J Mater Sci (2008) 43:413–416
DOI 10.1007/s10853-007-2169-6

LETTER

# Physical properties of a reactive graphitic nanofiber-reinforced epoxy

**Soumen Jana · Wei-Hong Zhong**

Received: 25 May 2007 / Accepted: 14 September 2007 /

The dielectric constants, and electrical and thermal conductivities of epoxy composites containing 0.2–0.5 wt.% of reactive graphitic nanofibers (r-GNFs) have been studied. In each case, epoxy composite with 0.3 wt.% r-GNFs showed the highest enhancement. Addition of more r-GNFs to the epoxy matrix degraded the properties. Incremental rates of dielectric constants at high frequency (from 10 KHz to 1 MHz), is higher compared to that at low frequency (less than 10 KHz).

For various engineering applications, epoxy resins are widely used as matrices for composite materials due to their low density compared to metals, high specific mechanical properties and good processability [1, 2]. In addition, both anhydride and amide curing agents can be used for curing without emission [3]. However, low electrical and thermal conductivities of epoxy resins make them unusable in some applications. One approach to this class of problems is to incorporate nano-scale fillers which have inherently high electrical and thermal properties into the epoxy matrix [4, 5]. For electronic applications, dielectric properties are also important.

Among various conductive nanofillers such as graphitic nanofibers (GNFs), carbon nanotubes (CNTs), etc., GNFs have relatively low cost and high performance [6, 7]. In addition, the edges of GNFs may be utilized for generation of covalent bond between GNFs and polymer resin molecules [8, 9]. In our previous studies, reactive graphitic nanofibers (r-GNFs) from functionalized herringbone graphitic nanofibers with 3,4′-oxydianiline (GNF-ODA) [9, 10] were produced, which resulted in enhancing mechanical properties. The reactive hydrogen in the –OH– group of the r-GNF takes part in curing reaction of an epoxy resin. Therefore, r-GNFs and epoxy matrix can form a unified resin system, which were named “nano-epoxy” because it is not a “simple physical nanocomposite” (physical mixing). Based on the r-GNFs, series of nano-epoxy matrices with different concentrations of r-GNFs were developed and the various mechanical properties were characterized in our previous studies. The results showed that among all concentrations of r-GNFs (up to 1.3 wt.%), the nano-epoxy with 0.3 wt.% concentration showed the highest interfacial adhesion properties between UHMWPE fiber and matrix, mechanical properties (flexural strength and modulus), ageing resistance, dynamic mechanical properties and other properties compared to the pure epoxy specimens [10–14]. In this study, our main objective is to find out whether r-GNFs could facilitate the improvement in certain physical properties. For this purpose, dielectric properties, thermal conductivity and electrical conductivity tests were conducted.

A mixture of GNF-ODA nanofibers (from Vanderbilt University) and diluent butyl glycidyl ether (BEG) (Sigma–Aldrich Co.) (1:50 by weight) was sonicated by a sonifier (Branson® 450) with power level 70 W for 3 h at room temperature and the length of the GNF-ODA nanofibers was reduced to 400–800 nm. The mixture left for 36 h for reaction and r-GNFs were obtained [12]. The ratio of solution r-GNF/BGE to 1:6 was obtained by vacuuming (125 °C) the solution in a vacuum oven. The curing agent, Epikure$^{TM}$ W (Miller-Stephenson Chemical Inc.) was added to the epoxy resin, Epon 828 (Miller-Stephenson Chemical Inc.) in a ratio of 24:100 by weight to produce pure epoxy matrix. Exact amounts of r-GNF/diluent solutions were added to the pure epoxy matrix to fabricate nano-epoxy matrices having 0.2, 0.3, and 0.5%

---

S. Jana · W.-H. Zhong (✉)
School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA
e-mail: katie_zhong@wsu.edu

r-GNFs loadings by weight. Low-level sonication was conducted for each mixture for an hour at room temperature to disperse the r-GNFs into the pure-epoxy matrix. Pure epoxy and nano-epoxy matrices with different r-GNF concentrations were degassed, cured for 4 h at temperature 150 °C and then cooled naturally to room temperature. Detailed information about preparation of the specimens can be found in Ref. [10]. A Keithley Instrument Model 6517A with 8009 fixture was used to measure the surface conductivity by applying a voltage of 500 V DC at ambient temperature (298 K). A Novocontrol GmbH Concept 40 broadband dielectric spectrometer was used to measure the real ($\varepsilon'$) of complex dielectric permittivity ($\varepsilon^{\bullet}$) at ambient temperature. Thermal conductivities were measured at room temperature using a TC-30 (Mathis Inc.).

Figure 1 shows the enhancement in dielectric constant with addition of r-GNFs in the epoxy matrix. It can be seen that the specimen with 0.3 wt.% concentration results in the highest dielectric constant among all concentration levels. It is believed that the optimum combination of r-GNFs, BGE and epoxy molecules occurred in the nano-epoxy with 0.3 wt.%. Greater amounts of r-GNFs may increase the r-GNF density in the matrix, and Van der Waals force among nanofibers will cause their aggregation which in turn disrupts the formation of an evenly dispersed network of r-GNFs throughout the matrix. TEM images of specimens with different r-GNF concentration confirm this idea (Fig. 2a–c). From the images, it is clear that the nanofillers dispersed well in the nano-epoxy with 0.3 wt.% of r-GNFs. In the nano-epoxy with 0.2 wt.% r-GNFs, even though they were well dispersed, there were insufficient amounts to establish an effective network of r-GNFs, whereas in the 0.5 wt.%, agglomeration was clearly observed. However, various models which demonstrate the enhancement in dielectric constant with increase of nanofillers volume fraction, are not valid to these experimental results [15, 16].

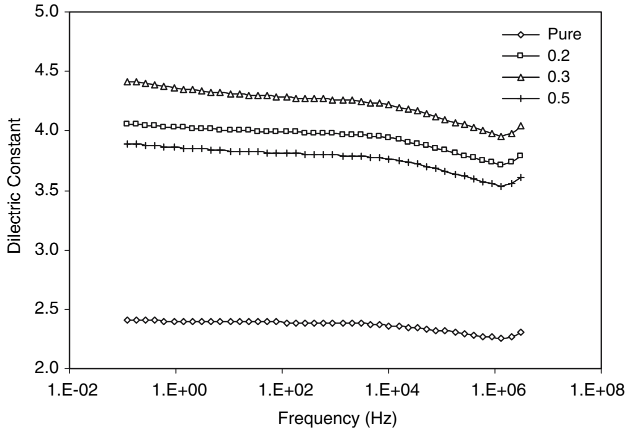

**Fig. 1** Dielectric constant vs. frequency curves of pure epoxy and nano-epoxy

It was also found that the increment rate at high frequency (10 K–1 MHz) is greater compared to that at low frequency (<10 KHz). When an electrical field is applied to a material, the dipoles in the material have a tendency to orient themselves in the direction of the applied field. However, mobility of the dipoles depends on the ductility of the materials. In our previous experiments, it was observed that r-GNFs/BGE solution increases the toughness/ductility of the epoxy resin [12]. At low frequency, dipoles are able to follow an oscillating electric field more easily than at a high frequency at a given temperature. Near to 1 MHz frequency, there is a sudden decrease in dielectric constant and it is thought that this occurred from field distortion which was caused by a decrease in dipolar polarization of the matrix and accumulation of charges at the interface of the nanofibers and epoxy resin.

Figure 3 shows the plot of log of resistivity versus r-GNF concentration (wt.%) at room temperature. Specimens with 0.3 wt.% concentration showed the lowest resistivity with a decrease by more than 2 orders of magnitude compared to the pure epoxy. They also showed the highest thermal conductivity (increased from 0.225 to 0.240 W/mK) compared to the nano-epoxy with other concentration levels (Fig. 4). The reactive nanofibers, r-GNFs, were produced from graphitic fibers which have significantly higher conductivity properties compared to that of epoxy resins, thus an effective linking of r-GNFs can improve the thermal/electrical conductivities. In the case of the 0.3 wt.% samples, the amounts of epoxy, diluent and r-GNFs were proportionate in the nano-epoxy composite which resulted in a maximum conductivity enhancement among all samples. In specimens with 0.2 and 0.5 wt.% concentrations, r-GNFs were either not able to develop sufficient network contiguity due to insufficient amount of r-GNFs, or their aggregation at the higher amount had the same effect. In consideration of the error bars in Figs. 3 and 4, it seems that the network density of r-GNFs is not uniform throughout the specimen even in the specimens with 0.3 wt.% concentration.

In considering the above results and discussions it should be noted that there is a growing desire among commercial applications of composites, especially in the aerospace and wind energy sectors, for multi-functional structures with not only high performances, but lower costs. This epoxy composite reinforced with r-GNFs has now been shown to not only have improved mechanical properties [14], but also significant electrical conductivity improvements as reported here, and is based on an economical form of nano-reinforcement, nanofibers. It is expected that these results could have value in such applications.

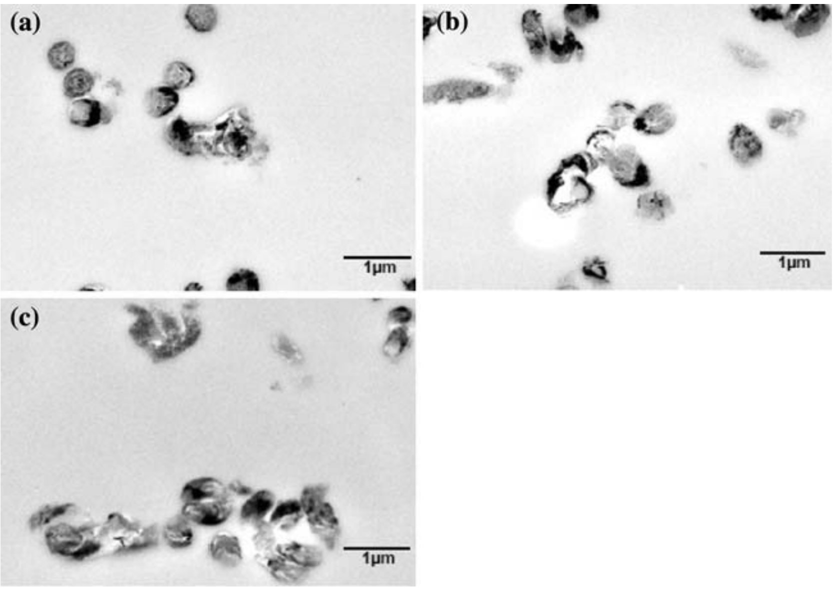

**Fig. 2** TEM images of the cured nano-epoxy specimens with: (**a**) 0.2 wt.%, (**b**) 0.3 wt.%, and (**c**) 0.5 wt.% of nanofibers

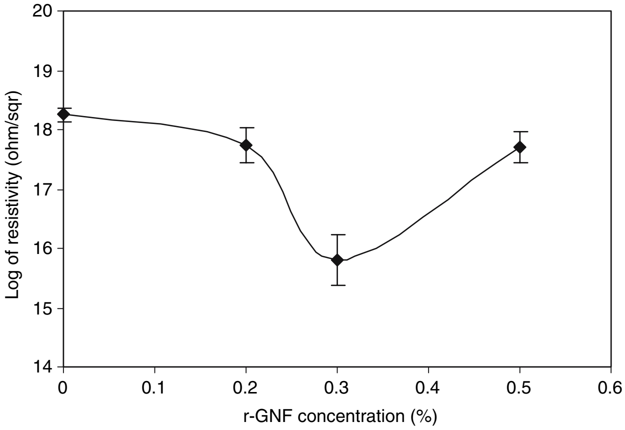

**Fig. 3** Log of resistivity vs. r-GNF concentration (%) curves of pure epoxy and nano-epoxy

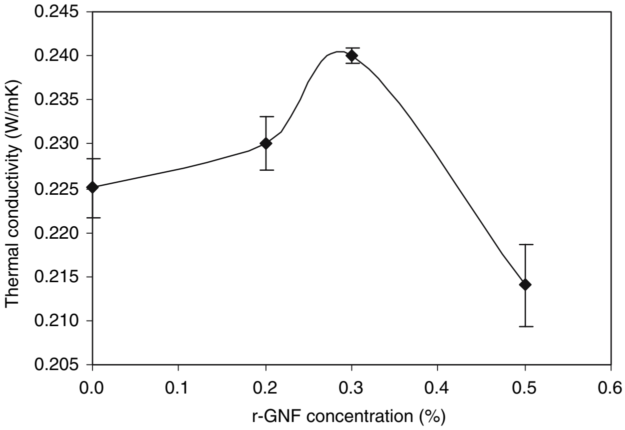

**Fig. 4** Thermal conductivity vs. r-GNF concentration (%) curves for pure epoxy and nano-epoxy

In conclusion, it can be stressed that the addition of very small amounts r-GNFs, 0.2–0.5 wt.%, can improve the dielectric constant of the epoxy resin, and reduce the surface resistivity as much as orders of magnitude compared to the pure epoxy. It was shown that an optimum value (0.3 wt.%) exists between the insufficient material levels and the excessive agglomerating levels. This same value produced an optimum level of thermal conductivity although that level was too low for many thermal management applications. More work needs to be done to comprehend this result.

**Acknowledgements** The authors gratefully acknowledge support from NASA through Grant NNM04AA62G and from NSF through NIRT grant 0506531. Dr. W. H. Zhong also gratefully acknowledges Dr. Charles M. Lukehart and Mr. Jiang Li (Vanderbilt University) for providing the derivatized graphitic carbon nanofibers.

## References

1. Donnet JB (2003) Compos Sci Technol 63:1085
2. Frisch HL, Mark JE (1996) Chem Mater 8:1735
3. Jang BZ (1994) Advanced polymer composites: principles and applications. ASM International, Materials Park, OH
4. Valebntini L, Puglia D, Frulloni E, Armentano I, Kenny JM, Santucci S (2004) Compos Sci Technol 64:23
5. Ramajo L, Reboredo M, Castro M (2005) Compos: Part A 36:1267
6. Yue ZR, Jiang W, Wang L, Gardner SD, Pittman CU (1999) Carbon 37:1785
7. Wong EW, Sheehan PE, Lieber CM (1997) Science 277:1971
8. Chen XH, Wang JX, Yang HS, Wu GT, Zhang XB, Li WZ (2001) Diam Relat Mater 10:2057
9. Li J, Vergne MJ, Mowles ED, Zhong WH, Hercules DM, Lukehart CM (2005) Carbon 43:2883
10. Zhong WH, Li J, Xu LR, Lukehart CM (2005) Polym Compos 26:128

11. Jana S, Zhamu A, Zhong WH, Gun YX (2006) J Adhesion 82:1157
12. Salehi-Khojin A, Jana S, Zhong WH (2007) J Nanosci Nanotech 7:1
13. Jana S, Zhong WH, Gun YX (2007) Mater Sci Eng A 445–446:106
14. Zhamu A, Hou YP, Zhong WH, Stone JJ, Li J, Lukehart CM (2007) Polym Compos 28:606
15. Nan CW (2001) Phys Rev B 63:176201
16. Yamada T, Ueda T, Kitayama TJ (1982) Appl Phys 53:4328