Research on BNNTs/Epoxy/Silicone Ternary Composite Systems for High Thermal Conductivity

Hua Lei, Qian Shi and Jia Chen*

The Materials and Metallurgy College, Guizhou University, Guiyang, Guizhou, P.R.China, 550003
E-mail: xxlhtt@sina.com

Abstract. A kind of composites based on organ silicon resin modification epoxy filling with Boron Nitride Nanotube (BNNT) was prepared. The composite could be used in the area of printed circuit boards (PCBs) and the electronic packaging industry. The influences of the BNNT and organ silicon resin content on the thermal conductivity of the composites were investigated. The structures of the composites were measured with DSC, SEM and Raman analysis. It was found that the thermal conductivity (TC) values of the composites linear varied by different filler contents. The thermal conductivity of neat epoxy is 0.1 W/(m K), and when the BNNT content increased to 5.0 wt %, the thermal conductivity of the composite reached 0.45 W/(m K), approximately four times increase compared with neat epoxy. Also, further result showed that combining organ silicon resin with BNNT (5.0%wt filling content), the TC value of the modified epoxy composite reached to 0.79 W/(m K), almost eight times that of the original epoxy resin.

1. Introduction
The applications of printed circuit boards (PCBs) have driven technical demand for the future evolution of high-frequency appliances. As the working frequency of electronic appliances increasing, the losses of signal intensity become more sensitive. Circuit substrates with poor dielectric properties will maintain unfavorable signal-conveying efficiency. Therefore, demand is high in the high-frequency appliance markets for a small dielectric constant (Dk) and low dissipation energy substrates to increase the speed of signal propagation [1–4]. Meanwhile, thermally conductivity is increasingly important for electronic packaging because the heat dissipation ability limits the reliability, performance, and miniaturization of electronics [5–7]. In addition to high-thermal conductivity and high-electrical resistivity, a low coefficient of thermal expansion (CTE) is needed for resistance to thermal fatigue [8]. Thus, materials used for PCBs need to have more multifunctional properties, such as excellent thermal, electrical, and mechanical properties at the same time. Up to now, a sole polymer material is hard to satisfy the demand for more multifunctional properties because of its high CTE and low-thermal conductivity [9]. Thermal-conductive ceramic particles-filled composites are potentially used as the primary materials for PCBs, because of their high-thermal conductivity. However, they have unacceptable dielectric constant for use in high frequency appliances [10–12]. In addition to the thermal and electrical properties, the mechanical properties of substrate and packaging materials are also very important. However, polymers usually exhibit low stiffness and strength. To offset these deficiencies, adding inorganic particles to a polymer is a common method. To effectively solve the thermal dissipation problem, different fillers have been investigated. These include oxides(Al2O3, SiO2, ZnO, and BeO), carbide(SiC), nitrides (AlN and BN)[13–15], and carbon materials (graphite and carbon nanotubes). Among these fillers, AlN has once been considered an ideal candidate due to its
higher thermal conductivity, no toxicity, stable crystal structure, and relatively low cost. Many researchers have observed significant increase in the thermal conductivity of different polymer–AlN composites. Boron Nitride Nanotubes (BNNTs) not only have high chemical stability at elevated temperatures, but exhibit unusual high thermal conductivity (~600 W/mK along the tube axis) due to low-dimensional effects, and, for example, is notably higher than the value ~ 400 W/mK for copper. It is found that an isolated single-walled BNNT can possess a thermal conductivity even higher than that of a carbon nanotube (~3000 W/mK). On the basis of the above considerations, the BNNTs content dependence on thermal property and the structure of epoxy/organic-si/BNNs hybrid composites were studied in this paper, and, the crucial thermal conductivity of the epoxy–BNNTs composite was also tested. Raman and SEM tests also were used for structure analysis of the composites. The purpose of systemic investigations of these properties is to develop a new composite for printed circuit board (PCB) substrates.

2. Experimental details

2.1 Materials and preparations

2.1.1 Raw materials. BNNTs, as nano fibers, with an average diameter of about 40nm, were purchased from ACSMATERIAL. The coupling agent was 3-glycidoxypropyltrimethoxysilane (C₉H₂₀O₅Si), purchased from AlFAAesar and also was used for synthesis of organ silicon resin. The epoxy resin used was D.E.R. 332(C₃H₃₄O₄), purchased from Dow Co., Ltd.

2.1.2 Procedure for composite preparation. The organ silicon resin was synthesized from 3-glycidoxypropyltrimethoxysilane through the hydrolytic polycondensation method.

The organ silicon resin was mixed with epoxy D.E.R. 332 according to the proportions of 3:7 as modified epoxy resin, the uniformly formed mixtures were cast in a mold and were pumped forever 1h to remove the air bubbles and solvent as the temperature gradually increased from 80 to 150°C; and (v) finally, they were heated to 175°C for 4 h to complete the polymerization so as to obtain high thermal conductivity composites.

3. Characterization

3.1 Thermal conductivity

The thermal conductivity is given by the product of the thermal diffusivity, specific heat, and density. The thermal diffusivity and specific heat of the composites were measured by Flashline™ 3000Thermal Properties Analyzer (Anter Corp.).

3.2 Phase and microstructure characterization

Micro-Raman spectroscopy of BNNTs and the composites were performed using a Micro-Raman/Photoluminescence system (Model: InVia (Renishaw)) with a Ti-sapphire crystal as target. Scanning electron microscopy (SEM) images of the materials were captured using the JEOL-6300 SEM system.

4. Results and discussion

4.1 Thermal conductivity

The thermal conductivity (TC) values for composites with different filler content are shown in Figure 1. As the BNNT content increases, Fig.1 (a), the thermal conductivity (TC) increases. The thermal conductivity of neat epoxy is 0.1W/(m K), and when the BNNT content increases to 5.0wt %, the thermal conductivity of the composite reaches 0.45 W/(m K), approximately four times that of neat epoxy. Also, the TC values increase with increasing content of organosilicon resin, as shown in Fig.1.(b), but the filling quantity of organosilicon resin is more larger than that of BNNT. Compared with the results shown in Fig.2, the TC value of the composite was 0.21 W/ (m K) when the filling...
content of AlN reached 10%wt. From the results shown in Fig.2, combining organosilicon resin with BNNT (5.0%wt filling content), the TC value of the modified epoxy matrix composite reached 0.79 W/(m K), almost eight times that of plain epoxy resin (0.1 W/(m K)).

**Figure 1.** The thermal conductivity (TC) of composites as a function of filler content (a) BNNTs, (b) the organosilicon resin

**Figure 2.** Comparison of different kinds of composites

**Figure 3.** The SEM morphology of the composites
Figure 4. Mode of formation of stable conducting paths with different materials: (a) conventional particle filler and (b) fiber-like nano powder forming chain structure

From the images in Figure 3, it can be observed that a BNNT network formed in the epoxy matrix with a surface modification beneficial for heat transformation. When the fiber-like BNNTs were filled in the resin matrix, acicular particles of nanowhiskers contacting each other can form, and stable conducting paths are created with minor filling quantities of BNNT nanowhiskers, see Figs. 3 and 4(b). Compared with conventional particle fillers, as in Fig. 4(a), a greater filling content is needed to form heat conducting paths, and the fiber-like BNNT shows more ability to create such a space conducting network.

The particle size also affects the thermal conductivity. To compare the effect of micro-AlN and BNNT, as shown in Fig.2, column 2 and 4, the effect of BNNT for thermal conductivity was better than micro-AlN. The mechanism is that specific surface areas of nano size materials are much larger than the micro size particles and that increase the contact surface between the filler. The forming probability of the thermal conductivity network leads to a decrease of heat resistance between the interfaces. On the contrary, micro particles have little surface area in contact with the resin matrix, surrounding with resin makes the heat flux spread in the matrix resin, then increasing the thermal resistance of the materials.

On the above basis, if organic-Si molecules were chemically induced in the epoxy resin matrix, the thermal stability and conductivity would be improved. The structure of organosilicon resin is the terminal hydroxyl groups contained in the molecular chain. They can form physical crosslinking center in the epoxy resin matrix. On the other hand, the terminal hydroxyl groups also improve interface interaction between the BNNT powder and the epoxy resin matrix as chemical crosslinking points that result in an increase of the crosslinking density with the filling of BNNT powder. The formation of the heat flow network of the composite system occurs more easily. This is the reason that by combining organosilicon resin with BNNT, the thermal conductivity (TC value), as shown in Fig.2, column 5, and the stability of the composites improved.

4.2 Raman analysis

Figure 5. Raman analysis of the composites
The BNNT showed a peak at 1362 cm\(^{-1}\), and the peaks of pure epoxy resin are at 1311, 1465, 1614 cm\(^{-1}\). The composite peak of epoxy and BNNT showed red-shift in the epoxy/organosilicon resin/BNNT composite as marked in the figure. Fig. 5 showed the micro-Raman spectrum for the as-received BNNTs and the polymer composite films. The BNNT itself showed a peak at 1362 cm\(^{-1}\) that is attributed to the E\(_{2g}\) mode\[^{30,31}\]. The same peak was observed in epoxy–BNNT composites red-shifted to 1383 cm\(^{-1}\), but absent in pure epoxy resin. This observation clearly indicates the presence of BNNTs in both epoxy–BNNT composites. However, the copolymer peaks at 1311, 1465, 1614 cm\(^{-1}\) in the pure epoxy shift to 1326, 1484, 1627 cm\(^{-1}\) in the epoxy/organosilicon resin/BNNT. The shift in the peak to a higher wave number was attributed to the compressive stress present in the polymer matrix in the composite system. Raman peaks were associated with lattice vibration and hence are affected by the atomic bond and chemical structure of the material. Therefore, the stress present in the structure can affect the Raman peaks. The compressive stress in the copolymer matrix should improve the physical contact between the BNNT and matrix, thus aiding good interfacial bonding.

5. Conclusions

The effects of BNNT and organosilicon resin on the thermal conductivity performance of PCB epoxy substrates were investigated in detail. The results show that the properties of composites are strongly dependent on the BNNT content, and excellent TC properties were obtained at a small filling content of 5.0 wt % in this study. Compared with neat epoxy, it was found that the thermal conductivity (TC) values of composites varied with different filler content; as the BNNT content increases, the thermal conductivity (TC) increases. The thermal conductivity of neat epoxy is 0.1 W/ (m K), and when the BNNT content increases to 5.0wt %, the thermal conductivity of the composite reaches 0.45 W/(m K), approximately four times that of neat epoxy. Also, the TC values increase with increasing content of organosilicon resin, but the filling quantity of organosilicon resin is larger than that of BNNT. The TC value of the composite was 0.21 W/(m K) when the filling content of AlN reached 10%wt. Combining organosilicon resin with BNNT(5.0%wt filling content), the TC value of the modified epoxy matrix composite reached 0.79 W/(m K), almost eight times that of plain epoxy resin(0.1 W/(m K)). Raman analysis shows red-shift in the epoxy/organosilicon resin/BNNT composite. Evidence of good wetting of the polymer on the BNNT surface with the effect of organosilicon resin to improve interface interaction between the BNNTs and the epoxy resin matrix that result in an increase of the crosslinking density. The formation of heat flow network of composite system occurs more easily. From the images of SEM, it can be observed that a BNNT network formed in the epoxy matrix with the surface modification beneficial for heat transformation.

Due to the significant improvement of the epoxy performance, we can conclude that these composite materials have good potential for use as PCB substrates.

6. Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51463005), the Cooperation Project of Guizhou Province (Grant No. LH [2016]7441)

7. References

[1] A. Balandin and K. L. Wang, “Significant decrease of the lattice thermal conductivity due to phonon confinement in a free-standing semiconductor quantum well” Phys. Rev. B, 58, 1544, 1998.
[2] C. K. Leong, D. D. L. Chung, “Carbon black dispersions as thermal pastes that surpass solder in providing high thermal contact conductance” Carbon, 41, 2459, 2003
[3] W. Zhou, S. Qi, Q. An, H. Zhao, N. Liu, “Thermal conductivity of boron nitride reinforced polyethylene composites” MRS. Bull. 42, 1863, 2007.
[4] R. Andrews, M. C. Wiesenberger, “Carbon nanotube polymer composite” Curr. Opin. Solid State Mater. Sci. 8, 31, 2004.
[5] K. C. Yung, B. L. Zhu, J. Wu, T. M. Yue, C. S. Xie, “Effect of AlN content on the performance of brominated epoxy resin for printed circuit board substrate” J. Polym. Sci. Part B, 45, 1662, 2007.
[6] A. Rubio, J.L. Corkill, M.L. Cohen, “Theory of graphitic boron nitride nanotube”, Phys. Rev. B 49, 5081, 1994.
[7] N.G. Chopra, R.J. Luyken, K. Cherrey, V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, “Boron nitride nanotubes”, Science 269, 966, 1995.
[8] G. X. Chen, Y. J. Li, and H. Shimizu, “Ultrahigh-shear processing for the preparation of polymer/carbon nanotube composites” Carbon, 45, 2334, 2007
[9] D. Golberg, Y. Bando, C. C. Tang, C. Y. Zhi. “Boron nitride nanotubes” Adv. Mater. 19, 2413, 2007.
[10] Y. Chen, J. Zou, S. J. Campbell, G. Le Caer. “Nano Au-decorated boron nitride nanotubes: Conductance modification and field-emission enhancement” Appl. Phys. Lett. 84, 2430, 2004.
[11] C. W. Chang, A. M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Y. Li, A. Majumdar, A. Zettl. “Isotope effect on the thermal conductivity of individual boron nitride nanotube” Phys. Rev. Lett. 97, 085901, 2006.
[12] D. A. Stewart, I. Savic, N. Mingo. “First-principles calculation of the isotope effect on boron nitride nanotube thermal conductivity” Nano Lett. 9, 81, 2009.
[13] I. Savic, D. A. Stewart, N. Mingo. “Phonon transport in isotope-disordered carbon and boron-nitride nanotubes: is localization observable?” Phys. Rev. B 78, 235434, 2008.
[14] C. W. Chang, W. Q. Han, A. Zettl. “Thermal conductivity of B-C-N and BN nanotubes” J. Vac. Sci. Technol., B 23, 1883, 2005.
[15] N. G. Chopra, A. Zettl. “Measurement of the elastic modulus of a multi-wall boron nitride nanotube,” Solid State Commun. 105, 297, 1998.