

Study on Reactive Carbon Nanotube Reinforcement and Its Application in Advanced Carbon Fibers Composites

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Introduction

Epoxy resin is a widely used polymer matrix for advanced composites. But with the increasing demand for higher mechanical properties, the strength, modulus and toughness of epoxy resins need to be further improved to match the advanced reinforcing fibers, such as Toray T1000[®] carbon fiber. In our previous studies, we developed a kind of reactive carbon nanofibers which showed effective enhancement in the strength and toughness for polymers.[1-3] In this paper, the reactive carbon nanotubes (CNTs) was prepared to realize the improvement of the interface bonding and the mechanical properties of Toray T1000[®] carbon fiber/epoxy resin composites.

Experimental

TDE-85 epoxy resin, a type of diglycidyl ester of aliphatic cycle, was supplied by Tianjin jindong chemical industrial factory, China (epoxy value, 0.85). DETDA (a mixture of two diethyltoluene diamines, Lonza, Switzerland) were used as curing agent in the experiment. T1000[®] carbon fibers were supplied by Toray Company, Japan. Multi-walled CNTs were purchased from Shenzhen Nanotech Part Co., Ltd, China (purity >95%). The diameters of raw nanotubes vary from 10 to 20 nm, and lengths vary from 5 μ m to 15 μ m. All of these materials were used in this experiment without further purification.

The raw CNTs were dipped in a blended acid solution with a volume ratio between nitric acid and sulfuric acid of 1:3. The loading of CNTs was 1g for 10ml of blended acid solution. The mixing solution was boiled and refluxed for 0.5h, and then the CNTs were carefully washed and filtrated with deionized water until chemically neutral. After drying in vacuum at 80°C, the 200mg of carboxylated CNTs were stirred in 60 ml of mixture with a volume ratio between

thionyl chloride (SOCl₂) and dimethylformamide (DMF) of 20:1 at 70°C for 24h. After the acyl chlorination, SOCl₂ and DMF were removed through vacuum distillation. The CNTs were washed by THF and then reacted with the mixture ethylenediamine/DMF (110ml, 10:1 in volume ratio) at 100°C for 72h. After washed using THF and dried in vacuum at 70°C for 12h, the amino-functionalized CNTs were obtained. The reactive CNTs were developed through the reaction of the cut amino-functionalized CNTs by digital sonifier with butyl glycidyl ether (BGE). The detailed synthesis procedures were described in [1,2]. In our previous studies, the H⁺ in the reactive group OH⁻ has been shown reactive to form covalent bonding with epoxy resin [1,2]. Then the excess BGE was removed by using a vacuum oven and the final mass ratio of reactive CNFs to BGE was optimized into 1:6.

For preparation of the reactive CNT/epoxy composites, the reactive CNTs were added into the epoxy resin and the mixture was stirred at 60 °C for 3 h. Then, the curing agent was added and an ultrasonic cleaner was used for further mixing at room temperature for 2 h. Subsequently, the mixture of reactive CNTs and epoxy was degassed under vacuum condition. The capability to transfer load and the interfacial adhesion of the carbon fiber/epoxy composite can be reflected and assessed by Naval Ordnance Laboratory (NOL) Ring. In this study, NOL-rings were prepared by using a filament winding machine (MAW 20-LS1-6, MIKROSAM Co.) with a winding tension of 25 N. Then NOL-rings were cured via a thermal cycle (120 °C for 1 h and 150 °C for 2 h).

Results and Discussion

The FTIR spectra of amino-functionalized CNTs and reactive CNTs are shown in Fig.1. In Fig.1 (a), the formation of acylamide groups CO-NH is supported by the peaks at 1655 cm⁻¹ and 1565cm⁻¹ and the peak at 3444 cm⁻¹ can be assigned to the N-H stretching vibrations. These results indicate the existence of amide groups. Fig.1 (b) exhibits the FTIR spectra of reactive CNTs. After treated by digital sonifier with epoxides, a new peak appears at 1198 cm⁻¹, which can be attributed to the C-O-C stretching vibrations in chemical structure of epoxide. At the same time, the appearance of peaks located in 600 cm⁻¹~800 cm⁻¹ that corresponds to N-H vibrations and peaks at 1470 cm⁻¹ that corresponds to C-N vibrations, reveals the chemical

reaction between the $-NH_2$ on the CNTs surface and epoxy functional groups. Therefore, the reactive CNTs with interface compatibility and chemical reactivity were obtained in experiment. The reactive CNTs existing in small amount of BGE forming the solution could facilitate the easy dispersion and reaction of the reactive CNTs in the epoxy composites.

The tensile strength, flexural strength and interlaminar shear strength (ILSS) of Toray T1000[®] carbon fiber/TDE-85 epoxy resin composite NOL-rings are shown in Table 1. After adding 1wt% raw CNTs, the NOL-rings of epoxy resin composites displayed weaker mechanical properties than the neat epoxy composites. At the same time, the reactive CNTs resulted in effective reinforcing effect to the epoxy composites. It is worth mentioning that, after adding 1 wt% reactive CNTs, the 30% enhancement in ILSS were observed in the NOL-rings of epoxy resin composites. These results were derived from a strong covalent bonding exists between the reactive CNTs and epoxy and good dispersion of reactive CNTs in epoxy matrix.

Fig.2 shows the DMTA curves of the loss factor of the pure epoxy and composites vs. temperature. The temperature at the peak is assigned as the glass transition temperature (T_g). The T_g shifted towards higher temperatures: 3 °C and 8 °C higher than the pure epoxy composites due to the additions of 1 wt% raw CNFs and 1 wt% reactive CNFs, respectively. With the increase of the nanofillers, the height of $\tan\delta$ peaks of epoxy composites decreased. These can be attributed to the stiffness effect of the nanofillers and their obstruction to the mobility of the polymer segments. The reactive CNFs showed stronger obstruction effect to epoxy molecular chain.

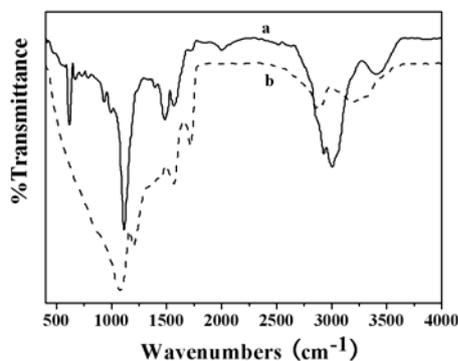


Fig. 1 FT-IR spectra: (a) amino-functionalized CNTs; (b) reactive CNTs

Table 1. Mechanical properties of Toray T1000[®] carbon fiber/TDE-85 epoxy composites

	NOL tensile strength (MPa)	NOL flexural strength (MPa)	NOL ILSS (MPa)
without CNTs	3010±318	1520±279	73±2
1wt% raw CNTs	2540±510	1307±485	70±2
1% wt% reactive CNTs	3020±280	1580±326	95±2

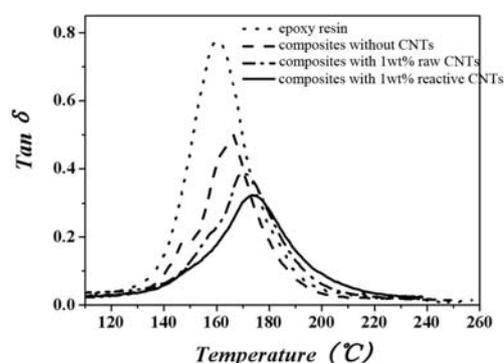


Fig. 2 $\tan\delta$ vs. temperature for epoxy composites

Conclusions

The reactive CNTs were prepared by chemical synthesis under ultrasonic treatment. The reactive CNTs exhibited obviously effects on enhancing the interface bonding and the mechanical properties of Toray T1000[®] carbon fiber/TDE-85 epoxy resin composites. After adding 1wt% reactive CNTs, the ILSS of epoxy resin composites increased by 30%. DMA results showed there was an obvious increase in glass transition temperature for the epoxy composites containing 1wt% reactive CNTs compared to that of the neat epoxy composites.

References

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