

Increasing the thermal conductivity of boron nitride and aluminum nitride particle epoxy-matrix composites by particle surface treatments

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Abstract—The thermal conductivity of boron nitride and aluminum nitride particle epoxy-matrix composites was increased by up to 97% by surface treatment of the particles prior to composite fabrication. The increase in thermal conductivity is due to decrease in the filler–matrix thermal contact resistance through the improvement of the interface between matrix and particles. Effective treatments for BN involved acetone, acids (nitric and sulfuric) and silane. The most effective treatment involved silane such that the coating resulted from the treatment amounted to 2.4% of the weight of the treated BN. The effectiveness of a treatment was higher for a larger BN volume fraction. At 57 vol.% BN, the thermal conductivity reached 10.3 W/m·K. The treatments had little effect on the specific surface area of the BN particles. Silane treatments were also effective for AlN. At 60 vol.% AlN, the thermal conductivity reached 11.0 W/m·K.

Keywords: Composite; thermal conductivity; polymer; epoxy; boron nitride; aluminum nitride; surface treatment; silane.

1. INTRODUCTION

Thermally conducting but electrically insulating materials are needed for die attachments, encapsulations, dielectrics and substrates used in electronic packaging. Metals are both thermally and electrically conducting, so they cannot be used for this purpose. Diamond is outstanding in its high thermal conductivity while it is electrically insulating, but it is expensive, even in powder form. Almost all polymers are electrically insulating, but they are also thermally insulating. Thus, polymers alone cannot be used for this purpose. On the other hand, polymers have low processing temperatures, which allow them to be easily made into polymer-matrix composites in bulk or coating forms. By using a filler which is thermally conducting but electrically insulating, a polymer-matrix composite can become thermally conducting while electrically insulating. Aluminum nitride particles [1, 2]

and boron nitride particles [3–7] are among the most effective ceramic fillers for these composites, due to their high thermal conductivity. Aluminum nitride suffers from its reactivity with water. Boron nitride does not have this problem. This paper is focused on the use of boron nitride and aluminum nitride particles as the filler.

For a given filler composition, there are methods to increase the thermal conductivity of the composite. They are (i) maximizing conductive paths, (ii) minimizing thermal resistance in each conductive path [7], and (iii) decreasing the thermal contact resistance at the filler–matrix interface. This paper addresses the third method, because this method has received little previous attention. The value of the third method stems from the tendency for gaps or other flaws to occur at the filler–matrix interface due to the insufficient affinity between filler and matrix. Such interfacial flaws cause a high thermal resistance at the interface, thus reducing the thermal conductivity of the composite [8, 9]. Richard Hill mentioned the importance of surface modification to the thermal conductivity of BN epoxy-matrix composites [3], but the method of modification was proprietary and not disclosed. This paper uses surface treatment of the filler to improve the affinity between filler and matrix, thereby significantly increasing the thermal conductivity of the composite. In particular, this paper uses silane coupling agents for surface treatment. Silane acts as a bridge to connect the ceramic filler and the polymer matrix together, because it has two different chemical structures at the two ends of the molecule. One end is chemically reactive with the polymer; the other end is chemically reactive with the surface of the ceramic filler. The surface treatment of AlN may have an additional function; the coating on the surface may protect AlN from the attack of water.

2. EXPERIMENTAL MATERIALS AND METHODS

The boron nitride particles were hexagonal BN, equiaxial in shape (as shown by scanning electron microscopy), 5–11 μm size, 280 W/m·K thermal conductivity, as provided by Advanced Ceramics Corporation, Cleveland, OH (Polartherm 180). Four types of surface treatments were used. They involved (i) acetone, (ii) nitric acid, (iii) sulfuric acid, and (iv) silane (Dow Corning Corp., Midland, MI, Z-6040, $\text{OCH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$). The epoxy structure at one end of the silane molecule allowed coupling to the epoxy matrix in the composites of this work.

Surface treatment of BN particles using silane Z-6040 involved (i) making a silane-water solution at a selected concentration, (ii) adding BN to the solution and stirring with a magnetic stirrer, (iii) heating at 60–70°C for 20 min, (iv) rinsing with water by filtration, and (v) drying at 110°C for 12 h.

Surface treatment of BN particles using an acid involved (i) immersing BN in acid in a beaker, (ii) stirring for 2 h with a magnetic stirrer, (iii) adding water and stirring

for 2 min, (iv) rinsing with water by filtration until water is neutral, and (v) drying at 110°C for 12 h.

Surface treatment of BN particles using acetone involved (i) immersing BN in acetone, (ii) stirring for 2 h, (iii) filtering, and (iv) drying at 110°C for 12 h.

The aluminum nitride particles were obtained from Advanced Refractory Technologies, Inc. (Buffalo, NY). The particles were made by direct nitridation, with average diameter 7 μm . In contrast to the BN particles, two types of silanes (Dow Corning Corp. Midland, MI, Z-6040 and Z-6020 $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$) were used to treat the surface of AlN particles. The amine group at one end of the silane Z-6020 molecule and the epoxy group at one end of the silane Z-6040 molecule allowed coupling to the epoxy matrix in the composite of this work. The amine group in the silane Z-6020 serves as a catalyst for the curing of the epoxy and consequently allows the silane coating to fully bond to the epoxy matrix and yields a better interface than in the case of silane Z-6040. Surface treatment for AlN using silanes involved (i) making an ethyl alcohol (200 proof) aqueous solution at a selected concentration, (ii) adding silane to the solution and stirring for 10 min by using a magnetic stirrer in a flask, (iii) adding AlN particles to the solution made in (ii) and stirring for 20 min, (iv) heating to 80°C and refluxing for 30 min while stirring and then cooling to room temperature, (v) rinsing with alcohol by filtration, and (vi) drying at 110°C for 12 h.

The polymer used was epoxy, Epon (R) Resin 813 and EPI-Cure (R) 3234 Curing Agent from Shell Chemical Co. (Houston, TX). The epoxy-matrix BN or AlN composites were fabricated by (i) mixing epoxy resin and curing agent in the weight ratio 100:13, (ii) adding filler and mixing, (iii) pressing at room temperature and 10.5 MPa for 2 h, and (iv) heating at 45°C and 10.5 MPa for 1 h to complete polymerization.

The particles with and without surface treatment were tested by measuring the weight loss upon heating to 600°C at 20°C/min under nitrogen gas flow (30 ml/min) protection, using a Perkin-Elmer TGA7 thermogravimetric analyzer. A sample in the amount of 25 mg was used for each test. The weight loss provides an indication of the amount of volatile or decomposable material on the particle.

The specific surface area (BET) of the BN particles with and without surface treatment was determined by nitrogen adsorption at 77 K and measurement of the pressure of the gas during adsorption using the Micromeritics ASAP 2010 instrument.

The surface elemental composition of the particles with and without surface treatment was analyzed by electron spectroscopy (ESCA).

The thermal conductivity (in $\text{W/m}\cdot\text{K}$) was given by the product of the thermal diffusivity (in mm^2/s), specific heat (in $\text{J/g}\cdot\text{K}$) and density (in g/cm^3). For measuring the thermal diffusivity, the laser flash method was used as shown in Fig. 1 [10, 11]. The pulse type Nd glass laser used for impulse heating was Coherent General Everpulse Model 11, which had a pulse duration of 0.4 ms, a wavelength of 1.06 μm , and a pulse energy up to 15 J. Adjustment of the capacitor

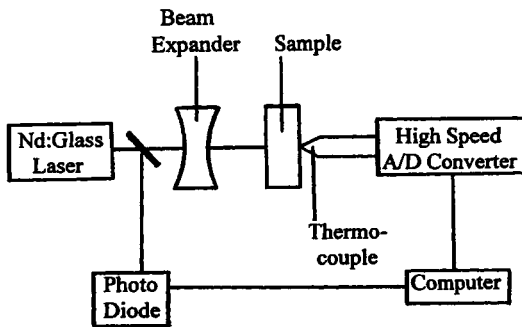


Figure 1. Schematic set-up of the laser flash thermal diffusivity analyzer used in this work.

discharge voltage permitted variation of the energy per pulse. The cylindrical sample to be measured was 0.5 in diameter, 2.0 to 3.5 mm in thickness, ground flat on both sides, coated with a thin gold layer on both sides and subsequently coated with carbon on the front side surface (the side on which the laser beam would hit). The gold layer was used to enhance the thermal contact and to prevent direct transmission of laser beam through the specimen (such as a transparent polymer sample). The carbon coating served to enhance absorption rather than reflection of the incident beam. The energy per pulse was adjusted so that the temperature rise of the specimen was between 0.8 to 1.0°C. The temperature of the specimen at the rear side was measured after the laser flash as a function of time by using a fast response (2 to 5 ms) and thin (5 μm) type E thermocouple (Omega CO2-E), which was attached directly to the rear surface of the sample. The temperature response of the thermocouple was monitored with a high resolution interface card (Omega WB-AAI-B) and with Labtech Notebook data acquisition software. The precision analog/digital interface card was set to measure DC volts with a resolution of 0.8 μV . The maximum data acquisition rate was 200 readings per second. The recording of the temperature rise was triggered by the laser, which was deflected upon firing to a PIN silicon photodiode (Hamamatsu Model S1223-01).

From the temperature *vs.* time curve, the thermal diffusivity in the direction through the thickness of the specimen was calculated by using an equation [6] through an iterative procedure, which was based on the least-squares method and optimization algorithm.

A stainless steel (NBS 1461) standard specimen (0.5 in diameter, 0.2 in thickness) obtained from National Institute of Standards and Technology (NIST) was used to calibrate the laser flash thermal diffusivity analyzer. Table 1 shows the thermal diffusivity of the standard sample measured as well as the value from NIST. From the comparison, one can see that the data measured using our laser flash thermal analyzer is close to the value from NIST.

A Perkin-Elmer differential scanning calorimeter (DSC-7) with UNIX specific heat software was used for measuring the specific heat. The specimen was in the

Table 1.

Thermal properties of NIST standard reference material (stainless steel) at 23 °C. Standard deviations are shown in parentheses

	From NIST	This work
Density (g/cm ³)	8.007 (0.002)	
Heat capacity (J/g·K)		0.47012 (0.00913)
Thermal diffusivity (mm ² /s)	3.8	3.67 (0.05)
Thermal conductivity (W/m·K)	14.32	13.81 (0.46)

form of a disc of diameter 6 mm and thickness 1 mm. The weight of each sample was in the range from 45 to 55 mg. All samples were crimped in non-hermetic aluminum pans with lids. A three-curve analysis method was used; it involved obtaining DSC sample, baseline, and reference material data. Sapphire was selected as the reference material.

3. RESULTS AND DISCUSSION

Figure 2 shows SEM photographs of as-received BN (Fig. 2a) and AlN (Fig. 2b) particles. Surface treatments did not cause any observable difference in the SEM photographs. Figure 3 shows SEM photographs of BN epoxy-matrix composite surfaces, which had been etched by an ethanol–NaOH solution for 30 h at 45 °C. Figure 3a shows the composite with 50 vol% BN and Fig. 3b shows the composite with 57 vol% BN. BN particles in the latter composite are more densely packed than those in the former composite. Figure 4 shows SEM photographs of the cross-section (obtained by fracture under shear in the direction perpendicular to the composite slab) of AlN epoxy-matrix composites with as-received AlN (Fig. 4a), silane (Z-6040) treated AlN (Fig. 4b) and silane (Z-6020) treated AlN (Fig. 4c) particles. Figure 4a shows cracks between the matrix and particles, and also bare particles due to the weak particle–matrix interface. Figure 4b shows no cracks and essentially no bare particles, indicating a stronger interface than that in the as-received AlN composite. Figure 4c shows no cracks and that all particle surfaces were covered by the matrix, indicating an even stronger interface and failure occurring within the matrix. Figure 5 shows SEM micrographs of the cross-section of BN epoxy-matrix composites containing as-received BN particles (Fig. 5a) and silane (2.4%) treated BN particles. Figure 5a shows cracks, bare particles, and holes caused by particle pull-out due to the poor interface between particles and matrix. Figure 5b shows no cracks, less bare particles and less holes, indicating the improvement of the interface.

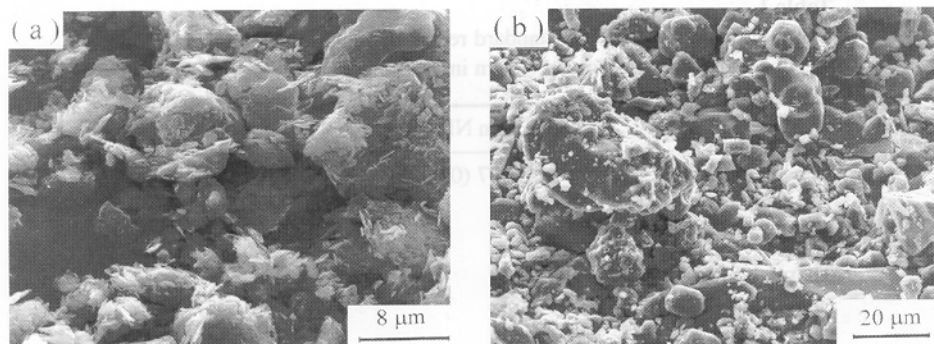


Figure 2. SEM micrographs of as-received BN (a) and AlN (b) particles.

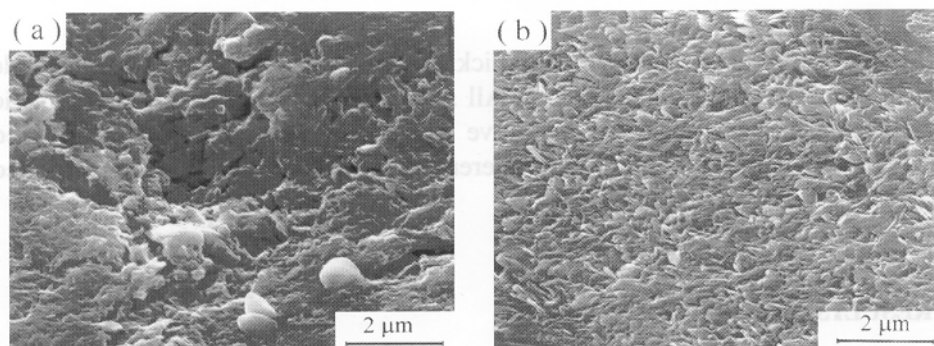


Figure 3. SEM micrographs of BN epoxy-matrix composite surfaces (after mechanical polishing and etching) (a) 50 vol.% BN, (b) 57 vol.% BN.

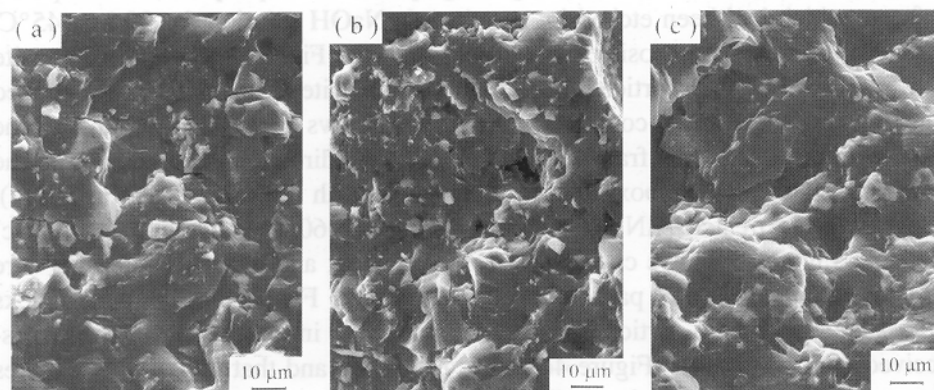


Figure 4. SEM micrographs of cross-section of AlN epoxy-matrix composites (without polishing or etching) containing (a) as-received AlN particles, (b) Z-6040 treated AlN particle, (c) Z-6020 treated AlN particles.

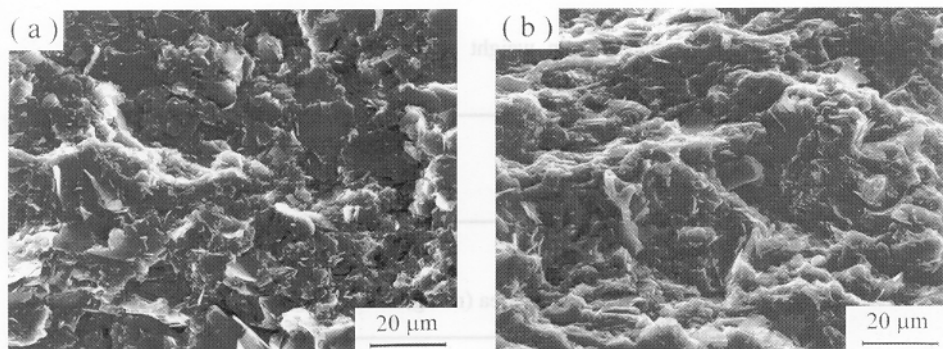


Figure 5. SEM micrographs of cross-section of BN epoxy-matrix composites containing (a) as-received BN particle, (b) silane (2.4%) treated BN particles.

Table 2.

Fractional loss in weight of BN particles upon heating to 600°C

As received	0.15%
Acetone treated	0.14%
HNO ₃ treated	0.10%
H ₂ SO ₄ treated	< 0.10%
Silane (0.7%)	0.7%
Silane (0.8%)	0.8%
Silane (2.4%)	2.4%

The fractional loss in weight of treated BN upon heating to 600°C is shown in Table 2. The amounts of volatile/decomposable material on the as-received, acetone treated and acid (HNO₃ or H₂SO₄) treated BN particles were negligible, indicating that treatments involving acetone and acids did not result in a coating on the particle. However, the amounts of weight loss on the silane treated BN particles were much higher, indicating that the silane treatment resulted in a coating on the particle, since the weight loss resulted from the decomposition of the coating at high temperature. By using silane-water solutions of three different concentrations, different amounts of coating resulted. The higher was the silane concentration in the solution, the greater was the amount of coating. The four silane treatments are hereby labeled by the corresponding fractional weight loss, e.g. silane (2.4%) treatment.

Table 3 shows the fractional loss in weight of treated AlN upon heating to 600°C. The volatile/decomposable materials on the silane Z-6040 and silane Z-6020 treated particles were higher than that on the as-received AlN particles, indicating that treatments involving silane resulted in a coating on the particles. The fractional loss in weight of silane treated AlN particles did not change much with the concentration of silane in the treatment solution, in contrast to the BN case. This difference between AlN and BN is due to the relatively

Table 3.

Fractional loss in weight of AlN particles upon heating to 600°C

As received	0.11%
Silane Z-6040 treated	0.35%
Silane Z-6020 treated	0.80%

Table 4.

BET specific surface area (m²/g) of BN particles

As received	10.8
Acetone treated	16.4
HNO ₃ treated	14.9
H ₂ SO ₄ treated	12.5
Silane (2.4%)	10.5

smooth AlN particle surface and the limited amount of active sites on the AlN surface.

Table 4 shows the specific surface area (BET) of BN particles with and without surface treatment. Acetone treatment increased the specific surface area from 10.8 to 16.4 m²/g, due to its cleansing function and consequent exposure of the true surface of the particle. Treatment with either acid also increased the specific surface area, but only by small amounts. Nitric acid treatment resulted in a slightly higher specific surface area than sulfuric acid treatment. However, both acid treatments resulted in lower specific surface areas than acetone treatment. The acid treatments also have a cleansing function, but acids are reactive and may change the surface morphology. On the other hand, the acid treatments did not have much effect on the surface, as shown by the maintaining of a low specific surface area after acid treatments. Silane (2.4%) treatment resulted in essentially no change in the specific surface area, compared to the as-received case. However, compared to the acetone washed case, the specific surface area was decreased, since the acetone washing allowed the true surface to be exposed and the silane treatment coated the surface.

The surface composition of the BN particles with and without surface treatment was analyzed by ESCA. The surface carbon, oxygen and silicon concentrations were much higher after silane (2.4%) treatment than for the as-received, acetone treated or H₂SO₄ treated particles (Table 5). This is because of the presence of these three elements in silane. The silane treated BN particle surface had less boron and nitrogen compared to as-received, acid treated and acetone treated BN particles (Table 5), because treated particles were partially covered by silane. The charge corrected binding energies (Si_{2p} and O_{1s}) of silane treated BN surface (Table 6) confirmed the existence of silane. Table 7 shows the ESCA results of AlN particles with and without treatment. The as-received particle surface has oxygen, probably in the form of aluminum oxynitride. Compared to the as-received AlN particles, that the Z-6040 treated particle surfaces have more silicon atoms, less nitrogen

Table 5.

Surface elemental composition (in at.%) of BN

Element	As-received	Acetone treated	H ₂ SO ₄ treated	Silane (2.4%) treated
B	44.2	44.6	42.7	34.8
N	41.5	40.2	38.2	31.2
C	11.1	12.5	13.6	19.8
O	3.2	2.8	4.4	11.0
Si	—	—	1.1	3.2

Table 6.

Charge corrected binding energies (eV) and possible assignment for silane treated BN

Energy level	Binding energy (eV)	Assignment
C _{1s}	285.0	(CH ₂) _n
	287.2	C—O
Si _{2p}	102.1	Organic silicone
B _{1s}	189.8	BN
O _{1s}	531.8	Si—O
N _{1s}	396.1	Metal nitride (tentative)
	397.8	BN

Table 7.

Surface elemental composition (in at.%) of AlN

Element	As-received	Silane Z-6040 treated	Silane Z-6020 treated
Al	33.9	28.4	25
N	15.5	12.2	15.8
C	26.8	22.4	30.2
O	23.8	35.5	23.7
Si	—	1.5	5.3

atoms, less aluminum atoms and more oxygen atoms is consistent with the fact that the surface is partly covered by the silane coating and that Z-6040 contains Si and O atoms. Compared to the as-received AlN particles, that the Z-6020 treated particle surface has more silicon atoms, fewer aluminum atoms and slightly more nitrogen atoms is consistent with the fact that the surface is partly covered by the silane coating and that Z-6020 contains Si, N and O atoms. Compared to silane Z-6040 treated AlN particles, that the silane Z-6020 treated AlN particle surface have fewer aluminum atoms, more carbon atoms and more silicon atoms resulted from that the silane Z-6020 treated AlN particle surface has been coated by more silane (which contains Si and C), as shown by thermogravimetric analysis (Table 3).

Table 8.

Charge corrected binding energies (eV) and possible assignment for silane Z-6020 treated AlN

Energy level	Binding energy (eV)	Assignment
C _{1s}	285.0	(CH ₂) _n
Si _{2p}	102.1	Organic silicone
Al _{2s}	120.2	AlN
Al _{2p}	74.1	AlN, Al ₂ O ₃
O _{1s}	531.7	Si—O
N _{1s}	397.0	AlN

That the silane Z-6020 treated AlN particle surface contains more nitrogen atoms and less oxygen atoms than the silane Z-6040 treated AlN particle surface is due to each silane Z-6020 molecule containing two nitrogen atoms and each silane Z-6040 molecule containing no nitrogen atom but more oxygen atoms. Table 8 shows the charge corrected binding energies of silane Z-6020 treated AlN particles, confirming the existence of silane groups on the particle surface. Tables 5–8 all indicate that BN and AlN particles have been coated by silane molecules after either silane treatment.

The thermal diffusivity, specific heat and thermal conductivity are shown in Tables 9 and 10 for composites with different volume fractions of BN and AlN particles (with and without treatment). The thermal conductivity increased with increasing filler volume fraction and the specific heat decreased with increasing filler volume fraction for each type of filler particles, due to the high thermal conductivity and low specific heat of filler compared to the polymer. At a fixed BN volume fraction, the thermal conductivity was increased by any of the treatments. The different treatments were different in their effectiveness in enhancing the thermal conductivity. Table 11 shows the fractional increases in thermal conductivity due to the treatments for two BN volume fractions. At either BN volume fraction, silane (2.4%) gave the greatest fractional increase in thermal conductivity; the lower was the silane content, the lower was the fractional increase in thermal conductivity, except for the silane (3.2%) treatment. At 57 vol.% BN, silane (0.8%) was more effective than H₂SO₄, whereas, at 44 vol.% BN, silane (0.8%) was less effective than H₂SO₄. H₂SO₄ was more effective than HNO₃ at either volume fraction of BN, though the difference was small at 57 vol.% BN. Silane (0.7%) was more effective than acetone, but was less effective than HNO₃ or H₂SO₄. Silane (3.2%) was less effective than silane (2.4%) or silane (0.8%) at either volume fraction of BN. Acetone was least effective at either volume fraction of BN.

The fractional increase in thermal conductivity due to surface treatment was much higher at 57 vol.% BN than at 44 vol.% BN for any BN condition. As shown in Table 11, the effect of all treatments at low volume fraction is not significant; however, it is remarkable at a high volume fraction. This means that the surface

Table 9.

Thermal conductivity, specific heat and thermal diffusivity of BN epoxy-matrix composites

BN Filler	Thermal diffusivity (mm ² /s)	Specific heat (J/g·K)	Thermal conductivity (W/m·K)
As received			
44 vol.%	2.70 (0.032)	0.941 (0.021)	4.27 (0.268)
57 vol.%	3.15 (0.047)	0.930 (0.020)	5.27 (0.49)
Acetone treated			
44 vol.%	2.83 (0.034)	0.943 (0.02)	4.48 (0.388)
57 vol.%	4.68 (0.045)	0.926 (0.019)	7.80 (0.72)
HNO ₃ treated			
44 vol.%	2.85 (0.027)	0.942 (0.02)	4.51 (0.354)
57 vol.%	5.11 (0.075)	0.927 (0.019)	8.52 (0.824)
H ₂ SO ₄ treated			
44 vol.%	3.03 (0.03)	0.941 (0.018)	4.79 (0.348)
57 vol.%	5.15 (0.057)	0.928 (0.021)	8.60 (0.80)
Silane (0.7%)			
44 vol.%	2.55 (0.027)	0.942 (0.021)	4.03 (0.248)
57 vol.%	4.58 (0.046)	0.930 (0.020)	7.67 (0.54)
Silane (0.8%)			
44 vol.%	2.91 (0.037)	0.943 (0.021)	4.61 (0.321)
57 vol.%	5.39 (0.064)	0.934 (0.023)	9.06 (0.87)
Silane (2.4%)			
44 vol.%	3.04 (0.03)	0.948 (0.022)	4.84 (0.293)
54 vol.%	4.24 (0.05)	0.938 (0.020)	7.08 (0.472)
57 vol.%	6.13 (0.11)	0.934 (0.023)	10.31 (0.754)

treatments are more important at a higher BN volume fraction, probably because of a higher tendency for adjacent particles to touch one another at the higher BN volume fraction and the positive effect of the treatments on the filler–filler interface quality.

The highest thermal conductivity was 10.3 W/m·K, exhibited by the composite with 57 vol.% BN particles that had been treated by silane (2.4%). This value is less than the value of 12.9 W/m·K for a BN epoxy-matrix composite containing 56 vol.% BN particles that had been surface treated by a proprietary process [3]. The higher thermal conductivity of the composite prepared by Hill [3] is at least partly due to the platelet shape of the BN particles there, in contrast to the equiaxial shape of the BN particles of this work.

HNO₃ treatment resulted in a higher specific surface area than H₂SO₄ treatment. Yet it resulted in a lower fractional increase in thermal conductivity than H₂SO₄ treatment. This indicates that a high specific surface area is not needed to attain a high thermal conductivity. The effectiveness of the acid treatments in enhancing

Table 10.

Thermal conductivity, specific heat and thermal diffusivity of AlN epoxy-matrix composites

AlN Filler	Thermal diffusivity (mm ² /s)	Specific heat (J/g·K)	Thermal conductivity (W/m·K)
As received			
40 vol.%	0.68 (0.022)	0.940 (0.020)	1.30 (0.108)
50 vol.%	1.74 (0.045)	0.921 (0.021)	3.52 (0.316)
60 vol.%	3.31 (0.05)	0.875 (0.027)	6.99 (0.668)
Silane Z-6040 treated			
40 vol.%	1.13 (0.05)	0.941 (0.02)	2.16 (0.23)
50 vol.%	2.19 (0.065)	0.923 (0.025)	4.45 (0.43)
60 vol.%	3.58 (0.072)	0.894 (0.02)	7.71 (0.067)
Silane Z-6020 treated			
40 vol.%	1.34 (0.046)	0.942 (0.022)	2.56 (0.26)
50 vol.%	2.60 (0.052)	0.925 (0.03)	5.29 (0.47)
60 vol.%	5.18 (0.067)	0.88 (0.03)	10.98 (0.97)

Table 11.

Fractional increase in thermal conductivity of BN epoxy-matrix composite due to BN surface treatment

	Fractional increase in thermal conductivity due to surface treatment	
	44 vol.% BN	57 vol.% BN
Acetone treated	4.9%	48%
HNO ₃ treated	5.6%	62%
H ₂ SO ₄ treated	12%	63%
Silane (0.7%)	-5.6%	46%
Silane (0.8%)	8.0%	72%
Silane (2.4%)	13%	96%

the thermal conductivity is probably due to certain surface functional groups that resulted from the treatments.

All silane treatments were effective in increasing the thermal conductivity. As the amount of silane coating on the particles increased, the thermal conductivity was enhanced more, until the silane concentration reached 2.4%. Further increase of the silane concentration to 3.2% caused the thermal conductivity to decrease. Hence, silane (2.4%) treatment was the most effective. This means that the coating resulting from the silane treatment must be sufficiently thick in order for the treatment to be fully effective. The coating serves as an interlayer at the filler-matrix interface, thereby improving the quality of the interface. However, if the coating is too thick, the interlayer will become less effective or even a thermal barrier, thereby decreasing the thermal conductivity.

Table 12.

Fractional increase in thermal conductivity of AlN epoxy-matrix composites due to AlN surface treatment

	Fractional increase in thermal conductivity due to silane surface treatment		
	40 vol.% AlN	50 vol.% AlN	60 vol.% AlN
Z-6040 treated	66.5%	26.4%	10.3%
Z-6020 treated	96.9%	50.3%	57.1%

Acetone treatment was effective due to its cleansing function. However, its effectiveness was not great.

At a fixed AlN volume fraction, the thermal conductivity was increased by either silane treatment. Table 12 shows that the fractional increase in thermal conductivity due to surface treatment is high for all three AlN volume fractions, especially for 40 vol.% AlN, in contrast to the trend for the BN case shown in Table 11. A possible reason is that the BN particle surface is not as smooth as the AlN particle surface (as shown in Fig. 2). A part of the silane coating in the BN case is absorbed by the BN particle surface instead of coupling to the reactive sites of the BN surface. Therefore the effectiveness of surface treatment in the BN case at low particle volume fractions is not as great as in the AlN case. At high particle volume fractions, the fractional increase in thermal conductivity is higher for BN than AlN, possibly because BN has higher thermal conductivity than AlN (BN 280 W/m·K, AlN 200 W/m·K). At the same AlN volume fraction, silane Z-6020 treatment was more effective than silane Z-6040 treatment for enhancing the thermal conductivity.

4. CONCLUSIONS

1. Surface treatment of BN and AlN particles is useful for increasing the thermal conductivity of BN and AlN particle epoxy-matrix composites by up to 97%.
2. At 44 vol.% BN, surface treatment effectiveness increases in the order: acetone, silane (3.2%), silane (0.7), HNO₃, silane (3.2%), silane (0.8%), H₂SO₄, silane (2.4%).
3. At 57 vol.% BN, surface treatment effectiveness increases in the order: acetone, silane (0.7%), acetone, HNO₃, H₂SO₄, silane (0.8%), silane (2.4%).
4. Surface treatment using silane Z-6040 (2.4%) is most effective for BN. At 57 vol.% BN, the thermal conductivity is 10.3 W/m·K.
5. Both silane Z-6020 and Z-6040 treatments are effective for AlN epoxy-matrix composites.
6. Silane Z-6020 treatment is more effective than silane Z-6040 treatment for AlN particles in enhancing the thermal conductivity. At 60 vol.% AlN treated by silane Z-6020, the thermal conductivity is 11.0 W/m·K.

7. The effectiveness in enhancing thermal conductivity by surface treatment is due to the decrease in the thermal contact resistance at the filler-matrix interface.

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