ELSEVIER

Thermochimica Acta 320 (1998) 177–186

thermochimica acta

Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine

Hatsuo Ishida*, Sarawut Rimdusit

The NSF Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science,
Case Western Reserve University, Cleveland, Ohio 44106-7202, USA

Received 2 March 1998; received in revised form 18 June 1998; accepted 22 June 1998

Abstract

A thermal conductivity of 32.5 W/mK is achieved for a boron nitride-filled polybenzoxazine at its maximum filler loading of 78.5% by volume (88% by weight). The extraordinarily high conductivity value results from outstanding properties of the polybenzoxazine matrix and the boron nitride filler. The bisphenol-A–methylamine-based polybenzoxazine possesses very low A-stage viscosity which aids in filler wetting and mixing. The filler particles with an average size of ca. 225 μm are large aggregates of boron nitride flake-like crystals. It has bimodal particle size distribution which assists in increasing the particle packing density. This filler–matrix system provides a highly thermally conductive composite due to the capability of forming conductive networks with low thermal resistance along the conductive paths. The SEM picture of the composite fracture surface reveals good interfacial adhesion between the boron nitride filler and polybenzoxazine matrix. Water absorption of the filled systems at 24 h is <0.1% and decreases with increasing filler content. © 1998 Elsevier Science B.V.

Keywords: Boron nitride; Electronic packaging material; Highly filled system; Polybenzoxazine; Thermal conductivity of polymer composite

1. Introduction

The heat dissipation problem in microelectronic packaging is becoming increasingly important as the demands in denser and faster circuits intensify. The incorporation of highly thermally conductive ceramic materials in polymers in order to improve the thermal conductivity of encapsulant or substrate has long been studied [1–9]. The composite should exhibit balanced properties of high thermal conductivity and thermal stability of the ceramic component while retaining ease of processing and low dielectric constant of the polymer matrix.

Bujard [3] studied the temperature dependence and influence of sample preparation in thermal conductivity of boron nitride-filled epoxy resin as a function of filler content. He used flake-like boron nitride crystals with small particle size and was able to make a composite with a maximum filler content of 31 vol% and a corresponding thermal conductivity value of 2.3 W/mK. The author mentioned the use of percolation theory to explain the formation of filler networks in his composite system. However, his system did not show a sharp discontinuity associated with a percolation threshold at 15 vol% which was normally observed in electrically conductive composites. He suggested that there were two important parameters that regulated the conductivity in the composite, i.e. the number of conducting paths and the real

---

*Corresponding author. Tel.: +1-216-368-4172; fax: +1-216-368-4202.

PII S0040-6031(98)00463-8

particle density along the heat-flow paths. The effect of the mode of sample preparation can lead to different particle distributions in the matrix which produces the variations in the thermal conductivity.

One of the highest thermal conductivity values was also reported by Bujard et al. [9] for alumina loaded bisphenol-F epoxy resin. He obtained a value of 4.5 W/mK at 80 vol% of alumina. The value was even higher than the A1N-filled epoxy resin reported by the same author i.e. 4.235 W/mK at 62 vol% [4]. In the latter report, Bujard explained the formation of the conductive networks in the aluminum nitride-filled epoxy using bond percolation. The obtained percolation threshold, ϕ_c, was 0.15 ± 0.03 with the percolation exponent, t, of 1.85 ± 0.1 which is close to the currently accepted values of $\phi_c=0.198$ and the theoretical value of the exponent of 2 [10].

The concept of effective thermal management by maximizing the formation of conductive networks while minimizing the heat resistance along the heat-flow path is well recognized. Berman [11] explained the transport of heat in non-metals by the flow of phonons or lattice vibrational energy. The thermal resistance is caused by various types of phonon scattering processes, e.g. phonon–phonon scattering, boundary scattering, and defect or impurity scattering. Therefore, in order to maximize the thermal conductivity in materials, these phonon scattering processes must be suppressed. Phonons travel in matter with the speed of sound. In theory, the scattering of phonons in composite materials is mainly due to the existence of an interfacial thermal barrier from acoustic mismatch, or the damage of the surface layer between the filler and the matrix [12,13]. These interfacial phonon scattering phenomena are similar to the scattering of light due to differences in refractive indices of the media. Consequently, we generated the idea of maximizing the formation of highly thermally conductive networks and minimizing the thermal resistance along the conductive paths by first choosing the filler which should be able to form many heat-flow paths. The maximum packing of the filler in the matrix is one way to assure the formation of near-perfect conductive networks. To achieve high packing density composites, the use of large size particles with multimodal particle size distribution and low aspect ratio with smooth surface texture as a second phase were suggested [14]. Secondly, the thermal resistance would be reduced by the combination of various techniques. The selection of particles which have perfect lattice or crystal structure as much as possible to suppress the scattering of phonons by lattice defects is essential. This kind of filler is normally found in highly thermally conductive ceramics, such as boron nitride or aluminum nitride. The large particle size, i.e. low particle surface area, is desired to minimize the scattering of phonons due to the interfacial thermal barrier. Moreover, the use of large particle size tends to form fewer thermally resistant junctions of the polymer layers than the small particle size at the same filler content. Finally, the layer of the matrix resin between the particles must be as thin as possible, to such a degree that its mechanical properties are still high enough for the application, to reduce the thermal resistance due to the resin itself. This can be achieved by using a resin which has low melt viscosity. Furthermore, the low viscosity resin generally aids in filler mixing during the molding compound preparation. These hypotheses are based on one important assumption that the adhesion between the filler and the matrix resin is good; otherwise, the third phase, an air gap, may occur and will also have a high contribution to the overall conductivity of the composites. Therefore, the choice of resin which possesses low melt viscosity and excellent adhesion with the selected filler is preferred.

The purpose of this study is to develop highly thermally conductive molding compounds for electronic packaging applications. The effects of filler and resin on the thermal conductivity of the polymer composites are studied. Other essential properties, such as modulus, glass-transition temperature, and water absorption, are also examined. Boron nitride-filled polybenzoxazine is the system to be investigated.

2. Experimental

2.1. Materials

The polybenzoxazine used is a bisphenol-A–methylamine type. The monomer synthesis followed the procedure reported by Ning and Ishida [15]. The resin was used as-synthesized without further purification. The monomer is solid at room temperature. It was ground into fine powder and kept in a refrigerator.

Table 1
Properties of bisphenol A–methylamine type polybenzoxazine

Properties	Values
Density	
monomer ($\times 10^{-3}$ kg/m^3)	1.159
polymer ($\times 10^{-3}$ kg/m^3)	1.122
Thermal exp. coef.($\times 10^6$ m/m°C)	69
Glass transition temperature (°C)	180
Heat capacity (J/kg°C)	1415
Water absorption at room temperature (wt.%)	
24 h	0.17
120 days	1.15
G'_{RT} (GPa)	1.8
Melt viscosity at 100°C (Pa S)	1.2

Properties of this type of polybenzoxazine are shown in Table 1.

The filler used was hexagonal boron nitride (grade HCJ48) supplied by Advanced Ceramics. The powder consists of large aggregates of flake-like boron nitride crystals fabricated by hot-pressing technology. The powder has bimodal size distribution with mean particle size of ca. 225 μm.

2.2. Sample preparations

The monomer powder was dry mixed well with boron nitride at a desired volume fraction. The mixture was then heated up to ca. 80°C in a mixer and was mixed by hand for ca. 10 min. The compound in the form of paste was then compression molded into various dimensions depending upon the types of experiments. All the specimens were thermally cured at 200°C with pressure of 0.1 MPa for 2 h. The specimens were left to cool down at room temperature in the open mold for ca. 2 h before using.

2.3. Thermal conductivity and thermal diffusivity measurement

The effect of particle size on thermal conductivity was studied using Schroder's technique [20]. The principle of this technique is based on the steady-state Fourier's law of heat conduction and can be expressed by the equation below.

$$q = -k(\mathrm{d}T/\mathrm{d}x) \tag{1}$$

where q is the heat flux (W/m^2), k the thermal conductivity (W/mK), and ($\mathrm{d}T/\mathrm{d}x$) the temperature gradient. The apparatus that was made in our laboratory based on this technique gave only relative values of thermal conductivities of different specimens. The thermal diffusivity measurement was done at Virginia Polytechnic Institute and State University using the pulsed laser method which is the non-steady-state technique and can be expressed as the relation with heat flux as follows.

$$q = -\alpha(\mathrm{d}U/\mathrm{d}x) \tag{2}$$

where α is the thermal diffusivity (m^2/s), and ($\mathrm{d}U/\mathrm{d}x$) the energy gradient. The specimens were in the form of disks with 12.7 mm diameters and 2 mm thicknesses. The absolute values of thermal conductivities of the specimens were calculated from the thermal diffusivity value of each specimen using the relationship,

$$\alpha = \frac{k}{\rho \times C_\mathrm{p}} \tag{3}$$

where ρ is the density and C_p the heat capacity of the specimen.

2.4. Dynamic mechanical analysis

The dynamic mechanical spectra were obtained using Rheometrics Dynamic Mechanical Spectrometer (RMS-800) which was equipped with a 2000–200 g cm dual range force rebalance transducer. The dimensions of the specimen were ca. 51×13×2.5 mm^2 and were tested under the rectangular torsion fixture. The strain used was 0.015% after determining the linear viscoelastic region by strain sweep. The strain was applied sinusoidally with a frequency of 1 Hz in the temperature sweep experiment. The specimens were heated at a rate of 2°C/min from 30°C to the temperature beyond the glass-transition temperatures of each composites.

2.5. Composition and density measurement

The density of the composites were determined using a water displacement technique (ASTMD792-91). The specimens were disk-shaped with a 51 mm diameter and a 2.0 mm thickness. The amount of resin for each specimen was confirmed with TGA using heating rate of 20°C/min under air from 50°C to ca. 1000°C. Sample weights were ca. 20 mg. No mass of remaining resin was observed.

2.6. Water absorption

Water absorption measurements were conducted following ASTM D570 using disk-shaped specimens having a 51 mm diameter and a 3.2 mm thickness. All specimens were conditioned, weighed, and submerged in distilled water at 25°C. The specimens were occasionally removed, wiped dry, weighed, and immediately returned to the water bath. The amount of water absorbed was calculated based on the initial conditioned mass of each specimen.

2.7. Scanning electron microscopic analysis

A Philips scanning electron microscope was used to investigate the adhesion between boron nitride filler and polybenzoxazine. The specimens were the fracture surface of the composites of 20% by weight of flake-like particle of the boron nitride filler in the 80% by weight of polybenzoxazine matrix. The fracture surface was coated with a thin film of evaporated gold before insertion into the apparatus. The applied voltage was 25 kV with magnification of ×2000.

2.8. Heat capacity measurement

Specific heat capacities of the samples were measured using a modulated differential scanning calorimeter (MDSC) model 2920 from TA Instruments. All samples were crimped in non-hermetic aluminum pans with lids. The weight of reference and sample pans with lids were measured to be 23±0.1 mg. The weight of the sample is in the range of 15–20 mg. The instrument was calibrated for heat capacity measurement using sapphire as a reference material. The calibration method and the experiment were performed using the same conditions as follows:

- isothermal equilibration for 5 min at −10°C;
- temperature amplitude ±1°C with period of 80 s;
- ramp at 5°C/min to 100°C or 200°C.

3. Results and discussion

Fig. 1 shows the density of boron nitride-filled polybenzoxazine as a function of filler content. The theoretical densities of the composites were calculated based on the density of boron nitride of 2.25 g/cm^3 and the density of polybenzoxazine, B-m, of 1.122 g/cm^3 [19]. In Fig. 2, the composition of the composites were confirmed again by using TGA. Most observed composite densities especially at higher filler contents showed good agreement with the values calculated from the compositions analyzed by TGA, suggesting negligible amount of voids. The reason that the densities of specimens at low range of filler contents are somewhat higher than those of the original molding compound is due to the greater loss of resin by overflowing out of the mold than that in case of higher filler contents. In this study, we defined the maximum

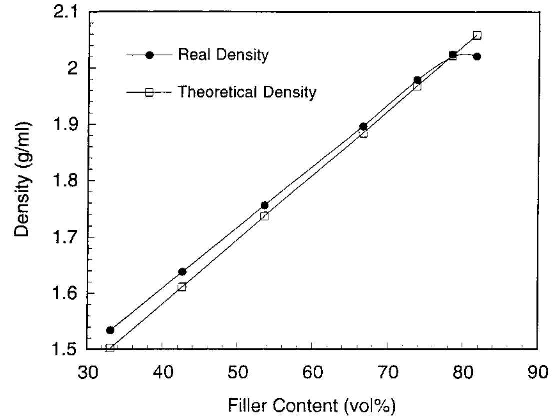

Fig. 1. The maximum packing density of boron nitride-filled polybenzoxazine using boron nitride grade HCJ48. (□) theoretical density, (●) experimental density.

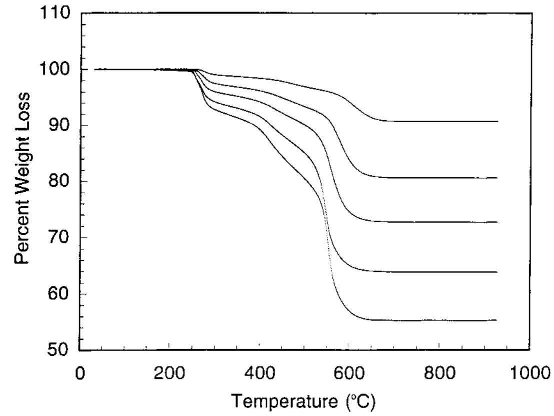

Fig. 2. TGA experiment for composition determination of composite samples.

Table 2
The effect of particle size on composite packing densities

Boron nitride (grade)	Average particle size (μm)	Type	ϕ_m (wt%)
HCPH	9	Flake	60
HCJ325	45	Aggregate	75
TS1890	75	Aggregate	85
HCJ48	225	Aggregate	88

packing density of each type of filler by its maximum observed density that is equal to the theoretical density. Using boron nitride grade HCJ48, we were able to make a specimen with maximum packing density up to 78.5% by volume (88% by weight) as shown in Fig. 1. The attempt to add boron nitride beyond 78.5% by volume tended to decrease the observed composite packing density to a value lower than the theoretical value due to void formation.

The maximum packing densities of four grades of BN are summarized in Table 2. From the result, we can see that the larger the average particle size of boron nitride, the higher the maximum packing density of the composite, which is in good agreement with the theory of particle packing [14]. One of our reasons to choose a large average particle size of boron nitride filler is to be able to obtain the maximum packing density in the specimen as thermal conductivity seems to have characteristics of both a path dependent property, i.e. the conductivity values increase rapidly beyond the percolation threshold, and a bulk property, i.e. the conductivity values are strongly dependent on filler loading. The use of maximum packing density of filler in the composite can, at the same time, render a large number of conductive networks in the composite which fulfils both path dependent and bulk properties.

The maximum achievable boron nitride loading in our system, 78.5% by volume, surpassed the maximum boron nitride loading reported by Bujard, 31% by volume [3]. This is due to the fact that our boron nitride powder has a large average particle size (225 μm) and has low effective aspect ratio as it is an aggregate of flake-like crystals. Moreover, the filler also has bimodal particle size distribution. The effect of particle size on a packing density was investigated by Ruschau et al. [17,18]. Their observation was consistent with the theory of particle packing [14] which states that, in an unimodal particle size distribution, the packing density decreases with smaller particle size due to an increase in particle surface area, lower particle mass, and a greater importance of weak short-range forces including electrostatic fields and surface adsorption of moisture and other wetting liquids that can lead to agglomeration. The high aspect ratio particles, such as flake or fiber, greatly exhibit the bridging phenomenon in compacts. Though the bridging assists in the formation of the conductive network by lowering the percolation threshold, it lowers the packing density. The multimodal distribution of the particles also plays a significant role in enhancing the packing density. Although packing density is higher in multimodal particle mixtures, German [14] observed that there is less benefit to make the mixtures beyond the bimodal system to a trimodal or more complex system which are more difficult to obtain and handle. As a consequence, the use of boron nitride grade HCJ48 having a bimodal particle size distribution with large average particle size should be sufficient in obtaining high particle packing.

The effect of particle size on thermal conductivity was studied using an apparatus for steady-state thermal conductivity measurement based on the Colora thermoconductometer or Schroder technique [20]. All specimens used were the composites of 30% by weight of polybenzoxazine and 70% by weight of boron nitride, which is the composition beyond the typical percolation threshold of bond percolation. The boron nitride used was a mixture of large particle size grade (HCJ48 with 225 μm average particle size) and a smaller particle size grade (TS1890 with 75 μm average particle size). Increasing the composition of the large particle size grade of boron nitride resulted in higher thermal conductivities as shown in Fig. 3. This is due to the fact that the network formation of the large particle filler has less heat resistant junctions than that of the smaller size filler. As a result, the thermal conductivity of the specimens beyond the percolation threshold increases with increasing the fractional composition of the large particle size grade of boron nitride filler.

Fig. 4 shows the thermal diffusivities of boron nitride-filled polybenzoxazine as a function of filler content. These values can be converted into thermal conductivity by the relationship expressed in Eq. (3) In order to determine the thermal conductivities of the

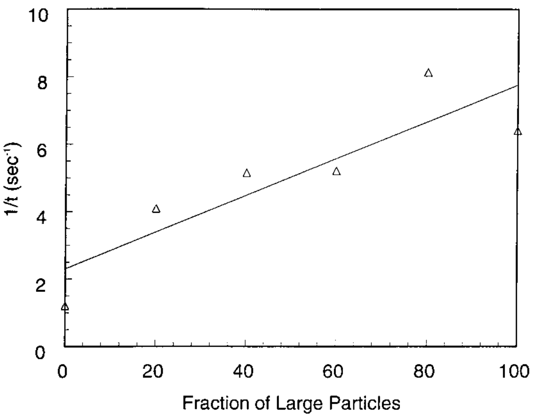

Fig. 3. Effect of particle size on the composite thermal conductivity.

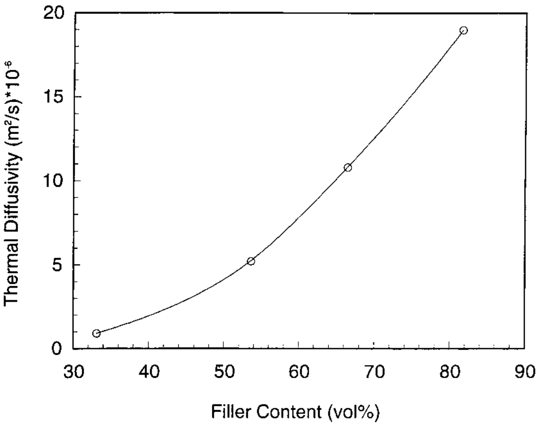

Fig. 4. Thermal diffusivity of boron nitride-filled polybenzoxazine as a function of filler contents.

composites, densities and heat capacities of the composites are needed. The heat capacity of each specimen was determined by MDSC. Table 3 shows the thermal diffusivities, heat capacities, and composite densities of specimens at different compositions and the corresponding values of thermal conductivities determined by Eq. (3).

From Fig. 5, we can see that, once the conductive networks of the large particle size are formed, the thermal conductivity of the composites will exceed that of the smaller particles as the formation of the conductive paths of the large particles renders less thermal resistance along the paths [16]. The phenomenon is more pronounced at the filler content exceeding the maximum packing of smaller particles since the maximum packing of smaller particle size is less than the maximum packing of the larger particles [17,18]. Our experimental results are in good agreement with the above statement.

Table 3
Thermal conductivity of boron nitride-filled polybenzoxazine

Filler content	$\alpha\times10^6$ (m^2/s)	C_p (J/kg K)	ρ ($\times10^{-3}$ kg/m^3)	k (W/mK)
33	0.91	1069	1.539	1.50
54	5.22	933	1.758	8.56
66	10.8	897	1.889	18.3
78.5	19.2	841	2.012	32.5

We have produced a composite with a remarkably high value of thermal conductivity of 32.5 W/mK at 78.5% by volume of boron nitride filler. The value was averaged from the value of 30.8 W/mK at the center of the sample and 34.2 W/mK at the edge of the sample. This value is ca. 15 times higher than the maximum achieved thermal conductivity value found in epoxy filled with small flake-like boron nitride [3] and about eight times greater than the state-of-the-art value found in alumina-filled epoxy [9].

An anisotropic behavior of this composite was also observed. By measuring linear thermal expansion coefficient, LCTE, of 80% by weight of boron nitride-filled polybenzoxazine, we obtain the LCTE

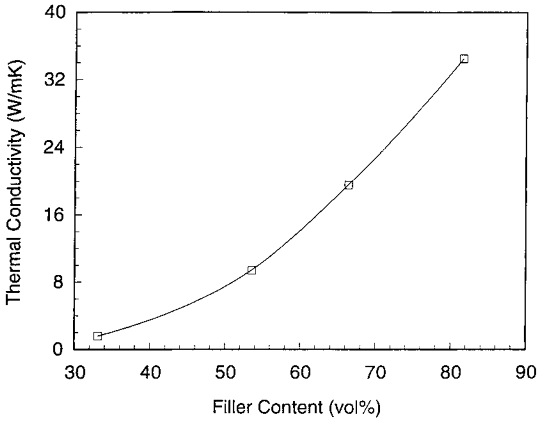

Fig. 5. Thermal conductivity of boron nitride-filled polybenzoxazine as a function of filler contents.

value of the sample measured along the z-direction to be 44.2×10^{-6} m/m°C while the LCTE value measured in the x- and y-directions is 7.17×10^{-6} m/m°C. The result reveals an anisotropic behavior of this composite material. This is due to the fact that boron nitride powder has anisotropic property and possesses high aspect ratio from its flake structure which can strongly contribute to the anisotropic LCTE of this composite. Although, the boron nitride powders used are the aggregates of the flake crystals which have low effective aspect ratio, the anisotropic LCTE obtained implies the anisotropic orientation of the flakes in the aggregates.

Bond percolation is used to explain formation of conductive networks by the filler in the composite materials. This theory can normally explain the insulator–conductor transition well in path-dependent properties of materials such as electrically conductive composites as a point at which the first conductive path is formed. The filler content, ϕ, at this transition point is called the percolation threshold, ϕ_c. However, thermal conductivity seems to be an intermediate property between a path-dependent property and a bulk property. Hence, the thermal conductivity value in the composite material depends on both the formation of the filler network and the filler loading. Generally, the percolation threshold of thermally conductive composite is difficult to define. Agari et al. [22,23] demonstrated an indirect technique used to identify the percolation threshold of the composite by using filler which can affect both electrical and thermal properties of the composites, such as carbon black. In our system, we use a percolation threshold of 0.198 which is the currently accepted percolation threshold for a three dimensional network [10]. Fig. 6 is the plot between log k and log $(\phi-\phi_c)$. The slope of the plot is the critical percolation exponent. From the plot, we obtained the critical exponent having the value of 2.02 which is in good agreement with the value of 2 in bond percolation for a three dimensional system [10].

Fig. 7 shows the storage shear moduli of the composites with filler loadings ranging from 50 to 85% by weight. The moduli of the composites expectedly increase with increasing amount of boron nitride. This corresponds to the high conductivity value of the specimen as heat conducts better in a stiffer material, i.e. higher acoustic velocity. The modulus at room temperature of 85% by weight filler is very high, exceeding 10 GPa which is a value comparable to continuous fiber glass-reinforced phenolics. Thus, the formation of a network from low aspect ratio filler produces a similar composite strength as that from a high aspect ratio reinforcement, such as glass fibers. Moreover, the storage modulus of the composite at all compositions exhibited fairly stable values up to ca. 200°C due to the high performance properties of the polybenzoxazine matrix. From Fig. 7, the moduli of these composites increase rapidly and non-linearly with increasing filler contents.

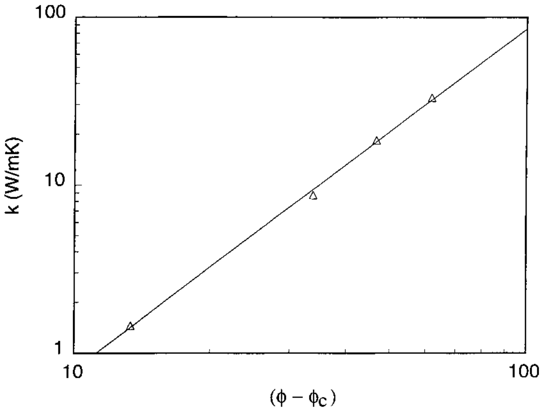

Fig. 6. Percolation theory of thermal conductivity of boron nitride-filled polybenzoxazine.

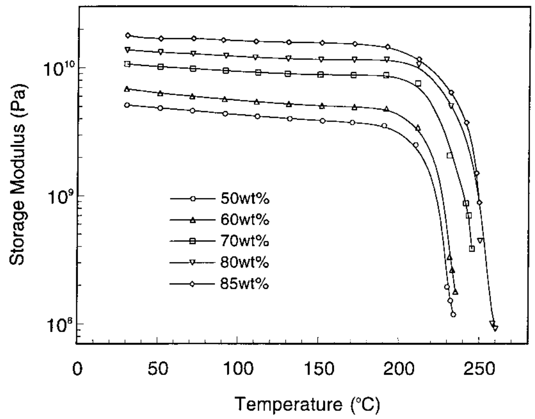

Fig. 7. Storage modulus of boron nitride-filled polybenzoxazine as a function of temperature at different filler loading. (○) 50 wt.% BN, (△) 60 wt.% BN, (□), 70 wt.% BN, (▽) 80 wt.% BN, (◇) 85 wt.% BN.

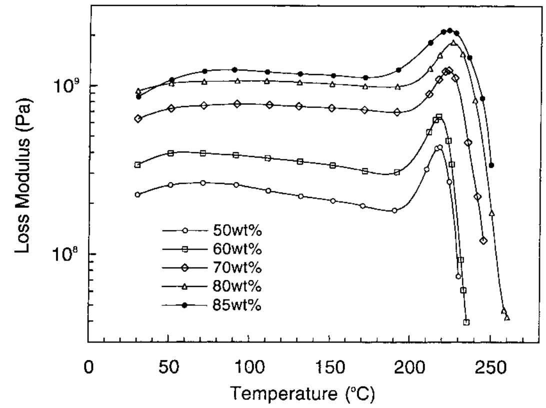

Fig. 8. Loss modulus of boron nitride-filled polybenzoxazine as a function of temperature at different filler loading. (○) 50 wt.% BN, (□) 60 wt.% BN, (◇) 70 wt.% BN, (△) 80 wt.% BN, (●) 85 wt.% BN.

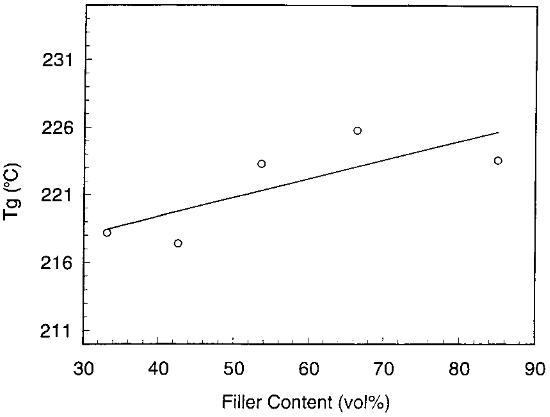

Fig. 9. The effect of filler loading on glass-transition temperature of boron nitride-filled polybenzoxazine.

The glass-transition temperatures of the filled systems were obtained from the maximum value of G″ as shown in Fig. 8. We observe a large increase of ca. 40–45°C in the glass-transition temperatures of the composites relative to the glass-transition temperature of the homopolymer made from B-m resin, i.e. 180°C [19]. The implication of this phenomena is possibly due to the contribution of the good interfacial adhesion between the boron nitride filler and polybenzoxazine matrix. The stiff boron nitride filler can highly restrict the mobility of the polymer matrix which adheres on the filler surface and could lead to the large increase in the glass-transition temperatures of their composites. It is also possible that the boron nitride surface acted as a catalyst and the molecular architecture of the crosslinked polybenzoxazine was affected. Fig. 9 shows the plot between the glass-transition temperature as a function of filler contents. From the plot, we observed an increasing tendency of the glass-transition temperature as filler contents increased.

The electron micrograph of the fracture surface of the composite is shown in Fig. 10. The picture shows

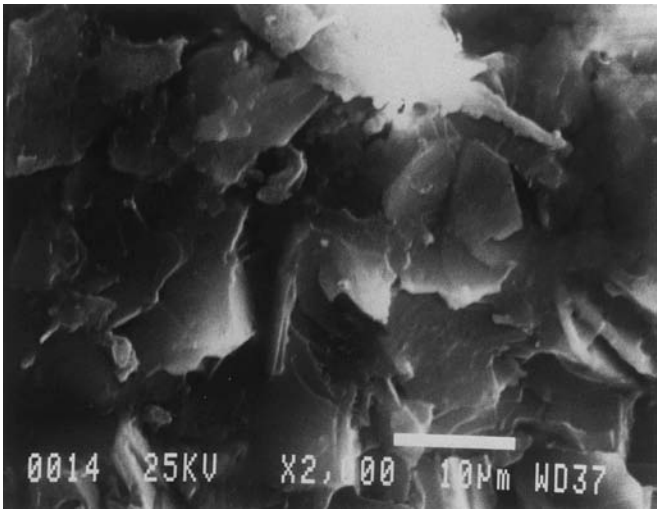

Fig. 10. Scanning electron micrograph of the fracture surface of 20 wt% of boron nitride flake in polybenzoxazine matrix.

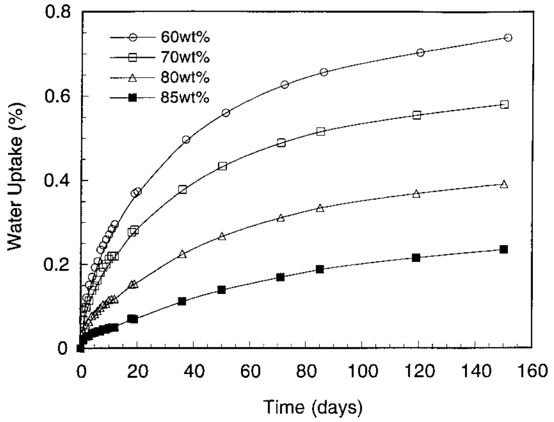

Fig. 11. Water uptake of boron nitride-filled polybenzoxazine up to 150 days at different filler contents. (○) 60 wt.% BN, (□) 70 wt.% BN, (△) 80 wt.% BN, (■) 85 wt.% BN.

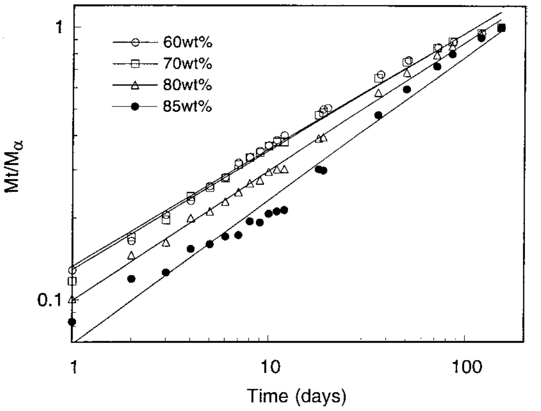

Fig. 12. Plots between log M_t/M_α and time to determine the diffusion exponents in Eq. (4). (○) 60 wt.% BN, (□) 70 wt.% BN, (△) 80 wt.% BN, (●) 85 wt.% BN.

smooth interfaces between the filler and the resin which signifies good interfacial adhesion of the boron nitride filler and polybenzoxazine matrix. The good adhesion of boron nitride and polybenzoxazine is one of the significant contributions to the high thermal conductivity values of their composites as poor interfacial adhesion can lead to strong scattering of heat energy at the filler–matrix interfaces.

Fig. 11 shows the water absorption of the composites at different filler contents ranging from 60 to 85% by weight up to 150 days. As the filler content increases, the water uptake decreases. These composites show very low room temperature water uptake having values much <0.2% which is the value desired in the industrial standard of typical composites for electronic packaging. The water uptake of all compositions at 24 h is <0.1% and only ca. 0.02% at a filler content of 85% by weight. From the curves, the water uptake up to 150 days is <0.8% at a filler content of 60% by weight and lower at higher filler contents, which is considered to be very low. The generalized equation to explain the diffusion in the materials can be expressed as:

$$M_t/M_\alpha = k_n t^n \tag{4}$$

where M_t is the mass of sample at time t and M_α the mass of sample at saturation or infinite time.

The diffusion behaviors can be classified as: supercase II($n>1$), case II ($n=1$), anomalous ($1/2<n<1$), classical/Fickian ($n=1/2$), or pseudo-Fickian ($n<1/2$) [21].

Fig. 12 illustrates log M_t/M_α versus log t plots which show the slopes ranging from 0.43–0.53. Thus, we can conclude that our composite material exhibited a behaviour close to Fickian type diffusion.

4. Conclusions

The thermal conductivity of boron nitride-filled polybenzoxazine exhibited a very high conductivity value. The remarkably high value was obtained using the well-recognized concept of thermal management in composite materials by maximizing the formation of conductive networks while minimizing the thermal barrier resistance along the heat-flow path. The concept was accomplished by using highly thermally conductive filler with a matrix resin which has low melt viscosity and good adhesion to the filler. In addition, a large particle size with multimodal particle size distribution was used. Boron nitride and polybenzoxazine have properties that meet all these requirements and thus exhibit a very high thermal conductivity value. This molding compound also exhibits high and stable mechanical strength up to 200°C with a high T_g value of ca. 220°C. Water absorption at room temperature for 24 h of this composite is very low. Boron nitride-filled polybenzoxazine has many outstanding properties which makes it suitable for an application as a molding compound for the electronic packaging industry and other applications with high thermal conductivity.

References

[1] K.W. Garrette, H.M. Rosenberg, J. Phys. D: Appl. Phys. 7 (1974) 1247.

[2] J.D. Bolt, R.H. Prench, Adv. Mat. and Proc. inc. Met. Prog. 7 (1988) 32.

[3] P. Bujard, Proc. I-THERM 1988, Los Angles, May 11–13, IEEE, 1988, p. 41.

[4] P. Bujard, J.P. Ansermet, Proceedings of SEMI-THERM 1989, San Diego, February 7–9, IEEE, 1989, p. 126.

[5] Y. Agari, A. Ueda, M. Tanaka, S. Nagai, J. Appl. Polym. Sci. 40 (1990) 929.

[6] P. Procter, J. Solc, 41st ECTC, Atlanta, May 11–16, IEEE, 1991, p. 835.

[7] N. Tsutsumi, N. Takeuchi, T. Kiyotsukuri, J. Polym. Sci., Part B, Polym Phys. 29 (1991) 1085.

[8] M. Michael, L. Ngugen, Intersoc. Conf. on Thermal Phenomena, IEEE, 1992, p. 246.

[9] P. Bujard, G. Kuhnlein, S. Ino, T. Shiobara, IEEE Transac. Compn. Packg. Manu. Tech., Part A 17 (1994) 527.

[10] M. Sahimi, Applications of Percolation Theory, Taylor and Francis, London, 1994.

[11] R. Berman, Contemp. Phys. 14 (1973) 101.

[12] R. Ruth, K.Y. Donaldson, D.P.H. Hasselman, J. Am. Ceram. Soc. 75 (1992) 2887.

[13] S. Pettersson, G.D. Mahan, Phys. Rev. B 42 (1990) 7386.

[14] R.M. German, Particle Packing Characteristics, Metal Powders Industries Federation, Princeton, 1989.

[15] X. Ning, H. Ishida, J. Polym. Sci. Chem. Ed. 32 (1994) 1121.

[16] A. Padilla, A. Sanchez-Solis, O. Manero, J. Comp. Mat. 22 (1988) 616.

[17] G.R. Ruschau, R.E. Newnham, J. Comp. Mat. 26 (1992) 2727.

[18] G.R. Ruschau, S. Yoshikawa, R.E. Newnham, Proceedings IEEE 1992, Piscataway, May 18–20, IEEE, 1992, p. 481.

[19] H. Ishida, D.J. Allen, J. Polym. Sci. Phys. Ed. 34 (1996) 1019.

[20] J. Schroder, Rev. Sci. Instru. 34 (1963) 615.

[21] P. Neogi (Ed.), Diffusion in Polymers, Marcel Dekker, New York, 1996.

[22] Y. Agari, T. Uno, J. Appl. Polym. Sci. 30 (1985) 2225.

[23] Y. Agari, A. Ueda, S. Nagai, J. Appl. Polym. Sci. 52 (1994) 1223.