

Effect of BN filler on thermal properties of HDPE matrix composites

Yeon Kyung Shin^a, Woo Sung Lee^b, Myong Jae Yoo^b, Eung Soo Kim^{a,*}

^aDepartment of Materials Engineering, Kyonggi University, Suwon 443-760, Republic of Korea

^bElectronic Materials & Device Research Center, Korea Electronics Technology Institute, Seongnam 463-816, Republic of Korea

Available online 16 October 2012

Abstract

The effects of boron nitride (BN) content and particle size on the thermal properties of BN/high density polyethylene (HDPE) composites were investigated. The thermal conductivities and thermal diffusivities of the composites were dependent on the BN content. For composites with same amount of BN, the thermal conductivity and thermal diffusivity increased with an increase in the size of the BN particles. Composites with a mixture of different-sized BN particles exhibited higher thermal conductivities than those of composites with single-sized BN particles. The specific heat capacities of the composites were also affected by the BN content and particle size. Several theoretical models were employed to predict the effective thermal conductivities of the composites, and the predicted values were compared with those obtained experimentally.

© 2012 Published by Elsevier Ltd and Techna Group S.r.l.

Keywords: A. Extrusion; B. Composites; C. Thermal conductivity

1. Introduction

For electronic packaging applications, materials with high thermal conductivities are required to dissipate the heat generated by the electronic component effectively. Polymers are often used in these applications, in addition to being employed as substrate materials, because of their low dielectric properties and ease of processing. However, the thermal conductivities of polymers are usually very low. Therefore, there is a need to investigate ceramics-filled polymer composites that have high thermal conductivities [1–4].

Generally, the thermal conductivity of ceramic-filled polymer composites increases with increasing ceramic content and particle size. Particles with a high aspect ratio such as flake- or fibre-shaped particles exhibit the bridging phenomenon to a larger degree. This assists in the formation of a conductive path because the percolation threshold for such particles is lower than that of spherical particles. However, high-aspect-ratio particles have low packing densities due to their increased porosity [3]. Usage of a mixture of different-sized ceramic particles would increase the thermal conductivity of composites [5–8], as the

packing densities of such composites would be higher than those of composites with single-sized ceramic particles.

Flakes of BN were used as the filler in this study due to their high conductivity, excellent temperature resistance, light-weight nature, and moderate cost [1]. High-density polyethylene (HDPE) was used as the polymer matrix since HDPE is an engineering thermo-plastic used in several industrial applications due to its low cost, desirable mechanical properties, and ease of processing.

Therefore, the thermal conductivity of BN/HDPE composites was investigated on the basis of the volume fraction (V_f) and size of the BN flakes. In addition, several theoretical models were employed to predict the effective thermal conductivities of the composites, and the predicted values were compared with those obtained experimentally.

2. Experimental procedures

Powders (99.5%, Changsung Corp., Korea) comprising BN flakes of different sizes were chosen as the fillers for the polymer matrix composites. The sizes of the BN flakes in the ceramic powders used in this study were 3 μm , 10 μm , and 20 μm . HDPE (99.9%, Yuhwa Korea Petrochemical Ind. Co., Korea) was used as a matrix for the composites. The BN powders and HDPE were weighed as per the

*Corresponding author. Tel.: +82 31 249 9764; fax: +82 31 244 6300.
E-mail address: eskim@kyonggi.ac.kr (E.S. Kim).

desired composite compositions and mixed in a chamber at 200 °C at a speed of 30 rpm for 20 min. The mixture was hot-pressed under a pressure of 15 MPa for 30 min at 200 °C and cooled to room temperature.

The apparent densities of the composites were measured by the Archimedes' method. X-ray diffraction (XRD) analysis (D/Max-2500V/PC, Rigaku, Japan) was used to determine the content and the size of the particles in the BN powders. The microstructures of the composites were observed by scanning electron microscopy (SEM) (JSM-6500F, Jeol, Japan). The specific heat capacities (C_p) and the thermal diffusivities were measured by differential scanning calorimetry (DSC) (Model DSC 200F3, Netzsch, Germany) and by a laser flash apparatus (LFA) (Model LFA447, Netzsch, Germany), respectively. The thermal conductivities of the composites were obtained using their densities, specific heat capacities, and thermal diffusivities.

3. Results and discussion

3.1. Physical properties of composites

The X-ray diffraction patterns for the BN/HDPE composites with various volume fractions (V_f) and BN-particle sizes are shown in Fig. 1. The semi-crystalline phase of HDPE and the single crystalline phase of BN (JCPDS no. 37-109) could be detected. With an increase in the BN content, the intensity of the peak for HDPE decreased. For a given BN content, the intensity of the peak for HDPE increased with a decrease in the size of the BN particles.

The peaks for the composites with a mixture of 3 μm - and 20 μm -sized BN particles exhibited intensities that were between the intensities of the peaks for the composites with BN particles with sizes of 3 μm and 20 μm ,

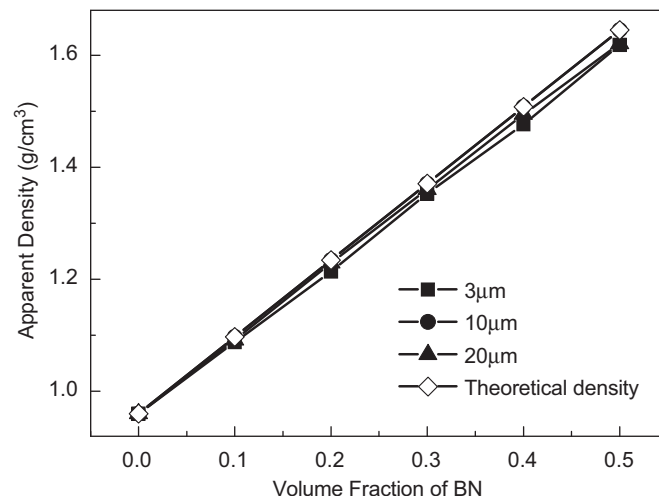


Fig. 2. Apparent and theoretical densities of the BN/HDPE composites with various volume fractions and BN-particle sizes.

respectively. The XRD patterns did not show peaks for any reaction compounds of BN and HDPE, suggesting that no chemical reaction took place between the BN particles and HDPE.

Fig. 2 shows the apparent and theoretical densities of the composites with various volume fractions (V_f). The apparent and theoretical densities of the composites increased with an increase in the BN content as the density of the BN particles is higher than that of HDPE. For composites with same amount of BN particles, the apparent density did not change markedly with BN-particle size. With increasing BN content, the difference between the apparent and theoretical densities of the composites increased because of the pores induced at the interface between polymer and ceramics [3].

SEM micrographs of the composites with various volume fractions and BN-particle sizes are shown in Fig. 3. With increasing BN content (Fig. 3(a–c)), the distance between the BN particles decreased. That is to say that connectivity among the BN particles as well as the interfacial area between BN and HDPE increased. The composites with a mixture of 3 μm - and 20 μm -sized BN particles showed larger conductive networks than did the composites with single-sized BN particles (Fig. 3(d) and (e)). The composites with various volume fractions and BN-particle sizes had the BN particles uniformly dispersed within the HDPE matrix, with melted HDPE completely covering the BN particles, resulting in the low porosity of the composites.

3.2. Thermal properties of composite

The thermal diffusivities and specific heat capacities of the composites with various volume fractions and BN-particle sizes are shown in Table 1. With increasing BN content, the thermal diffusivity of the composites increased, while the specific heat capacity decreased. These

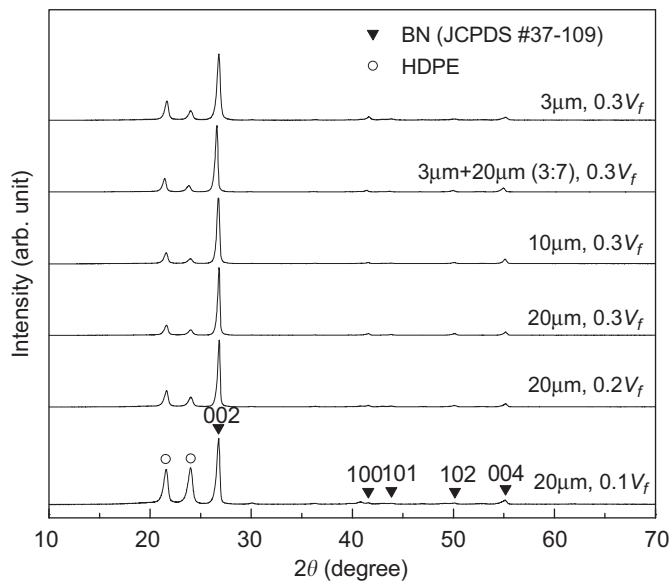


Fig. 1. X-ray diffraction patterns for the BN/HDPE composites with various volume fractions (V_f) and BN-particle sizes.

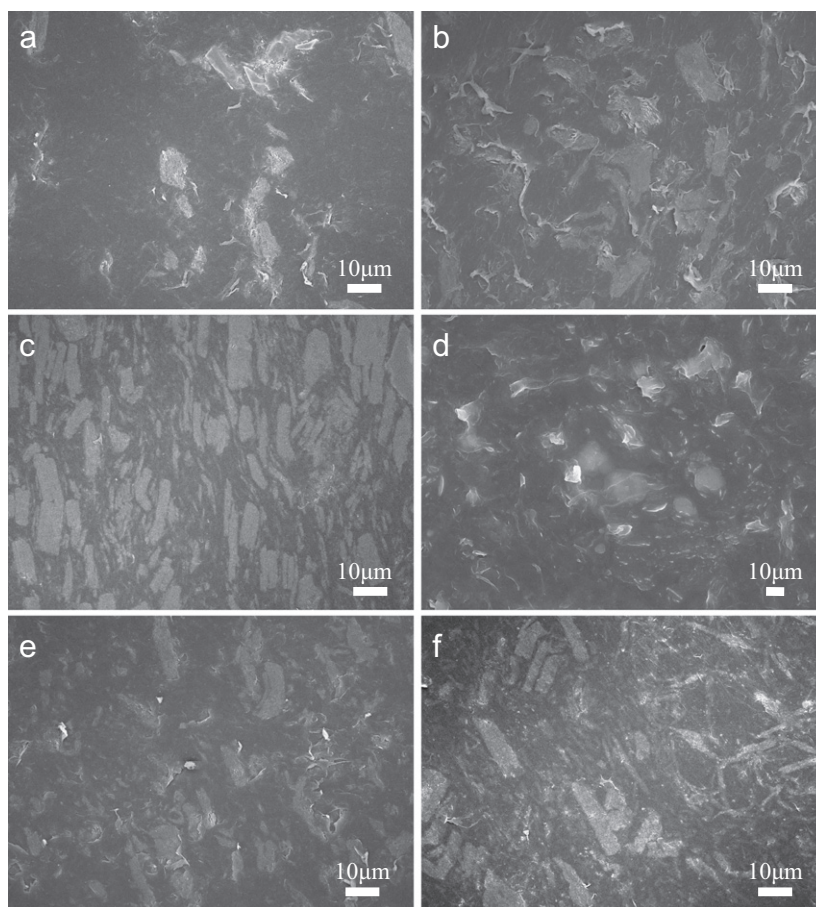


Fig. 3. SEM micrographs of the BN/HDPE composite with various volume fractions (V_f) and BN-particle sizes: (a) V_f of 0.1, 20 μm , (b) V_f of 0.3, 20 μm , (c) V_f of 0.5, 20 μm , (d) V_f of 0.3, 3 μm , (e) V_f of 0.3, 10 μm and (f) V_f of 0.3, 3 μm and 20 μm .

Table 1
Thermal diffusivities and specific heat capacities of the BN/HDPE composites with various volume fractions (V_f) and BN-particle sizes.

Particle size (μm)	Volume fraction (%)	Thermal diffusivity (mm^2/s)	Specific heat capacity (J/gK)
3	10	0.379	1.481
	20	0.528	1.360
	30	0.827	1.238
	40	1.269	1.128
	50	2.253	1.064
10	10	0.435	1.376
	20	0.644	1.331
	30	0.993	1.214
	40	1.599	1.103
	50	2.548	1.021
20	10	0.494	1.533
	20	0.852	1.323
	30	1.314	1.235
	40	1.769	1.212
	50	2.653	1.051

results are due to the fact that the thermal diffusivity of BN is higher than that of HDPE, and its specific heat capacity is lower than that of HDPE. The thermal diffusivity of the

composites increased with an increase in the size of the BN particles due to the decrease in the interfacial thermal barrier between BN and HDPE. However, the specific heat capacity of the composites did not change markedly with the size of the BN particles. A similar tendency has been confirmed in BN/polybenzoxazine composites [9].

Fig. 4 shows the experimentally determined and theoretically calculated thermal conductivities of the composites with various volume fractions and BN-particle sizes. The experimentally determined thermal conductivity of the composites increased with increasing BN content due to the thermal conductivity of BN being higher than that of HDPE. For a given ceramic content, the thermal conductivity of the composites increased with increasing BN-particle size because the heat conducting paths were thicker and the junctions had lower thermal resistance in the composites with the larger particles of BN than in the composites with smaller BN particles.

For electronic packaging applications, the ability to predict the thermal conductivity of the composites effectively should be considered when designing ceramic/polymer composites with high thermal conductivity. Several theoretical models were employed to predict the thermal conductivity of the composites with various volume fractions and BN-particle sizes. The Bruggeman and Russell

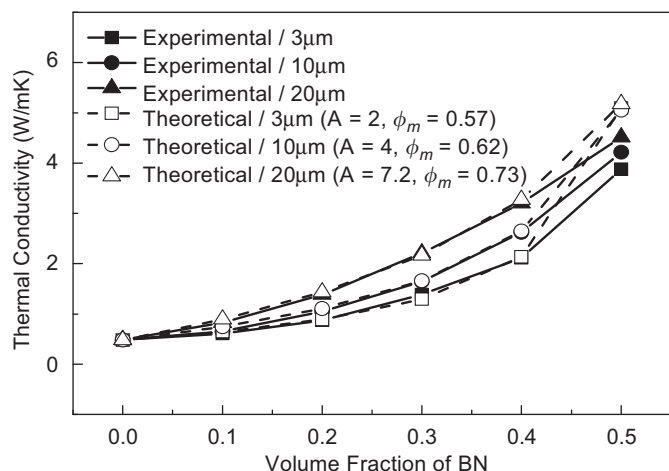


Fig. 4. Theoretically calculated and experimentally obtained values of thermal conductivity of the BN/HDPE composites with various volume fractions and BN-particle sizes.

models [6] were not used to fit the experimental data due to the fact that the fillers used in this study were not spherical or cubic in shape. However, the Nielsen–Lewis model [6,10] was in good agreement with the experimental values well up to V_f of 0.4, above which the model failed because of the presence of pores, as shown in Fig. 4.

This result is due to the fact that, unlike the other models, the Nielsen–Lewis model includes a fitting parameter A (morphology factor) to describe the shape of the filler. The Nielsen–Lewis model is based on the following equation:

$$\lambda_{eff} = \lambda_p \frac{1 + ABV_f}{1 - \psi BV_f}, \quad B = \frac{(\lambda_c/\lambda_p) - 1}{(\lambda_c/\lambda_p) + A}, \quad \psi = 1 + \frac{1 - \phi_m}{\phi_m^2} V_f \quad (1)$$

where λ_{eff} , λ_p , and λ_c are the thermal conductivities of the composites, polymer, and ceramic, respectively; V_f is the volume fraction of the ceramic; constant A is related to the morphology of the composites (irregular-shaped particles have a larger value of A than do spherical particles ($A=1.5$)); ϕ_m is maximum packing fraction. For composites with same amount of BN particles, the values of A and ϕ_m increased with increasing BN-particle sizes (Fig. 4).

Fig. 5 shows the thermal conductivity of BN/HDPE composites with the volume fraction of BN equal to V_f of 0.3 and a mixture of 3 μm - and 20 μm -sized BN particles. For the composites with the V_f of 0.3 and a mixture of 3 μm - and 20 μm -sized BN particles, the thermal conductivity increased when V_f of the 3 μm -sized BN particles was 0.09. It then decreased with a further increase in the volume fraction of the 3 μm -sized BN particles. These results can be explained by the fact that the 3 μm -sized BN particles fill the space between the 20 μm -sized BN particles until V_f of the 3 μm -sized BN particles reaches 0.09 (Fig. 3(f)). This leads to an increase in the number of conductive paths.

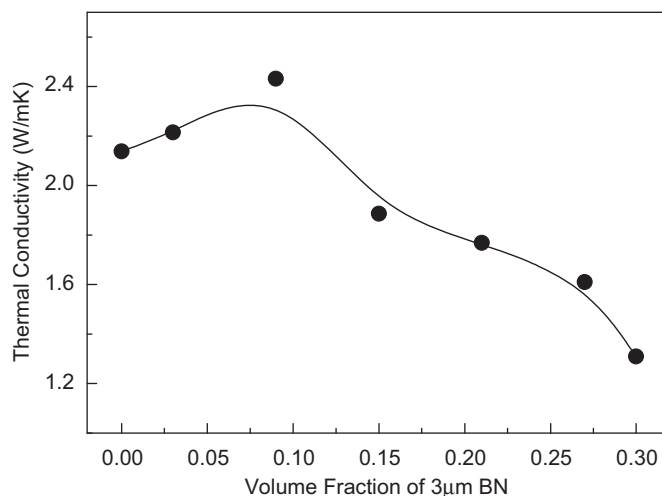


Fig. 5. Thermal conductivity of BN/HDPE composites with volume fraction of 0.3 and that containing a mixture of 3 μm - and 20 μm -sized BN particles.

4. Conclusions

With increasing BN content, the thermal conductivities and the thermal diffusivities of BN/HDPE composites increased, while the specific heat capacities decreased. For a given BN content, the thermal conductivity and the thermal diffusivity of the composites increased with an increase in the sizes of the BN particles. However, the specific heat capacity of the composites did not change markedly with the BN-particle size. The thermal conductivity of composites containing a mixture of different-sized BN particles was higher than that of composites containing only single-sized BN particles (3 μm or 20 μm). The experimentally determined values of thermal conductivity were in good agreement with those obtained using the Nielsen–Lewis model.

Acknowledgments

This work was supported by the Industrial Strategic Technology Development program, funded by the Ministry of Knowledge Economy (MKE, Korea).

References

- [1] W.Y. Zhou, S.H. Qi, Q.L. An, H.Z. Zhao, N.L. Liu, Thermal conductivity of boron nitride reinforced polyethylene composites, *Materials Research Bulletin* 42 (2007) 1863–1873.
- [2] W.Y. Zhou, S.H. Qi, H.D. Li, S.Y. Shao, Study on insulating thermal conductive BN/HDPE composites, *Thermochimica Acta* 452 (2007) 36–42.
- [3] H. Ishida, S. Rimdusit, Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine, *Thermochimica Acta* 320 (1998) 177–186.
- [4] R.F. Hill, P.H. Supancic, Thermal conductivity of platelet-filled polymer composites, *Journal of the American Ceramic Society* 85 (2002) 851–857.

- [5] W.Y. Zhou, S.H. Qi, H.Z. Zhao, N.L. Liu, Thermally conductive silicone rubber reinforced with boron nitride particle, *Polymer Composites* 28 (2007) 23–28.
- [6] S. Li, S. Qi, N. Liu, P. Cao, Study on thermal conductive BN/novolac resin composites, *Thermochimica Acta* 523 (2011) 111–115.
- [7] B.L. Zhu, J. Ma, J. Wu, K.C. Yung, C.S. Xie, Study on the properties of the epoxy-matrix composites filled with thermally conductive AlN and BN ceramic particles, *Journal of Applied Polymer Science* 118 (2010) 2754–2764.
- [8] K.C. Yung, H. Liem, Enhanced thermal conductivity of boron nitride epoxy-matrix composite through multi-modal particle size mixing, *Journal of Applied Polymer Science* 106 (2007) 3587–3591.
- [9] H.Y. Ng, X. Lu, S.K. Lau, Thermal conductivity of boronnitride-filled thermoplastics: effect of filler characteristics and composite processing conditions, *Polymer Composites* 26 (2005) 778–790.
- [10] L.E. Nielsen, B.L. Lee, Dynamic mechanical properties of some polystyrene composites, *Journal of Composite Materials* 6 (1972) 136–146.