EFFECT OF FILLER SIZE AND ITS BIMODAL DISTRIBUTION FOR HIGHLY THERMAL-CONDUCTIVE EPOXY COMPOSITES

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1 Introduction

As microelectronic devices become highly integrated often used at high frequencies, the highly thermal-conductive composite systems are required because the generated heat in those electronic devices is substantially high, e.g., in light emitting diode (LED) and highly-integrated memory chips [1,2]. In those systems, the generated heat must be dissipated through the printed circuit board (PCB) or epoxy molding compound (EMC) to achieve sustained performance and life time of the devices [3], since the accumulated heat often causes thermal fatigue and chemical reaction to reduce the service life. For example, LED performance is reported to degrades exponentially with the increased temperature above 90 ℃ due to the thermal degradation of light-emitting material [4].

For developing polymeric composites with high thermal conductivity, many thermally-conductive but electrically-nonconductive fillers have been introduced such as silica, aluminum oxide, silicon carbide, aluminum nitride(AlN), boron nitride(BN) [1, 5-8]. In those filler systems, the particle size and the filler content have been reported to be the major factors for achieving high thermal conductivities [7,9,10], where the efficient packing gives an increased loading density of fillers in polymer matrices. Compared with a unimodal particle distribution, the bimodal distribution of fillers has been reported to give an increased thermal conductivity by 130 % [11]. In the bimodal distribution characteristics (Figure 1), smaller particles can desirably fill the interstitial space of larger particles to give an increased packing density of the fillers, which may be represented by a continuous valley formed by the overlapped unimodal distribution curves. If the unimodal curves are placed apart without overlapping of the curves, we believed that the interstitial space is not efficiently filled with the other particles.

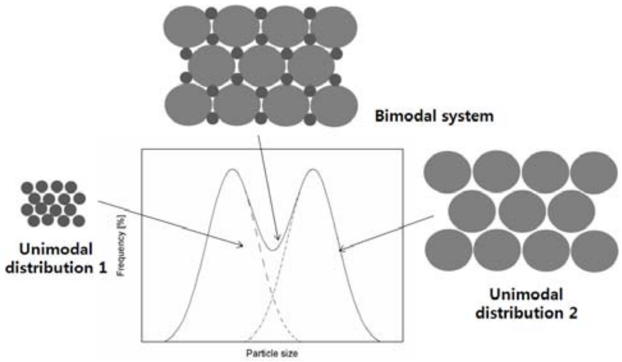

Fig. 1. Schematic of the unimodal and the bimodal distribution, and the continuity vally formed by overlapped two unimodal distribution curves.

Although AlN has higher thermal conductivity, 180~200 W/mK, than BN, 60~100 W/mK, the thermal conductivity of BN composites is higher than AlN composite, e.g., giving 1.2 W/mK and 0.6 W/mK at 30 vol.%, respectively, [12]. It is likely that the BN particle, which is in the planar shape, has a favorable filler packing and network formation for facile heat dissipation through the composites. Since heat dissipation is greatly influenced by the shape of fillers, it may be quantified by the aspect ratio of particles termed as "shape factor". The thermal conductivity of composites has been reported to increase with the shape factor [12,13]. In addition, it should be addressed that the particle size may very well influence the thermal conductivity because the particle size determines the overall contact area of fillers, interfacial thermal resistance, conducting path, etc.

Accordingly, hybrid multimodal composite systems were investigated in this study using different sizes and shapes of AlN and BN particles in the epoxy matrix. The dispersion of AlN and BN particles was analyzed to identify for developing the efficient conducting path in hybrid composite system in

		A150	A50	A20	A1	B18	B5	B1
Chemical formula		AlN	AlN	AlN	AlN	BN	BN	BN
Commercial grade		A500-150	A500-50	A500-20	H	SGP	HGP	MBN
Tap Density(g/cm^3)		2.09	1.9	1.6	0.43	0.8	0.4	0.3
Particle Size (μm)	D10	4.2	3.3	2.5	-	5.4	1.9	-
	D50	25.5	14.4	8.67	1.13	18	6	1
	D90	113.2	39.9	18.8	-	41.6	10.6	-

Table 1 Properties of thermal conductive filler used in this study.

epoxy matrix system. The ratio of mean particle sizes of two different fillers was also investigated identifying the optimal size distribution for high thermal conductivity of the composites.

2 Experimental

The four types of AlN and three types of BN particles were used for hybrid filler systems in this study. As summarized in Table 1, the mean particle size (D_{50}) of AlN and BN was 1.13 ~ 25.5 ㎛ and 1 ~ 18 ㎛, respectively, as represented by A1, A20, A50 and A150 (SURMET ,USA) for AlN particles, and B18, B5 and B1 (DENKA ,Japan) for BN particles.

Epoxy and hardner used as a matrix system in this study were bisphenol A diglycidyl ether (DGEBA) and methyl tetrahydrophthalic anhydride (MTHPA), respectively, purchased from Kukdo Chemical. The catalyst was 1-methylimidazole (1-MI), and the surface modifier of fillers was 3-aminopropyl-triethoxy silane (aminosilane), both purchased from Aldrich.

Three different hybrid systems were investigated and shown in Table 2: Case 1 as AlN bigger than BN ($D_{AlN} > D_{BN}$), Case 2 as AlN similar to BN ($D_{AlN} \approx D_{BN}$), and Case 3 as AlN smaller than BN ($D_{AlN} < D_{BN}$) in the mean particle sizes. In addition, compared with Case 2, Case 2′ was designed to compare the AlN particle sizes while maintaining $D_{AlN} \approx D_{BN}$. More specifically, the particle sizes of AlN in Case 2 and Case 2′ were 14.4 μm and 25 μm, respectively, at the same BN size of 18 μm, which comply well with $D_{AlN} \approx D_{BN}$.

The surface of AlN and BN particles was treated using an aminosilane for improving filler dispersion and minimizing the thermal resistance at the particle surface, more details of which can be found elsewhere [1,14]. The epoxy resin system of YD-128, MTHPA, and 1-MI was mixed with the silane-treated fillers at room temperature for 20 min with mechanical stirring. Total filler contents were adjusted to 80 vol.%. The mixture was cured in a mold at 3,000 psi and 80℃ for 4 hours followed by 2 hours of holding at 145℃. The resulting composite samples had a thickness of 1±0.5 millimeters in a diameter of 12.7 millimeters.

The surface was analyzed using a scanning electron microscope (JEOL JSM6700F, Japan). Thermal conductivity was measured by the improved modified laser flash method [15,16], where the thermal diffusivity and specific heat were estimated using a Netzsch Nanoflash 447. All the thermal measurements were performed three times and the average was taken to calculate the thermal conductivity and thermal diffusivity. The density was measured using the Archimedes' principle.

3 Results and discussion

Figure 2 shows the schematic of fillers at different sizes and shapes of fillers in the AlN and BN bimodal hybrid composites systems investigated in

Ratio of AlN to BN	Composition (Total 80 vol.%)											
	Case 1 (D_{AlN}>D_{BN})			Case 2 (D_{AlN}≈D_{BN})			Case 3 (D_{AlN}< D_{BN})			Case 2′ (D_{AlN}≈D_{BN})		
	A50	B5	B1	A50	B18	B1	A20	B18	B1/A1	A150	B18	B1+A1
2:1	48	24	8	48	24	8	49	25	3/3	48	24	4/4
1:1	36	36	8	36	36	8	37	37	3/3	36	36	4/4
1:2	24	48	8	24	48	8	25	49	3/3	24	48	4/4

Table 2 The ratio of filler by volume percent (vol.%) for multi-modal distribution.

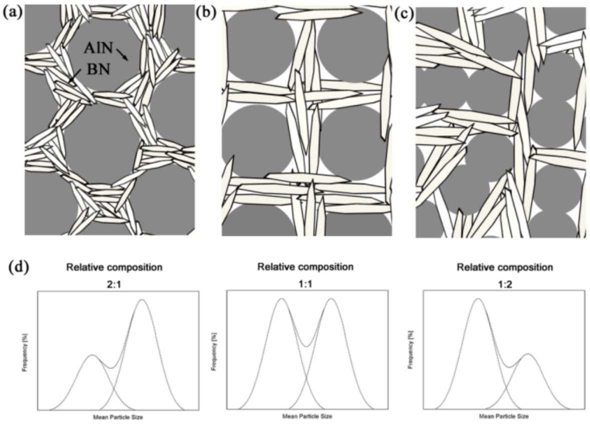

Figure 2. Schematic of the prepared composite systems in Case 1 (a), Case 2 (b), and Case 3 (c) comparing morphologies of different filler sizes, and the bimodal distribution characteristics with relative composition of 2:1, 1:1, and 1:2 (d).

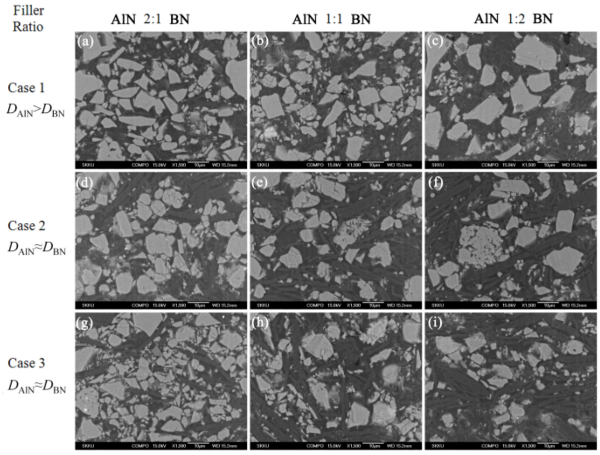

Figure 3. The SEM images of cross sections for Case 1 (a,b,c), Case 2 (d,e,f), and Case 3 (g,h,i) at different ratios of AlN to BN at 2:1, 1:1, and 1:2.

this study. The circular- and needle-shape particles represent polygonal AlN and planar BN particles, respectively. Comparing Figures 2(a) and (b), each representing Case 1 and Case 2, respectively, they are composed of the same size of the AlN particle but the BN particle size of Case 1 is smaller than that of Case 2. Comparing Figures 2(b) and (c), the BN particle size is the same, but the AlN particle size of Case 3 is smaller than that of Case 2. Figure 2(d) shows the continuous probability curve of the AlN/BN hybrid bimodal system with relative compositions of 2:1, 1:1, and 1:2. In our preliminary investigation, we found that the thermal conductivity of the AlN/BN hybrid systems depends on the absolute value of the particle size as well as the relative compositions of AlN to BN. Collectively, the prepared bimodal hybrid systems of Case 1, 2, and 3 represent the most significant factors affecting the thermal transport properties of AlN/BN composites, which should be considered in design and fabrication of thermal-dissipation parts and devices.

The cross sections of the prepared composite specimens are presented at Figure 3 for Case 1, 2, and 3, each having three different AlN-to-BN ratios at 2:1, 1:1, and 1:2. In the SEM images, the AlN, BN particles, and epoxy matrix are indicated by the polygonal shape in white, the needle shape in grey, and the ocean area in black color, respectively. Figures 3(a), (b), and (c) show that the AlN particles are bigger than BN particles corresponding to Case 1, where the BN particles are located in the interstitial space formed by the large AlN particles. Figures 3(d), (e), and (f) represent the composite systems containing similar sizes of AlN and BN particles corresponding to Case 2. Figures 3(g), (h), and (i) exhibit the hybrid composites corresponding to Case 3, where the AlN particle size is relatively smaller than BN. The prepared composite specimens in Figure 3 show different composite morphologies, i.e., different relative compositions, different particulate network, different interfaces, and so forth. It is believed that those different topological characteristics would provide different heat-dissipation paths allowing the thermal energy to flow through the AlN/BN particulate network in the direction toward minimal thermal resistance. Overall, the prepared composite specimens do not contain micro-cracks or entrapped voids seemingly demonstrating that there is a good interfacial adhesion between the fillers and matrix polymer.

Figure 4 shows the thermal conductivity and diffusivity of hybrid composite plotted at different ratios of AlN to BN comparing the composite systems in Case 1, 2, and 3. The thermal conductivity and thermal diffusivity of Case 1, where the AlN is larger than BN, decrease with the increment of BN particles or increase with the increased amount of the large-sized AlN fillers. In addition, the thermal properties of Case 2, where the AlN and BN sizes are similar but the BN size is larger than that of Case 1, shows a parabolic shape in the AlN-to-BN ratio, giving maxima at 6.06

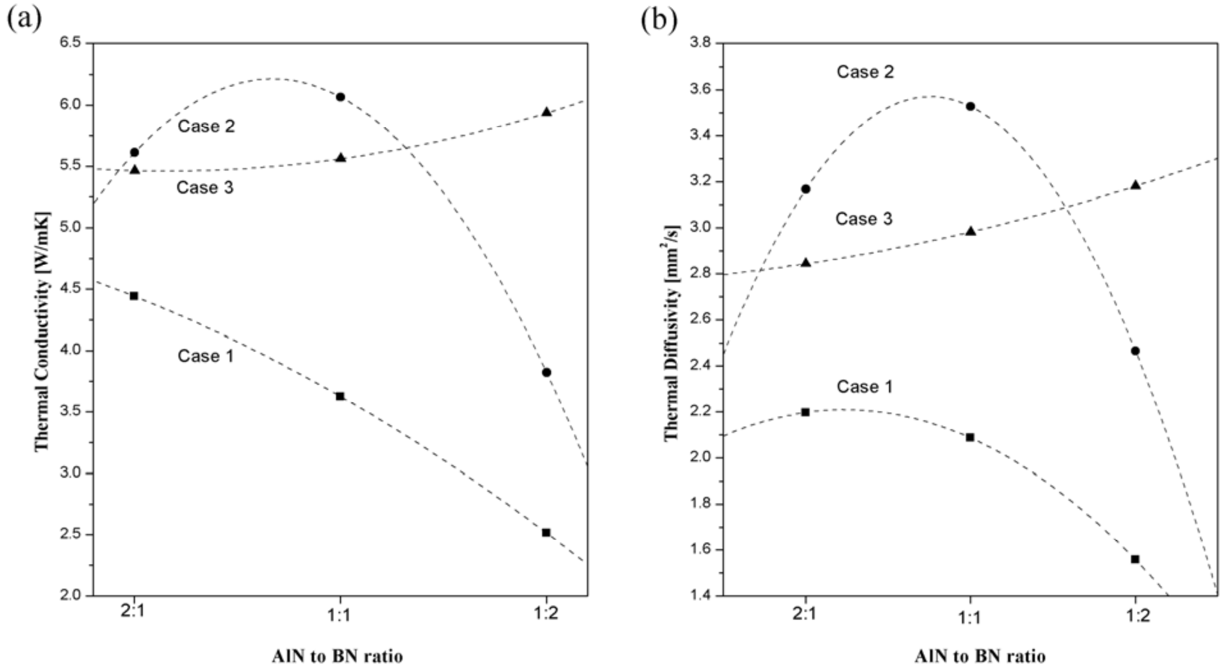

Figure 4. Thermal conductivity (a) and thermal diffusivity (b) of AlN-BN epoxy composites corresponding to Case1, Case 2, and Case3.

W/mK of thermal conductivity and 3.53 mm2/s of thermal diffusivity at 1:1 ratio. It should be noticed that the thermal conductivity and diffusivity of Case 2 are higher than Case 1 in the whole range of compositions.

As also can be seen in Case 3 (Figure 4), where the BN size is similar to Case 2 with a decreased size of AlN, the thermal properties increase with the BN content or increase with AlN content, which is contrary to Case 1. Comparing Case 2 and Case 3, both having similar particle sizes except that the AlN size of Case 3 is smaller than Case 2, there seem topological factors affecting the thermal properties in a critical and sensitive way. It was reported that the efficient packing capability is critically affected by the BN content because the high aspect ratio particles of BN could provide the thermal conducting path [12,13]. However, it should also be addressed that BN particles have a large contact area, which gives increased interfacial thermal resistance. When similar-sized particles of AlN and BN are loaded in epoxy matrix like Case 2, the filler contact area seems to be minimized and, consequently, the highest thermal properties are achieved. Subsequently when AlN and BN particle sizes are similar, the relative compositions of AlN-to-BN is likely affected by the interfacial thermal resistance and packing efficiency in a sensitive way, resulting in different behaviors of Case 2 and Case 3 in Figure 4. Overall, the highest thermal conductivity and diffusivity are obtained at the AlN-to-BN ratio of 1:1 in Case 2.

Since Case 2 gives the highest thermal properties, Case 2′ was specifically designed to investigate the

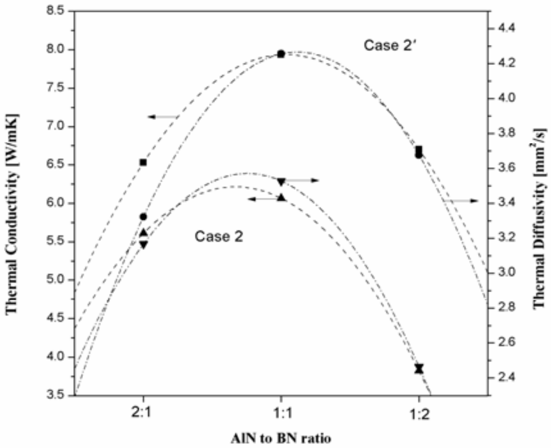

Figure 5. Thermal conductivity and thermal diffusivity comparing Case 2 and Case 2′ in order to investigate the thermal conducting paths using the different size of AlN particle while maintaining $D_{\mathrm{AlN}} \approx D_{\mathrm{BN}}$ at similar AlN-to-BN ratio to Case 2.

conducting path of our hybrid system in detail using a similar AlN-to-BN ratio to Case 2 but the different size of AlN particle. The mean particle size of AlN of Case 2′ (D_{AlN} = 25.5 μm) is slightly bigger than that of Case 2 (D_{AlN} = 14.4 μm), while the D_{BN} is fixed at 18 μm for both cases. Figure 5 compares the thermal conductivity and diffusivity of Case 2 and Case 2′, both exhibiting a parabolic behavior in the AlN-to-BN ratio. The maxima of the thermal properties appear at 1:1 in the AlN-to-BN ratio for both cases, but Case 2′ shows the thermal conductivity ca. 33% higher than that of Case 2.

As observed in the results in Figure 5, the relative size of the fillers seems to influence the thermal properties in a sensitive way. Accordingly, the particle size ratio (RD) of the AlN and BN particles may be defined as

$$R_D = \frac{D_{AlN}}{D_{BN}} \quad (1)$$

Using RD, the effect of relative particle sizes on the thermal conductivity and diffusivity may be examined. As summarized in Table 3 and Figure 6, RD of Case 1, Case 2, Case 2′, and Case 4 are 2.4, 0.8, 1.41, and 0.48, respectively. The corresponding thermal conductivities at the AlN-to-BN ratio of 1:1 are plotted as a function of RD in Figure 6(a). As can be seen, the thermal conductivity is high at around RD ≈ 1. Figure 6(b) schematically shows the bimodal distribution of particle sizes for Case 1, Case 2, Case 2′, and Case 3. The particle sizes of Case 2 and Case 2′ are close (RD ≈ 1) and, thus, the bimodal distribution gives a continuous shape at the valley of the two unimodal curves. We believe that this continuous valley lead two different particles packed well in the interstitial space to result in high thermal properties. On the other hand, the particles sizes of Case 1 and Case 3 are quite different (RD=2.4 and 0.48), two unimodal distribution curves of AlN and BN cannot be overlapped but disconnected. In this case, the interstitial space formed by each particle may not be efficiently filled by the other particle, which may very well give a poor thermal property. In addition, it should be mentioned that the composite systems having continuous bimodal distribution (Case 2 and 2′) show a parabolic feature and maximum value in thermal properties (see Figures 5 and 6). Overall, the highest thermal-transport properties may be achieved at the 1:1 ratio in AlN-to-BN composition having similar particle sizes (RD ≈ 1). When these two conditions are satisfied, it is preferred that DAlN > DBN to give thermal conductivity and

Case	Mean particle size (D_{50}) AlN	BN	Mean Particle size ratio, *R*
Case 1 (D_{AlN}>D_{BN})	14.4	6	2.4
Case 2	14.4	18	0.8
Case 2′ (D_{AlN}≈D_{BN})	25.5	18	1.41
Case 3 (D_{AlN}≈D_{BN})	8.7	18	0.48

Table 3 Comparing the effect of the mean

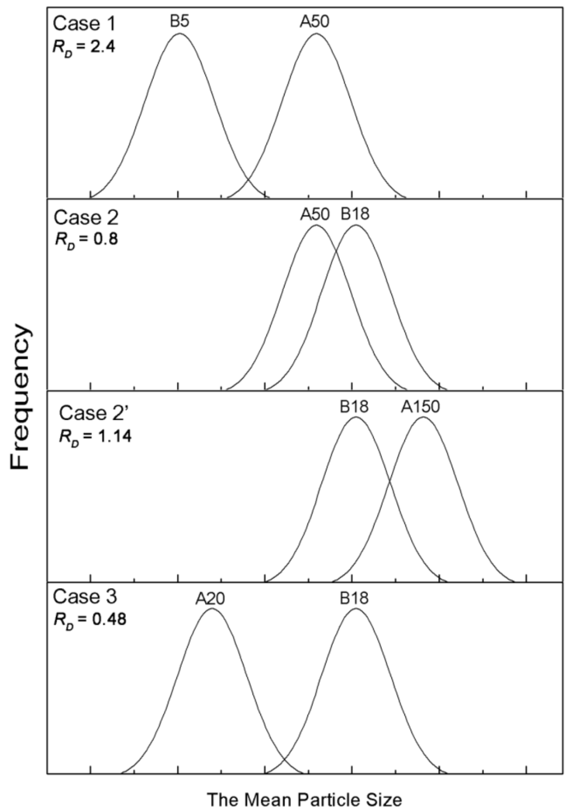

Figure 6. Thermal conductivities of hybrid composite systems at AlN to BN ratio of 1:1 plotted as a function of the particle size ratio, RD (a), bimodal distribution characteristics corresponding to Case 1, Case 2, Case 2′, and Case 3 (b).

diffusivity as high as 8.0 W/mK and 4.3 mm/sec, respectively, in this study.

4 Conclusion

The thermal conductivity of hybrid composite system was investigated using bimodal filler distribution with the different sizes and shapes of AlN and BN fillers. The thermal transport properties of composite in hybrid system are related in interfacial resistance, packing efficiency and bimodal size distribution characteristics due to the different particulate network, different interfaces formed with the relative compositions of AlN-to-BN. The optimal thermal conductive paths was found at the 1:1 ratio in AlN-to-BN composition having similar particle sizes (RD ≈ 1) due to the efficient packing and reduction of interfacial thermal resistance.

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