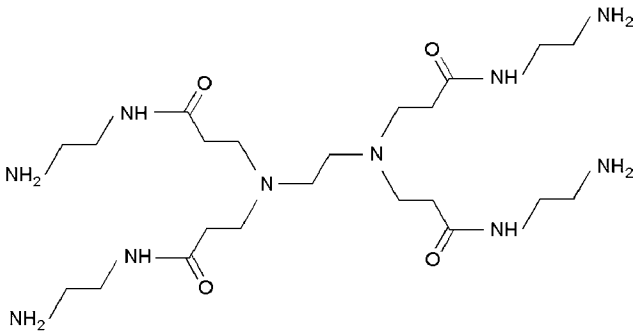

Fig.S1 0 generation PAMAM molecular structure

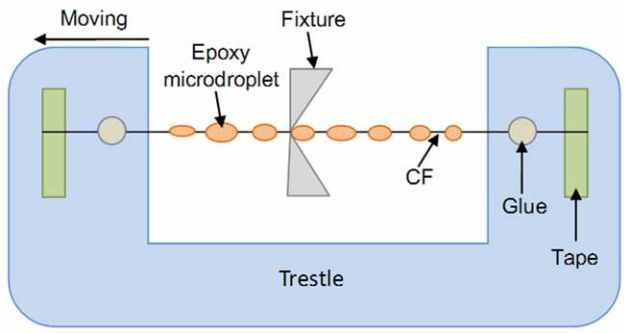

Fig. S2 The sketch of single fiber-microbond test