Enhanced Thermal Conductivity of Boron Nitride Epoxy-Matrix Composite Through Multi-Modal Particle Size Mixing

K. C. Yung, H. Liem

Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Received 2 April 2007; accepted 26 June 2007
DOI 10.1002/app.27027
Published online 28 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Castable particulate-filled epoxy resins exhibiting excellent thermal conductivity have been prepared using hexagonal boron nitride (hBN) and cubic boron nitride (cBN) as fillers. The thermal conductivity of boron nitride filled epoxy matrix composites was enhanced up to 217% through silane surface treatment of fillers and multi-modal particle size mixing (two different hBN particle sizes and one cBN particle size) prior to fabricating the composite. The measurements and interpretation of the curing kinetics of anhydride cured epoxies as continuous matrix, loaded with BN having multi-modal particle size distribution, as heat conductive fillers, are highlighted. This study evidences the importance of surface engineering and multi-modal mixing distribution applied in inorganic fillered epoxy-matrix composite. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3587–3591, 2007

Key words: boron nitride; thermal conductivity; epoxy; composite; thermogram

INTRODUCTION

Excellent electrical insulation properties have made epoxy resins the basis of rather ideal molding compounds. They are, however, also good thermal insulators, and current trends in encapsulating heat-dissipating electronic components with epoxy resins have stimulate interest in the thermal conductivity of particulate filled epoxy resins. Although, epoxy resins have a low thermal conductivity ($\sim$ 0.2 W/mK[1,2]), it can be enhanced by the addition of inorganic particles with a high thermal conductivity. The electrical insulation is maintained if these particles are electrically insulating.[3,4] Since the thermal conductivity of an inorganic filler is much larger than that of the resin matrix, the magnitude of the thermal conductivity of the imbedded particles plays a minor role, compared with the role of the geometrical arrangement of the particles. Experimental and theoretical investigations[5–7] indicate that the temperature within each particle is approximately uniform, but depends on the location of the particle. Temperature gradients occur in the resin between the particles. A thermal conductivity greater than 20 W/mK appears sufficient to consider particles as heat-flow shunts.[8]

In general, when the filler particles are of low concentrations, heat flows uniformly through the filled epoxy since all particles are well separated. Increasing the filler concentration promotes the formation of preferential paths for heat conduction passing through the composite.[7,9] It is worth to emphasis that the different geometrical arrangement of the chains as well as their variable lengths yields different thermal conductivities for the same volume loading of particle. On top of the concentration of the reinforcement, fiber aspect ratio has an impact on increasing the thermal conductivity.[10] This is an inherent property of heterogenous systems.

Silicone carbide (SiC),[11,12] alumina (Al_2O_3),[12,13] aluminum nitride (AlN),[14–16] and boron nitride (BN)[17] have been added into resin matrix to form a composite having satisfactory properties. The dielectric constants of SiC, Al_2O_3, and AlN are relatively high (>8), which are marginal satisfactory for electronic encapsulation. The hexagonal boron nitride (hBN) has a crystal structure similar to graphite with lattice parameters a = 0.25040, c = 0.66612, and a low dielectric constant $\kappa_{\parallel} = \kappa_{\perp} \sim 4$[18] except for the difference in the stacking of layers. In its powder form, hBN is a naturally lubricious material and is often called white graphite. It is also an electrical insulator and exhibits excellent resistance to oxidation, performs exceptionally well at high temperatures (up to 3000°C), and is resistant to corrosive attack. Most of the applications of hBN are thermal dissipation, lubricant, hot-pressed shapes, and pyrolytic

Correspondence to: K. C. Yung (mfkcyung@inet.polyu.edu.hk).

© 2007 Wiley Periodicals, Inc.
WILEY InterScience® DISCOVER SOMETHING GREAT

TABLE I
Type of Fillers and Sizes in BN Samples

Sample	Material/size
Single hBN(untreated)	hBN, 0.6 μm
Single hBN	hBN, 0.6 μm
Double hBN	hBN, 0.4 and 0.2 μm
Double Hbn + cBN	hBN, 0.4 and 0.2 μm, and cBN, 1μm

shapes.[19] Cubic boron nitride (cBN) is synthesized from hBN at high temperature and pressure. Powdered hBN is heated to ~ 1500°C at a pressure in excess of 60 kbars. This process transforms the atomic structure from hexagonal to cubic, making the material hard and of high abrasivity. One important fact about cBN is that, unlike hBN, it does not react with ferrous alloys.

Previous work on BN epoxy-matrix composites was limited to the use of resin as the matrix,[20] and use of either AIN or SiC or BN as the sole filler.[21–24] The highest thermal conductivity was measured to be 11.5 W/mK for an AIN-resin composite. It was suggested that the combination of AIN whisker and its particle with appropriate ratio gave the highest thermal conduction value.[24] Accordingly, this work is aimed to develop highly thermal conductive composite materials through (i) the combined use of hBN and cBN of different size, ultizing the idea of combined use of whisker (hBN in our case) and particle (cBN), to enhance the formation of thermally conductive network and (ii) the improvement of interface between the filler matrix by surface treatment.

EXPERIMENTAL

Material preparation

Both the hBN and cBN powders were provided in pyrolytic form by Shineso Co. China. Two hBN possessed average particle sizes ~ 0.6 and 0.3 μm (density = 2.10 g/cm^3), and one cBN having an average size ~ 1 μm were used (density = 3.48 g/cm^3). Their powders were dried and degassed under vacuum (10^{-2} torr) at 300°C several hours prior to use. The range of volume loading percentage spanned from 0 to 26.5%. Each sample was prepared manually by adding gradually the appropriate amount of BN to the epoxy resin/hardener mixture, stirring with a high shear 3-roll miller (efficient particle de-agglomeration), degassing the mixture, and casting into a mold. Table I summarizes the sample notation and the constituent BN components. That is, a 10 vol % of a ''single hBN'' sample has 10 vol % of hBN having an average size of 0.6 mm inside while a 10 vol % of a ''double hBN'' sample has 5 vol % of hBN having an average size of 0.4 μm and 5 vol % of hBN having a size of 0.2 μm.

A silane coupling agent Z-6020 ($H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$) from Shinesc Co. China was used for the surface treatment of BN. The amine group in the silane serves as a catalyst for the curing of the epoxy and consequently allows the silane coating to completely bond to the epoxy matrix and gives a better interface.

Surface treatment for BN using silane coupling agent involved (i) making an ethanol (200 proof) aqueous solution at a selected concentration; (ii) mixing silane with this solution and stirring for 10 min using a magnetic stirrer in a beaker; (iii) adding BN particles into the solution prepared in (ii); (iv) rinsing with alcohol by filtration and (v) drying at 110°C for 12 h.

An epoxy resin with trade name Epon 8008 from Huntsman Co. was used in the study. It is a kind of brominated epoxy resin having an epoxide equivalent weight of 410–460 g/equiv, with 19.0–21.0% bromine content. The curing agent dicyandiamide (DICY, purity >99%) were obtained from Neuto Products and Tokyo Kasei Kogyo, respectively. The DICY particles had an average diameter of <1 mm. The epoxy resin, DICY, and 2-MI were used as received. They were mixed by a magnetic stirrer for 4 h at a specific ratio listed in Table II. The composites were cast in a mold heated to 80°C in an oven. They were then heated to 100°C and pumped for 15 min. Finally, they were heated to 180°C for 4 h to complete polymerization.

Thermal characterisation

Curing kinetics of resins

A differential scanning calorimeter (DSC, Perkin Elmer DSC7) was employed to analyze the curing kinetics of the resins in samples. Samples with notation summarized in Table I was individually loaded into a DSC pan and isothermal scans were performed in a nitrogen purged chamber at 180°C subsequently. The evolution of the curing reaction or the resin conversion against time can be determined by integrating the isothermal curve area using the equation in literature.[25]

$$\text{Conversion}(\%) = \frac{1}{\Delta H_T}\int_0^t \frac{dH}{dt}dt \times 100 \qquad (1)$$

TABLE II
Basic Recipe of BN-Epoxy Resin Composite

Material	Ratio of materials by volume
Epon 8008	100
DICY	3
2-MI	1
BN	0–26.5

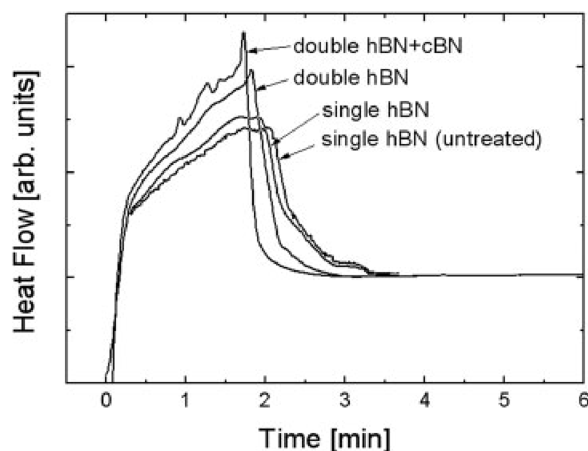

Figure 1 Isothermal DSC thermograms of BN resins.

where ΔH_T is the total enthalpy change of the sample which can be mathematically presented by the area of the enthalpy change from $t = 0$ to $t = \infty$

The glass transition temperatures (T_g) of the samples are measured by DSC technique. The composites were heated in DSC cell to 180°C at a rate of 5 °C/min. The obtained thermographs showing transition features were adopted as the T_g's of composite resins.

Coefficient of thermal expansion

A Perkin Elmer (Norwalk, CT) thermo-mechanical analyzer (TMA7) was used to determine the coefficient of thermal expansion (CTE). Samples containing 4.2, 8, 12.1, 13.4, 15.2, 21, 26.5 vol % BN filler/fillers were cured and cut by a diamond saw into square shape with dimensions $\sim 5 \times 5 \times 3$ mm^3. The temperature of the sample was increased from room temperature to around 180°C at a rate of 5 °C/min after it was loaded into the TMA cell. The thermal expansion was then presented as a function of temperature.

Thermal conductivity

The thermal conductivity, κ, was calculated by the product of the thermal diffusivity (mm^2/s), specific heat (J/g K), and density (g/cm^3), with the additional information of the sample density. Flashline™ 3000 is employed to automatically determine the thermal conductivity using the measured heat capacity and thermal diffusivity, with separately entered density data. Samples containing 4.2, 8, 12.1, 13.4, 15.2, 21, 26.5 vol % BN filler/fillers were cured and prepared in cylindrical shape of 12.8 mm in diameter and 1.0–3.0 mm in thickness, depending on the actual thermal conductivity. The lower this value is, the thinner the sample required to give a reliable value. They are ground flat on both sides, coated with a silver layer on the bottom side and a carbon layer on the front surface, respectively. The former layer was used to enhance the thermal contact and to prevent direct transmission of flash light through the specimen, especially in the case of a semi-transparent resin, while the latter layer is to optimize the absorption of the flash light. Their weights and dimensions were measured by a balance and a vernier caliper, respectively. A standard copper block was used as calibration.

RESULTS AND DISCUSSION

Curing kinetics

On the basis of the isothermal DSC characterization, the heat flow of hBN-resins at 180°C as a function of time is plotted in Figure 1. All the samples contain 26.5 vol % of filler/fillers. The curves in Figure 1 show a peak featuring the initial reaction rate followed by a leveling down tail (time > 4 min) and the slope of profile (rate of change of heat flow) becomes the steepest when fillers are hBN and cBN. The second steepest peak is from the double hBN sample, the third is the single hBN, and the last is the untreated single BN. The flat nonzero reaction rate tails reveal that there is a continuous curing reaction followed by the initial reaction. These tails evidence the existence of the diffusion controlled reaction mechanism because of the increase of viscosity resulted from the peak reaction. The onset of the diffusion-controlled process indicates that fast transportation of the molecules in the resin system is prevented by the increase of viscosity.[26]

The ΔH_T's of resins containing various amounts of filler were calculated based on the data of Figure 1, which were then substituted into eq. (1) to calculate the conversions of composite resins as shown in Figure 2. Both Figures 1 and 2 shows that when the fillers are hBN together with cBN, the time to complete

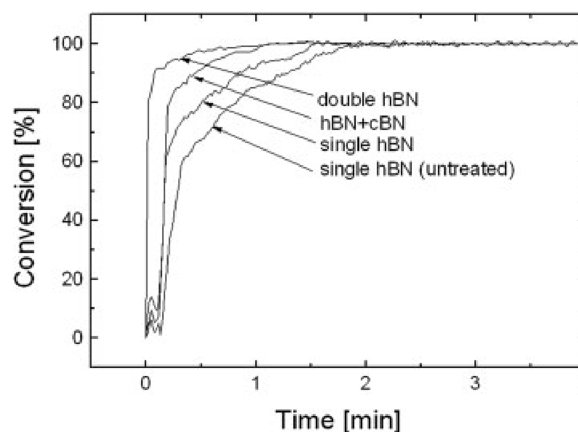

Figure 2 Percentage conversion of BN-resins.

TABLE III
T_g of BN-Resins Measured by Using DSC

Sample	T_g (°C)
Single hBN(untreated)	138
Single hBN	145
Double hBN	150
hBN + cBN	158

the curing of resin is faster than that of the samples contain solely untreated/treated/double hBN. This happens when their total volume of filler loading are the same, suggesting that more amine groups on the edge planes of hBN are available to react with epoxy group of epoxide resin so as to accelerate the polymerization.[27,28] With the presence of cBN, the hBN fillers have more amine groups participating in the reactions with epoxide resin. This enhances the crosslinking, and therefore the T_g's of epoxide resins as listed in Table III.

The shorter curing time of double hBN-cBN-resin again evidences the better geometrical arrangement of the hBN platelets and cBN and thus increasing the availability of amine groups on hBN that promotes the polymerization of the epoxide resins.

Coefficient of thermal expansion

Figure 3 shows the post CTE with various BN contents in the resins. It can be observed that the addition of inorganic filler effectively reduces the CTE of organic resin. This suggests that the mechanical interlock at the organic–inorganic interface may constrain the CTE mismatch of the two components in composite resin. Figure 3 also shows that higher BN content (>12.5 vol %) alleviates the reduction of CTE, which is similar to the behaviors in SiO_2-resin reported.[29,30] In our measurement, the CTE of the single untreated hBN-resin composite at 26.5 vol % is 46.5 ppm, which is larger than 23.0 ppm for the double hBN-cBN-resin at the same filler loading. It is worth mentioning that the reduction in CTE is 43.0% because of the use of cBN as one of the fillers. This was attributed to the more uniform dispersion of BN filler in resin and thus possesses a lower CTE value.

Thermal conductivity

Heat dissipation becomes an important issue in micro-electronic packaging and printed circuit boards (PCBs) since the increase of device density drastically increases the electrical energy consumption and thus raises the need for better heat dissipation. In comparison with metals and ceramics, polymers possess lower thermal conductivity because of relatively low

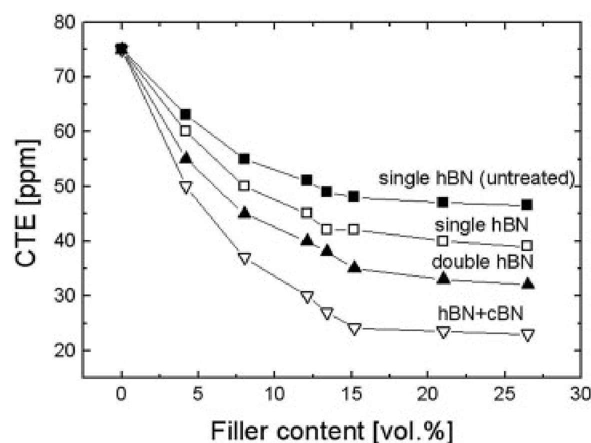

Figure 3 Coefficient of thermal expansion of BN-resins with various filler contents.

atomic density. Nevertheless, as explained in the Introduction Section, such a deficiency could be improved by adding inorganic filler with high thermal conductivity in organic matrix.

Figure 4 shows the variation of thermal conductivity with the filler content for BN resins. In general, the thermal conductivities of different types of BN resins are enhanced with the increase of filler content, and the addition of hBN exhibits a better effect on the thermal conductivity enhancement. Although, hBN has a high thermal conductivity ($\kappa_{\parallel}$ = 121 W/mK; $\kappa_{\perp}$ = 71 W/mK), only limited amount of it is shared by the composite due to the presence of epoxy (~ 0.2 W/mK) used as the matrix. For the treated hBN-resin containing 26.5 vol % filler, κ is increased by 75.0% compared with that of single untreated hBN sample; this is attributed to the decrease in thermal resistance by silane surface treatment of BN, in agreement with the observation reported by Xu et al.[24] For the double hBN samples,

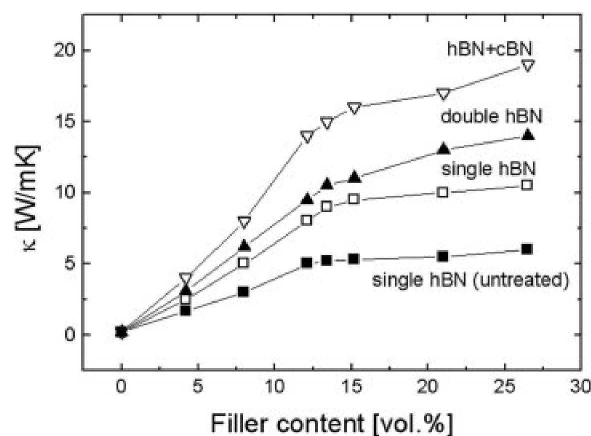

Figure 4 Thermal conductivity of BN resins with various filler contents.

κ is enhanced by 133.3%. Similar enhancement is observed in combine use of AIN whisker and its particle fillered composite [14]. The underlying physics is that the smaller particles fill the gaps between the bigger whisker and epoxy matrix. For the double hBN-cBN-resin, the thermal conductivity reaches as high as 19.0 W/mK. The overall increase in κ is 217%. It is suggested that the distribution of the two kinds of fillers in the epoxy matrix might arrange themselves in a way that the surface areas of filler are maximized by adding cBN into hBN-resin. The plate-like shape of Hbn, hence, must have a better inter-filler contact in comparison with the double hBN filler sample at the same volume loading so that a better thermal conductivity property is observed in double hBN-cBN-resin. The isothermal thermogram of this composite shown in Figure 1 supports this explanation as its thermogram has a steeper peak which occurs earlier than that of the double hBN-resin. The same effect can be achieved by using higher filler vol % in the double hBN-resin. It is worth nothing that the addition of the cBN has an average size ~ 1 μm, however, the overall packing density is higher, forming more preferential paths for heat conduction than that of the sample having solely hBN fillers.

CONCLUSIONS

This work investigated the effects of combined use of hBN and cBN fillers on the physical properties of composite resin for device encapsulation and multilayer PCBs construction. The overall increase in κ is about 217% compared with that of single untreated hBN sample, while the CTE is decreased by 43% through silane surface treatment of fillers and multimodal particle size mixing. Thermal property analysis using DSC indicated that the enhancement in κ is due to decrease in the filler-matrix thermal contact resistance through the improvement of the interface between matrix and particles. Through multi-modal particle mixing, the fillers arrange themselves in a way that their contact areas are maximized, resulting in further enhancing the thermal conductivity.

References

1. Fishcher, M.; Schmid, R. Polymere Werkstoff, Band I; Verlag: New York, 1986.
2. Nicholls, C. I.; Rosenberg, H. M. J Phys C: Solid State Phys 1984, 17, 1165.
3. Garret, K. W.; Rosenberg, H. M. J Phys D: Appl Phys 1974, 7, 1247.
4. Ott, H. J. Plast Rubber Process Appl 1981, 1, 9.
5. Bigg, D. M. Polym compos 1986, 7, 125.
6. Hasselman, D. P. H.; Johnson, L. D. J Compos Mater 1987, 21, 508.
7. Batchelor, G. I.; Brien, R. W. O. Proc Royal Soc London Ser A 1977, 355, 313.
8. Nozad, I.; Carbonnell, R. G.; Whitaker, S. Chem Eng Sci 1985, 40, 843.
9. McCullough, R. L. Compos Sci Technol 1986, 22, 3.
10. Milton, G. W.; Golden, K. Therm cond 1985, 18, 571.
11. Solomo, A. A.; Fourcade, J.; Lee, S. G.; Kuchibhotla, S. K.; Revankar, S. Latta, R.; Holman, P. L.; McCoy, J. K. Proceedings of the 2004 international Meeting on LWR Fuel Performance, Orlando, Florida, 2004; pp 1028.
12. Hussain, M.; Oku, Y.; Nakahira, A.; Niihara, K. Mater Lett 1996, 26, 177.
13. Bujard, P.; Kühlein, G.; Ino, S.; Shiobara, T. IEEE Trans Compon Packaging Manuf Technol A 1994, 17, 527.
14. Xu, Y.; Chung, D. D. L.; Mroz, C. Compos A 2001, 32, 1749.
15. Kim, W.; Bae, J. W.; Choi, I. D.; Kim, Y. S. Polym Eng Sci 1999, 39, 756.
16. Bae, W.; Kim, W.; Park, S. W.; Ha, C. S.; Lee, J. K. J Appl Polym Sci 2002, 83, 2617.
17. Huang, M. T.; Ishida, H. J Polym Sci Part B: Polym Phys 1999, 37, 2360.
18. Pease, R. S. Acta Crystallogr 1952, 5, 236.
19. Park, J.; Lee, J. S.; Lee, C. C. Electronic Components and Technology Conference, 2003, Proceedings, 53rd, New Orleans, LA, 2003; p 1800.
20. Chiang, T. H.; Hsieh, T.-E. J Inorg Organomet 2006, 16, 175.
21. Xu, Y.; Chung D. D. L. Compos Interface 2000, 7, 243.
22. Bujard, P.; Ansermet, J. P. The Fifteenth Annual IEEE Semiconductor Thermal Measurement and Management Symposium, San Diego, CA, 1989; p 126.
23. Li, L.; Chung, D. D. L. J Electron Mater 1994, 23, 557.
24. Xu, Y.; Chung, D. D. L.; Mroz, C. Compos A 2001, 32, 1749.
25. Mohsen, N. M.; Craig, R. G.; Filisko, F. E. J Biomed Mater Res 1998, 39, 252.
26. Wu, S. X.; Zhang, C.; Yeh, C. P.; Wille, S.; Wyatt, K. Proceedings of the 47th Electronic Components and Technological Conference, 1997; p 550.
27. Higginbottom, H. P. U.S. Pat. 4,501,864 (1985).
28. Higginbottom, H. P.; Drumm, M. F. U.S. Pat. 4,557,979 (1985).
29. Wong, C. P.; Bollampally, R. S. J Appl Polym Sci 1999, 74, 3396.
30. Qu, J.; Wong, C. P. IEEE Trans Compon Packaging Technol 2002, 25, 53.