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Effects of amphiphilic agent on thermal conductivity of boron nitride/poly(vinyl butyral) composites☆

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ABSTRACT

Dependence of thermal conductivity of boron nitride (BN)/poly(vinyl butyral) (PVB) composites on the orientation and particle size of BN with an amphiphilic agent was investigated. The platelet BN particles were oriented in the polymer matrix by physical processes such as tape-casting process. A comparison of the thermal conductivity of the specimens with that of pristine BN showed that the BN/PVB composite treated with amphiphilic agents such as $C_{14}H_6O_8$ and $C_{27}H_{27}N_3O_2$ showed a higher thermal conductivity than the PVB composite with pristine BN. It was also found that the thermal conductivity of the $C_{14}H_6O_8$-treated BN/PVB composite was higher than that of the $C_{27}H_{27}N_3O_2$-treated composite due to the good dispersion and interfacial adhesion with $C_{14}H_6O_8$. Also, the thermal conductivity of the composite with an in-plane orientation of 8-μm-sized BN was higher than that of the composites with different particles sizes because of the improvement in the high degree of orientation.

1. Introduction

In the power industry, electrical insulating polymers incorporated with ceramic fillers are used to achieve specific electrical, mechanical, and thermal properties and to reduce the cost [1,2]. For solving heat-dissipation problems in microelectronics, several types of ceramics with high thermal conductivities have been used in ceramic/polymer composites to enhance heat dissipation [3–8]. The heat-transfer efficiency of ceramic/polymer composites depends greatly on the contact point between the ceramic filler and the matrix, the orientation of the ceramic filler that forms the path for heat dissipation, and the particle size and amount of the ceramic filler.

Hexagonal boron nitride (h-BN) is known to be a nonmetallic filler with a high intrinsic thermal conductivity, high temperature resistance, and excellent oxidation resistance. BN has a graphite-like structure, and changes its thermal conductivity with its anisotropy. When the platelet BN is aligned parallel to the heat flow, its thermal conductivity increases by a factor of nearly 20 compared to when the plane is aligned perpendicular to the heat flow [9]. Poly(vinyl butyral) (PVB) is widely used as a binder in ceramic processing because of its excellent adhesion to ceramic filler. Additionally, PVB has been used in ceramic polymer composites as the polymer matrix because of its good thermal conductivity (0.24 W/mK) [10].

It has been shown that surface treatments of the filler, such as the silane treatment, greatly improve the heat-transfer capability of the composites by enhancing the interfacial adhesion between the filler and the polymer matrix [11–15]. Takeshi studied catechin molecules, having numerous aromatic rings, that effectively interacted with a BN nanotube surface via π—π bonding in such a way that the catechin species acted as a mediator between the BN nanotubes and the polymer, improving the heat transfer between the matrix and the polymer [16].

Generally, an amphiphilic agent is composed of two groups; one is hydrophobic groups worked for hydrophobic ceramics, the other is hydrophilic groups worked for hydrophilic polymer. The interfacial behavior between ceramics and polymers could be improved due to these two groups of amphiphlic agents. However, the effects of the hydrophilic —OH groups of the catechin molecule on the thermal properties of the composites were not studied. The effect of the hydrophilic —OH group of an amphiphilic agent on the interfacial adhesion is of interest as part of the search for new amphiphilic agents, as well as the improvement of the thermal conductivity of ceramic/polymer composites.

In this study, the factors influencing the thermal conductivity of BN/PVB composites were investigated, i.e., the orientation and particle size of the BN. The dependence of the thermal conductivity

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of the BN/PVB composites on the type of amphiphilic agent was also studied using $C_{27}H_{27}N_3O_2$ and $C_{14}H_6O_8$, which have the same number of aromatic rings but different numbers of hydrophilic —OH groups. It is believed that the aromatic rings of $C_{27}H_{27}N_3O_2$ and $C_{14}H_6O_8$ promote strong π–π interactions with the BN surface. There is only one hydrophilic —OH group in $C_{27}H_{27}N_3O_2$, while $C_{14}H_6O_8$ has four per molecule. The effects of the amphiphilic agents with different numbers of hydroxyl bonds on the thermal conductivity of the BN/PVB composites are also discussed.

2. Experimental procedure

2.1. Materials

Hexagonal BN powders of different particle sizes were used as the thermal conductive fillers of the composite. The particle sizes of these ceramic powders were 4, 8, and 10 μm. The average diameters of these platelet powders were determined using a particle size analyser (Model S3500, Nikkiso, USA). A polymeric compound (BM2L380, CS Technology, Korea) comprising PVB was chosen as the matrix for the composites. 2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol ($C_{27}H_{27}N_3O_2$, Sigma–Aldrich, USA) and ellagic acid hydrate ($C_{14}H_6O_8 \cdot xH_2O$, Sigma–Aldrich, UK) were used as the amphiphilic agents.

2.2. Specimen preparation

To prepare the amphiphilic-agent-treated BN, the amphiphilic agents and BN powders were mixed in a toluene/dimethyl sulphoxide (DMSO) mixture at 150 °C for 6 h by magnetic stirring. Afterwards, the powders were transferred to a suction flask, filtered and washed with ethanol, and then dried at 80 °C for 24 h. To the polymeric compound, which is liquid at room temperature, was added the BN powders to obtain the desired volume fraction (V_f) of 0.3. The ceramic and polymer compound was then mixed and transferred to a vacuum chamber to remove air. To obtain composites filled with oriented ceramic particles, the air-free slurry was poured into a tape-casting machine and then laminated to a height of 5 mm at 5 MPa and 70 °C. These laminated films were re-pressed at 10 MPa and 90 °C for 200 s by a hot press. To measure the composites with orientation, the prepared bulk specimens were cut in dimensions of $5 \times 5 \times 1\,mm^3$. The composites with the oriented BN particles were prepared such that the platelet BN was aligned parallel (in-plane orientation) or perpendicular (transverse orientation) to the thermal path.

2.3. Analysis of properties

The surface-treated particles were tested by measuring the weight loss upon heating to 700 °C at a heating rate of 20 °C/min under vacuum using an elemental analysis system (EA, Model CE1110, CE instrument Ltd., UK). The weight loss value provides an indication of the amount of the amphiphilic agent present on the BN particle. Fourier-transform infrared spectroscopy (FT-IR) of the particle was performed on a Bruker IFS-66/S spectrometer (Bruker UK Ltd., Convetry, UK) from 4000 to 400 cm^{-1}. The changes in the amphiphilic-agent-treated BN were observed in the FT-IR spectra. The density of the specimens was measured using a gas pycnometer (GP, Model AccuPyc1330, Micromeritics, USA). X-ray diffraction analysis (XRD, Model D/Max-3C, Rigaku, Japan) was conducted to determine the degree of orientation of the BN ceramics in the polymer composites. The orientation of the platelet fillers in the composites was observed using scanning electron microscopy (SEM, Model JSM-7500F, Jeol, Japan). The thermal conductivity of the composite was obtained using a laser flash apparatus (LFA, Model LFA-447, Netzsch, Germany), along with the thermal diffusivity and specific heat capacity. Differential scanning calorimetry (DSC, Model EXSTAR-6000, Seiko, Japan) was used to obtain the specific heat capacity of the composite at room temperature.

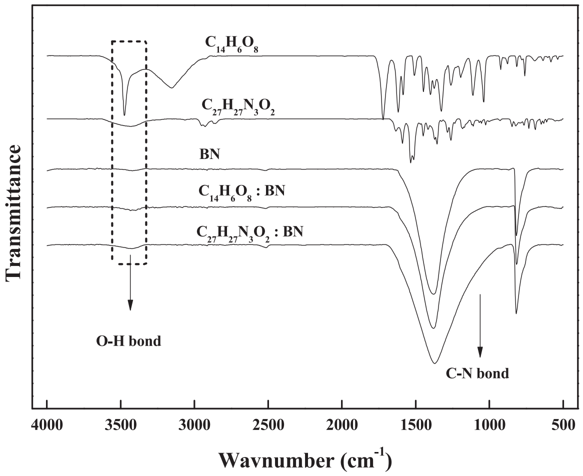

Fig. 1. Fourier-transform infrared spectroscopy (FT-IR) spectra of pristine BN and amphiphilic-agent-treated BN.

3. Results and discussion

To prepare the amphiphilic-agent-treated BN, the relative ratio of the amphiphilic agent to the BN was determined to be 5–1. $C_{27}H_{27}N_3O_2$ and $C_{14}H_6O_8$ were dispersed in different solvents (toluene and DMSO, respectively) at 150 °C in concentrations of 20 wt%. Each amphiphilic agent completely dissolved in its respective solvent. The BN particles were added to the solution, followed by magnetic stirring, suction flask filtering with ethanol washing, and drying at 80 °C for 24 h.

Fig. 1 shows the FT-IR spectra of the pristine BN, amphiphilic agents, and amphiphilic-agent-treated BN. The pristine BN exhibits characteristic absorption bands at 1363 and 817 cm^{-1} from the in-plane vibrations of hexagonal B—N and transverse vibrations of B—N—B bonds, respectively [17]. Compared with the spectrum of the pristine BN, the O—H bond intensity was slightly increased in the spectra of amphiphilic-agent-treated BN (~3500 cm^{-1}). This result was obtained due to the hydroxyl groups in the amphiphilic agent. Additionally, the $C_{27}H_{27}N_3O_2$-treated BN showed C—N bond stretching (~1000 cm^{-1}) [18]. From these results, we confirmed that the hydrogen signal in the elemental analysis arises from the amphiphilic agent molecules.

The fractional loss in the weight of the amphiphilic-agent-treated BN upon heating to 700 °C is shown in Table 1. The weight loss is observed only in the amphiphilic-agent-treated BN particles, indicating that these BN particles contain organic materials. As the size of the particles increased, the weight loss of the specimens decreased. This result could be attributed to the decrease in the specific surface area with the increase in the particle size. The surface composition of the amphiphilic-agent-treated 8-μm-sized BN particles was compared with that of the

Table 1
Fractional weight loss of boron nitride (BN) particles upon heating to 700 °C.

Particle size of BN	Amphiphilic agent	Weight loss (%)	Carbon (%)
4 μm	$C_{27}H_{27}N_3O_2$	0.158	2.0314
8 μm	Pristine BN	0.052	–
	$C_{14}H_6O_8$	0.148	1.2572
	$C_{27}H_{27}N_3O_2$	0.149	1.8818
10 μm	$C_{27}H_{27}N_3O_2$	0.142	1.7538