Interphase control of boron nitride/epoxy composites for high thermal conductivity

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Abstract

The effects of the surface treatment of boron nitride (BN) particles on the thermal conductivity of BN/epoxy composite systems was investigated. By coating an amino silane compatibilizer on the BN surface, the interfacial space could be decreased so as to minimize the phonon scattering and thermal-interface resistance. When an excessive amount of silane compatibilizer was present at the BN/epoxy interphase boundary, it acted as a thermal insulation layer, resulting in the reduction of the thermal conductivity. Accordingly, the thermal conductivity was maximized when the optimal amount of silane compatibilizer was used, which was associated with the specific surface area or the size of the incorporated BN particles. In the case of the BN particles, whose specific surface areas were 14.3 m²/g and 11 m²/g (average particle size: 1 µm and 5 µm, respectively), the highest thermal conductivity was observed at 3.0 wt% and 2.5 wt% of the silane compatibilizer, respectively. By converting the particle size and specific surface area into the shape factor, the optimal amount of amino silane required to maximize the thermal conductivity was discussed in relation with the interphase structure and thermal resistance.

Keywords: thermal conductivity, silane treatment, boron nitride

1. Introduction

Boron nitride (BN) has a similar plate structure to graphite and thus superior thermal conductivity, but it is a nonconductor of electricity(Yung and Liem, 2007). BN has been studied extensively as a filler to improve the thermal conductivity of a variety of polymer-based composite systems, most often in epoxy composite systems, which are applied to the packaging of electronic parts such as PCBs and EMCs(Lee et al., 2006; Nagai and Lai, 1997; Yung et al., 2007; Hsieh and Chung, 2006). In short, composite materials have different thermal conductivities depending on the size or loading content of the particles, characteristics of the interfaces, or relative thermal conductivities of the particles and resin.

The surface treatment of fillers is widely known to be an important factor for reducing the thermal resistance of the interfaces between the polymer and filler. Surface modification using silane in particular is the most widely known method. Based on the results of research on the surface treatment of particles using silanes, it is known that surface treatment can indeed play an important role in reducing the thermal resistance between the filler and polymer depending on the amount of silane; note, however, that the thermal conductivity may be reduced when an excessive amount of silane is used (Hsieh and Chung, 2006; Xu and Chung, 2000; Xie et al., 2004). In other words, using silane may initially increase the thermal conductivity, since it lowers...
the interface resistance, but an excessive amount may actually reduce the thermal conductivity. This suggests that there must be an optimum amount of silane to be used. Estimating and fully understanding this optimum amount of silane to secure the maximum thermal conductivity are very important in designing composite materials with guaranteed high thermal conductivity.

In this research, the change of the thermal conductivity depending on the amount of amino silane was studied using an epoxy composite material and BN fillers with a certain specific surface area; the optimum amount of amino silane for obtaining the maximum thermal conductivity was then monitored for each filler system. Furthermore, the relation between the amount of silane coating and the specific surface area and size of the particles was analyzed using the shape factor.

2. Experiment

2.1. Materials

In this research, BN with an average size of 5 µm purchased from DENKA (Japan) and BN with an average size of 1 µm purchased from SINTEC (England) were used. The detailed characteristics of the filler are shown in Table 1. Fig. 1(a) shows a scanning electron microscope image of the particles with an average size of 1 µm used in the experiment.

The epoxy resin was YD-128, a liquid-type standard epoxy resin derived from bisphenol A diglycidyl ether (DGEBA) supplied by Kukdo Chemical. The hardener, methyl tetrahydrophthalic anhydride (MTHPA), was HN-2200, also provided by Kukdo Chemical. The catalyst was 1-methylimidazole (1-MI) and the surface modifier was 3-aminopropyl-triethoxy silane (aminosilane); both were purchased from Aldrich.

Table 1. Fillers properties

<table>
<thead>
<tr>
<th>Filler</th>
<th>B1</th>
<th>B5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial grade</td>
<td>MBN</td>
<td>HGP</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>BN</td>
<td>BN</td>
</tr>
<tr>
<td>Tap Density (g/cm³)</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Particle Size(µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>-</td>
<td>1.9</td>
</tr>
<tr>
<td>D50</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>D90</td>
<td>-</td>
<td>10.6</td>
</tr>
<tr>
<td>Particle thickness</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>14.4</td>
<td>11.0</td>
</tr>
<tr>
<td>Oxygen Content (wt %)</td>
<td>5.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Fig. 1. The SEM image of (a) B1 particle, (b) its mixture with resin at 60 vol%, and (c) cured composite specimen of 60 vol% of B1 particle.

2.2. Preparing samples

Moderate amounts of filler and amino silane were added to acetone. After more than three hours of agitation at ambient temperature, the filler, whose surface was coated with silane, was obtained using a filter. The obtained filler was then placed in a vacuum oven at 120°C for two hours to dry (Hsieh and Chung, 2006). YD-128, MTHPA, and 1-MI were placed in a moderately-sized container and stirred well. The stirred resin was mixed with the surface-coated fillers evenly. The filler content was adjusted to 60 vol%. The mixture was then put into a 1 millimeter thick mold and a pressure of 3,000 psi was applied for 4 hours at 80°C and then for 2 hours at 145°C. Figs. 1(b) and 1(c) show the BN/epoxy mixture and cured specimens with a coin shape, respectively.

2.3. Analysis of properties

The scanning electron microscope was an FEI Helios 600 NanoLab. The specific surface area was measured using a Micromeritics Instruments Corporation ASAP 2020 (USA). The thermal diffusivity and specific heat were obtained using a Netzsch Nanoflash 447. The measurements were performed twice and the average was taken to calculate the thermal conductivity. The density was measured using Archimedes’ principle. The coin-shaped sample that was used had a thickness of 1 ±0.5 millimeters and diameter of 12.7 millimeters.

3. Results and Discussion

In the case of aluminum nitride (AIN), which is frequently used to increase the thermal conductivity of composite materials, the surface reacts sensitively to moisture in the air. The surface of AIN is converted into Al(OH)₃ as a result of the reaction with moisture in the air, and ammonia gas is produced as a byproduct (Kameshima et al., 1998). The surface roughness of AIN increases due to the reaction with moisture; contact with moisture over an extended period of time may reduce the thermal conductivity of AIN, because its surface will have been covered with coarse lumps created as a result of hydrolysis (Li et
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According to a research report, surface treatment using silane is very effective in protecting inorganic particles against moisture. Furthermore, surface treatment using silane in the case of a composite material is highly recommended to maximize the thermal conductivity, because the coupling agent allows the matrix to be connected with the filler through the various functional groups of silane, which can minimize the interfacial gap or space (Xu and Chung, 2000). Among the various silane chemicals, amino silane gives higher thermal conductivity than glycidyl silane in epoxy and amino systems (Xu et al., 2001).

Scheme 1 shows the reaction mechanism of amino silane to form silane layers on the surface of BN particles. The BN particles are produced through the thermal hydrolysis reduction process and, thus, –OH groups are present on its surface by nature (Li et al., 2005; Hubáček and Ueki, 1996). As shown in Scheme 1(a), the alkoxy groups (-OR) of silane react with the hydroxy groups (-OH) on the surface of the BN particles to form Si-O bonds through silanization reactions. In addition, as shown in Schemes 1(b) and (c), some of the -OR groups in the silane are converted to Si-OH by the alcoholysis reaction. These –OH and -NH₂ groups in the silane form hydrogen bonds with other silane molecules as well as –OH groups in the BN surface to form a robust aminosilane layer (see Scheme 1(d) (Fiorilli et al., 2008)). Finally, the -NH₂ groups in the aminosilane layer would react with the epoxide groups in DGEBA to give chemical bondings eventually connecting BN and the epoxy matrix, as shown in Scheme 1(e).

The aminosilane layer formed between the BN surface and epoxy matrix eventually determines the thermal resistance through the composites. If the amount of aminosilane is not sufficient to wet the BN surface, the air gap would insulate it, resulting in high thermal resistance. On the other hand, if the amount of aminosilane is excessive, forming a thick coating on the BN surface, the thermal resistance would become high, due to the coating thickness. In this sense, Fig. 2 shows four different cases corresponding to different features of the aminosilane layers, giving different thermal resistances or thermal conductivity. Fig. 2(a) shows the case where the aminosilane is absent and an air gap is developed to give an interfacial thermal resistance mostly due to the air gap ($R' = R_{air}$).
stemming from the phonon-scattering. The conductivity of air is fairly low at 0.026 W/mK as compared with epoxy (0.165 W/mK) or BN (60 W/mK) and, thus, \( R_a \) may well be very high. When the BN particles are treated with an amount of aminosilane which is not sufficient to fill the interfacial gap, as represented in Fig. 2(b), the thermal resistance of the total interfaces becomes the sum of the thermal resistances of the air gap \( R_{air} \) and aminosilane layer \( R_S \), viz. \( R^b = R_{air} + R_S \). In this case, the phonon scattering taking place in the air gap could be reduced by the silane layers and, thus, the thermal conductivity may well be slightly improved or similar to that of the air gap, i.e., \( R^a \geq R^b \). Fig. 2(c) shows the case where the air gap is completely filled, without excessive aminosilane existing at the interface, which may well give the lowest thermal resistance \( R^c = R_S \). Subsequently, when the amount of aminosilane becomes excessive at the interface, as shown in Fig. 2(d), the thermal resistance would increase with increasing thickness of the aminosilane layer, viz. \( R^d = R_S \). Comparing the cases in Fig. 2(c) and (d), it can be realized that \( R^c < R^d \), in the case where the aminosilane layers act as a thermal barrier to give a thermal resistance which increases with increasing thickness(Xu and Chung, 2000).

In the case of BN, the maximum thermal conductivity was reportedly obtained with 2.4 wt% of silane when the particle size was in the 5~11 µm range(Xu and Chung, 2000). Similarly, the thermal conductivity values vary with the amount of silane coupling agents in AlN composite systems. For example, when the average AlN particle size was 6.3 µm with a specific surface area of 0.6 m²/g, the maximum thermal conductivity was obtained at 1.0 wt% of aminosilane(Hsieh and Chung, 2006). Figs. 3 (a) and (b) show the thermal conductivities of the BN composite systems at 60 vol% of BN particles plotted as the amount of aminosilane coupling agent for BN particles with sizes of 1 µm (specified as B1) and 5 µm (specified as B5), respectively. The B1 composite specimen in Fig. 3(a) has an average particle size and specific surface area of 1 µm and 14.3 m²/g, whereas those of B5 in Fig. 3(b) are 5 µm and 11 m²/g, respectively. As can be seen, the maximum thermal conductivities of B1 and B5 appear at 3.0 and 2.5 wt% of aminosilane, respectively. Since the specific surface area (surface area per unit weight) depends on the particle size, the coating thickness of aminosilane may well be dependent on the particle size, resulting in different thermal conductivities. Thus, effective thickness of aminosilane can be calculated and expressed as:

\[
effective\text{ thickness} = \frac{\text{amount of aminosilane} \times \frac{1}{\rho}}{\text{specific surface area of filler}} \tag{1}
\]

where \( \rho \) is density of aminosilane. Based on Fig 3, calculating eqn. (1) using 3 and 2.5 wt% of aminosilane at the highest thermal conductivity of B1 and B5 composite, the optimal thickness of aminosilane layer is 2.2~2.4 nm, and which may well give the lowest thermal resistance. Also,
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aminosilane layer thickness becomes 3.6–3.8 nm using 5 and 4 wt% of aminosilane at the lowest thermal conductivity, which may become thermal insulator.

The effect of the particle shape on the thermal conductivity has been analyzed using the shape factor, which may quantify the particle packing with its size and thickness (Nielsen, L. E., 1974). Since the specific surface area depends on the size of the particles and the thermal conductivity depends on the thickness of the aminosilane layer, the shape factor \( A \) may be defined as follows to represent the thermal conductivity of our composite systems:

\[
A = \sqrt{\frac{D}{L}} \log \frac{D}{L}
\]

where \( D \) is the average particle size and \( L \) is the thickness of the particles. In the case of plate-type particles, the shape factor largely depends on the aspect ratio, which itself is affected by the particle size (Progelhof et al., 1976; Droval et al., 2006). The smaller the specific surface area is, the greater the shape factor becomes, corresponding to the fact that the specific surface area is inversely proportional to the particle size. In the case of B1, the shape factor \( A \) is 5.47, whereas that of B5 is 8.66, corresponding to the specific surface areas of B1 and B5 of 14.3 m\(^2\)/g and 11 m\(^2\)/g, respectively. Accordingly, as the shape factor decreases, the specific surface area increases and, consequently, the amount of aminosilane coating on the BN particles increases. As a result, the optimal amount of aminosilane which maximizes the thermal conductivity becomes 3 wt% for B1 and 2.5 wt% for B5, as also represented by their shape factors.

4. Conclusion

The thermal conductivity of BN particle/epoxy composite systems was investigated in order to identify the optimal amount of an aminosilane compatibilizer. The aminosilane coupling agent was expected to reduce the gap between the polymer and the surface of the BN filler, thereby improving the thermal conductivity of the composite material. If the thickness of the silane layer was in excess of a certain value, the thermal conductivity of the composite material decreased, due to the thermal resistance of the silane layer. The specific surface area was converted into the shape factor using the filler size and thickness, and the shape factor successfully represented the maximum thermal conductivity of the composite systems.

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References


