Thermal Characterization of Carbon-Nanofiber-Reinforced Tetraglycidyl-4,4'-diaminodiphenylmethane/4,4'-Diaminodiphenylsulfone Epoxy Composites

Hongfeng Xie,[1] Binghua Liu,[1] Hu Yang,[1] Zhiliu Wang,[1] Jianyi Shen,[1] Rongshi Cheng[1,2]

[1]Key Laboratory for Mesoscopic Chemistry of the Ministry of Education, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China
[2]College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

ABSTRACT: The thermal properties of carbon nanofibers (CNF)/epoxy composites, composed of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) resin and 4,4'-diaminodiphenylsulfone (DDS) as a curing agent, were investigated with differential scanning calorimetry (DSC), thermogravimetric analysis, and dynamic mechanical thermal analysis. DSC results showed that the presence of CNF had no pronounced influence on the heat of the cure reaction. However, the incorporation of CNF slightly improved the thermal stability of the epoxy. Furthermore, the storage modulus of the TGDDM/ DDS epoxy was significantly enhanced, whereas the glass-transition temperature was not significantly affected, upon the incorporation of CNFs. The storage modulus of 5 wt % CNF/ epoxy composites at 25°C was increased by 35% in comparison with that of the pure epoxy. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 295–298, 2006

Key words: composites; high performance polymers; thermal properties
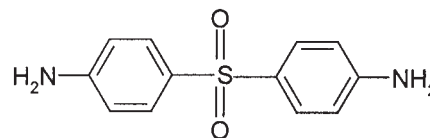
INTRODUCTION

Carbon nanofibers (CNF) are vapor-grown carbon fibers (VGCF) with diameters of 60–200 nm. VGCFs are a relatively new type of carbon fiber and are produced from a hydrocarbon gas, such as benzene and methane, in the presence of hydrogen at temperatures around 900–1200°C with transition metal catalyst particles (usually Fe, Co, and Ni) supported on an inert substrate.[1–3] Depending on the preparation conditions, VGCF can be made with diameters of several tens of nanometers up to tens of micrometers and with lengths from several micrometers up to several centimeters. Because of their high specific tensile modulus and strength, excellent electrical and thermal properties, high aspect ratios, and potentially low production cost, CNFs are of great scientific interest as reinforcements for polymer matrices.[4–12]

Tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)
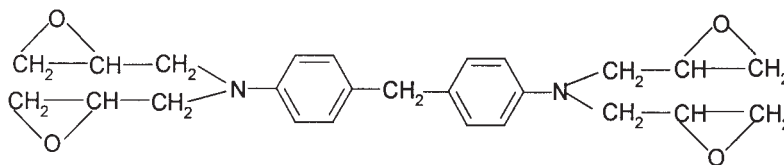
cured with 4,4'-diaminodiphenylsulfone (DDS)

shows a high glass-transition temperature (T_g) because of the presence of polar sulfone groups that favor hydrogen bonding and the regular packing of the polymer chains.[13,14] Furthermore, the tetrafunctionality of TGDDM leads to a high-density crosslinked network on curing, giving a very tough polymer. These characteristics have promoted the use of the TGDDM/DDS system as a binder for high-performance and light-weight composites employed
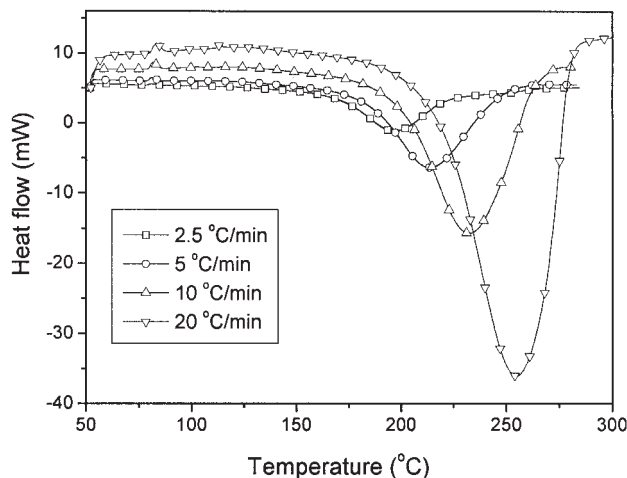
Figure 1 Dynamic DSC thermograms at different heating rates for 5 wt % CNF/epoxy composites.

in the aerospace industry.[15,16] In most of these applications, carbon fibers have been used as reinforcements.[17,18] However, very few efforts have been made to study the effects of carbon nanofillers on the physical properties of TGDDM/DDS epoxy. In our previous publications,[19,20] the influence of both multiwalled carbon nanotubes (MWNTs) and CNF on the cure kinetics of TGDDM/DDS systems was studied through isothermal differential scanning calorimetry (DSC). It was found that MWNTs had an acceleration effect on the cure reaction of the resin, whereas CNF had a negligible influence. In this article, the effects of CNF on the thermal properties of the epoxy are reported.

EXPERIMENTAL

Materials

The epoxy resin used in this research was TGDDM (AG80), with a weight per epoxy equivalent of 120 g/equiv, from the Shanghai Synthetic Resin Institute (Shanghai, China). The curing agent was DDS, with a molecular mass of 248.31 and a purity greater than 99% according to the supplier. CNFs were prepared from propylene over a Ni–Cu catalyst in a conventional horizontal tube furnace. The diameter of the CNFs was about 200 nm.

Sample preparation

An epoxy resin/CNF mixture was sonicated for 2 h before curing. Subsequently, the mixture was placed in an oil bath at 120°C, and a stoichiometric amount of DDS was slowly added with continuous mechanical stirring until a homogeneous mixture was observed; this took about 10 min. Several DSC aluminum pans

were filled with the reaction mixture. The mixtures (ca. 10 mg) were then cooled and stored in a freezer until they were required for the DSC measurements. Other mixtures were immediately poured into polytetrafluoroethylene molds. Curing was conducted at 80°C for 2 h, at 140°C for 2 h, and at 180 for 2 h and was followed by a postcuring step at 220°C for 5 h. The weight fractions of CNF in the TGDDM/DDS system were 1, 2.5, and 5 wt %.

DSC

A PerkinElmer (Boston, MA) Pyris 1 differential scanning calorimeter (supported by a PerkinElmer computer for data acquisition/analysis) was used for the dynamic cure experiments and data analysis under an argon flow of 20 mL/min. The dynamic (nonisothermal) DSC experiments were conducted at heating rates of 2.5, 5, 10, and 20°C/min.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical tests were carried out on specimens 25 mm long, 8 mm wide, and 1 mm thick with a model DMTA V dynamic mechanical thermal analyzer from Rheometric Scientific, Inc. (Piscataway, NJ). The geometry of deformation was the rectangular tension mode. The tests were performed in the scanning temperature mode, in the range of 30–300°C, at a heating rate of 3°C/min, with an oscillating frequency of 1 Hz.

Scanning electron microscopy (SEM)

Morphology observations were performed with a Hitachi X650 scanning electron microscope (Tokyo, Japan), before which cured samples were fractured under liquid nitrogen, and then the etched surfaces were vacuum-coated with a thin gold layer.

Thermogravimetric analysis (TGA)

A PerkinElmer Pyris 1 TGA instrument (Boston, MA) was used for thermogravimetric examinations,

TABLE I
Heats of Reaction of Epoxy Composites with Various CNF Contents at Different Heating Rates

Heating rate (°C/min)	ΔH_0 (J/g)			
	0 wt %	1 wt %	2.5 wt %	5 wt %
2.5	602.9	570.0	552.9	551.7
5	668.6	658.8	643.5	613.4
10	671.1	650.8	656.4	624.2
20	707.9	688.4	688.7	643.3
$\overline{\Delta H_0}$ (J/g)	662.6	642.0	635.4	608.2
$\overline{Q}_0$ (kJ/mol of epoxide)	120.3	117.7	118.3	116.2

TABLE II
T_p **Values for All CNF/Epoxy Composites**

Heating rate (°C/min)	T_p (°C)			
	0 wt %	1 wt %	2.5 wt %	5 wt %
2.5	198.2	197.0	196.6	196.6
5	216.8	215.3	214.3	213.6
10	237.0	235.8	235.5	232.2
20	261.0	260.8	255.5	254.8

operating under a continuous flux of nitrogen (20 mL/min) from 20 to 700°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the heat flow measured by DSC during curing at different rates between 2.5 and 20°C/min for 5 wt % CNF/epoxy composites. To calculate the total heat of reaction generated to reach the full conversion (ΔH_0), the total area under the thermogram was determined for all composites. The individual values of ΔH_0 and average values ($\overline{\Delta H_0}$) for different epoxy composites with various nanofiber contents at different heating rates are shown in Table I. The total heat of reaction is influenced by the presence of CNF, and the average values of ΔH_0 decrease with the nanofiber content in the epoxy composites. The normalized values of $\overline{\Delta H_0}$ ($\overline{Q_0}$) also are given in the table, and the fact that the normalized values are practically constant suggests that the decrease in ΔH_0 can be directly attributed to the proportional reduction of the epoxy concentration in the composites.

Table II gives the temperatures of the DSC thermogram peaks (T_p) for all CNF/epoxy composites. The peak shifts to high temperatures as the heating rate increases for a certain system, whereas T_p slightly shifts to a lower temperature with increasing CNF
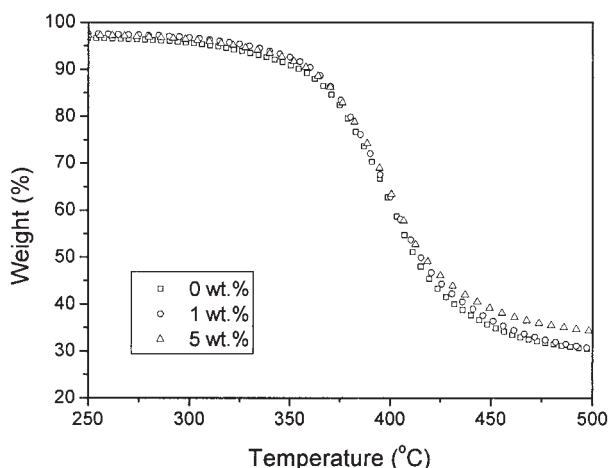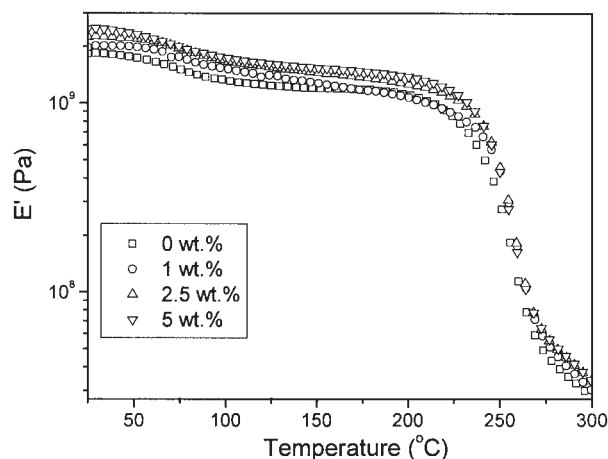
Figure 3 Dynamic mechanical spectra in terms of E' for the CNF/epoxy composites.

content. This indicates that nanofibers slightly accelerate the cure reaction of the epoxy.[20,21]

Figure 2 shows TGA curves of TGDDM/DDS epoxy and its CNF composites. The thermal stability of the epoxy is slightly improved by the incorporation of nanofibers. The better thermal stability of the CNF/epoxy composites could be attributed to the slightly enhanced interfacial adhesion between the nanofibers and the epoxy.[22]

The elastic modulus and damping properties of the composites were characterized by DMTA as a function of the nanofiber content and temperature. The storage modulus (E') as a function of temperature for the epoxy and its CNF composites is shown in Figure 3. Evidently, E' increases with increasing CNF content. E' (2.47 GPa) of 5 wt % CNF/epoxy composites at 25°C increased by 35% in comparison with that of the pure epoxy (1.82 GPa). Figure 4 shows the loss tangent
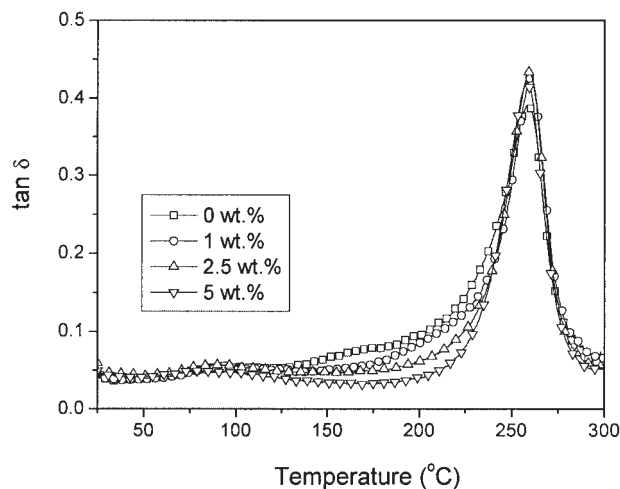
Figure 2 TGA curves of the epoxy and its CNF composites.

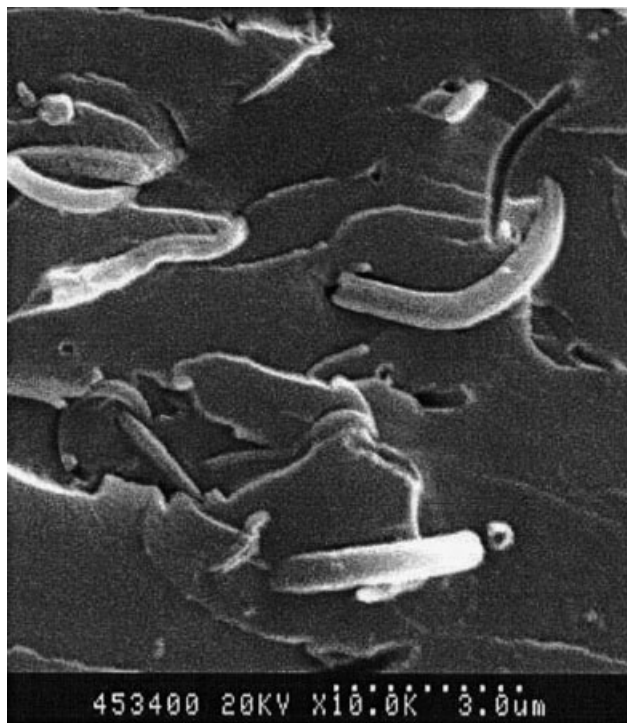**Figure 4** Dynamic mechanical spectra in terms of tan δ for the CNF/epoxy composites.

Figure 5 SEM image of 1 wt % CNF/epoxy composites.

(tan δ) as a function of temperature for CNF/epoxy composites. T_g (ca. 259°C), defined as the temperature at which tan δ is maximum, was not affected by the presence of nanofibers. Such results have also been observed in nanofiber-reinforced rubbery epoxy,[23] but it is different from the results of the MWNT-reinforced TGDDM/DDS system, for which T_g slightly increased with increasing nanotube content.[24] Furthermore, with increasing CNF content, the onset of the glass transition shifts to a higher temperature. Clearly, the CNF immobilizes the nearby epoxy segments, partly by specific interactions, thus delaying the onset of their motions to a higher temperature.[25] Hence, it can be followed that good interfacial interaction between the epoxy and the CNF exists in the composites and could be the main reason for the observed improvement in E'.

An SEM image of 1 wt % CNF/epoxy composites is shown in Figure 5. A good dispersion of nanofibers in the epoxy can be observed. However, the SEM image of the fractured surface also shows nanofibers pulled out of the epoxy. The diameters of many nanofibers in the composites are greater than those of the original CNF, which appear coated by a cylindrical shell of the polymer matrix. This indicates the interfacial bonding between the nanofibers and the epoxy is strong. Thus, the enhancement of the thermal stability and E' could be attributed to the interfacial bonding. Such a feature was also observed in CNF/poly(ether ether ketone) composites.[26]

CONCLUSIONS

In this article, the thermal characterization of a CNF-reinforced TGDDM/DDS system has been studied through DSC, TGA, and DMTA. The presence of nanofibers in the epoxy has no pronounced influence on the heat of the cure reaction, but T_p slightly decreases with increasing nanofiber content. The addition of CNF slightly improves the thermal stability of the epoxy. Furthermore, E' of the epoxy increases with increasing nanofiber content, but the presence of CNF has no influence on T_g of the epoxy. A good dispersion of nanofibers in the epoxy has been observed in an SEM image. The improvement in the thermal stability and dynamic mechanical properties can be attributed to the strong interfacial bonding between the nanofibers and the epoxy.

References

1. Tibbets, G. G. Carbon 1989, 27, 745.
2. Chung, D. D. L. Carbon 2001, 39, 1119.
3. Endo, M.; Kim, Y. A.; Hayashi, T.; Nishimura, K.; Matusita, T.; Miyashita, K.; Dresselhaus, M. S. Carbon 2001, 39, 1287.
4. Patton, R. D.; Pittman, C. U., Jr.; Wang, L.; Hill, J. R. Compos A 1999, 30, 1081.
5. Lozano, K.; Barrera, E. V. J Appl Polym Sci 2001, 79, 125.
6. Lozano, K.; Bonilla-Rios, J.; Barrera, E. V. J Appl Polym Sci 2001, 80, 1162.
7. Zeng, I. J.; Saltysiak, B.; Johnson, W. S.; Schiraldi, D. A.; Kumar, S. Compos B 2004, 35, 173.
8. Brandl, W.; Marginear, G.; Chirila, V.; Warschewski, W. Carbon 2004, 42, 5.
9. Cortes, P.; Lozano, K.; Barrera, E. V.; Bonilla-Rios, J. J Appl Polym Sci 2003, 89, 2527.
10. Sandler, J.; Windle, A. H.; Werner, P.; Altsadt, V.; Es, M. V.; Shaffer, M. S. P. J Mater Sci 2003, 38, 2135.
11. Ran, S.; Burger, C.; Sics, I.; Yoon, K.; Fang, D.; Kim, K.; Avila-Orta, C.; Keum, J.; Chu, B.; Hsiao, B. S.; Cookson, D.; Shultz, D.; Lee, M.; Viccaro, J.; Ohta, Y. Colloid Polym Sci 2004, 282, 802.
12. Kumar, S.; Doshi, H.; Srinivasarao, M.; Park, J. O.; Schiraldi, D. A. Polymer 2002, 43, 1701.
13. Van Hoorn, H. J Appl Polym Sci 1968, 12, 871.
14. Levchik, S. V.; Camino, G.; Luda, M. P.; Costa, L.; Costes, B.; Henry, Y.; Muller, G.; Morel, E. Polym Degrad Stab 1995, 48, 359.
15. Epoxy Resins: Chemistry and Technology, 2nd ed.; May, C. A., Ed.; Marcel Dekker: New York, 1988.
16. Morgan, R. J. Adv Polym Sci 1985, 72, 1.
17. Mijovic, J. J Appl Polym Sci 1986, 31, 1177.
18. Opalicki, M.; Kenny, J. M.; Nicolais, L. J Appl Polym Sci 1996, 61, 1025.
19. Xie, H. F.; Liu, B. H.; Yuan, Z. R.; Shen, J. Y.; Cheng, R. S. J Polym Sci Part B: Polym Phys 2004, 42, 3701.
20. Xie, H. F.; Liu, B. H.; Sun, Q.; Yuan, Z. R.; Shen, J. Y.; Cheng, R. S. J Appl Polym Sci 2005, 96, 329.
21. Wu, J. H.; Chung, D. D. L. Carbon 2004, 42, 3039.
22. Jang, J.; Bae, J.; Yoon, S. H. J Mater Chem 2003, 13, 676.
23. Richard, P.; Prasse, T.; Cavaille, J. Y.; Chazeau, L.; Gauthier, C.; Duchet, J. Mater Sci Eng A 2003, 352, 344.
24. Xie, H. F.; Liu, B. H.; Yang, H.; Wang, Z. L.; Shen, J. Y.; Cheng, R. S. Polym Int, submitted.
25. Goh, H. W.; Goh, S. H.; Xu, G. Q.; Pramoda, K. P.; Zhang, W. D. Chem Phys Lett 2003, 379, 236.
26. Sandler, J.; Werner, P.; Shaffer, M. S. P.; Demchuk, V.; Altsadt, V.; Windle, A. H. Compos A 2002, 33, 1033.