Development of Thermal Conductive PMMA/BN Electric Insulating Composite Material Using Electrostatic Adsorption Method

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Abstract—An electrostatic adsorption method can produce composite materials with an arbitrary structure by changing the ratio of the main particles to the adsorption particles. To develop a composite material with both a higher thermal conductivity and an acceptable breakdown strength (Fb: Field of Breakdown), the DC breakdown test and thermal conductivity test of polymethylmethacrylate (PMMA)/boron nitride (BN) composite material were performed. The Fb of the samples increased regardless of the type of BN filler as the pressure increased. The higher bonding force among the composite particles due to a high pressure leads to a higher Fb. The higher orientation probability of the longer direction of BN, which is perpendicular to the field (press) direction, might induce the higher Fb in the high-pressure sample. The thermal conductivity of the sample with a mixture of the agglomerate of the platelet BN and the platelet BN was higher than those of the other BN samples. The longer directions of the platelet BN and the agglomerate of the platelet BN were oriented perpendicular to the thickness direction. These results suggested that the reasonable strength and higher thermal conductivity were due to the orientation of the agglomerate of the platelet BN and the platelet BN mixture by the press.

Keywords—Electrostatic adsorption method; Breakdown strength; Thermal conductivity; Composite material

I. INTRODUCTION

Polymeric insulating materials are commonly applied to power apparatuses due to their higher insulating properties and excellent maintenance performances [1] [2]. Traditionally, additives and fillers have been used to improve the mechanical, the thermal, and sometimes electrical insulating properties [3] [4]. To achieve specific requirements, various composite materials as well as functional insulating materials, which have higher thermal conductivities with acceptable electrical breakdown strengths, have been developed. However, aging failures of insulating materials, which are important phenomena in terms of reliability and how each property (e.g., average distance between fillers) affects the electrical performance and thermal conductivity, must be understood to develop functional composites.

The electrostatic adsorption method can produce composite materials with arbitrary structures by changing the ratio of the main particles to the adsorption particles [5]. Because the electrostatic method does not require expensive or specially manufactured equipment, this method may reduce the cost to prepare functional composite materials. Furthermore, this method is easily scaled-up due to its simplicity. We have reported that the breakdown strength and the thermal conductivity of a polymethylmethacrylate (PMMA)/aluminium oxide (alumina) composite material using the electrostatic adsorption method can easily be adjusted by changing the pressure and the particle size[6].

To develop a composite with a higher thermal conductivity compared with that of the PMMA/alumina composite, a PMMA/boron nitride (BN) composite material is produced using an electrostatic adsorption method. Its breakdown strength and the thermal conductivity, which are important factors for the insulating and heat dissipation performances, are estimated.

II. SAMPLE AND EXPERIMENTAL PROCEDURE

Figure 1 schematically depicts the electrostatic adsorption method. PMMA particles with an average diameter of 4 μm were prepared as the “adsorption particles”. The PMMA...
adsorption particles, whose surface potential was adjusted to have a negative polarity using sodium deoxycholate (surfactant agent), were immersed in poly (diallyldimethylammonium chloride) (PDDA) (10 g/L), which is a polyelectrolyte. Because PDDA has a positive polarity that covers PMMA adsorption particles, the PMMA surface potential becomes positive. Then the solution was agitated at 20 rpm for 15 minutes using a stirrer. Afterwards, the particles were separated from the solution using a centrifugal machine. The rotation number and the centrifugal separation time were 3000 rpm (1720 xg) and 5 minutes, respectively. Next the PMMA adsorption particles with a positive surface potential were immersed in poly (styrenesulfonatesodium salt) (PSS) (10 g/L), reversing the polarity of the surface potential of the PMMA adsorption particles. The particles were again separated from the solution using a centrifugal machine. Finally, the polarity of the surface potential on the PMMA adsorption particles was adjusted so that it was negative. In a similar manner, PMMA adsorption particles with a positive surface potential and with a three-layer polyelectrolyte on the surface were also prepared.

On the other hand, BN particles with four different configurations were prepared as the main particles: platelet, a mixture of platelet agglomerate and platelet, spherical agglomerate, or low-density agglomerate. The platelet BN is a common hexagonal crystal. The other types were prepared to understand the influence of the BN configuration on each property.

The polyelectrolytes were stacked in four layers by a similar procedure, and the BN main particles with a negative surface potential were prepared. The PMMA adsorption particles with a positive surface potential and the BN main particles with a negative surface potential were mixed in deionized water; the PMMA adsorption particles were absorbed to the BN main particle surface by Coulomb force (Fig. 1). A composite particle consisting of the PMMA adsorption particle and a BN main particle was produced using the above procedure. The composite particles were cast into a disk configuration with a 10-mm diameter and 1-mm thickness by a hot-press after the composite particles were dried. The pressure, temperature, and hot-pressing time were 10 or 100 MPa, 200 °C, and 60 minutes, respectively.

The structures of the BN fillers, the composite particles, and the composite materials after hot-pressing were observed using a scanning electron microscope (SEM). In the electrical breakdown test, the sample was an approximately 0.3-mm-thick PMMA/BN composite. The material thickness was adjusted by polishing.

Figure 2 shows the experimental setup for the breakdown test, where the breakdown voltage was measured using a McKeown type electrode [7] under a DC ramp voltage with an increase rate of 1 kV/s at 30 °C. Furthermore, the thermal conductivity of the composite materials was also estimated using a laser flash method [8].

### Table 1. PMMA/BN composite materials produced by electrostatic adsorption method.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Main particle (particle size[μm])</th>
<th>Absorption particle (particle size[μm])</th>
<th>BN content [vol. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pBP-100</td>
<td>Single-Crystal Platelet(45)</td>
<td>PMMA(4)</td>
<td>62.4</td>
</tr>
<tr>
<td>pBP-10</td>
<td></td>
<td></td>
<td>60.7</td>
</tr>
<tr>
<td>mBP-100</td>
<td>Platelet Agglomerate and Platelet(15-20)</td>
<td></td>
<td>58.6</td>
</tr>
<tr>
<td>mBP-10</td>
<td></td>
<td></td>
<td>54.0</td>
</tr>
<tr>
<td>sBP-100</td>
<td>Spherical Agglomerate(55-65)</td>
<td></td>
<td>35.2</td>
</tr>
<tr>
<td>sBP-10</td>
<td></td>
<td></td>
<td>60.1</td>
</tr>
<tr>
<td>aBP-100</td>
<td>Low-Density Agglomerate(60)</td>
<td></td>
<td>16.9</td>
</tr>
<tr>
<td>aBP-10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

III. EXPERIMENTAL RESULT AND DISCUSSION

Table 1 shows the produced composite materials. The initial character, the second character, the third character, and the numerical number after the hyphen “-” in the sample name represent the BN configurations (p: platelet, m: mixture agglomerate of the platelet and platelet, s: spherical agglomerate, a: low-density agglomerate), the main particle substance (B:BN), the adsorption particle substance (P:PMMA) and the pressure of the hot-press (10 or 100), respectively. The BN content of the composite material $\nu_f$ (vol.%) was also estimated using the equation below on the assumption that the air gap do not exist in these composites [9].

$$\nu_f = \frac{\rho_c - \rho_e}{\rho_f - \rho_e} \times 100$$

where $\rho_c$ (g/cm³) is the mastered density of the composite material, $\rho_f$ (=2.2 g/cm³ [10]) is the density of BN, and $\rho_e$ (=1.19 g/cm³ [11]) is the density of PMMA. The mBP composite, the sBP composite, and the aBP composite contain BN agglomerates. The density of the BN agglomerate decreases in the following order: the agglomerate of the platelet BN in mBP composite > the spherical agglomerate BN in sBP sample > low-density agglomerate BN in aBP composite. Figure 3 shows the SEM images of the BN fillers and the composite particles. The PMMA adsorption particles absorb uniformly onto the BN main particle’s surface. Figure 4 shows the SEM images observed from the fracture surface perpendicular to the thickness direction. The longer direction...
of the BN particles in the composite material hot-pressed at a high pressure were oriented perpendicular to the press (or perpendicular to the thickness) compared to those at a low pressure regardless of the BN particle configuration. The BN contents of all the composite materials increased as the pressure increases (Table 1). The differences of the BN contents due to pressure in the sBP sample or the aBP sample were larger than those in the other samples. The BN agglomerate that collapsed at high pressure and air in the BN agglomerate may be removed.

Figure 5 shows the DC breakdown strength (Fb) and the thermal conductivity. The Fb was estimated by dividing the breakdown voltage by the thickness. The white and the black plots denote each Fb and the average Fb of four to five samples, respectively. The Fb of the sample hot-pressed at high pressure increased compared to that hot-pressed at a low pressure regardless of the BN particle configuration. The high pressure increased the bonding force between the PMMA adsorption particles. In addition, the longer direction of the BN particles was oriented perpendicular to the electrical field (or perpendicular to the press and the thickness). The thermal conductivities of the mBP composites showed higher values.
compared to the others. The existence of the agglomerate of the platelet BN in the mBP composite might prevent the longer direction of the platelet BN, which corresponds to the direction of higher thermal conductivity, from being oriented perpendicular to the thickness direction. As shown in Fig. 4 (c) and (d), it was observed that the longer direction of the platelet BN is actually oriented parallel to the thermal conduction measurement direction (=thickness direction) compared with those in the other samples. Therefore, the orientation probability of the longer direction of the platelet BN in the agglomerate in the thickness direction might be higher. In the mBP composite, the thermal conductivity of the sample hot-pressed at high pressure decreased compared to that hot-pressed at low pressure. The longer direction of the platelet BN was oriented perpendicular to the thickness direction due to high pressure.

In case of the pBP composite, the thermal conductivity of the sample hot-pressed at high pressure increased compared to that hot-pressed at low pressure. The longer direction of the platelet BN was naturally oriented perpendicular to the thickness direction regardless of the pressure intensity. The higher density of the sample hot-pressed at high pressure may induce the higher thermal conductivity.

For the sBP composite and the aBP composite, the thermal conductivities of the samples hot-pressed at high pressure agreed with those at low pressure. For low pressure, the spherical agglomerate of BN or the low-density agglomerate of BN due to low pressure do not collapse. At high pressure, the density increases due to the collapse of the agglomerates of BN due to high pressure, leading to the higher thermal conductivity. On the other hand, the orientation ratio of longer direction of the BN to electric field decreases, leading to the lower thermal conductivity. Therefore, the thermal conductivities between the samples hot-pressed at high pressure or at low pressure were apparently agreed.

Employing a mixture consisting of an agglomerate of the platelet BN and the platelet BN led to a reasonable breakdown and a higher thermal conductivity due to the appropriate orientation of the platelet BN and the agglomerate of the platelet BN.

IV. CONCLUSION

To develop a composite material possessing both a high thermal conductivity and acceptable breakdown strength, PMMA/BN composites was produced using an electrostatic adsorption method. The orientation of BN determined the breakdown strength and the thermal conductivity. Currently, a mixture of the agglomerate of the platelet BN and the platelet BN is the preferable filler configuration.

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