

HIGH THERMAL CONDUCTIVE COMPOSITES BASED ON POLYPHENYLENE SULFIDE, BORON NITRIDE AND CARBON NANOTUBES

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1 Introduction

High thermal conductivity composites are required recently for the objective of weight savings that thin inner parts of cellular phones and metallic or ceramic automotive parts are substituted by the composites having high mechanical properties [1, 2]. In especial, pelletized, injection moldable and high thermal conductivity composites are demanded based on the thermoplastic polymer matrix because of convenience of postprocessing.

Polyphenylene sulfide (PPS) is one of the most suitable thermoplastic polymers as the matrix of the composite due to its high mechanical and heat resistant properties [3]. Boron nitride (BN) particles and carbon nanotubes (CNTs) are promising fillers for the high thermal conductivity composites due to their high thermal conductivity. Thermal conductivity of the BN is about 200 W/m·K and that of the CNTs in axial direction is 3000 W/m·K [4-6]. Several PPS/BN composites were prepared with respect to the BN weight fraction in order to develop pelletized, injection moldable, and high thermal conductivity composites having high mechanical properties. PPS/BN/CNT hybrid composites were also prepared by adding both small amount of CNTs and optimum amount of BN to improve thermal conductivity of the PPS/BN composites and examine the hybrid effect [7] of BN-CNT fillers on thermal conductivity of the composite. Effects of the CNT surface treatments [8] on thermal conductivity of the composites were investigated by modifying the CNT surface with acid and peroxide treatments.

2 Experimental

2.1 Materials

PPS used in this study was supplied from Toray Resin Co. and initial state of the PPS was powders. Average particle size of the used BN powers (ESK Ceramics GMBH & Co.) was 30 μm . The used multi-walled CNTs (MWCNT, Carbon Nano-materials Technology, Pohang, Korea) produced by the catalytic chemical vapor deposition method have the diameter of 5 to 20 nm, the length longer than 10 μm , and therefore the aspect ratio larger than five hundred.

2.2 Chemical modification of MWCNTs

Chemical modification of the MWCNT surface was performed by acid and hydrogen peroxide treatments. Acid treatment was performed as follows. Firstly, MWCNTs were dispersed in a 65% solution of 3:1 mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3$ in water. Then, the suspension was treated by ultrasonic excitation for 1 h at 80°C to attach carboxyl and hydroxyl groups onto the surface of MWCNTs. After acid treatment, the MWCNTs were cleaned several times with distilled water, filtered by using filtering paper with pore size of 1 μm , and then dried at 50°C in vacuum oven for 2 days. Hydrogen peroxide treatment was performed as follows. MWCNTs were dispersed in the 1:1 mixture of H_2O_2 /distilled water. Then, the mixture was sonicated for 1 h at 80°C to generate carboxyl and hydroxyl groups onto the surface of MWCNTs. After hydrogen peroxide treatment, the mixture was cleaned several times with distilled water and filtered by using a paper with pore size of 1 μm . Hydrogen peroxide treated MWCNTs were dried at 50°C in vacuum oven for 2 days.

2.3 Preparation of Composites

Various PPS composites were prepared with respect to BN weight fraction, CNT weight fraction and

CNT surface treatment by using melt compounding with a twin-screw extruder (TEK20, SM PLATEK Co., Ansan, Korea) as listed in Table 1. The composite melt was quenched in a water bath and then pelletized using a cutting machine. Before melt compounding, the PPS resin, BN and CNT powders were dried in an oven for 5 h at 100 °C to avoid void formation and degradation induced by moisture. Specimens shaped stairs were prepared by injection molding of the compounds with an injection molding machine (HPMMC Co., Ltd., South Gyeongsang, Korea) for measurement of thermal conductivity.

2.4 Characterization

Morphological properties were observed with a scanning electron microscopy (SEM, JSM-6390LV, JEOL, Tokyo, Japan) to investigate dispersion of reinforcements in the composite pellets. Fractured surfaces of the pellets were coated with platinum in vacuum for 80 s by using a sputter coating machine (Sputter Coater-108, Cressington Scientific Instruments, Watford, UK) and then SEM observation was carried out at 25.0 kV.

A hot-disk modified transient plane source thermal constant analyzer was used for the measurement of thermal conductivity of the composites. Experiments were carried out at room temperature. The measurements were performed using the injection molded specimens. The thickness of the used samples should preferably not be less than the diameter of the hot disk sensor and this must always be much larger than the cell diameter.

3 Results and Discussion

3.1 Moldability

Fig. 1 shows appearance of the injection molded specimens with respect to BN weight fraction. The injection specimen was composed of three different thicknesses in order to evaluate moldability of the injected material. As shown in Fig. 1 (c), the thin part of the injection molded specimen of the PPS/BN composite with BN of 50 wt% was not filled due to the increase of viscosity of the composites with increasing BN weight fraction. Therefore, much higher loading composites were not preferable because of the poor moldability of the composite materials.

3.2 Thermal Conductivity

Thermal conductivity of the composites is listed in Table 1 with respect to BN weight fraction and the thermal conductivity was improved with increasing BN loading. Therefore, BN is one of the effective fillers for elevation of thermal conductivity of polymer based composites. Teng et. al [xx] recently reported synergetic effect of chemically treated hybrid boron nitride and MWCNTs on the thermal conductivity of epoxy composites. The significant improvement of thermal conductivity of the composites was observed in this study by adding small amounts of MWCNTs using conventional melt compounding and the synergetic effect was significantly depended on the MWCNT surface treatments. These results indicated that the synergetic effect was caused by physical properties of BN and MWCNTs and especially MWCNTs.

3.3 Morphology

SEM images of the PPS/BN composites are shown in Fig. 2 with respect to BN loading. BNs of polygon shapes were occasionally found in the surface of the composites. SEM images of the PPS/BN/MWCNT composites are displayed in Fig. 3 and the results clearly showed the synergetic effect of the PPS/BN/MWCNT composites was caused by three-dimensional thermal transfer pathway between BN and MWCNTs due to high aspect ratio of MWCNTs.

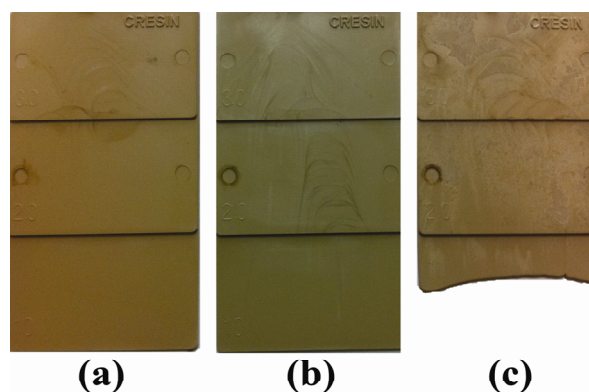
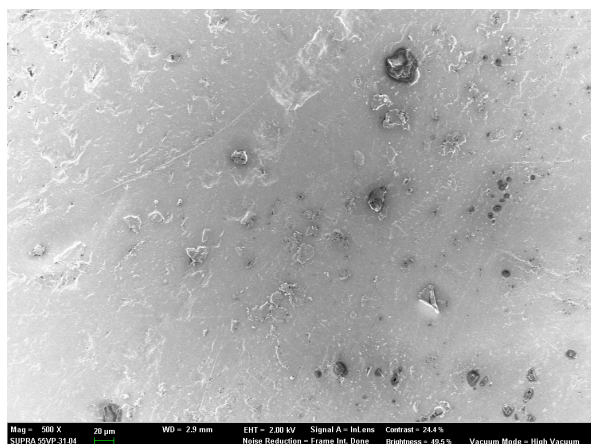
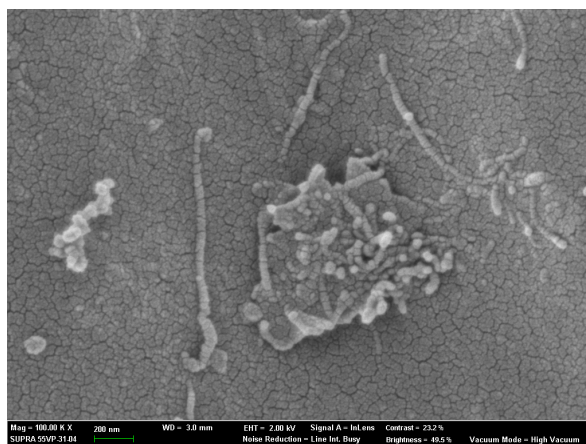


Fig. 1. Appearance of the injection molded specimens: (a) PB-30, (b) PB-40 and (c) PB-50.

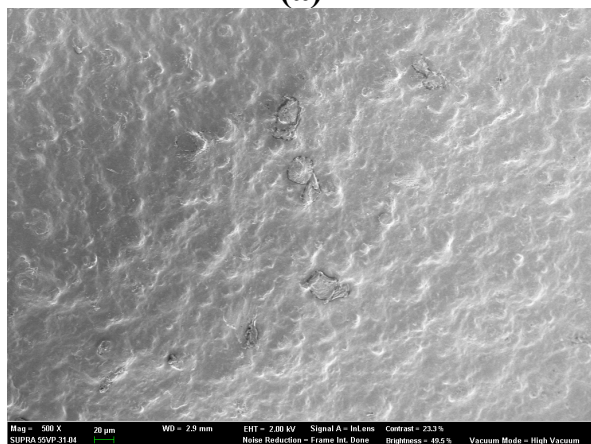
*The abbreviation is represented in the following Table 1.



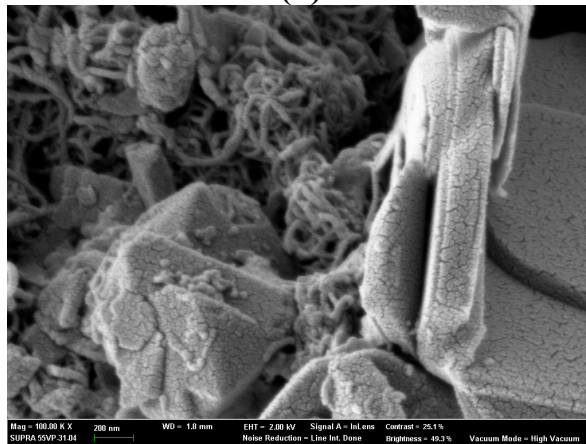
(a)



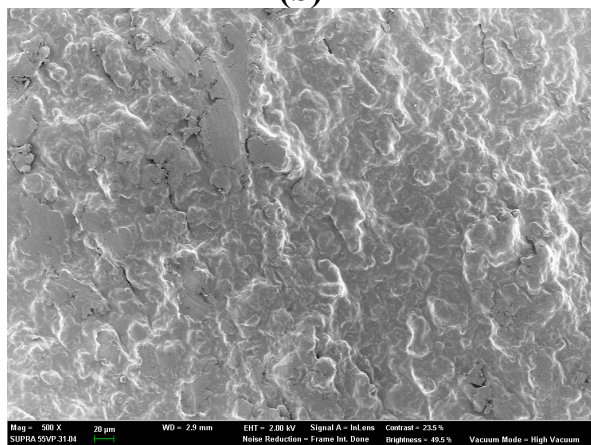
(a)



(b)



(b)



(c)

Fig.3. SEM images of (a) PBHM-1.0 and (b) PBAM-1.0. *The abbreviation is represented in the following Table 1.

Fig.2. SEM images of (a) PB-30 (b) PB-40 and (c) PB-50. *The abbreviation is represented in the following Table 1.

Table 1. Sample preparation and Thermal conductivity of the composites

Sample	PPS (wt%)	BN (wt%)	MWCNT (wt%)	Thermal conductivity
PB-0	100	0	0	0.31
PB-30	70	30	0	0.62
PB-40	60	40	0	0.87
PB-50	50	50	0	1.00
PBM-0.5	49.5	50	0.5	1.54
PBM-1.0	49	50	1	1.45
PBHM-1.0	49	50	1(H ₂ O ₂ treated)	1.74
PBAM-1.0	49	50	1(acid treated)	1.31

References

- [1] G. Pernot, M. Stoffel, I. Savic, F. Pezzoli, P. Chen, G. Savelli, A. Jacquot, J. Schumann, U. Denker, I. Mönch, Ch. Deneke, O. G. Schmidt, J. M. Rampnoux, S. Wang, M. Plissonnier, A. Rastelli, S. Dilhaire and N. Mingo "Precise control of thermal conductivity at the nanoscale through individual phonon-scattering barriers". *Nature Materials*, Vol. 9, pp 491-495, 2010.
- [2] S. Shaikh, K. Lafdi and E. Silverman "The effect of a CNT interface on the thermal resistance of contacting surfaces". *Carbon*, Vol. 45, pp 695-703, 2007.
- [3] Y. F. Zhao, M. Xiao, S. J. Wang, X. C. Ge and Y. Z. Meng "Preparation and properties of electrically conductive PPS/expanded graphite nanocomposites". *Composites Science and Technology*, Vol. 67, pp 2528-2534, 2007.
- [4] K. C. Yung and H. Liem "Enhanced thermal conductivity of boron nitride epoxy-matrix composite through multi-modal particle size mixing". *Journal of Applied Polymer Science*, Vol. 106, pp 3587-3591, 2007.
- [5] H. Huang, C. Liu, Y. Wu and S. Fan "Aligned carbon nanotube composite films for thermal management". *Advanced Materials*, Vol. 17, pp 1652-1656, 2005.
- [6] S. T. Huxtable, D. G. Cahill, S. Shenogin, L. Xue, R. Ozisik, P. Barone, M. Usrey, M. S. Strano, G. Siddons, M. Shim and P. Keblinski "Interfacial heat flow in carbon nanotube suspensions". *Nature Materials*, Vol. 2, pp 731-734, 2005.
- [7] A. Yu, P. Ramesh, X. Sun, E. Bekyarova, M. E. Itkis and R. C. Haddon "Enhanced thermal conductivity in a hybrid graphite nanoplatelet-carbon nanotube filler for epoxy composites". *Advanced Materials*, Vol. 20, pp 4740-4744, 2008.
- [8] S. H. Lee, S. H. Choi, S. Y. Kim and J. R. Youn "Effects of thermal imidization on mechanical properties of poly(amide-co-imide)/multiwalled carbon nanotube composite films". *Journal of Applied Polymer Science*, Vol. 117, pp 3170-3180, 2010.
- [9] C. C. Teng, C. C. Ma, K. C. Chiou, T. M. Lee and Y. F. Shih "Synergetic effect of hybrid boron nitride and multi-walled carbon nanotubes on the thermal conductivity of epoxy composites". *Materials Chemistry and Physics*, Vol. 126, pp 722-728, 2011.