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Enhanced Thermal Conductivity of Polyimide Films via a Hybrid of Micro- and Nano-Sized Boron Nitride

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ABSTRACT

A new thermally conductive polyimide composite film has been developed. It is based on a dispersion of different particle sizes of boron nitride (BN) in a polyimide (PI) precursor, polyamic acid (PAA). Subsequently, thermal imidization of PAA at 350 ^{o}C produced the corresponding polyimide composites. 3-Mercaptopropionic acid (MPA) was used as the surfactant to modify the boron nitride (BN) surface for the dispersion of boron nitride (BN) in the polymer. The PI/BN composites showed different thermal conductivities at different proportion of BN particle sizes and film thicknesses. The thermal conductivity of the PI/BN composite was up to 4 W/m-k, for a mixture containing 30 wt% of micro and nano-sized BN fillers in the polyimide matrix. The PI/BN composites had excellent thermal properties. Their glass transition temperatures were above 360 ^{o}C, and thermal decomposition temperatures were over 536 ^{o}C.

1. INTRODUCTION

Polymer composites have versatile applications in different fields, because of their unique electrical, thermal, mechanical and optical properties. Especially, the dispersion of thermally conductive fillers in an insulating polymer matrix can result in an increase in thermal conductivity of the polymer. Owing to the demands in denser and faster circuits in electronic devices, the dissipation of heat generated in electronic components has attracted more attention and is considered as a critical issue to be resolved. To solve the heat dissipation problem, ceramic fillers, such as alumina (Al_2O_3), silica (SiO_2), silicone carbide (SiC), silicon nitride (Si_3N_4), aluminum nitride (AlN) and boron nitride (BN), were used as the thermal conductive materials embedded in a polymer matrix. Among them, the BN with a hexagonal structure (h-BN) has the greatest potential due to its high thermal conductivity (up to 400 W/m-k) and relatively low dielectric constant (around 4), compared with SiC, Si_3N_4, Al_2O_3 and AlN. The h-BN also exhibits excellent resistance to oxidation and chemical corrosion. The heat transport mechanism of the non-metals is explained by the flow of phonons or lattice vibration energy. Hence, the polymer/ceramics composites form a thermally conductive path or network, which can decrease the heat generated by the phonon scattering in the polymer matrix. The conventional method to fabricate the thermally conductive composites is to use different filler-type mixtures or high solids loading of thermally conductive fillers to form a thermally conductive network. However, these polymers are mostly epoxy resins, which cannot be operated at high temperatures, and the thermal conductive composite of these film types are seldom discussed.

Polyimides are widely used in microelectronics and aerospace industries as a material for electronic packaging and electrical insulating due to its excellent thermal stability, mechanical properties and low dielectric constant. Here, we report the preparation and properties of high temperature, highly thermally conductive composite materials, containing different proportions of micro-sized and nano-sized BN particles dispersed in the polyimide (PI) matrix. The combination of micro-sized and nano-sized BN particles with an appropriate ratio gives the highest thermal conductivity. To the best of our knowledge, no one has reported this method used in polyimide films before. The surface modification of the BN fillers, and the thermal properties of the thermal conductive PI/BN composite films will be discussed.

2. Results and discussion

2.1. Preparation and homogeneity of PI/BN composites

PMDA-ODA polyimide was used as the polymer matrix due to its thermal stability and conventional use in microelectronic applications. The formulations of BN compositions in polyimide matrix are shown in Table 1. Different sizes of thermal conductive BN fillers were used as the conductive filler in this study, because of their excellent thermal conductivity and low dielectric constant in comparison to other ceramic fillers, such as SiC, Al_2O_3, AlN. However, the dispersion of the BN particles into the polymer matrix is an important issue for the composite film fabrication. Simple blending of BN particles and PI precursor resulted in the aggregation of BN particles due to the different polarities between the organic and inorganic phases. One of the best ways to uniformly disperse the inorganic phase into a polymer matrix is to functionalize the surface of the inorganic phase with organic surfactants. 3-Mercaptopropionic acid (MPA) was used as the surfactant in this study to functionalize the BN surface. The carboxylic acid group of the surfactant can be used to modify the BN surface to prevent agglomeration, and enhance its compatibility with the polymer matrix. The FT-IR spectra were used to investigate the MPA-modified BN particles. The absorption peak at 818 cm^{-1} was attributed to out-of-plane bending absorption of the amino groups, and the absorption peak at around 1385 cm^{-1} was B-N bond vibration. The MPA-modified BN with an absorption peak at 1681 cm^{-1}, which can be clearly distinguished from the unmodified BN due to the carboxylic acid (C=O) group of MPA. The EDX analysis also confirmed that the BN fillers were embedded in the polyimide matrix.

TABLE 1: Formulations of BN Compositions in Polyimide Matrix

Filler type	Material/size/ratio
mBN	h-BN[a]/1 μm/100%
7mBN	h-BN/1 μm/70%, h-BN/70nm/30%
3mBN	h-BN/1 μm /30%, h-BN/70nm/70%
nBN	h-BN/70nm/100%

[a] h-BN: hexagonal boron nitride.

2.2. Thermal properties of PI/BN composite films

The thermal properties of PI/mBN, PI/7mBN, PI/3mBN and PI/nBN exhibited similar behavior. The pure PI displayed high thermo-oxidative stability. The thermo-oxidative decomposition behavior of PI/BN composites was similar to that of pure PI. The decomposition temperature of PI/7mBN composites shifted to a slightly higher temperature, which indicated that the thermo-oxidative stability of PI membranes can be increased slightly with the increase of BN content. The thermal properties of the PI/7mBN composites are summarized in Table 2. The glass transition temperatures of the PI/BN composites are higher than the parent PI. This indicates that the BN fillers could increase the Tg of polymers. Coefficient of thermal expansion (CTE) of PI/BN composite films is also crucial to prevent the mismatch with other electronic components, such as copper and aluminum (16~23 μm/m ^{o}C). The in-plane CTEs of PI/BN composite membranes are shown in Figure 4. The CTE of pristine PI film was 44 (μm/m ^{o}C). It was found that the CTEs of PI/BN composite films decreased with increasing amounts of BN. The CTE of PI/mBN30 composite was reduced to 19 μm /m ^{o}C, a decrease of 57 % relative to that of pure PI. In addition, the PI/nBN30 was reduced to 32 μm /m ^{o}C, a decrease of 27 % relative to that of pure PI. The CTEs of PI/7mBN30 and PI/3mBN30 were around 27 μm /m ^{o}C. The magnitude of the CTE depends on the structure of the materials. For composite materials, the CTE are dependent on each component phase and also the interactions between each phase. Hence, the significant reduction of CTE in PI/BN films should originate from adequate dispersion and interfacial physical bonding between the BN and polyimide matrix. The higher BN filler loading and higher micro-size BN particles ratio can restrain the mobility of loose molecular bonds in the polymer chains during the increase of temperature.

TABLE 2. Thermal Properties of PI/BN Composites

	Tg[a]	CTE[b] (μm/m ^{o}C)	T$_5$[c] wt% loss (^{o}C)	Residue
PI	368	44	523	0
PI/7mBN10	380	30	536	8.2
PI/7mBN20	382	29	538	19.5
PI/7mBN30	382	27	537	28.9

[a] Coefficient of thermal expansion, measured by TMA in the temperature range of 100–250 ˚C.

[b] Glass transition temperature, identified by TMA.

[c] Temperature of 5% weight loss, as determined by TGA .

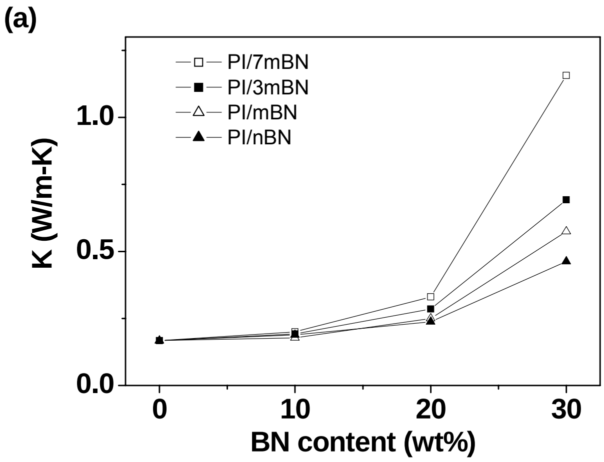
2.3. Thermal Conductivity of PI/BN composite films

Compared with other thermally conductive fillers, BN is a softer filler, which can attain a higher packing density at a low filler content and provide a larger surface contact between micro- and nano-particles than other ceramic thermally conductive fillers. Lee's study also confirmed that the BN fillers have a maximum packing fraction below 30 vol% (around 68 wt%) that can form a thermally conductive network when compared to other fillers. Hence, the BN filler is the best candidate for fabricating the thermally conductive composite films at low filler content. Figure 1 shows the thermally conductivity values of

PI/BN composite films with different micro and nano-sizes of BN particles measured by the Hot Disk equipment. The thermal conductivity of the composite films increased with increasing BN fraction. The PI/7mBN and PI/3mBN have higher conductivity than PI/mBN and PI/nBN, due to the mixture of different BN particle sizes. The PI/7mBN composite films show the highest thermal conductivity of 1.16 W/m-K at 30 wt% of BN content as shown in Figure 7(a). The high thermal conductivity can be explained by the appropriate ratio of micro to nano-sized BN particles in the polyimide film, which forms a random conductive bridge or network. In the PI/BN composite films with both micro- and nano-sized BN particles as thermally conductive fillers, the thermally conductive network can be easily created. The micro-sized BN particles formed the main thermally conductive path in composites, and the nano-sized BN particles played as the connection role between micro-sized BN particles to enhance more contact to obtain high thermal conductivity. This thermal conductivity value is about five times higher than that of the polyimide matrix. Figure 7(b) exhibits the thermal conductivity with various PI/BN composite film thicknesses. Thermal conductivity increased with increasing film thickness. This is due to that the thermal conductivity (κ) is related to thermal diffusivity (α) as in the following equation:

$$\kappa(W/mK)=\alpha(m^2/s)\rho(kg/m^3)c(J/kgK)$$

where ρ and c are the density and specific heat of the film, respectively. Thermal conductivity is an intrinsic property of a homogeneous material and should not be dependent on its thickness. However, in our study, the thermal diffusivity of the composite films is dependent on the film thickness due to the heterogeneous phases between the BN fillers and the polyimide matrix. The reasonable account for this phenomenon is that the variation of thermal diffusivity with the thickness of the film may originate from either the microstructure dependent thermal diffusivity of the thin film material or a change in the interface thermal resistance between the different phases, or from both. At the film thickness of 70 μm, the PI/7mBN composite film displayed the highest thermal conductivity of 4 W/m-K. PI/BN composite films with high thermal conductivity could have a great potential for use as heat dissipative materials in microelectronics and flexible print circuit boards.



(b)

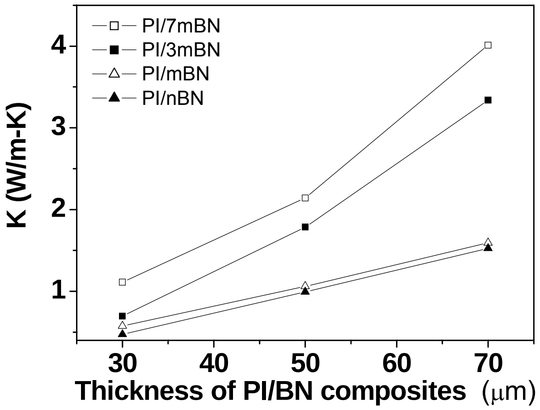


Figure 1. Thermal conductivity of PI/BN composite films with (a) different BN contents and (b) different film thicknesses.

3. Conclusions

The polyimide composites containing a hybrid filler of micro and nano-sized BN filler were found to have enhanced thermal conductivity. A thermally conductive composite can be prepared from surface modified BN particles embedded in a polyimide. The composites became highly thermally conductive when an appropriate ratio of micro and nano-sized BN particles was added into the insulating polymer matrix. This phenomenon appeared when the BN weight fraction was sufficient to form the thermally conductive path to dissipate the generated heat. The polyimide composites consisting of 30 wt% of micro and nano-sized BN at the weight ratio of 7:3 showed the highest thermal conductivity. Due to the excellent thermal properties, the PI/BN nanocomposite films have the potential for use in high temperature microfabrication of heat dissipative components in microelectronic industry.

REFERENCES

Shimazaki, Y.; Hojo, F.; Takezawa, (2009) Y. *Appl. Mater. Interfaces*. *1*(2), 225-227.

Lee, W. S.; Yu, (2005) J. *Diamond Relat. Mater. 14*, 1647-1653.

Hussain, M.; Oku, Y.; Nakahira, A.; Niihara, K. (1996) *Mater. Lett. 26*, 177-184.

Zhou, W.; Wang, C.; Ai, T.; Wu, K.; Zhao, F.; Gu, H. (2009) *Compos. Part A 40*, 830-836.

Wang, J.; Yi, X. S. (2003) *J. Appl. Polym. Sci. 89*, 3913-3917.

Yung, K. C.; Liem, H. (2007) *J. Appl. Polym. Sci. 106*, 3587-3591.