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Surface modification and ultrasonication effect on the mechanical properties of carbon nanofiber/polycarbonate composites

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Abstract

The effect of plasma surface modification and ultrasonication time on the mechanical properties of multi-wall carbon nanofiber polycarbonate composites were investigated. The study showed that plasma polymerization treatment of multi-wall carbon nanofibers enhanced the dispersion of the nanofibers in the polymer, and hence improved the mechanical properties of the nanocomposite. The study also showed that the mechanical properties of the nanocomposite depended on the ultrasonic dispersion time. Long term dispersion damaged the surfaces of both untreated and plasma polymerized carbon nanofibers. The interface behavior and strengthening mechanisms are discussed.
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1. Introduction

Carbon nanotubes (CNT) have demonstrated great potential in many practical applications especially in composite materials since their discovery [1]. Recently, it has been shown in laboratory scale tests that the physical properties and performance of composite materials can be significantly improved by the addition of small percentages of carbon nanotubes [2–4]. However, the experimental strength values of these composites are still lower than the theoretical predictions due to severe nanotube aggregation and poor interfacial bonding between the nanotubes and the polymer matrix. Therefore, these critical issues must be addressed by surface modification.

As is well known, the as-synthesized nanotubes usually form aggregates that behave differently in response to a load as compared with individual nanotubes [5]. To maxi-

mize the advantage of nanotubes as reinforcing particles in high strength composites, the aggregates need to be broken up and dispersed well in the polymer matrix to avoid stress concentrations, and areas of the matrix without nanotubes which will degrade the mechanical properties of the composite. Ultrasonication using a bath ultrasonicator is one of the main methods used to disperse carbon nanotubes [6,7]. Although ultrasonication of carbon nanotubes in organic solvents is widely used, the mechanism of dispersion and the factors that optimize its efficiency are not well understood.

Furthermore, the strong interface between the nanotube and the polymer matrix is essential to transfer the load from the matrix to the nanotubes and thereby to enhance the mechanical properties of the composite. However, the surfaces of the nanotubes are not ideal to bond strongly to the polymer matrix. Therefore, pullouts and slippage often occur during loading. One of the most effective ways to improve interfacial bonding is through plasma surface modification. In our previous studies, by

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plasma polymerization, an ultrathin polymer film was deposited on the surfaces of carbon nanofibers [8]. These surface modified nanofibers were used to reinforce a polystyrene matrix [9]. In this paper, we present results on the microstructure, dispersion, and mechanical properties of a polymer composite impregnated with coated and uncoated carbon nanofibers. Different ultrasonication times were employed to study the effects of dispersion and related mechanical properties.

Carbon nanofibers (CNF) are used in the experimentation performed in this paper. The CNF have multiple walls and diameters from 70 nm to 150 nm and one low cost compared to carbon nanofibers.

2. Experimental details

In this research, the substrate used for plasma deposition was a carbon nanofiber provided by Applied Science Inc., located in Cedarville, OH. A styrene monomer to coat the nanofibers was purchased from Alfa Aesar, Ward Hill, MA. The polycarbonate (PC) resin in which the CNF were cast was purchased from Fisher Scientific Inc., Chicago IL. The molecular weight of the PC is 64,000.

The plasma-coating facility is a specially designed system for small particle applications. The schematic diagram of the plasma reactor for thin film deposition of nanoparticles is shown in Fig. 1. It mainly consists of a radio frequency (RF) source, a glass vacuum chamber, and a pressure gauge. The vacuum chamber of the plasma reactor has a long Pyrex glass column about 80 cm in height and 6 cm in internal diameter [10,11]. The CNF powder was vigorously stirred at the bottom of the tube and thus the surface of the particles were continuously renewed and exposed to the plasma for thin film deposition during the plasma polymerization processing. A magnetic bar was

used to stir the powder. Before the plasma treatment, the basic pressure was pumped down to less than 50 mtorr, and then the styrene monomer vapors were introduced into the reactor chamber to coat the nanofibers. The operating pressure was adjusted by the gas/monomer mass flow rate. During the plasma polymerization processing, the input power was 10 W and the system pressure was 300 mtorr. The plasma treatment time was 1 h.

After the plasma treatment, the treated CNF was characterized using transmission electron microscopy (TEM) and infrared spectroscopy (FTIR). The high-resolution TEM (HRTEM) experiments were performed on a JEOL JEM 4000EX TEM. The fracture morphologies of nanotube composites were studied using a Philips XL30 FEG scanning electron microscopy (SEM).

A simple solution-evaporation method was used to prepare the CNF polycarbonate composite. First, 2 g of polycarbonate was weighed and totally dissolved in 30 ml of chloroform. At the same time, 1 wt% of uncoated and coated CNF was weighted and dispersed in 30 ml chloroform using ultrasound for 30 min. Then the dispersed CNF was mixed with the polycarbonate solution. After further ultrasonication for a period of time (0.5, 1, 2, 4, 8 and 12 h), the mixed solution was poured into an 80 mm × 60 mm × 6.5 mm aluminum mold. The solution was kept at room temperature and dried for seven days.

After the sample was completely dried, it was sectioned into 50 mm × 6 mm × 0.4 mm samples for tensile testing according to the ASTM D 822-97: "Standard Test Method for Tensile Properties of Thin Plastic Sheeting." An Instron mechanical testing machine, model 2525-818, with a 1 mm/min crosshead speed was used for the tensile test. Multiple measurements were performed in the tensile experiments. Five samples were tested and an average value was used for each data point.
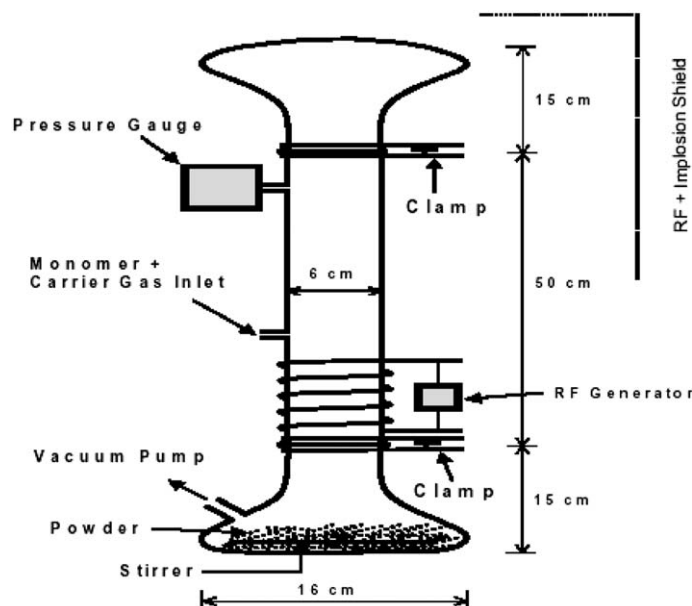

Fig. 1. The plasma reactor for thin film coating of the nanoparticles.

3. Results and discussion

HRTEM image (Fig. 2(a)) of the original CNF show the graphite structure with the interlayer spacing $d_{002} = 0.34$ nm. It is apparent that the CNF surface terminates at a graphite layer for the originally uncoated nanotubes. After plasma treatment, an ultrathin amorphous film can be clearly seen covering the surfaces of the CNF in Fig. 2(b). The thin film is uniform on outer surface, with a thickness approximately 5 nm surrounding the entire surface of the CNF. Fig. 2(a) shows the high resolution TEM images of the original uncoated CNF. Parallel graphite layers are clearly shown in Fig. 2(a).

To confirm the TEM observations shown in Fig. 2, FTIR was carried out to study the chemistry of the surface film on the CNF. Fig. 3 shows the FTIR spectrum of the treated carbon nanofibers. The FTIR spectrum exhibits several strong peaks between 1400 and 1600 cm^{-1}, which are identified as the C–C vibrating absorption of the benzene ring. These peaks are clear indications of the benzene rings in the surface amorphous coating.

As can also be seen in Fig. 3, the special absorption peaks at 758 and 700 cm^{-1} belong to benzene C–H out of plane bending. Two peaks appear together in the 700–790 cm range which is a typical spectrum for one hydrogen atom on a benzene ring substituted by other function groups. The spectrum shown in Fig. 3 is more complicated than the standard FTIR spectrum of polystyrene, but the special absorption peaks for styrene are almost the same as for regular polystyrene. This implies that in plasma polymerization, the molecular structure is destroyed by ion or electron bombardment, but the deposited film still maintains some polystyrene molecular
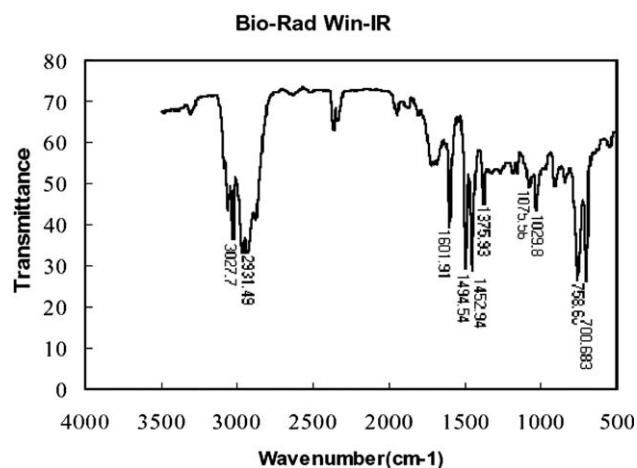

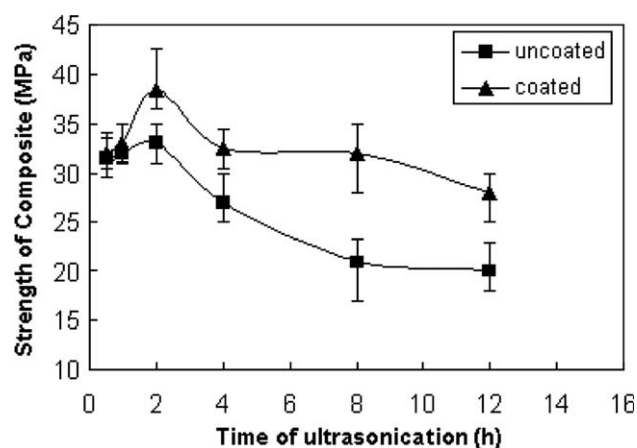Fig. 3. FTIR spectrum of plasma coated CNF.

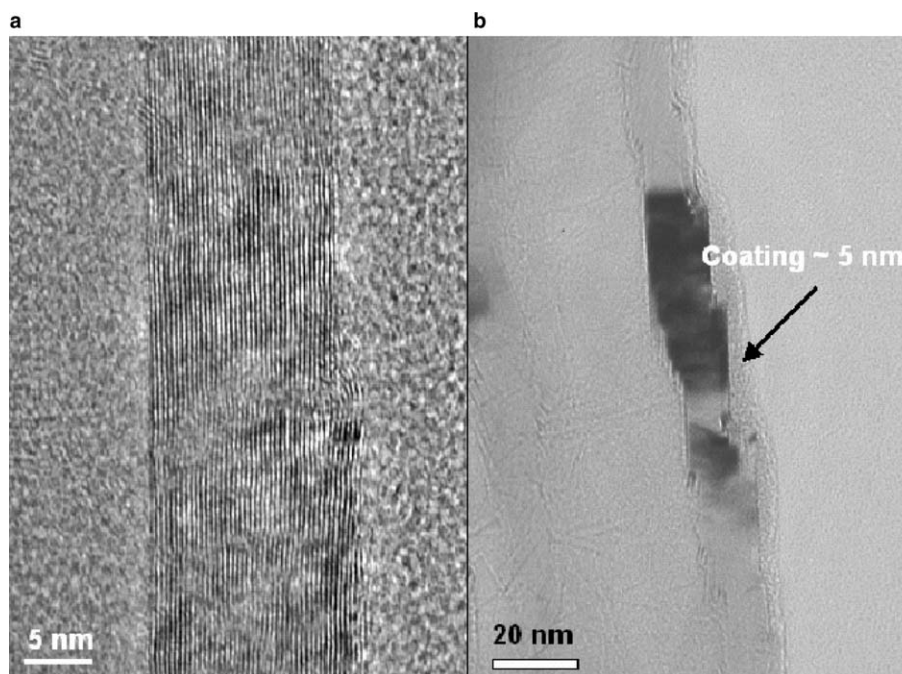Fig. 4. Strength vs. ultrasonic time for both coated and uncoated CNF composite at 1% concentration.

Fig. 2. HRTEM images of the nanotubes: (a) The uncoated CNF and (b) coated CNF.

structure which is desired for compatibility with the polycarbonate matrix.

Fig. 4 shows the strength of the CNF-PC composite for various ultrasonication times for a 1% concentration of CNF in the polymer. As can be seen, increasing the dispersion time from 0.5 to 2 h produces the maximum tensile strength of the composite. The tensile strength then gradually decreases to nearly half of the maximum value as the dispersion time is increased from 2 to 12 h. This trend was also observed for higher concentrations of CNF in the composite. The Young's modulus shows a similar trend as the tensile strength (Fig. 5).

The mechanism of deagglomeration lies in cavitation effects arising adjacent to particles or within loosely associated particle aggregates and the inability to follow the

Fig. 5. Modulus vs. ultrasonic time for both coated and uncoated CNF composite at 1% concentration.

induced wave front projected by the transducer. When two particles are separated by a distance of only a few particle diameters, hydrodynamic forces of repulsion and attraction are involved in the ultrasound field [12]. The maximum tensile strength is the balance of the contracting force and repelling force created in the ultrasound field. Study also showed the separation of the nanotube from the bundle is reversible, leading to a dynamic equilibrium for the system of the surfactant adsorption during ultrasonication [13]. The decrease of the tensile strength after maximum value may come from the decrease of the ultrasound velocity. Previous study [14] showed the sound velocity will decrease with the dispersion time and jump again for a long dispersion time.

Ultrasonication imparts a high energy density in the solution. Cavitation can break the aggregated nanotubes apart, which will improve the dispersion of nanotubes and improve the mechanical property of the nanocomposite. But at the same time, the high energy may damage the polymer chain and cause the polycarbonate to partially decompose. When the ultrasonication time further increases, the ultrasonication will even damage and break the CNF into short pieces [15,16]. This effect will degrade the mechanical properties of the nanocomposite. Thus, there is a trade-off between improving dispersion and damaging the nanotubes and polymer.

Generally, composites with coated CNF have higher tensile strength than with uncoated CNF. This indicates, in turn, that the coated CNF has better dispersion than uncoated CNF. Fig. 4 showed that uncoated MWNT CNF cluster even at the optimum ultrasonication time. That means controlled/CNF cannot give good mechanical
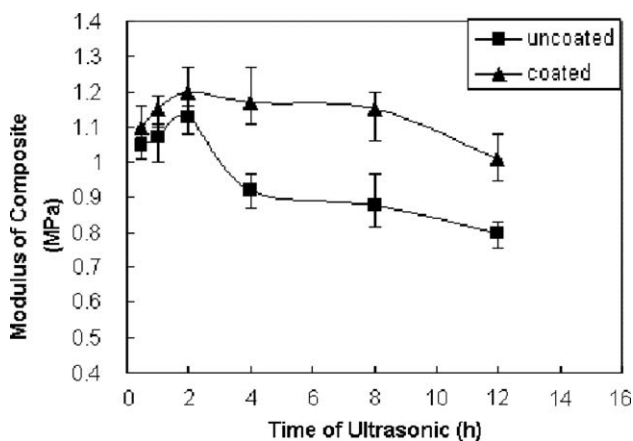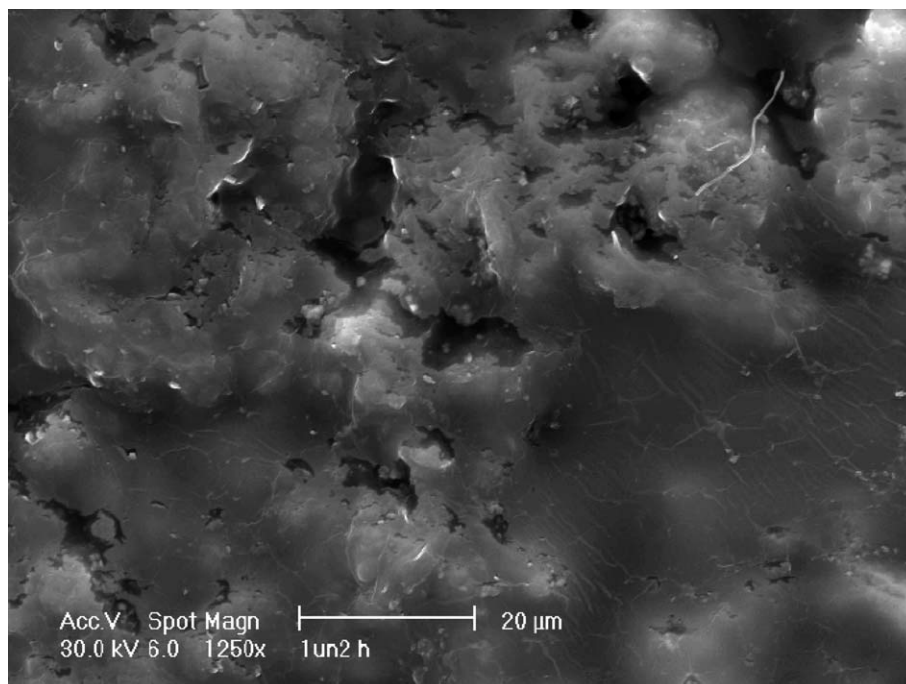

Fig. 6. SEM image of the fracture surface of 1 wt% uncoated CNF-polycarbonate composite (dispersed 2 h).
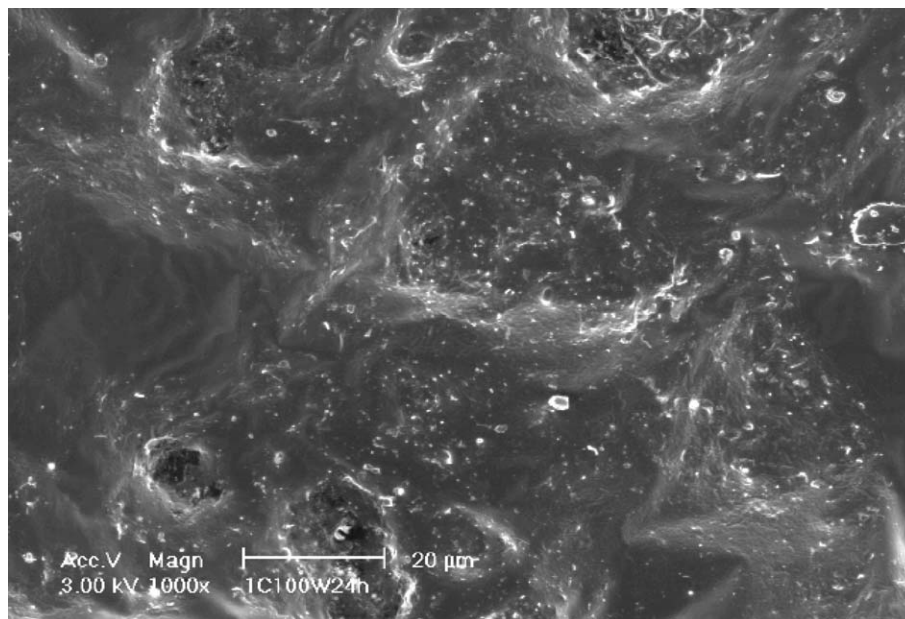
Fig. 7. SEM image of the fracture surface of 1 wt% coated CNF-polycarbonate composite (dispersed 2 h).

properties even at the optimum dispersion condition. Lau and Hui [17] showed that the use of multi-wall nanotubes for advanced composite structures may not improve the mechanical strength of the structure. The weak bond between the outer shell of the nanofibers and polymer matrix is mainly responsible for this behavior. However, this interfacial effect only takes place at the outer shell of the nanotubes. The inner shells can rotate and slide freely because of weak van der Waals force to link the individual graphene shells. This results in the non-uniform axial deformation inside the multi-wall nanotubes.

Another interesting trend that can be observed from Figs. 4 and 5 is that for the same processing conditions, the nanocomposites with the plasma treated CNF have better mechanical properties than those of the nanocomposites with the uncoated CNF. Fig. 6 shows the fracture surface of the nanocomposite with the uncoated nanotubes. Large pores in the polymer can be seen in this figure, which indicates the aggregation of nanofibers. On the other hand, Fig. 7 shows a smooth fracture surface and well dispersed CNF treated by plasma coating. No obvious aggregation of the CNF or clusters was found.

4. Conclusions

The experimental results presented in this research show that the plasma coating significantly enhances dispersion of CNF in the polymer matrix leading to improved mechanical properties of the nanocomposite. Although ultrasonic dispersion method is effective for dispersing nanotubes into polymer matrix, it can damage the deposited thin films resulting in the degradation of the mechanical properties of the composite. In order to further improve the mechanical properties of nanotubes composite, the ultrasonic time needs to be optimized. Ultrasonic dispersion without damaging the CNF and coating is an area where further research is needed.

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