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Pyrolysis behavior of polysilazane and polysilazane-coated-boron nitride for high thermal conductive composite

Kiho Kim, Hyun Ju, Jooheon Kim*

School of Chemical Engineering & Materials Science, Chung-Ang University, Seoul, 156-756, Republic of Korea

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A thermally conductive composite was fabricated using a BN filler and an epoxy matrix. Because of electrostatic repulsion force, the BN/epoxy composite had poor interfacial affinity, which led to a decrease in the thermal conductivity. To enhance the interfacial affinity, pre-ceramic polysilazane (PSZ) was introduced onto the BN surface and it was sintered in various conditions. PSZ was converted to different structure depended on pyrolysis conditions. After the pyrolysis, the PSZ was converted into a SiOC ceramic in nitrogen atmosphere, and to SiO_2 and ash in air atmosphere. The thermal conductivity of the BN-PSZ/epoxy composite decreased as the pyrolysis temperature was increased because of the decomposition of polar functional groups. Pyrolysis at 300 °C in nitrogen atmosphere yielded the highest performance, resulting in an increase in the thermal conductivity to 3.521 W $m^{-1}K^{-1}$ at 70 wt% of filler, which was a 1.35-fold increase compared with the raw BN/epoxy composite.

1. Introduction

Despite the rapid progress in the field of electronic devices over the last few decades, the continued miniaturization of electronic-device components faces significant problems associated with heat dissipation [1–3]. It is well known that there is an exponential relationship between the reliability of an electronic device and the operating temperature of the junction; a small difference in the temperature can result in a two-fold reduction in the lifespan of the device. Therefore, to maintain the operation temperatures of a device at the desired level, it is crucial that the heat generated by the device is dissipated as quickly and effectively as possible [4].

In electronic devices, three kinds of components are applied for heat dissipation. The first is a heat sink, which releases heat into the air via radiation. In this case, heat emissivity and thermal conductivity are important factors. A heat sink is made of aluminum and attached to the heating device or circuit board [5]. The second is a thermal interface material (TIM), which fill the gaps between asperities in order to minimize the thermal contact resistance between the device and the heat sink or printed circuit board (PCB) [6]. The third is a high-thermal-conductive plastic circuit board, which spreads the heat and transfers it from the device to the heat sink. In the case of TIMs and PCBs, high thermal conductivities and good mechanical properties are important [7]. Generally, TIMs and PCBs are made of epoxy resin because of their good processability, adhesive strength, and electrical insulation, which is one of the most important properties for packaging materials in order to prevent electrical leakage and shortage. Unfortunately, epoxy resin is a poor thermal conductor (~0.2 W/mK) for transporting unwanted heat out of hot spots. To enhance the thermal conductivity of epoxy resin, many researchers have introduced high thermal conductivity solid materials as fillers, such as carbonaceous materials (carbon nanotube, graphene), metallic materials (copper, aluminum), and ceramic materials (AlN, BN, Al_2O_3, SiC). Among these, carbonaceous and metallic materials have a good electrical conductivity, which is a limitation for fabricating high thermal conductive composite with a high filler concentration. Therefore, high thermal conductivity and electrical insulating ceramic materials have been widely applied as fillers in recent thermally conductive composites [8–10].

Among the ceramic materials, several studies have focused on hexagonal BN as a filler because of its high thermal conductivity, high chemical resistivity, attractive electrical insulating property, and low dielectricity. These properties make BN an attractive material for many applications, e.g., refractory materials, lubricants, optical coatings, and ceramic composites [11,12]. Unfortunately, BN is very difficult to handle because its surface is very inert, which leads to poor interfacial adhesion between BN and the matrix in a

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* Corresponding author.
E-mail address: jooheonkim@cau.ac.kr (J. Kim).

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composite [13]. The transport of heat in nonmetals occurs through lattice vibrations in the solid [14]. Hence, in a composite, the heat-transfer efficiency depends greatly on the contact point between the filler and the matrix. A good contact between the two phases is critical for the heat-flow efficiency. And, surface treatments of the filler is one of the promising method for improving the interfacial adhesion between the filler and the polymer matrix. Commonly, surface modification via chemical bonding significantly improve the heat transfer capability of composite [15,16]. However, due to the outstanding chemical resistivity and absence of functional group onto surface, chemical modification of BN is very hard and required strong chemical agent [17,18]. Therefore, in order to effectively use BN to thermal conductive filler, appropriate surface modification method should be demanded.

In this study, the organic polysilazane (PSZ) was adopted to BN surface coating material. Polysilazane is a polymer whose backbone consists of alternating Si and N atoms with pendent carbon-containing groups. It is widely used in precursors of ceramics, coating solutions, and blending applications. PSZ coatings have good thermal stability, are electrically insulating, and provide oxidation and corrosion resistance [19,20]. Moreover, the simple process step for particle coating is the most important advantage for BN due to its extremely high stability. The processing of coatings based on polymer-derived ceramics (PDCs) can be divided into two steps: (i) shaping (varnish techniques such as spraying or dip coating) followed by the crosslinking of the precursors to an infusible network and (ii) conversion into an amorphous or crystalline ceramic by pyrolysis. The microstructure, composition, and mechanical and chemical properties of PDCs mainly depend on the not only precursor system, the degree of crosslinking but also the pyrolysis temperature, humidity and the pyrolysis atmosphere [21,22]. Thus, sufficient knowledge of the conversion behavior of the precursors into polymeric- and ceramic-like coatings is essential. Moreover, it is almost not studied for BN particle surface modification and thermal conductive filler application. So, the structural difference was studied using FT-IR and XPS analysis after pyrolysis in various atmospheres and temperature. And, the resulting PSZ-coated BN was used as a filler for a high thermal conductivity ceramic/polymer composite material.

2. Experimental

2.1. Fabrication of PSZ-coated BN particle

PSZ was applied on BN (hexagonal plate shape, average size is 12 μm) via dip coating. First, BN particles were entirely dipped into a PSZ solution in a vacuum oven at room temperature for 1 h. Subsequently, the BN/PSZ mixture was filtered to remove the excess PSZ solution, and the filtered PSZ-coated BN was placed in a convection oven at 160 °C to allow the moisture-crosslinking of PSZ on the particle surface. During drying, the PSZ-coated BN was gently ground every 20 min to prevent aggregation for 2 h and then kept in an oven for 24 h. Finally, the dried particles were heat-treated at 300, 500, and 700 °C in air and N_2 atmospheres during 4 h for the sintering of the PSZ. The specimens name depended on pyrolysis conditions were summarized in Table 1.

2.2. Preparation of BN/epoxy composites

An epoxy-terminated dimethysiloxane (ETDS) oligomer was obtained from Shin-Etsu Silicones (KF-105, equivalent weight = 490 g/eq., density = 0.99 g/cm^3). On the basis of our previous study, the weight ratio of the epoxy to the curing agent was determined to provide efficient flexibility of the matrix. In the present study, the equivalent weight ratio of ETDS and 4.4′-Diamino diphenylmethane (DDM) was 1:2. 1.9 g of DDM was placed in a three-neck round flask equipped with a reflux condenser and preheated to 100 °C. 9.5 g of the ETDS resin was added, and the mixture was heated in an oil bath at 110 °C for 1 h in a N_2 atmosphere. The bubbles were removed by placing the mixture in a vacuum oven for 30 min at room temperature. The composites were prepared by solution blending and a casting method consisting of (a) adding filler to the epoxy resin (30, 40, 50, 60, 70 wt%) for ~2 h with the minimum amount of ethanol until the synthesized materials were completely mixed, (b) fabricating the composite films with a uniform thickness via a doctor blade on a Teflon mold, (c) pre-curing the films at 100 °C for 1 h in the vacuum oven until no air bubbles appeared on the surface followed by post-curing at 180 °C for 5 h, and (d) cooling to room temperature.

2.3. Characterization

Thermogravimetric analysis (TGA; TGA-2050, TA instruments) of the samples was carried out to examine the thermal degradation. Samples of 4 mg were heated to 800 °C at a heating rate of 10 °C/min under a nitrogen and air atmosphere. Fourier-transform infrared (FTIR; Parkin-Elmer Spectrum One) and X-ray photoelectron spectroscopy (XPS; VG-Microtech, ESCA2000) were employed to analyze the PSZ coating on BN and chemical structure after pyrolysis. For FTIR spectroscopy, the scans were performed using radiation in the frequency range of 400 to 4000 cm^{-1}. Field-emission scanning electron microscopy (FESEM, Carl Zeiss, Sigma) high resolution transmission electron microscopy (HR-TEM, JEM-3010, Japan) were used to inspect the particle morphologies before and after PSZ coating and to investigate the film cross-sections. The samples were sputtered with a thin layer of platinum before the FESEM observations to avoid charge accumulation. The thermal diffusivity (δ, mm$^2\cdot$s^{-1}) was measured at room temperature on disk samples using the laser-flash method (Netzsch Instruments Co. NanoFlash LFA 467). The specific heat, C (J$\cdot$g^{-1}K^{-1}), at room temperature was measured on the disk samples by differential scanning calorimetry (Perkin-Elmer Inc. DSC-7), and the bulk density, ρ_{comp} (g$\cdot$cm^{-3}), of the specimens was measured using the water-displacement method. The thermal conductivity κ (W$\cdot$m^{-1}K^{-1}) of the samples was calculated by multiplying their density, specific heat capacity, and thermal diffusivity. The contact angle of the sessile drop formed on PSZ films was directly measured using a contact angle goniometer (model:100-00-(115/220)-S, Rame-Hart,

Table 1
The specimen name of PSZ and PSZ-coated-BN according to various pyrolysis conditions.

	Atmosphere	Pyrolysis temperature [°C]		
		300	500	700
Raw PSZ	Nitrogen	PSZ-N_2-300	PSZ-N_2-500	PSZ-N_2-700
	Air	PSZ-air-300	PSZ-air-500	PSZ-air-700
PSZ coated BN	Nitrogen	BN-PSZ-N_2-300	BN-PSZ-N_2-500	BN-PSZ-N_2-700
	Air	BN-PSZ-air-300	BN-PSZ-air-500	BN-PSZ-air-700