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Enhancing the effective thermal conductivity of Kapton-type polyimide sheets via the use of hexagonal boron nitride

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ABSTRACT

The effect that filler size and content exerts on the out-of-plane effective thermal conductivities (TCs) of hexagonal boron nitride (hBN) and Kapton-type polyimide (PI) (hBN/PI) composite sheets was investigated in an effort to enhance the TCs of Kapton-type PI sheets. A TC-measurement apparatus that was devised based on the steady-state method was adopted. The apparatus was constructed in-house, and its validity was established. In this study, the effective TCs of composite sheets were increased with increases in the hBN size and volume fraction. The enhancement behaviors of the effective TCs obtained in the present work reasonably approximated the data in the literature regardless of the differences in either the preparation method of the composite or the monomer species of the PI. The Hamilton and Crosser model could reproduce the experimentally enhanced levels of effective TCs for all hBN/PI composites via adjustments to the configuration factors for hBN.

1. Introduction

As functional devices such as the electronic semiconductors and components of advanced motors in electric vehicles become smaller and more highly integrated, high levels of heat density and non-uniformity of temperature threatens to seriously reduce product lifetime. Therefore, advanced thermal management is required to ensure the performance of devices for long periods [1–3]. Among the materials that are used in electrical devices, polymers play important roles as electrical insulating material, shock-absorbing material, and as packaging material, because polymers offer many advantages compared with inorganic materials such as metals and ceramics [4]. In particular, one of the most important roles of polymers in these devices is as a thermal interface material (TIM) that can fill the gaps between a heat sink and a heat source. The TIM reduces the heat resistance caused by the air layers of a gap in order to effectively release the heat into a heat sink. However, the thermal conductivities (TCs) of polymers are normally quite low. Therefore, many research groups have sought to enhance the TCs of polymer materials via the addition of high thermal conductive fillers such as ceramics and functional carbons into the polymer [5–10].

Polyimides (PIs) show excellent thermal stability compared with other engineering plastics [11]. Therefore, PIs are expected to find use as TIMs for high-temperature applications. Research on thermal conductive filler/PI composites can be found in the literature, but only a few studies have focused on PI composites compared with epoxy resins. Ceramic fillers have shown relatively low levels of electrical conductivity, which is appropriate for use in electrical insulation. Among them, hexagonal boron nitride (hBN) has gained much attention due to a high level of TC and chemical stability. Only a limited number of studies on the effective TC for hBN/PI composites have been reported thus far. Li and Hsu investigated the effect that different sizes of mixed hBN fillers exert on the effective TC of the hBN/PI composites [12]. The effective TCs of hBN/PI composites and a mixture of (hBN + aluminum nitride)/PI composites were investigated by Kuo et al. In that case, PI synthesized from 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane and 4,4′-oxydiphthalic dianhydride that could be dissolved in tetrahydrofuran was used, and the fillers were mixed directly with the PI rather than with a polyamic acid (PAA) of a precursor of PI [13]. Recently, Yang et al. modified the surface properties of hBN using a silane coupling agent to improve the interfacial affinity between the hBN and the PI matrix to enhance the effective TC [14]. Diaham et al. also experimentally investigated the effective TCs of BN/PI composites using 120 nm of hBN and 40 nm of wurtzite type BN. They also performed a theoretical study using four types of well-known thermal conductive models, which are referred to as the Bruggeman and Hamilton-Crosser models [15].

Studies of hBN/PI composites are limited in number, although the films and sheets of hBN/PI composites are considered promising functional materials for use in a wide range of industrial fields, particularly in the electrical industry. Therefore, there remains a need for the systematic accumulation of data addressing the relationships between the properties of the materials and their effective TCs. Studies on a thermal

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conductive model are also required because only a few theoretical studies have focused on hBN/PI composites. In the present work, the effects of hBN size and content on out-of-plane effective TCs for hBN/PI composite sheets were investigated. This study was focused on Kapton-type PIs synthesized from pyromellitic dianhydride (PMDA) and 4,4′-diaminodiphenyl ether (ODA), which are considered to be among the most thermally stable PIs. In addition to the reports of the experimental values, the experimental results for the enhancement of the effective TCs were compared with values found in the literature values in order to discuss the influence of the differences in preparation methods and species of PIs. Moreover, the experimental data were correlated using the thermal conductive models to reinforce the discussion about hBN addition from a theoretical view. Furthermore, in the experiment, a hand-built apparatus was developed and used to evaluate the effective TCs of the composite sheets. Therefore, the procedure used to test the validity of the apparatus is also reported.

2. Experiment

2.1. Materials

PMDA with a purity > 97 mol% and ODA with a purity > 97 mol% are Kapton-type PI monomers that were purchased from Sigma-Aldrich Co. They were dehydrated at 150 °C for 60 min before use. N,N-Dimethylformamide (DMF) with a purity > 99.5 vol% was used as a reaction media and was purchased from Nacalai Tesque Co. The hBN fillers had median diameters of 11 μm (A_hBN) and 0.2–0.8 μm (C_hBN) and were supplied from Showa Denko Co., and hBN with a median diameter of 5 μm (B_hBN) was supplied from Denka Co. In order to convert weight fraction to volume fraction, a density of 2.27 g/cm^3 was adopted for hBN, regardless of the actual size. The values of the median diameters and density of hBNs reported by the suppliers were used in the present work.

Several thicknesses of Kapton sheets (Toray-Dupon Co.), polytetrafluoroethylene (PTFE) sheets (Nilaco Co.), and stainless steel (SUS304 for JIS, X5CrNi18-10 for ISO) plates were also used to evaluate the validity of the apparatus for the TC measurement. The crystallinity of PTFE sheets was estimated using differential scanning calorimetry and the literature values for the heat of fusion for 100% crystalline PTFE [16,17]. The average value of the crystallinity of the PTFE sheets was 27%.

2.2. Preparation of the composite materials

The scheme for the preparation of composite materials is summarized in Fig. 1. A glass flask containing ODA dissolved in DMF at a certain concentration was cooled in an ice bath, and the solution was mixed well using a stirring bar. PMDA with the same molar number as that of ODA was added to the ODA + DMF solution, and that solution was also stirred for 1 h. Stirring of the solution was then continued at room temperature for 23 h to obtain PAA. A certain amount of hBN was introduced into the PAA solution in the glass vial (ϕ27.5 mm, 20 mL), and they were stirred using a stirring bar at about 200 rpm. The stirring method is described in detail in the Results and Discussions section. The solution was then applied to a stainless (SUS304) plate using a spatula to form a sheet, which was then let stand under ambient atmosphere for 1 h. The solution on the plate was introduced into a vacuum oven (DP33, Yamato Scientific Co.) set to 60 °C. After 15 min had passed, the air inside the oven was evacuated. The temperature in the oven was maintained at 60 °C for 45 min. The sheet was then dried at 100 °C for 1 h, followed by further drying at 150 °C for 1 h. The sheet that had dried on the plate was ejected from the oven and was imidized on a hot plate at 250 °C for 1 h under ambient atmosphere. The hBN/PI composite sheet was then separated from the stainless plate. Estimation of the volume fraction of hBNs required the density of PI, and 1.42 g/cm^3 was used based on the values of commercial PIs. The dispersion

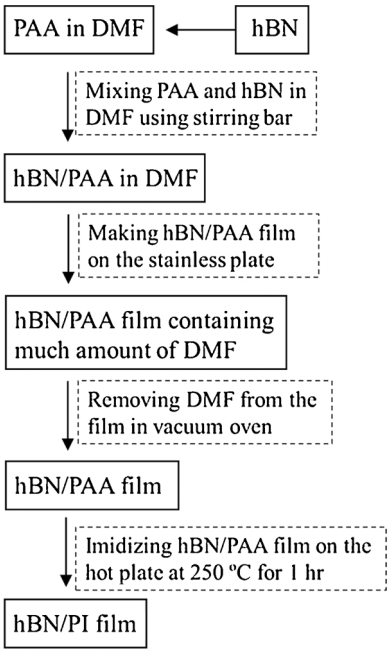

Fig. 1. Procedure of preparing hBN/PI composites.

behavior of the hBNs in the sheet was investigated using a digital microscope (VH-5500, Keyence Co.) and a field emission scanning electron microscope (SEM, S-4500, Hitachi Co.). Moreover, the degrees of imidization were checked via Fourier transform infrared spectroscopy (FT-IR, FT720, Horiba Co.) using the KBr method. The FT-IR spectra of plain PI and representative hBN/PI composites are described in Fig. S1 of the supplementary material. As shown in the figure, the PAA seemed completely imidized to the PI. The thermal stability was also measured under an air atmosphere using a thermogravimetric analyzer (TGA, TGA-50, Shimadzu Co.). The effective TCs of the composite sheets were measured using a hand-built apparatus that is explained in the next section.

2.3. Preparation and method for effective TC measurement

In the present work, out-of-plane TCs were measured using a self-built apparatus that was based on a temperature gradient, steady-state method reported in the literature [18,19]. The apparatus was self-built and validated by measuring the TCs of Kapton and PTFE sheets along with a SUS304 plate. The apparatus developed in the present work is shown in Fig. 2. It featured a band heater (MB1A1JN2, Sakaguchi E.H VOC Co.) as a heat source, two cylindrical rods made of tough pitch copper that conducted heat from the band heater to the sample and discharged it into a water bath. The rods were 20 mm in diameter, and the lengths of the upper and bottom side rods were 150 and 250 mm, respectively. A data logger (midi logger GL240, Graphtec Co.) recorded the temperatures that were measured at 10 different points of the copper rods using K-type thermocouples, as shown in the figure.

Each sample was cut into disc shapes with diameters of 20 mm, and their thicknesses were measured using a micrometer (MDC-25SX, Mitsutoyo Co.) before TC measurements. Both surfaces of the samples were thinly coated with a thermal conductive paste (SCH-20: 0.84 W/(m K), Sunhayato Co.) to reduce the thermal resistance at the interfaces between the samples and the copper rods. Each sample was then placed between the two copper rods with heat supplied from the top edge of the upper-side by the band heater with a constant AC voltage adjusted via an electric transformer. The temperature of the copper rods was monitored at 10 points in order to maintain a steady-state temperature distribution. For a 50 μm commercial Kapton sheet, the temperatures measured at the 10 points of the copper rods are shown in Fig. 2(b) after