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Surfactant-Assisted Processing of Carbon Nanotube/ Polymer Composites

Xiaoyi Gong, Jun Liu,* Suresh Baskaran, Roger D. Voise, and James S. Young

Pacific Northwest National Laboratory, Battelle Boulevard, Richland, Washington 99352

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Interfacial interaction is one of the most critical issues in carbon nanotube/polymer composites. In this paper the role of nonionic surfactant is investigated. With the surfactant as the processing aid, the addition of only 1 wt % carbon nanotubes in the composite increases the glass transition temperature from 63 °C to 88 °C. The elastic modulus is also increased by more than 30%. In contrast, the addition of carbon nanotubes without the surfactant only has moderate effects on the glass transition temperature and on the mechanical properties. This work points to the pathways to improve dispersion and to modify interfacial bonding in carbon nanotube/polymer composites.

Introduction

The discovery of carbon nanotubes and carbon nanotube based materials has inspired scientists for a range of potential applications.[1−4] The use of carbon nanotubes in polymer/carbon nanotube composites has attracted wide attention.[5,6] The carbon nanotubes have unique atomic structure, very high aspect ratio, and extraordinary mechanical properties (strength and flexibility), as directly measured by transmission electron microscopy,[7] making them ideal reinforcing fibers in nanocomposites. Carbon nanotube reinforced composites have been investigated for flame-retardant performances,[8] improved electrical conductivity and electrostatic charging behavior,[9,10] optical emitting devices,[8] and in lightweight, high strength composites. Recently, carbon nanotube/poly(vinyl alcohol) composites were prepared by direct mixing.[11] The presence of nanotubes stiffened the composites, especially at high temperatures, and retarded the onset of thermal degradation in some cases. However fabrication of homogeneous nanocomposites with carbon tubes remains a technical challenge.[5] Here we report the role of surfactants as processing aids in carbon nanotube/polymer composites. With the surfactant as the wetting agent, the addition of only 1 wt % carbon nanotubes in the composite increased the glass transition temperature from 63 °C to 88 °C. The elastic modulus was also increased by more than 30%. In contrast, the addition of carbon nanotubes without the surfactant only had moderate effects on the glass transition temperature and on the mechanical properties.

Experimental Procedure

AP (as-prepared)-grade carbon nanotube was purchased from Carbolex at the University of Kentucky and used as received. The bisphenol A epoxy resin and hydroxylated polyamine hardener H-917 were obtained from the Composite Materials Inc (Arlington, WA). Polyoxyethylene 8 lauryl, ($CH_3(CH_2)_{11}(OCH_2CH_2)_7OCH_2CH_3$) or $C_{12}EO_8$, was from Sigma. Reagent-grade acetone (99.5+%) was from Aldrich. A typical preparation of the carbon nanotube-epoxy composites is as follows: 19.2 mg $C_{12}EO_8$ was dissolved in 0.5 g acetone in a small beaker. 25.2 mg carbon nanotube was added to the as-prepared $C_{12}EO_8$ solution. This mixture was sealed with a plastic film (Parafilm) and magnetically stirred for 15 min with a stirbar at room temperature. Then 2.0 g epoxy and 0.5 g hardener were added. This produced a viscous suspension. The suspension was sealed and stirred for another 15 min until it appeared to be homogeneous. The mixture was poured into a mold with a dimension of 20 × 3 × 1 mm, cured at room temperature overnight, followed by an elevated temperature cure at 80 °C for 2 h and 120 °C for 2 h. The samples were removed from the oven and cooled to room temperature under ambient conditions. The control samples were made by using the same procedure without $C_{12}EO_8$, or without the nanotubes.

The samples were mounted on a Perkin-Elmer DMA 7e dynamic mechanical analyzer. We chose the dynamic testing technique because it only requires small samples and provides information on both the thermal and mechanical properties. Three-point bending test was performed with 50 mN static force and 50 mN dynamic force at frequency of 1.0 Hz. The samples were heated from −60 °C to 100 °C at a heating rate of 5.0 °C/min. The sample chamber was purged with nitrogen at 20 mL/min throughout the test.

Results

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (SEM) revealed

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* To whom correspondence should be addressed.

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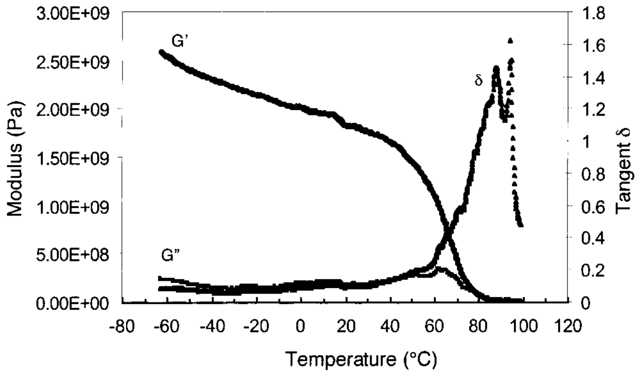

Figure 1. Storage modulus G', loss modulus G'', and loss tan δ as a function of temperature for epoxy plus 1 wt % carbon nanotubes with $C_{12}EO_8$.

that the as received carbon nanotubes are multiwalled and have a diameter from 2 to 4 nm. A small fraction of the carboneous materials are made of partially disordered spherical particles. Careful examination of the cross-section TEM image suggests that the partially disordered particles are also made of short carbon nanotubes centered around the nickel particles used in the preparation of the carbon nanotubes. The surface area of the as-received carbon nanotubes, as measured by nitrogen adsorption technique, is 252 m^2/g.

The dynamic mechanical analysis gave the storage modulus G', the loss modulus G'', and the loss tan δ as a function of temperature (Figure 1). The storage modulus G' is indicative of the elastic modulus of the composite, and the loss modulus G'' is indicative of the energy lost due to the friction of polymer chain movement. The loss tan δ is calculated as the ratio of G'' to G', which is very sensitive to the structural transformation. Generally, G' decreases very slowly as a function of temperature (due to increased chain mobility and flexibility) until the glass transition region is approached. Then G' decreases rapidly. At the same time, G'' increases and goes through a maximum. The damping factor (the energy lost), as expressed by the loss tan δ, also goes through a maximum. The glass transition temperature, T_g, is defined as the temperature at which a maximum of tan δ is observed, which is a common practice for polymer materials.[12] The storage modulus, and tan δ of different samples as a function of temperature are shown in Figure 2. These samples include pure epoxy (sample 1), epoxy plus $C_{12}EO_8$ (sample 2), epoxy plus 1 wt % C tubes (sample 3), and epoxy plus $C_{12}EO_8$ and 1 wt % C tubes (sample 4). As can be seen from Figure 2, the modulus and the glass transition behavior are both affected by the addition of the carbon nanotubes, as well as the surfactant. The addition of carbon nanotubes moderately increases the modulus and the glass transition temperature. The addition of the surfactant by itself has little effect on the glass transition temperature, but decreases the storage modulus. The decrease of the modulus by the surfactant is expected because the surfactant functions as a plasticizer.[13] The greatest effect comes from the addition of both carbon nanotubes and the surfactant. Both the modulus and the glass transition temperature were significantly increased.

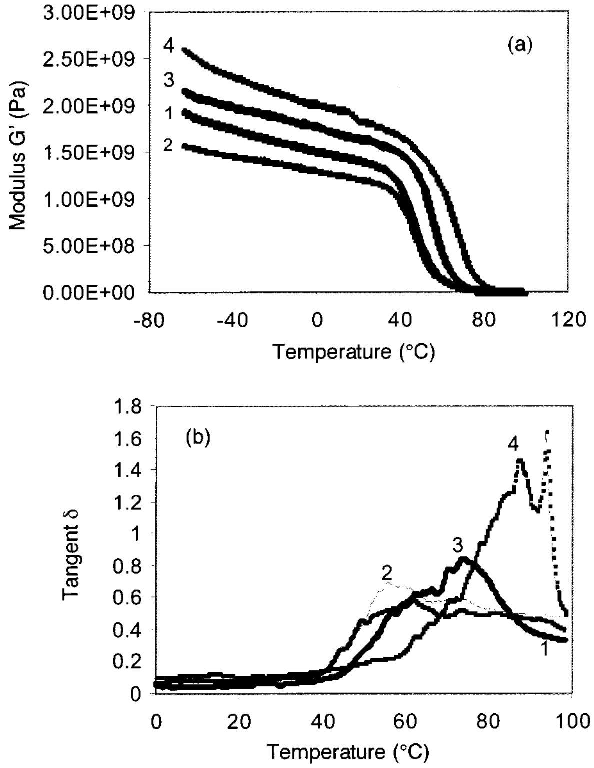

Figure 2. Storage modulus G', and loss tan δ, of different samples, as a function of temperature: (a) storage modulus G' and (b) loss tan δ. Sample 1 is the pure epoxy. Sample 2 is epoxy plus $C_{12}EO_8$. Sample 3 is epoxy plus 1 wt % carbon nanotubes. Sample 4 is epoxy plus 1 wt % carbon nanotubes with $C_{12}EO_8$.

Table 1. Storage Moduli and Transition Temperatures of the Epoxy Samples and Carbon Nanotube Composite Samples

	G' (GPa)			T_g (°C)	
samples	−60 °C	−20 °C	20 °C	tan δ	G''
(a) epoxy	1.90	1.65	1.43	63	50
(b) epoxy+$C_{12}EO_8$	1.53	1.38	1.20	62	47
(c) epoxy + 1% tube	2.12	1.90	1.60	72	53
(d) epoxy + $C_{12}EO_8$ + 1% tube	2.54	2.18	1.80	88	64

The storage modulus at several temperatures and the glass transition points of the different samples are summarized in Table 1. The storage modulus of carbon nanotube reinforced sample (with $C_{12}EO_8$) was increased by more than 30%, and the transition temperature was elevated from 63 °C to 88 °C, as compared with the pure epoxy sample. On the other hand, addition of pure carbon nanotubes only gave a moderate increase in storage modulus and glass transition temperature. In fact, it may be more informative to compare surfactant−carbon nanotube/epoxy sample with surfactant/epoxy samples, because the surfactant/epoxy sample, rather than the pure epoxy, was the base material for the surfactant−carbon nanotube/epoxy sample. This comparison gave a 50−70% increase in storage modulus with the addition of only 1 wt % carbon nanotubes.

The most likely role of the $C_{12}EO_8$ surfactant is to function as a dispersing agent. $C_{12}EO_8$ is a nonionic

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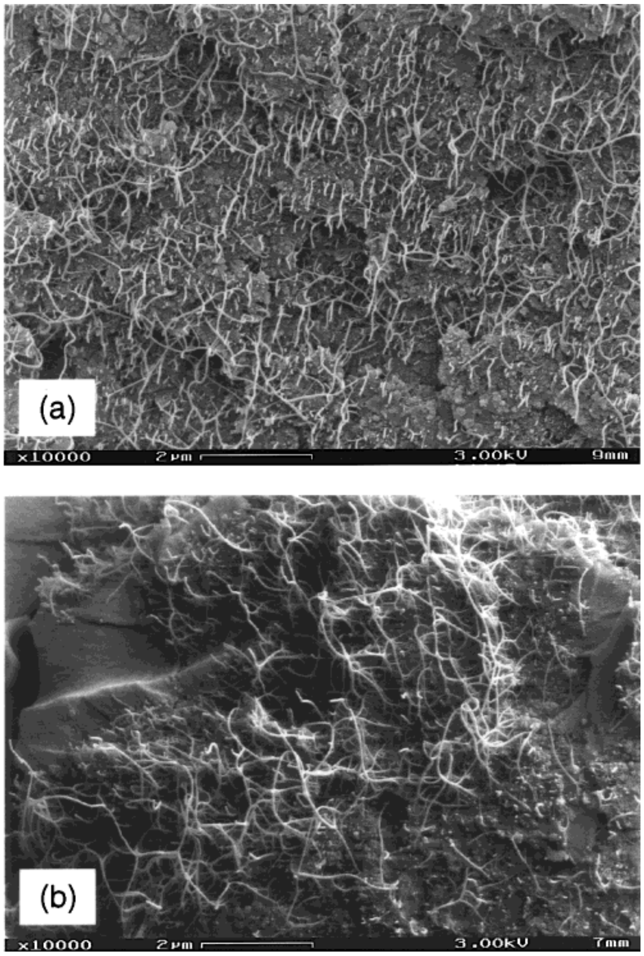

Figure 3. SEM photographs of carbon nanotubes on fracture surfaces of the composite samples: (a) with $C_{12}EO_8$ and (b) without $C_{12}EO_8$.

surfactant containing an oxyethylenated hydrophilic segment and a hydrocarbon hydrophobic segment, and a good dispersant for carbon.[14] Naturally the addition of the surfactant also has an effect on the wetting behavior, and on the interfacial adhesion, which in return has an impact on the surfactant's ability to disperse the nanotubes. More detailed study of the interfacial chemistry of carbon nanotubes should be an important subject for future research in this area. However on the basis of previous adsorption studies of hydrocarbon molecules on carboneous materials,[15] we suggest that the surfactant interact with carbon through the hydrophobic segment, at the same time, the hydrophilic segment can interact with the epoxy through hydrogen bonding. The surfactant as a coupling agent may introduce a steric repulsive force between the carbon nanotubes, which overcomes the van der Waals attractive force between the carbon surfaces in a poor solvent.[16] Figure 3 compares the morphologies of the carbon nanotubes on the fracture surface of the carbon nanotube/epoxy nanocomposites with (Figure 3a) and without (Figure 3b) the addition of the surfactant.

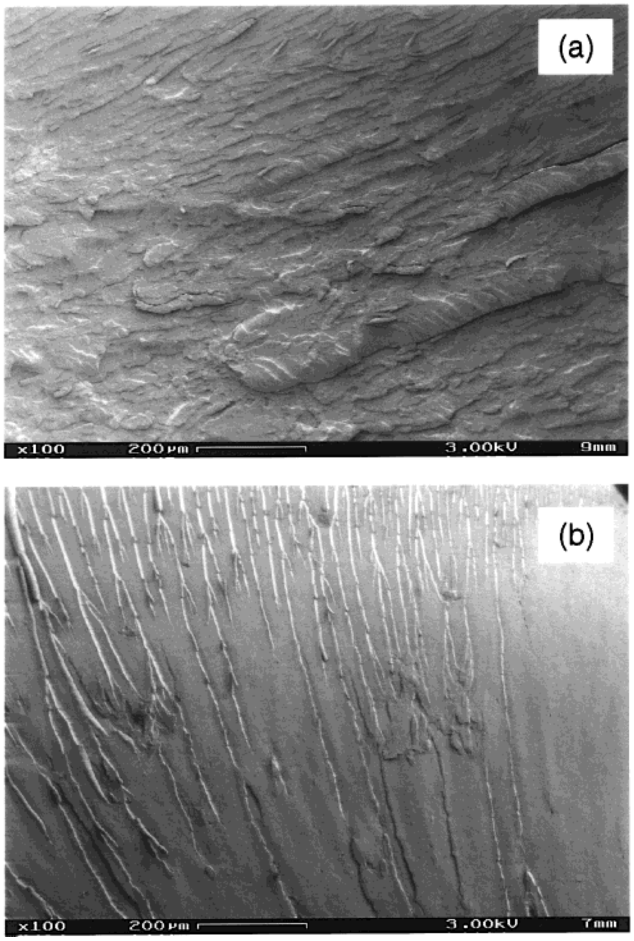

Figure 4. SEM photographs of fracture surfaces of the carbon nanotube composite samples: (a) with $C_{12}EO_8$ and (b) without $C_{12}EO_8$.

Typically the carbon nanotubes in the fractured sample without the surfactant appear to be very long, wavy, and are lumped together. This type of morphology is an indication of highly agglomerated carbon nanotubes and weak interactions with the matrix. The agglomerated carbon nanotubes can be easily separated from the matrix without breaking the nanotubes. On the other hand, the carbon nanotubes in the fractured sample with the surfactant appear to be more evenly distributed and aligned along one direction. Many nanotubes are terminated and dangling on the surface. These observations indicate that the nanotubes are better dispersed, and the load is transferred to the tubes during the fracture process. A low magnification macroscopic view of the fracture surfaces (magnification only ×100 instead of ×10 000) reveals signs of a tougher and stronger material for the composite with the surfactant than without, as shown in Figure 4. The fracture surface with just the carbon nanotubes is relatively smooth, while the fracture surface with the carbon nanotubes and the surfactant is relatively rough. The difference in the surface roughness suggests different fracture pathways.

Conclusion

In summary, we found that using surfactants as processing aids can improve the thermomechanical properties of carbon nanotube/polymer composites. The addition of only 1 wt % carbon nanotubes in the

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composite increases the glass transition temperature from 63 °C to 88 °C. The elastic modulus is also increased by more than 30%. In contrast, the addition of carbon nanotubes without the surfactant only has moderate effects on the glass transition temperature and on the mechanical properties. We should point out that even with the addition of the surfactant, complete homogeneous dispersion of the nanotubes was not achieved. The gas-phase synthesized carbon nanotubes usually contain agglomerate structures that can be very difficult to breakdown physically. There are regions with more carbon nanotubes, and regions with less carbon nanotubes. More carbon nanotubes are observed within the domains of an agglomerate. What is observed in the thermomechanical properties reflects the average containing contributions from the whole sample. However our work clearly illustrated the dramatic effect the carbon nanotubes can have on the composite materials with improved dispersion, and points to the pathways for dispersing carbon nanotubes in this type of new composite materials. Future improvement of this work may include better choices of surfactant types and concentration for different polymer materials, a more complete understanding of the interfacial chemistry and the mechanism dispersion, optimization of carbon nanotube contents in the composite for different applications, better understanding of the adhesion between the carbon nanotubes and the polymer matrix in the presence of surface modification agents, and the synthesis of more uniform and more dispersible nanotubes.

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