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Surfactants assisted processing of carbon nanotube-reinforced SiO_2 matrix composites

Jinwei Ning*, Junji Zhang, Yubai Pan, Jingkun Guo

The State Key Laboratory of High Performance Ceramics and Superfine Structure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding-xi Road, Shanghai 200050, People's Republic of China

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Abstract

The dispersion homogeneity of carbon nanotubes (CNTs) is one of the most critical problems in carbon nanotube matrix composites. The dispersive role to CNTs of three kinds of surfactant including cetyltrimethyl ammonium bromide (C_{16}TMAB cationic), polyacrylic acid (PAA anionic) and C_{16}EO ($CH_3(CH_2)_{14}CH_2(OC_2H_5)_{10}OH$ nonionic) was investigated. The dispersion mechanism may include steric repulsive effect and static electric effect. CNT/SiO_2 (5 vol.%) composites with and without C_{16}TMAB were fabricated by sol–gel process. The average bending strength and fracture toughness of sample prepared with C_{16}TMAB, compared with monolithic SiO_2 glass, were enhanced 88 and 146% respectively. The properties of sample fabricated without C_{16}TMAB were enhanced only 48 and 118%.

Keywords: A: Hot-pressing; A. Sol–gel processes; B. Composites; D. SiO_2; Carbon nanotubes (CNTs)

1. Introduction

Since their first observation by Iijima in 1991 [1], CNTs have been the focus of considerable research. Numerous investigators have reported remarkable physical and mechanical properties for this new form of carbon. From unique electronic properties and a thermal conductivity higher than that of diamond to mechanical properties where the stiffness, strength and resilience exceed those of any current material, CNTs offer tremendous opportunities for the development of fundamentally new material systems [2–4]. In particular, the exceptional mechanical properties of CNTs (E≈1–1.8TPa) [4], combined with their low density (about 2.0 g/cm^3) [5], offer scope for the development of nanotube reinforced composite materials. The potential for nanocomposites reinforced with CNTs having extraordinary specific stiffness and strength represents tremendous opportunities for application. Today, CNTs have been used to reinforce many kinds of materials including polymer [6], metal [7] and ceramic [8,9].

However, CNTs tend to form aggregates owing to strong van der Waals force interactions. This has a negative effect on the properties of CNT-reinforced composites. Good dispersion of CNTs in a matrix of composite materials is a critical problem, being a prerequisite for their applications as additives for the reinforcement of composite materials.

Here we investigate the dispersion of CNTs in different surfactant water solutions and report the role of surfactants as processing aids in CNT/SiO_2 composite fabricated by sol–gel process.

2. Experimental procedure

The multi-wall CNTs were provided by Shenzhen NANO Tech. Port. Co. Ltd.(China). They were fabricated by catalytic pyrolysis of hydrocarbon. TEOS ($Si(C_2H_5O)_4$ A.R.) was used as the raw material of SiO_2. PAA, C_{16}TMAB (A.R.) and C_{16}EO (A.R. Aldrich Chemical Company Inc.) were used as surfactants in present experiment.

In a typical experiment, 12 mg CNTs were added into a 40 ml water solution of C_{16}TMAB, C_{16}EO, PAA respectively, followed by ultrasonication to disperse the

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* Corresponding author. Fax: +86-21-52413903.
E-mail address: njw0236@163.com (J. Ning).

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CNTs. Then these three kinds of suspension solutions were held in the glass beaker statically for 24 h.

In this experiment, two routes (A and B) were used to fabricate the 5 vol.%CNT–SiO_2 composite. In process A (without C_{16}TMAB surfactant), firstly, CNTs were added into the TEOS alcohol solution, followed by ultrasonication to disperse the CNTs. Next, hydrochloric acid (1.16 M) was dropped into the solution stirred by a magnetic mixer until the pH value reached 0.5–1. Then the solution was stirred for 2 h. Finally, a dense ammonia solution (A.R. Shanghai Chemical Agent Company) was dropped into the solution to make it gel rapidly. The gel was washed with distilled water and alcohol then dried in a box furnace at 100 °C, and calcined in air at 500 °C to remove structural water. The dried lumps were crushed and passed through a 200- mesh plastic sieve. In process B, firstly, the C_{16}TMAB was dissolved into distilled water then the CNTs were added into the solution followed by ultrasonication to disperse the CNTs. Next, the hydrochloric acid (1.16 M) was dropped into the solution stirred by the magnetic mixer until the pH value reached 0.5–1. Then the solution was stirred for 2 h. The following procedure was the same as that of process A. Finally, the CNTs and SiO_2 mixture powder were fabricated.

Two kinds of mixture powders (made by A or B route) were loaded in graphite die and sintered by hot pressing (25 MPa at 1300 °C) in pure N_2 atmosphere, yielding CNT/SiO_2 composites. The sintered specimens were cut longitudinally with a diamond-blade saw and the surface was polished into a mirror surface. The final size of the specimen was 3×4×35 mm.

The bending strength was measured using a three-point method with a 30-mm span and a crosshead speed of 0.5-mm/min (Model INSTRON-1195). Vickers indentation, using loads of 4.9 N, was used to determine the fracture toughness. A micrograph of the mixture powder and CNTs was recorded by transmission electron microscope (TEM) (Model JEM-2010, Japan). High resolution transmission electron microscope (HREM Model JEM2010, Japan) was used to observe the interface between the CNT and SiO_2 matrix. The fracture surface and the micrograph of crack propagation were observed by field emission scanning electron microscope (FSEM; Model JSM-6700, Japan). Finally, the density was measured by Archimedes immersion method in distilled water.

3. Results and discussion

3.1. Micrograph of CNTs

Fig. 1 shows a micrograph of the CNTs used in the experiments. It can be seen that the CNTs are tangled together. Their diameter is between 20 and 40 nm and their length is about tens of microns (μm), resulting in an aspect ratio up to 100–1000. Most of the CNTs are not straight, but possess some defects and demonstrate a few local kinks and bends.

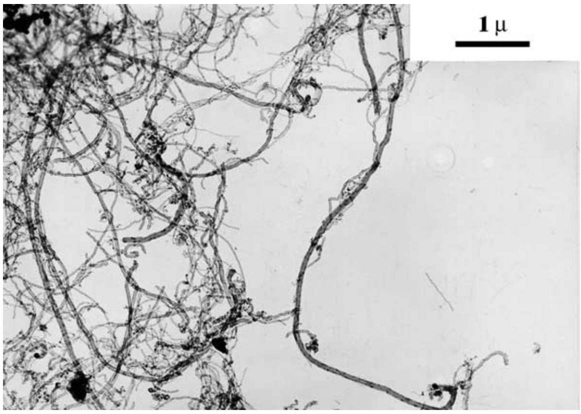

Fig. 1. TEM micrograph of CNT.

3.2. Dispersion mechanism of surfactants

After the ultrasonication, CNTs exist as a suspension in distilled water at the longest for about 5 min and then precipitate rapidly at the bottom of the beaker. But in the three kinds of surfactant solutions, the whole solution remained homogeneously black with no obvious precipitation observed after ultrasonication and holding for 24 h. This feature indicated that the surfactants have an excellent ability to disperse the CNTs homogeneously.

The surfactant molecules may absorb on the surface of CNTs. G-L. Hwang and K-C. Hwang think [10] that the surfactant molecules can form co-micelle structures with CNTs via a strong van der Waals force. A CNT with surfactant was observed by TEM, Fig. 2 is the TEM micrograph of a CNT with PAA. One can see that the PAA absorbs on the surface of CNTs homo-

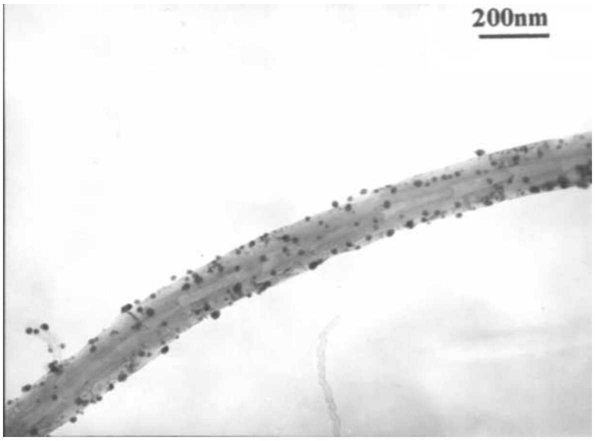

Fig. 2. TEM micrograph of CNT + PAA.

geneously in nano-particle style. All these particles have formed into nano-crystal (as shown in Fig. 3). But, PAA particles are not found in other sites. This phenomenon indicated that the PAA was absorbed on the surface of CNTs. It can be inferred that the other two surfactants absorb on the surface of CNTs due to their similar molecular structure.

All three kinds of surfactant molecules have a relatively long hydrocarbon chain, containing a hydrocarbon hydrophobic segment and hydrophilic segment. They absorb on the surface of CNTs through alkyl chain (hydrophobic segment) and the hydrophilic segment stretch into water [11]. The steric repulsive force between the surfactant molecules interact with each other to disperse the CNTs in the aqueous solution. Moreover, the ionic segment of ionic surfactant is charged, so there also exists a static repulsive force, which is beneficial to disperse CNTs further. These two kinds of force overcome the van der Waals attractive force between the CNTs surface with the result that the CNTs was dispersed homogeneously.

Table 1
Comparation of the properties of different sample

Properties Specimen	Relative density %	Bending strength MPa	Fracture toughness $MPam^{1/2}$
SiO_2 + 5 vol.%CNT + C_{16}TMAB	100	97.0 ± 10	2.46 ± 0.11
SiO_2 + 5 vol.%CNT	98.9	70.2 ± 5	2.18 ± 0.15
SiO_2 [12]	–	51.5	1.0

3.3. *Effect of surfactant on the mechanical properties and microstructure*

Table 1 gives the properties of 5 vol.%CNT–SiO_2 composites with and without C_{16}TMAB. One can see that the relative density, bending strength and toughness were enhanced obviously. Bending strength and fracture toughness of the sample with C_{16}TMAB were enhanced greater than that of sample without C_{16}TMAB.

Fig. 4 is the micrograph of fracture surface of the composite with and without C_{16}TMAB. One can see

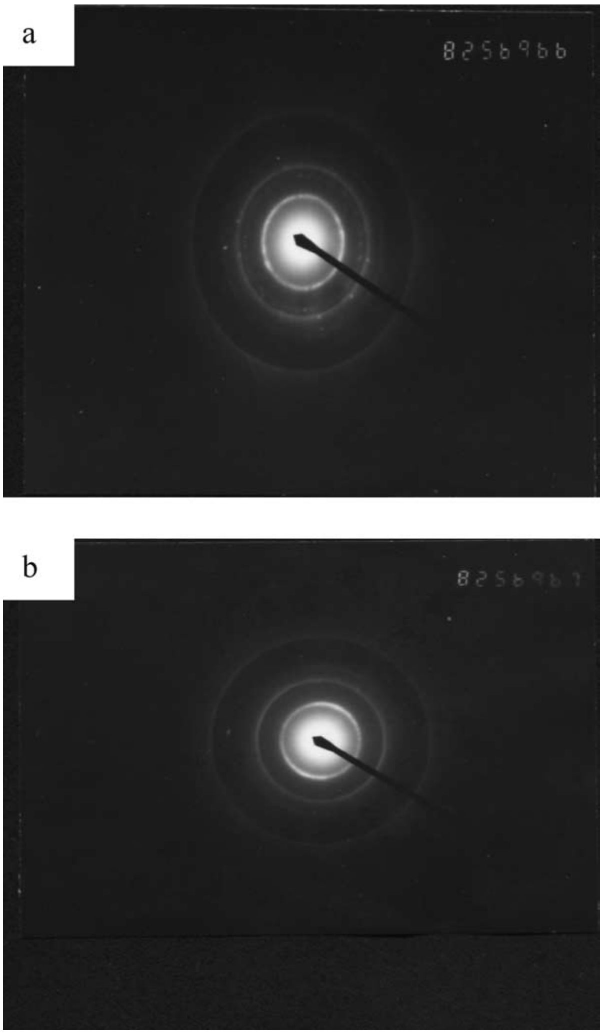

Fig. 3. Electron diffraction diagram of CNT(a) and CNT + PAA (b).

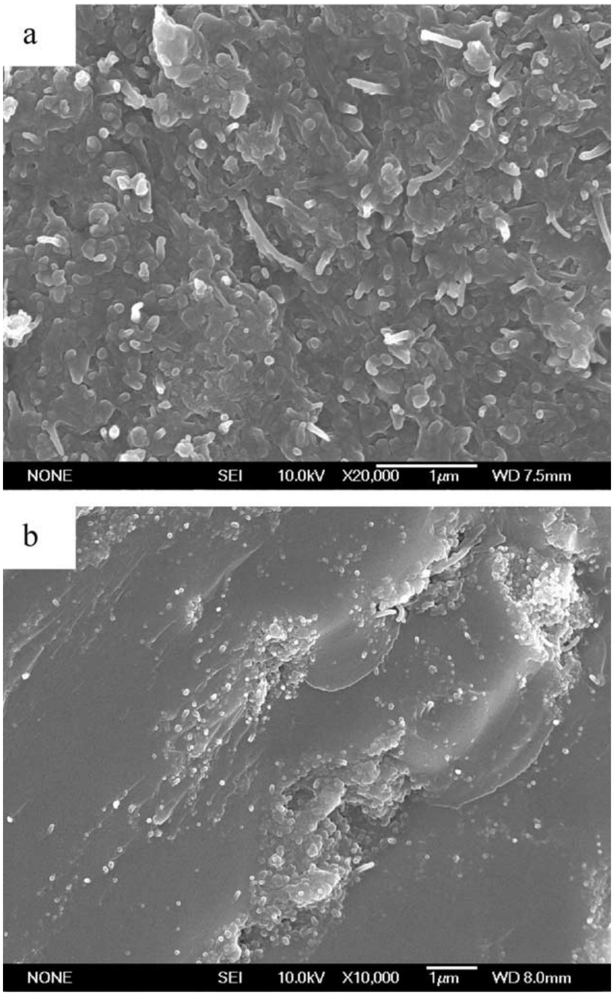

Fig. 4. FSEM micrograph of fracture surface of CNT/SiO_2 composite (a) Without C_{16}TMAB. (b) With C_{16}TMAB.

that carbon nanotubes lumped together in the sample without C_{16}TMAB. This type of morphology indicates that the CNTs agglomerate highly. But on the fracture surface of the sample with C_{16}TMAB, CNTs disperse more homogeneously and have little agglomeration. This difference in morphology indicates that C_{16}TMAB plays a positive role to improve the dispersion homogeneity of CNTs. It is the key factor to improve the properties of composites. The agglomeration of CNTs causes great damage to the properties of composite. Because the van der Waals force, by which CNTs form agglomeration, is relatively weaker, the agglomeration may form a hole and decrease the relative density. The C_{16}TMAB can improve the dispersion of CNT in the solution and reduce the agglomeration, so the relative density was increased. On the other hand, since the van der Waals force is far weaker than the force between the CNTs and SiO_2 matrix, as mentioned above, the agglomeration reduces the interface action between the matrix and CNTs. If the CNTs agglomerate, it is very easy to separate CNTs from the matrix without breaking the nanotubes. Fig. 5 is a HREM micrograph of the CNT/SiO_2 interface. It can be seen that there exists a good interface bonding between the CNT and the SiO_2 matrix. If the CNTs can be dispersed homogeneously, there are more interfaces between CNTs and SiO_2 matrix in the composite. Therefore, it has a stronger ability to absorb the crack energy and withstand the stress when an outside force acts on the composite. This can explain why the mechanical properties were enhanced in the composite with C_{16}TMAB compared with that prepared without C_{16}TMAB.

Moreover, the fracture surface of the sample prepared with C_{16}TMAB is rougher than that of the sample produced without C_{16}TMAB. There are obvious steps on the surface. The difference in the surface roughness shows different fracture pathways.

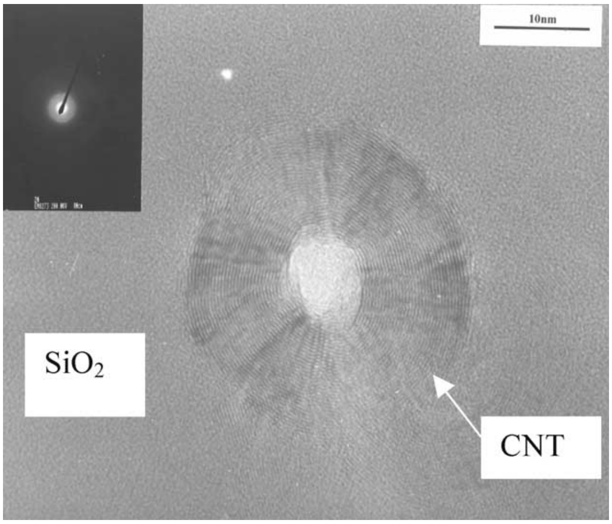

Fig. 5. HREM micrograph of CNT/SiO_2 interface.

4. Conclusions

In summary, all three kinds of surfactants can disperse the CNTs effectively. They absorb on the surface of CNTs through a hydrocarbon hydrophobic segments. The steric repulsive force and/or static repulsive force are the inherent mechanisms to disperse CNTs. The addition of 5 vol.% carbon nanotubes in the composite prepared with C_{16}TMAB enhances the bending strength and fracture toughness of amorphous SiO_2 glass by 88 and 146%, respectively. In contrast, the addition of carbon nanotubes without C_{16}TMAB has moderate effects on the mechanical properties. It should be pointed out that even with the addition of the surfactant, complete homogeneous dispersion of carbon nanotubes was difficult to achieve. But the present work clearly illustrated that the CNTs can have some dramatic effects on the properties of composite materials with improved dispersion by the surfactant. Therefore, the dispersion homogeneity and relative problems, including type of dispersion agent, interface chemistry and dispersion mechanism are still important subjects that need investigation in the future.

Acknowledgements

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