Study on the Properties of the Epoxy-Matrix Composites Filled with Thermally Conductive AlN and BN Ceramic Particles

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ABSTRACT: To develop new composites with sufficiently high thermal conductivity and suitably controlled D_k value for PCBs application, the composites were prepared from epoxy and AlN or BN fillers, and the effects of content, size, size distribution, and morphology of two fillers on the thermal and dielectric properties of the composites were investigated. The results showed that either AlN or BN fillers can greatly increase T_g and thermal conductivity, decreasing CTE and D_f, and suitably controlling the increase of D_k. At the same filler content, BN-filled composites exhibit better thermal performance and dielectric properties compared to AlN-filled composites. In the case of BN-filled composites, it is found that platelet-shaped micro-BN filled composite has lower T_g and higher CTE compared with particle-shaped nano-BN filled composite, but its thermal conductivity is remarkably higher than that of nano-BN filled composite. When hybrid BN fillers are used, thermal conductivity further increases. For micro- or nano-BN filled composite, the composite shows decreased T_g and increased D_k at high fraction of BN, but hybrid BN-filled composite still has high T_g and similar D_k with epoxy even if at high fraction of BN. Compared with single-sized AlN-filled composite, it is found that hybrid-sized AlN-filled composite has higher T_g and lower CTE, but has lower thermal conductivity. To predict thermal conductivity and D_k in the investigated materials system, different models reported in the literature were analyzed and compared with the experimental data. Finally, suitable models were recommended. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2754–2764, 2010

Key words: polymer-matrix composites (PMCs); dielectric properties; thermal properties; computational modeling

INTRODUCTION

With the advancement of electronics technology, more electronic components can be integrated into a single device to increase functionality and enhance performance. However, the miniaturization causes difficulty in heat dissipation, which will limit the reliability of devices. It is crucial to use electronic packaging and/or substrate materials that are capable of dissipating the heat generated and hence to maintain the operating temperatures of the device at a desired level. Polymers are often used as electronic packaging and/or substrate materials due to their high resistivity, low dielectric constant (D_k), and excellent processability. But their thermal conductivity is poor, which, nevertheless, can be improved with the use of electrically insulating fillers, such as alumina, boron nitride (BN), and alumina nitride (AlN) or other ceramic powders.[1–4] The thermal conductivity of polymer-filler composites can be maximized by minimizing thermal barrier resistance along the heat-flow path and forming thermal conductive network in the composites. Once a conductive network is formed by the filler, the composite shows a percolation behavior, i.e., the thermal conductivity increases steeply. Obviously, formation of conductive networks is related to the type, volume fraction, morphology, surface modification, and dispersion state of the fillers in composites. Composites with high thermal conductivity can be obtained using fillers with high intrinsic thermal conductivity. However, when the intrinsic thermal conductivity of the filler is 100 times greater than that of the polymer matrix, it is reported that no further significant improvement in the thermal conductivity of the

composite can be made.[1] The thermal conductivity usually increases with increasing filler volume fraction regardless of the filler type and normally shows a steep increase at a certain filler volume fraction.[1] For the same type of filler, the larger mean particles size gives higher thermal conductivity at a fixed volume fraction,[5–7] which may be attributed to the decrease in contact area between filler and polymer. However, mixed types of fillers with different particle sizes at a preferable ratio are reported to give higher thermal conductivity compared with the same type of filler with a single particle size at the same volume fraction.[5–7] This may be attributed to the high packing density and formation of conductive pathways inside matrix when mixed types of fillers are used. The specially shaped fillers, such as whiskers, exhibit a remarkable positive effect on the formation of conductive networks.[8–10] Also, the combination of whisker- and particle-shaped fillers with an appropriate ratio gives the highest thermal conductivity because of high packing density and formation of conductive pathways inside matrix.[10] Surface treatment of filler particles, if appropriately carried out, is useful for increasing the thermal conductivity of the composite, which is due to the decrease in the thermal contact resistance at the filler-matrix interface.[11] Generally, dispersion situation of the constitution of a composite investigated is the continuous polymer framework plus uniformly distributed fillers. Recently, some researchers proposed a new structural dispersion, which can be achieved by making the filler particles surrounding polymer matrix particles.[12–14] The results indicate that this special dispersion of filler in matrix gives the composites high thermal conductivity at low filler content; moreover, the smaller-sized filler or larger-sized polymer particles can more easily result in the formation conductive chains of filler compared to the larger-sized filler or smaller-sized polymer particles.

In addition to high thermal conductivity, electronic packaging and/or substrate materials also require other essential properties, such as high glass-transition temperature (T_g), low coefficient of thermal expansion (CTE), low D_k, and low dielectric loss factor (D_f). These properties can be also modified by the properties of fillers. However, addition of a single type of filler cannot produce a positive effect on all the properties of the composites simultaneously. For example, when a conventional ceramics powder, such as AlN or BN is used as a filler, thermal conductivity increases, and CTE and D_f decrease, but D_k increases, with filler content.[13,15] As discussed above, the filler with a larger particles size is usually preferred for improving thermal conductivity of the composites, but its effect on decreasing CTE is smaller compared with a filler with a smaller particle size.[16] Theoreti-

cally, T_g gradually increases as filler size decreases, especially at nanometer levels. Experimentally, reports about the effect of the nano-filler on the T_g of the polymer matrix is inconsistent.[17–19] Except that T_g of the polymer can be increased by the nano-filler in some cases, decreases in T_g, no obvious change in T_g and an initial increase in T_g followed by a T_g decrease with a higher nano-filler content have been also reported. The effect of filler size on the dielectric properties is also complex. Usually, the D_k increases as the size of the ceramic filler decreases due to the larger surface area of smaller fillers.[20] In addition to the surface area effect, other researchers consider the effect of the interphase between the polymer and the filler, and the integrality of the polymer matrix.[20–23] The bonding at the interphase between the polymer and the filler will result in the loss of one or more degrees of rotational and/or vibrational freedom, thus cause a decrease in effective D_k of the composite. The influence of the interphase will normally become more dominant when the size of the filler is small sufficiently, for example, at the submicrometer and nanometer ranges. It is also suggested that the degree of crosslinking of the polymer and the molecular weight of network chains decrease as filler content increases and/or filler size decreases, which subsequently influence the rotational and/or vibrational freedom of the main and/or side chains and the D_k of the composites increases as a result. As such, there may exist an optimum filler size that gives the lowest D_k for a certain composite system. The effects of filler shape on the thermal expansion behavior of composites have been examined both experimentally and theoretically.[24] It is found that spherical-particle-filled composites exhibit superior thermal expansion behavior compared with short-fiber- or flake-reinforced composites.[25] However, up to now, there has been little research into the effects of filler shape on the T_g and dielectric properties (D_k and D_f) of the composites.

In this study, composites are produced using brominated epoxy, a type of polymer widely used for making printed circuit boards (PCBs), as a matrix and AlN and BN particles as fillers. The effects of filler type, content, size, and shape on the thermal conductivity, T_g, CTE, and dielectric properties (D_k and D_f) of the composites are systematically studied. It aims to develop a new composite with sufficiently high thermal conductivity and suitably controlled D_k value for PCBs application.

EXPERIMENTAL PROCEDURE

Raw materials

The properties of AlN and BN powders used in this study are given in Table I. The coupling agent used was 3-glycidoxypropyltrimethoxysilane (trade name:

TABLE I
The Physical Properties of AlN and BN Fillers

	Average particle size (µm)	Particle shape	True density (g/cm^3)	CTE (ppm/°C)	D_k@1 MHz	Thermal conductivity (W/mK)
micro-BN	7	Platelet	2.28	<0.5	4	300
nano-BN	0.07	Polygon				
AlN	2.3	Polygon	3.26	4.5	8.5	270
	0.5					

Markosi® Silane KH-560). The epoxies were Epon 8008 and Epon 1031, purchased from Huntsman Co. Epon 8008 is a type of brominated epoxy resin that has been specially designed to meet the stringent requirements of the PCB industry. It has an epoxide equivalent of 410–460 g/Eq, and a bromine content of 19.0–21.0% w/w. Epon 1031 is a solid multifunctional epichlorohydrin/tetraphenylol ethane epoxy resin with an epoxy group content of 4350–5130 mmol/kg; it is usually used to improve the properties of cured epoxy resin systems, particularly at elevated temperatures. In this study, Epon 8008 and Epon 1301 were dissolved in acetone with a resin content of 80 and 70%w/w, respectively. The curing agent dicyandiamide (DICY, purity > 99.5%) with an average diameter of <1 mm and the accelerator 2-methylimidazole (2-MI, purity > 99.0%) were obtained from Neuto Products and Tokyo Kasei Kogyo, respectively. Both curing agent and accelerator were used as received.

Procedure for composite preparation

The composites were fabricated by firstly pretreating the surface of the filler powder with a KH-560 coupling agent, the amount used being 5 wt % of the weight of the filler powder. The Epon 8008 solution, Epon 1031 solution, DICY, and 2-MI were weighted out at a weight ratio of 100 : 7.349 : 2.552 : 0.056. The fillers were then weighted out at increasing percentages with respect to the weight of Epon 8008 solution, which 0, 10, 20, 40, 60, 80, 120 wt % in the case of AlN and 0, 10, 20, 30, 40 wt % in the case of BN. The mixtures were then diluted by a small quantity of acetone and were first stirred in a beaker for 45 min by an ultrasonic stirrer and subsequently by a high-speed mixing machine for 1 h. The uniformly formed mixtures were cast in a mold and pumped in a vacuum container for about 1 h to remove the air bubbles and solvent as the temperature gradually increased from 80 to 130°C. The casts were finally cured at 175°C and held at this temperature for 4 h.

Characterization

Filler volume fraction

The volume fraction of filler in the composites was determined using the following equation:

$$V_f = \frac{W_f}{W_f + (1 - W_f)\frac{\rho_f}{\rho_m}} \qquad (1)$$

where W_f was the weight fraction of the filler; ρ_f and ρ_m were the densities of the fillers and pure epoxy (1.3846 g/cm^3), respectively.

Thermal mechanical analysis

The CTE and T_g were measured with a Perkin-Elmer thermal mechanical analyser (TMA-7). The temperature range used was from 30 to 220°C and the heating rate was 10°C/min. All reported TMA data were obtained from a second heating cycle.

Thermal conductivity measurement

The thermal diffusivity and specific heat of composites were measured by Flashline™ 3000 Thermal Properties Analyzer (Anter Corporation) from cylindrical samples of 12.7 mm in diameter and 0.8–1.2 mm in thickness. Thermal conductivities were calculated from the measured values of thermal diffusivity, specific heat capacity, and density of the composites.

Dielectric properties measurement

D_k and D_f measurements were made using an Agilent-4294A impedance analyzer with an applied AC voltage of 500 mV; the frequency range used was 1 KHz–1 MHz. The samples used for the measurement were disc-shaped and both sides of the samples were coated with a silver paste. The D_k was calculated according to $D_k = Ct/\varepsilon_0 A$, where C was the capacitance of the composite, t the thickness of the discs, ε_0 the vacuum dielectric constant, and A the area of the major disc surface. The volume resistivity of the sample was measured using a high-resistance
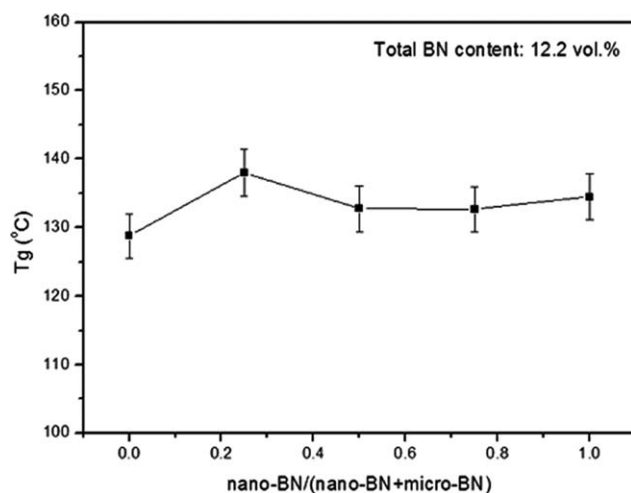
Figure 1 The T_g of the composites as a function of the nano-BN content in mixtures of micro- and nano-BN particles for the composites with a total BN content of 12.2 vol %.

& micro-current meter (Beijing Institute of Labor Protection, EST121) with a measure range of 10^4 to 10^{16} Ω for resistance and of 10^{-16} to 10^{-4} A for electric current.

SEM analysis

A field emission scanning electron microscope (FE-SEM, JEOL, JSM-6335F) was used to observe the fractured surfaces of the composite discs. The surfaces were sputtered with gold prior to SEM analysis.

EXPERIMENTAL RESULTS AND DISCUSSION

T_g and CTE

The T_g of the composites is plotted in Figure 1 as a function of the amount of nano-BN in mixtures of micro- and nano-BN particles for the composites with a total BN content of 12.2 vol %. The results show that T_g first increases, and then decreases with the fraction of nano-BN with a maximum T_g at a fraction of 0.25. The T_g as a function of filler content is presented in Figure 2, which shows that the T_g increases sharply with initial addition of AlN or BN filler. For example, the increase in T_g was approximately 20°C by adding only 4.6 vol % AlN or 30°C by adding only 6.5 vol % BN. The T_g continues to increase but at a slower rate with further increase in AlN filler content to 36.8 vol %, but it clearly decreases when the amount of BN filler added is above 12.2 vol %. Obviously, T_g of the composites depended on the particle size and size distribution of the filler. When AlN filler size is bimodal and hybrid ratio [0.5 um AlN/(2.3 μm AlN + 0.5 μm AlN)] is 025, the T_g of composites is higher than that for the composites filled single-sized AlN particles

(2.3 μm). Compared with T_g of the composites filled with single-sized BN, the T_g of the composites is higher for nanometer-sized BN filler. Also, if BN filler size is bimodal and hybrid ratio is 0.25, the T_g of the composite is further increased. As a whole, the T_g of AlN or BN-filled composite is 110–140°C, which basically reaches the T_g values of common commercial product manufactured by Polyclad Laminates (e.g., 110–150°C for PCL-FR-226 laminate/PCL-FRP-226 prepreg and PCL-FR-240 laminate/PCL-FRP- 240 prepreg).

The increase in T_g indicates that the interaction between filler and epoxy matrix can effectively restrict the mobility of epoxy chain. As for AlN filler, the interaction enhances with filler content. Thus, the T_g exhibits a increased trend with AlN content. But as for BN filler, the T_g begins to decrease with high filler content, which is related to the BN causing high viscosity of the mixture. Literature showed that BN caused a remarkable increase in viscosity of the mixture in comparison with other ceramic fillers even if at a small volume fraction, and thus the maximum filler content in the composite was 21.7 vol % in case of BN filler in this study.[3,26] The removal of solvent and bubble becomes difficult with increase in viscosity, and thus results in a weak interaction between the filler and the epoxy matrix. The weak interaction implies free volume of remove of epoxy chain increases and thus T_g decreases. On other hand, the increase in viscosity also results in a decrease in crosslinking density, which also causes a decrease in T_g.[27] As for smaller-sized filler, the interaction will further increase compared with larger-sized filler due to the increase in interface area. Thus, the T_g of nano-BN filled composites is higher that of micro-BN filled composites; hybrid-sized (2.3 μm + 0.5 μm) AlN-filled composite
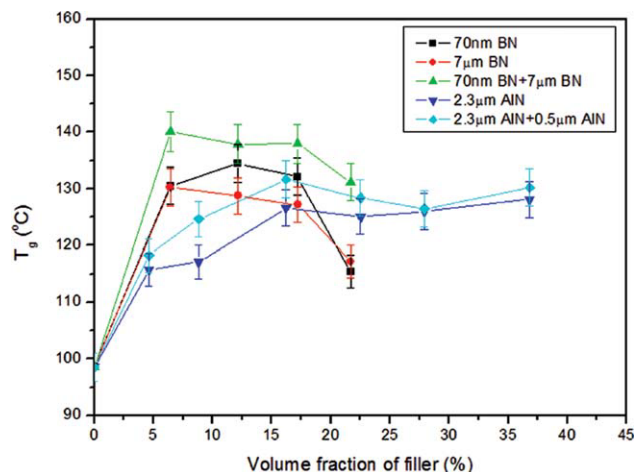

Figure 2 The relation of T_g of the composites and filler content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
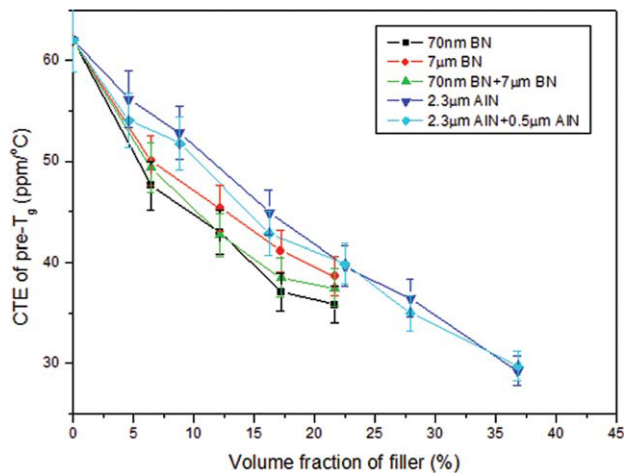
Figure 3 CTE of pre-T_g of the composites as a function of filler content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 CTE of post-T_g of the composites as a function of filler content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shows higher T_g than that of single-sized (2.3 μm) AlN-filled composite. Hybrid BN-filled composites show higher T_g than that of single nano-BN or micro-BN filled composites, which can be attributed to the decrease in viscosity of the mixture. When the total amount of the filler and the particle size are fixed, the viscosity of the mixture can be decreased at amount of the large-sized filler and the small-sized filler with suitable ratio.[28–30] The decrease of viscosity is beneficial to decrease the defect of the composites, and thus improves the T_g of the composites.

Figures 3 & 4 show the CTE of pre-T_g and post-T_g of the composites as a function of the filler content, respectively. It is found that the CTE of the composites decreases with increasing filler content. This is because the lower CTE of the filler than that of epoxy and the restriction of mobility of the epoxy chain due to the interaction between filler and epoxy. Note that intrinsic CTE of BN is smaller than that of AlN, thus CTE of BN-filled composite is smaller than that of AlN-filled composite at a given volume fraction of fillers, as seen from Figures 3 & 4. In case of BN or AlN filler, a composite containing with more smaller-sized filler shows lower CTE, indicating that smaller-sized filler seems to work more effectively in lowering CTE than that of larger-sized filler. This is because more interfacial area forms between the smaller-sized filler and the epoxy, and thus the thermal expansion of epoxy is more effectively restricted. From the standpoint of thermal-fatigue reliability, composites with low CTE are expected to have small thermal expansion mismatches among the chip, solder bumps, and substrate. In this study, CTE of the pre-T_g reaches minimum value of about 36 and 29 ppm/°C for BN- and AlN-filled composites, respectively, which are lower
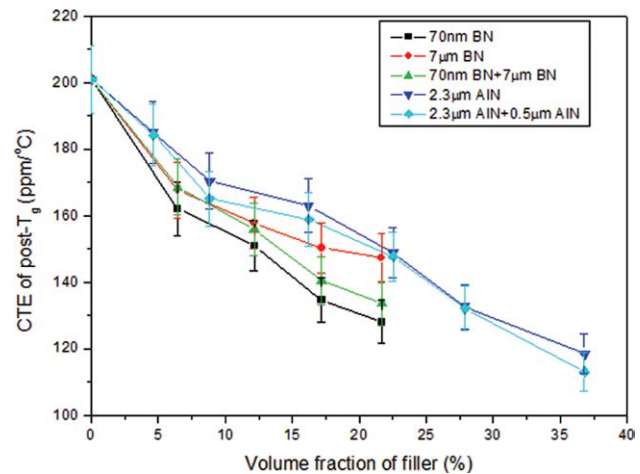
than those of other researcher's results[2,3] and the common commercial product (e.g., 50 ppm/°C for PCL-FR-226 laminate/PCL-FRP-226 prepreg and PCL-FR-240 laminate/PCL-FRP- 240 prepreg). The CTE of the composite after T_g, decreases to 128 and 113 ppm/°C for BN- and AlN-filled composites, respectively, and the values are also lower than that of the abovementioned product (250 ppm/°C).

Thermal conductivity

The thermal conductivity of the composite is plotted in Figure 5 as a function of the fraction of nano-BN particles in micro- and nano-BN mixtures with a fixed total fraction of 12.2 vol %. As shown in Figure 5, the epoxy incorporated by hybrid particles can exhibit higher thermal conductivity compared with the
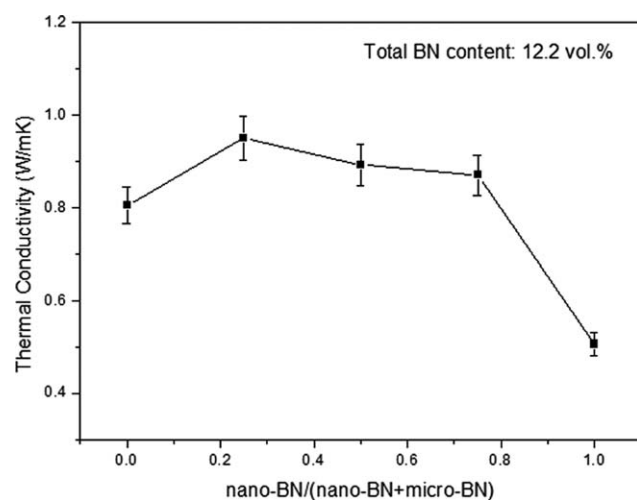

Figure 5 The thermal conductivity of the composites as a function of the nano-BN content in micro- and nano-BN mixtures with a fixed total BN content of 12.2 vol %.
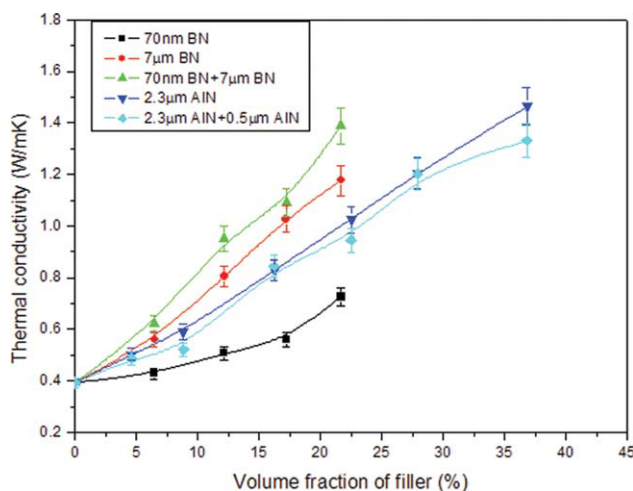
Figure 6 The thermal conductivity of the composites as a function of filler content. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

case of only single particle size, and the thermal conductivity reaches a maximum as the fraction of nano-BN changes to 0.25. Figure 6 shows the thermal conductivity of the composite as a function of filler content. It is found that the thermal conductivity of the composites increases with increasing filler content regardless of filler type or size. In addition to filler content, it is also found that the particles size and morphology have significant effect on thermal conductivity for BN particles filled composites. The maximal thermal conductivity of 1.39 and 1.46 W/mK is obtained for 21.7 vol % BN and 36.8 vol % AlN-filled composites, respectively. As reported in the literature, the thermal conductivity of AlN- and BN-filled epoxy could reach above 10 W/mK when the composites were fabricated by a process involving surface modification of filler combined with a high filler content,[6,10,11] but the thermal conductivity is usually about 1–1.5 W/mK for the same filler volume fraction as in this study.[2,3,13] For the common commercial product, the thermal conductivity is lower (e.g., 0.36 W/mK for PCL-FR-226 laminate/ PCL-FRP-226 prepreg and PCL-FR-240 laminate/ PCL-FRP- 240 prepreg), thus this kind of the composites can be used to improve the heat dissipation of the PCBs.

From Figure 6, we observe that the micro-BN filled composite has a much higher thermal conductivity than that of nano-BN filled composites, and the thermal conductivity of hybrid BN-filled composite is further improved. This is because larger-sized filler causes smaller contact resistance, and platelet-shaped filler more easily forms conductivity chain. Thus, it is obvious that the thermal conductivity of platelet-shaped micro-BN filled composites is higher than that of particle-shaped nano-BN filled

composites. When the epoxy is filled with hybrid BN filler, particle-shaped nano-BN maybe fills into the pores in the packed structure obtained from platelet-shaped micro-BN particles. This implies that the filler packing is closer and thus more thermal conductive chains are formed, which leads to higher thermal conductivity for hybrid BN-filled composites. However, as for AlN-filled composites, the thermal conductivity of single-sized AlN-filled composites is slightly higher than that of hybrid-sized AlN-filled composites although the hybrid ratio is same as the case of BN (0.25). Considering that the two sizes of AlN filler is close and formation of network structure by particle-shaped filler is difficult compared with platelet-shaped filler, no more conductivity chains are formed by hybrid-sized AlN filler. Oppositely, the thermal conductivity of hybrid-sized AlN-filled composites is lowered due to smaller-sized AlN causing increase of contact resistance. At a given volume fraction, micro-BN filled and hybrid BN-filled composites show higher thermal conductivity than that of AlN-filled composites. This is related not only to platelet-shape and large size, as discussed above, but also to higher intrinsic thermal conductivity for BN filler. In fact, BN-filled composites show higher thermal conductivity compared with other ceramic filler filled composites at the same filler size and morphology.[3,26] As for nano-BN filled composite, the lower thermal conductivity than AlN-filled composite can be attributed to its too small size although BN possesses of higher intrinsic thermal conductivity.

To predict the thermal conductivity of polymer-matrix composites, many theoretical and semitheoretical models have been developed. The parallel and series models are the simplest alternatives, which suppose that the constituents in composites are arranged in either parallel or series with respect to heat flow.[31–33] These two models usually give the upper or lower bounds of effective thermal conductivity of composites, and the measured values lie between them. In addition to the two simple models, there are some advanced models on the basis of Maxwell model that assumes the spherical fillers distributing randomly in matrix.[32,34,35] The Cheng-Vachon model is based on Tsao's model that uses probabilistic theory and the additivity of conductances in parallel to predict the thermal conductivity of two-phase solid mixture, and further assumes distribution function of the discontinuous phase is parabolic.[32] Cheng-Vachon model has been modified by introducing a new parameter, permitting the new equation to describe the thermal conductivity of the composites for a wide variety of filler shapes and states of dispersion.[36] Nielsen model is one of important semitheoretical models, which originates from the Einstein model for the viscosity of a fluid
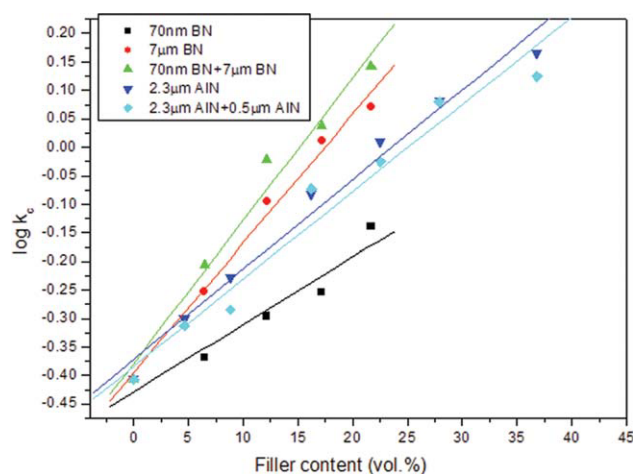
Figure 7 Comparison of the thermal conductivity of composite with Agari's model. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

with dispersed spheres.[31–33] This model considers constituent thermal conductivity, concentrations of each constituent, as well as aspect ratio, orientation, and packing of the fillers. From the parallel, series, Maxwell, and Cheng-Vachon models, the thermal conductivity of the composites is a function of thermal conductivity and volume fraction of constituents regardless of filer size and morphology. In Nielsen equation, particle shape (sphere, irregular particles, fibers), and packing order (random loose, random close, three dimensional random, etc.) are considered. However, it does not completely reflect the effect of filler size. Thus, these models do not predict the thermal conductivity of the composite filled with different sizes and morphologies filler in this study.

The Agari model is another important semitheoretical model, which considers the effects of dispersion state of filler by introducing factors C_1 and C_2[13,31,32,37]:

$$\log k_c = V_f C_2 \log k_f + (1 - V_f) \log(C_1 k_m) \qquad (2)$$

where k_c, k_f, and k_m are the thermal conductivity of the composites, filler, and epoxy matrix, respectively; V_f is the volume fraction of the filler and epoxy matrix. C_1 is a factor relating to the structure of the polymer, such as crystallinity and crystal size of

the polymer, and C_2 is a factor relating to the case in forming conductive chains of the filler. The more easily particles are gathered to form conductive chain, the larger the C_2 values are. So if the dispersion system is different, the thermal conductivity of the composites may be different even if the type and content of fillers in the composites are the same. The parameters C_1 and C_2 actually include the information about the effect of filler size and morphology, thus the thermal conductivity of the composites can be predicted once the constants are determined. When the thermal conductivity of the composites is plotted on a logarithm scale, as seen in Figure 7, linearity fitting of the experimental data indicates that thermal conductivity of the composites can be expressed by Agari equation. Through data fitting, C_1 and C_2 for the above composite systems are obtained and shown in Table II. From the Table II, it is found that the difference of numerical values of C_1 is small, indicating the uniform of structure of the epoxy regardless of filler type, size, and morphology. The numerical values of C_2 for micro-BN and hybrid BN-filled composite are obviously higher than other fillers filled composite, indicating more conductive chains of the filler are formed in these systems, as discussed above.

Dielectric properties

The curves of the D_k and D_f versus the frequency from 10^3 to 10^6 Hz showed that the D_k decreased but the D_f increased with increasing frequency for all the samples. The D_k at 1 MHz of the composites is plotted in Figure 8 as a function of BN or AlN fillers content. In the case of AlN, it is found that D_k increases with increase in AlN content. When the AlN content is below 22.5 vol %, the D_k of hybridsized AlN-filled composite is slightly higher than that of single-sized AlN-filled composite. However, when the amount of AlN is above 22.5 vol %, opposite result is found. The dielectric properties have a direct connection with the polarization of molecules. Epoxy is a weak polarization polymer; the addition of AlN increases the polarization of the system. Thus, the D_k of composites increases with increasing the AlN content. At the same AlN content, the interfacial area of epoxy-AlN increases with decreasing

TABLE II
C_1 and C_2 for Agari's Model for the Composites

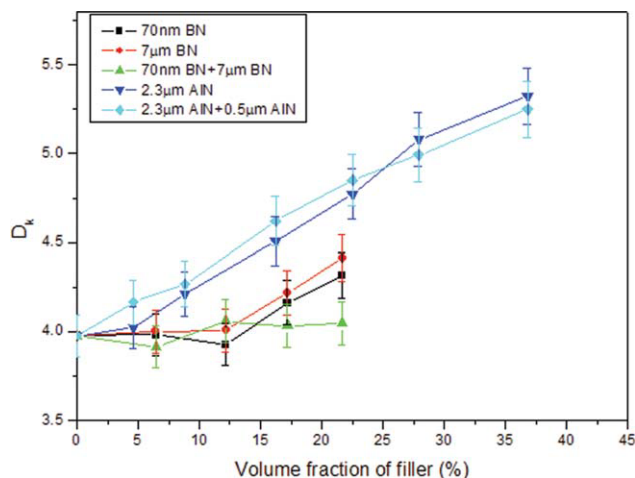| Coefficients | Filler size and type | | | | |
	70 nm BN	7 μm BN	70 nm BN + 7 μm BN	2.3 μm AlN	2.3 μm AlN + 0.5 μm AlN
C_1	0.9505	1.02769	1.06695	1.08509	1.05362
C_2	0.4967	1.23288	1.39836	0.49468	0.47215

Figure 8 The D_k at 1 MHz of the composites as a function of filler content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the AlN particle size, which implies that the effect of AlN filler increases and thus increases the overall polarization of the system. This can explain why the D_k of hybrid-sized AlN-filled composite is higher than that of single-sized AlN-filled composites. As for D_k of hybrid-sized AlN-filled composite being lower than that of single-sized AlN-filled composites as AlN content above 22.5 vol %, we have not completely understood at present. From the Figure 8, it is seen that the D_k of BN-filled composites is obviously lower than that of AlN-filled composites, which can be attributed to BN fillers having an almost same D_k as epoxy. Due to the similar D_k between BN filler and epoxy, the D_k of the composites should show a little change with increasing the BN filler regardless of filler size and morphology. However, this trend has been only seen in the case of hybrid BN-filled composite; the D_k of single nano-BN or micro-BN filled composite shows increased values when BN fraction above 12.2 vol %. It is thought that the increased values are related to the increased viscosity of the mixture caused by single-sized BN filler, as discussed above. Increased viscosity leads to survival of the solvent, which can increase the overall polarization of the system. In addition, it is worthy noting that the D_k of the composite shows a lower value compared with epoxy when BN fraction is below 12.2 vol %. For the present study, the D_k values of BN-filled composites (3.89–4.4) are smaller than that of common commercial product (e.g., 4.5 for PCL-FR-226 laminate/PCL-FRP-226 prepreg and PCL-FR-240 laminate/PCL-FRP- 240 prepreg). Although the D_k value of AlN-filled composites (4–5.25) is smaller than that of previously reported results (5–8),[4,10] it is higher than that of the above produce.

Figure 9 shows the D_f at 1 MHz as a function of filler content. In the case of AlN, the D_f decreases from 0.0366 to 0.019 by increasing filler content to 36.8 vol %. In the case of BN, the D_f can be decreased to 0.022 by increasing filler content to 21.7 vol %. The D_f values are much lower than those of some researcher's results (e.g. 0.08),[4] but slightly higher than that of the common commercial product (e.g., 0.015 for the PCL-FR-226 laminate/PCL-FRP-226 prepreg and PCL-FR-240 laminate/PCL-FRP- 240 prepreg). At the same volume fraction, it seems that the BN can more effectively decrease the D_f of the composite. The D_f of the composite gradually decreases because of the lower D_f for AlN and BN filler than that of epoxy. Theoretically, the D_f of the composites filled with smaller-sized AlN should has lower value because the interaction between AlN filler and epoxy enhances. However, it cannot be concluded the relationship between D_f and filler size and/or morphology from Figure 9. In the case of BN, it is worthy noting that hybrid BN-filled composite has a lower D_f at high filler content.

To predict the D_k of the composites, there are also many theoretical and semiempirical models. In the simplest case, it assumes that dielectric system consists of two different homogeneous dielectrics connected in series or in parallel. In this case, the D_k can be expressed by eq. (3)[38,39]:

$$\varepsilon_c^n = V_f \varepsilon_f^n + V_m \varepsilon_m^n \qquad (3)$$

where ε_c, ε_f, and ε_m are the D_k of the composite, filler, and matrix, respectively. When $n = -1$ and $n = 1$, the eq. (3) corresponds to assumption of capacitors in series and in parallel, respectively. However, in most general cases, composite dielectrics are
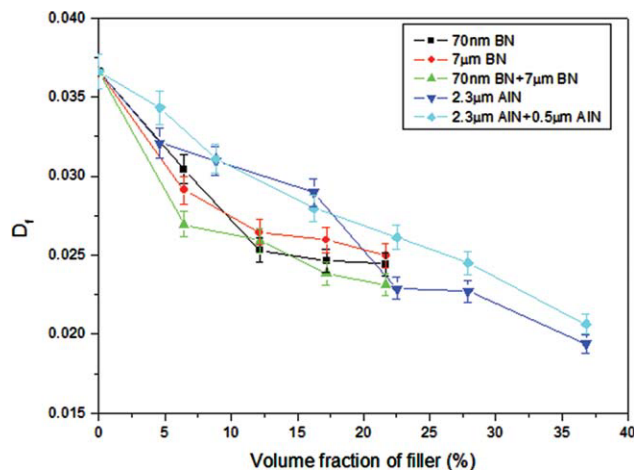

Figure 9 The D_f at 1 MHz of the composites as a function of filler content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
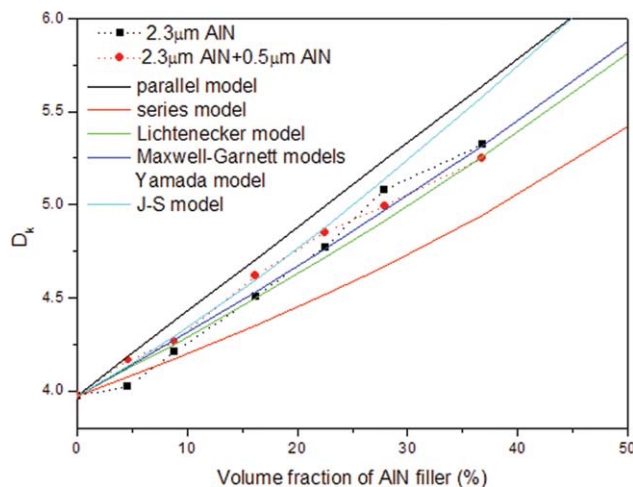
Figure 10 The comparison of measured D_k of AlN-filled composites and the theoretic models. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

chaotic or statistical mixtures of several components. Then the true value of D_k of a statistic composite should lie between the values determined by eq. (3) for $n = 1$ and $n = -1$.

In addition to series and parallel models, the other most commonly used equations include Lichtenecker logarithmic law of mixing (4),[38–41] Maxwell-Garnett model (5),[38,42–44] Yamada model (6),[38,39,42,45] and J-S model (7).[40,46,47]

$$\log \varepsilon_c = V_f \log \varepsilon_f + V_m \log \varepsilon_m \tag{4}$$

$$\varepsilon_c = \varepsilon_m \left[1 + \frac{3 V_f \times \frac{\varepsilon_f - \varepsilon_m}{\varepsilon_f + 2\varepsilon_m}}{1 - V_f \times \frac{\varepsilon_f - \varepsilon_m}{\varepsilon_f + 2\varepsilon_m}} \right] \tag{5}$$

$$\varepsilon_c = \varepsilon_m \left[1 + \frac{V_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n(\varepsilon_f - \varepsilon_m)(1 - V_f)} \right] \tag{6}$$

$$\varepsilon_c = \frac{V_m \varepsilon_m + V_f \varepsilon_f \left[\frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \right] \left[1 + \frac{3 V_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right]}{V_m + V_f \left[\frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \right] \left[1 + \frac{3 V_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right]} \tag{7}$$

In eq. (6), n is the morphology factor dependent on the shape of the particles. When $n = 1/3$ for spherical particles, the eqs. (6) and (5) will become same.

Figure 10 shows the comparisons between different theoretical models and experimental data for D_k of AlN-filled composites. It is observed that the theoretical data on the basis of series and parallel models deviate from the experimental data. The experimental data are just between the data on the basis of series and parallel models. The theoretical data on the basis of Lichtenecker logarithmic law of mixing, Maxwell-Garnett model, Yamada model, and J-S model are relatively close to the experimental data compared with series or parallel model, but the ex-

perimental data still show substantial deviation from the prediction of J-S model when AlN content above 22.5 vol %. Taking one with another, the calculated results from Lichtenecker, Maxwell-Garnett, and Yamada models are in agreement with the experimental data, indicating these models can be used to predict the D_k of epoxy-AlN composite in our study.

As mentioned in the introduction, when the filler size is at nanoscale, the D_k of the composites may be lower than that of pure polymer although the D_k of the filler is higher than that of polymer. In our study, when BN content below 12.2 vol %, the D_k of the composites is slightly lower than that of epoxy although their D_k is similar, as mentioned above. Obviously, the above models cannot predict the decreased D_k. To describe this case, Vo et al.[16] developed a theoretical model in which the effect of interphase region on the D_k of polymer composite was taken into account. In this model, the interphase region is described as a material having dielectric properties different from that of the polymer and filler phases.[20] Using this model, some researchers obtained more precise prediction of the D_k of the composite than that of the above models. In our study, we can use this model to qualitatively explain the decreased D_k for the composites containing nano-BN. Further quantitative analysis of the D_k of the composites will be undertaken in future study.

Except for D_k and D_f properties, the volume resistivity of the samples was also measured. The results show that the volume resistances of the samples have no obvious change with different filler type, size, and content, and the values are on the order of 10^{14} Ω cm. In fact, epoxy, AlN, and BN have high resistivity of above the order of 10^{13} Ω cm, thus the prepared composites show high resistivity, which is also important properties for electronic packaging and substrate materials.

Microstructure of the composites

Figure 11 shows the typical fractured surfaces of the composites containing different fillers. For nano-BN-filled composite [Fig. 11(a)], it is found the distribution of nano-BN is homogeneous. For micro-BN-filled composites [Fig. 11(b)], the orientation of the BN platelets in the composites is fairly random, and the composite morphology is thus isotropic. As it seems, the platelet-shaped particles of micro-BN are largely unbroken by the high shear force employed. For the hybrid BN-filled composites [Fig. 11(c)], it is observed that nano-BN particles occupy the space between micro-BN particles, resulting in high packing density of fillers in matrix, and thus heat conductive networks are easily formed in epoxy matrix, as discussed above. For the AlN-filled composites, few AlN filler can be observed on fractured surface,
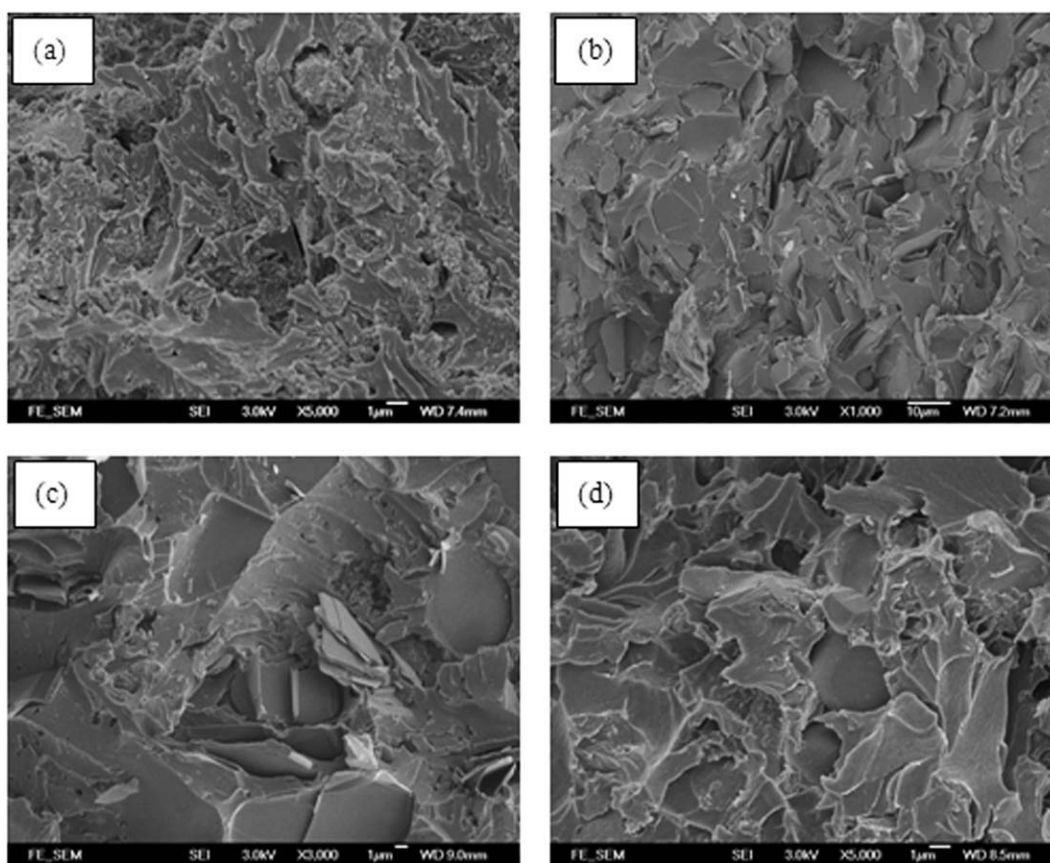
Figure 11 The fractured surface morphology of the composites: (a) 12.2 vol %, 70 nm BN; (b) 12.2 vol %, 7 μm BN; (c) 12.2 vol %, 70 nm BN + 7 μm BN; (d) 27.9 vol %, 2.3 μm AlN + 0.5 μm AlN.

as shown in Figure 11(d). This may be related to AlN filler size and sphere shape. The number of filler per unit area for the micro-filler filled composites is much smaller than that of nano-filler filled composites. For example, it is easy to see the BN filler on the fractured surface for nano-BN filled composites. On the other hand, sphere shape easily results in distinguishing AlN filler and epoxy matrix being difficult. For micro-BN filled composites, BN particles can be easily observed due to its platelet shape. In addition, it can be observed that some micro-BN and AlN particles are coated by epoxy, indicating a strong interfacial adhesion between filler and epoxy. The good adhesion of filler and epoxy is one of the significant contributions to modify the properties of the composite.

CONCLUSIONS

The results obtained with the investigated thermally conductive ceramic particle-filled epoxy composites allow us to draw the following conclusions:

1. Regardless of AlN or BN filler, the CTE and D_f of the composites decrease but T_g and thermal conductivity increase with increasing filler con-

tent, and a composite containing with more smaller-sized fillers shows lower CTE and higher T_g.

2. Due to the fact that intrinsic CTE, D_k, and D_f of BN are smaller than these of AlN, and thermal conductivity of BN is higher than that of AlN, thus CTE, D_k, and D_f of BN-filled composites are smaller than these of AlN-filled composite and the thermal conductivity of BN-filled composites is higher than that of AlN-filled composites at a given volume fraction of fillers.

3. Micro-BN filled composite has higher thermal conductivity than that of nano-BN filled composites due to its larger size and sphere shape. However, both of them show decreased T_g and increased D_k at high filler fraction, which is related to the BN causing high viscosity of the mixture.

4. Hybrid BN-filled composites show higher thermal conductivity than micro-BN filled composites due to the formation of more conductive chain. What's more, the viscosity of the hybrid BN-filled mixture can be decreased compared with micro- or nano-BN filled mixture, thus the hybrid BN-filled composites have higher T_g value and similar D_k value with epoxy even if

at high filler fraction. For the hybrid-sized AlN-filled composite, the thermal conductivity does not show a lower value than that of single-sized AlN-filled composites.

5. By analyzing the different theoretic models and experimental results about thermal conductivity, it is found that Agari model is suitable to predict thermal conductivity for present material system.

6. As for D_k of AlN-filled composite increasing with AlN content, it is found that Lichtenecker, Maxwell-Garnett, and Yamada models are in agreement with the experimental data. At the smaller fraction, lower D_k of composites containing nano-BN than that of epoxy can be qualitatively described by Vo et al. model.

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