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Synergetic effect of hybrid boron nitride and multi-walled carbon nanotubes on the thermal conductivity of epoxy composites

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ABSTRACT

This study investigates the synergistic effect of combining multi-walled carbon nanotubes (MWCNTs) and boron nitride (BN) flakes on thermally conductive epoxy composite. The surface of the two fillers was functionalized to form covalent bonds between the epoxy and filler, thereby reducing thermal interfacial resistance. The hybrid filler provided significant enhancement of thermal conductivity, adding 30 vol% modified BN and 1 vol% functionalized MWCNTs achieving a 743% increase in thermal conductivity (1.913 W mK^{-1}, compared to 0.2267 W mK^{-1} of neat epoxy).

1. Introduction

The development of polymer composites containing nanoscaled filler has become a popular topic in materials science recently. Polymer composites for electronic packaging and other applications require high thermal conductivity to dissipate heat [1]. Ceramic powders, including aluminum nitride [2,3], boron nitride [4,5] and silicon carbide [6] have been used extensively to enhance thermal conductivity in reinforced polymer composites. Although nanofiller has a positive effect on polymer matrices, their nanoscale dimensions, and high surface area make it difficult for nanocomposites to disperse. To optimize the thermal conductivity of nanocomposites, it is essential to consider the following model, $\kappa = \sim C_p v l$, where C_p, v, and l represent the specific temperature, the phonon velocity, and the mean phonon pathway, respectively. Thermal conductivity is sensitive to band velocity and scatting time. Thermal interface resistance obstructs the transfer of heat due to differences in phonon transfer in the complex phase and a weak interface between polymer and filler. The polymer matrix containing nanoscale filler with high surface area, forms a stronger boundary than the same volume using microscale filler. It is necessary to minimize the thermal interface resistance at the polymer composites by the functionalization of the filler. Secondly, increasing networks formation by using conductive filler promotes heat transfer and generates higher thermal conductivity. Filler with a large aspect ratio easily forms such networks and dominate the thermal conductivity of composites. Previous studies reported that carbon nanotubes (CNTs) had a high aspect ratio and high thermal conductivity (up to 3000 W mK^{-1}) [7], and therefore show potential as a heat transfer material. On the other hand, a polymer matrix containing a high CNT content may present some problems. For example, the CNTs may easily form bundle structure, which causes the reciprocal phonon vector phenomenon [8], and also increases composite viscosity. The increase of composite viscosity hinders the composite process. One solution to this problem might be the partial replacement of low-aspect-ratio filler with high-aspect-ratio filler, thereby forming a hybrid filler with a perfectly conductive network for next generation heat dissipation applications.

The effective hybrid filler system proposed in this study consisted of functionalized nano-scale boron nitride (BN) and functionalized multi-walled carbon nanotubes (MWCNTs). This filler was used to prepare thermally conductive epoxy composites. This study attempted to enhance the thermal conductivity of the composites, by increasing the number of heat transfer pathways with hybrid filler containing high-aspect-ratio MWCNTs and flaked BN. In the absence of covalent bonds at the interface, the difference in stiffness between pristine filler and the epoxy matrix created a small number of low frequency vibrational phonon modes. This was an indication that a high thermal resistance existed in the composite interface. We modified the filler to create covalent bonds on the epoxy-filler interface, which simultaneously minimized the interfacial thermal resistance and improved filler dispersion in the polymer matrix.

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2. Experimental

2.1. Materials

The diglycidyl ether of bisphenol A (DGEBA) epoxy NPEL-128 was supplied by the Nan Ya Plastics Co. Ltd., Taiwan, with an epoxide equivalent weight of 190 g equiv.$^{-1}$ 4,4-Diaminodiphenyl sulfone (DDS) acted as a curing agent and was supplied by Chriskev Company, Inc., USA. Boron nitride was supplied by Kallex Company LTD., Taiwan. Zirconate coupling agent (Ken-React® NZ37 (dineopentyl(diallyl)oxy, di(para amino) benzoyl zirconate)) was supplied by the Kenrich Perrochemicals, Inc., USA. 2,2′-Azobis-isobutyronitrile (AIBN) was obtained from the Showa Chemical Industry Co., Ltd., Japan. Glycidyl methacrylate (GMA) was received from the Acros Organic Co., Belgium. Multi-walled carbon nanotubes (MWCNTs) were produced by chemical vapor deposition (CVD) and were supplied by the CNT Company, Korea. The purity of the MWCNTs was 93%. The diameter of the carbon nanotubes was 10–50 nm; the length was 1–25 μm.

2.2. Surface modification of BN

The BN particles were modified by 1.0 wt% zirconate coupling agent with tetrahydrofuran under purified nitrogen. The detailed synthetic procedure is shown in Fig. 1(a). The slurry then was mechanical stirred at 80 °C for 24 h. After the modification, the slurry was filtered and dried at 100 °C. The functionalization procedure was via a zirconatization reaction and hydrolysis reaction.

2.3. Preparation of functionalized MWCNTs via free radical polymerization

Glycidyl methacrylate (GMA) monomer was de-inhibited using column with celite and sea sand to remove the monomethyl ether hydroquinone (MEHQ) inhibitor. The mole ratio of MWCNTs to GMA and to AIBN was 6.2:1:1. The mixture was dispersed in NMP and sonificated at 65 °C under nitrogen atmosphere for 2 h, and then stirred for 24 h. After reaction, the GMA-grafted MWCNT slurry was washed several times with acetone to remove all non-grafted GMA, and filtered with 0.2 μm Teflone microfiltration cell and then dried in a vacuum oven for 24 h. The synthetic procedure is shown in Fig. 1(b).

2.4. Preparation of hybrid filler/epoxy composites

Unfunctionalized or functionalized BN particles and MWCNTs with curing agent were dispersed in acetone in an ultrasonicator bath for 10 min. The epoxy resin and reform agent were then added; the slurry was stirred for 10 min to obtain acceptable homogeneity. The mixture was transferred to a mold and degassed in a vacuum oven at 60 °C until most of the solvent was removed by evacuation. The curing conditions were 1 h at 60 °C, 4 h at 120 °C, 2 h at 160 °C, and 2 h at 180 °C.

2.5. Instrumental analysis

Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Perkin Elmer RX1 spectrometer and collocated attenuated total reflectance (ATR) equipment. The morphological observations were executed by a field emis-

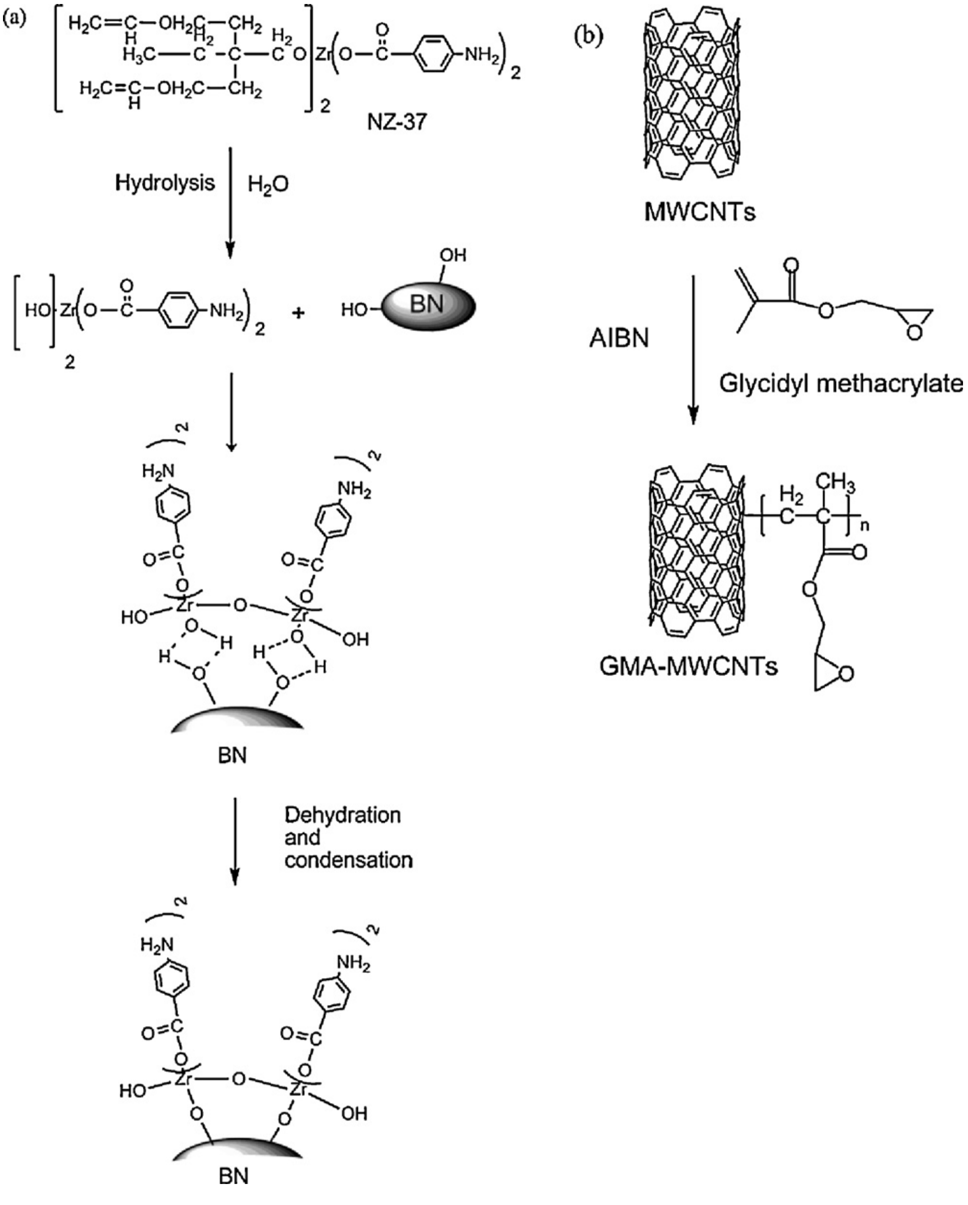

Fig. 1. (a) Scheme for chemical functionalization of BN and (b) scheme of the process of grafting GMA onto the MWCNTs.

sion scanning electron microscope (FESEM) (JEOL JSM-6700F) and transmission electron microscopy (TEM) (JEOL 2100). Curing reaction of the epoxy composites was measured using a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. Samples were heated from 30 to 200 °C at a heating rate, 5 °C min^{-1}. The thermal conductivity of nanocomposites was measured by a Hot Disk thermal analyser (TPS2500, Sweden), which was based upon the transient plane source method. The dimension of bulk specimens is 60 mm × 60 mm × 5 mm with the sensor placed between two similar slabs of materials. The senor supplied a heat pulse of 0.01 W for 10 s to the sample and recorded relevant temperature.

3. Results and discussion

3.1. Analysis of functionalized filler by infrared spectroscopy

An infrared spectrum of functionalized BN was compared with pristine BN and zirconate coupling agent in Fig. 2. The weak absorption band of pristine BN at 3600–3200 cm^{-1} was caused by the valence vibration of the O–H group on the BN, which was the reactive site with zirconate coupling agent by sol–gel reaction. The broad peak around 1627–1100 cm^{-1} could indicate in-plane stretching vibration of hexagonal BN (1358 cm^{-1}), but it also possibly included the vibration of B–O (1403 cm^{-1}). The peak at 773 cm^{-1} represented the out of plane bending vibration [9]. During further modification of BN surface, the additional peaks were observed at 3469, 3016, 2971–2952, 2135, 1714, 1230, and 1218 cm^{-1}. The absorption band at 3469 cm^{-1} was a NH_2 stretching band, while the peak at 3016 cm^{-1} indicated the aromatic C–H stretch. Some peaks around 2971–2952 cm^{-1} were valence stretching vibrations of aliphatic C–H. The peak at 2135 cm^{-1} could be attributed to N–H stretch. The peak at 1714 cm^{-1} corresponded to the C=O stretch, 1230 cm^{-1} could be attributed to C–N stretch and 1218 cm^{-1} was associated to C–(C=O)–O stretch. The above absorption bands were absent in the case of pristine BN. IR spectroscopy is not a strict proof for a covalent B–O–Zr bond, it is also possible that zirconate coupling agent is only physically adsorbed to the BN surface.

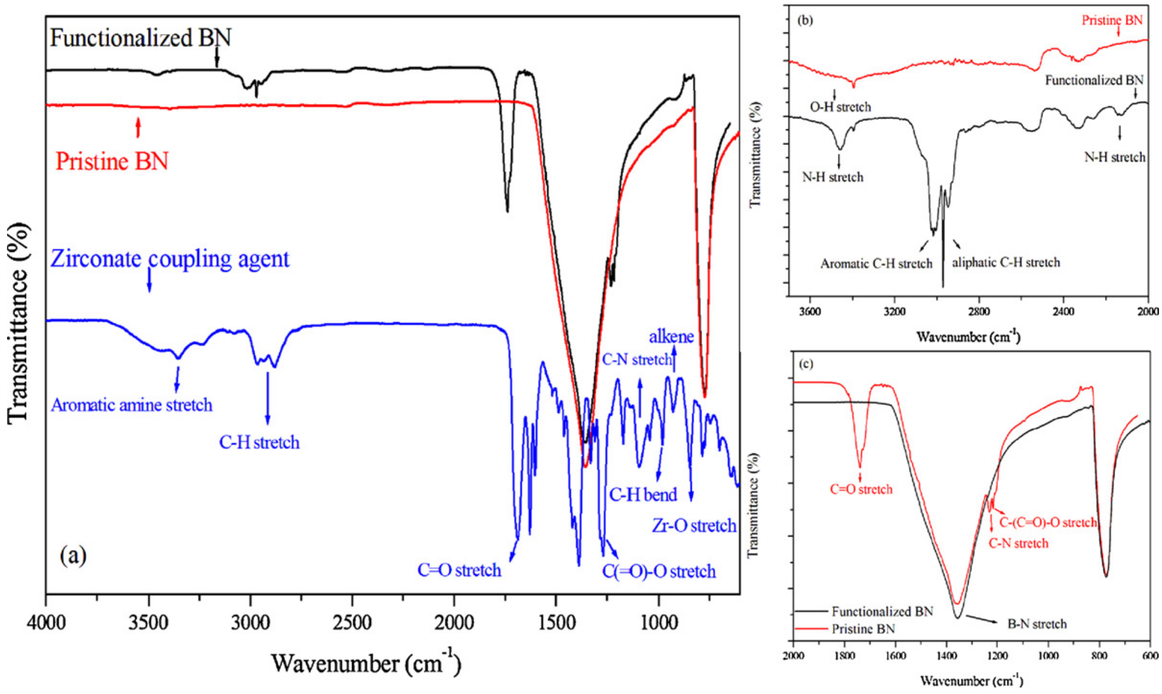

Fig. 2. FTIR spectra (a) of pristine BN, functionalized BN and zirconate coupling agent. FTIR spectra (b) of BN are at 3700–2000 cm^{-1}. FTIR spectra (c) of BN are at 2000–600 cm^{-1}.

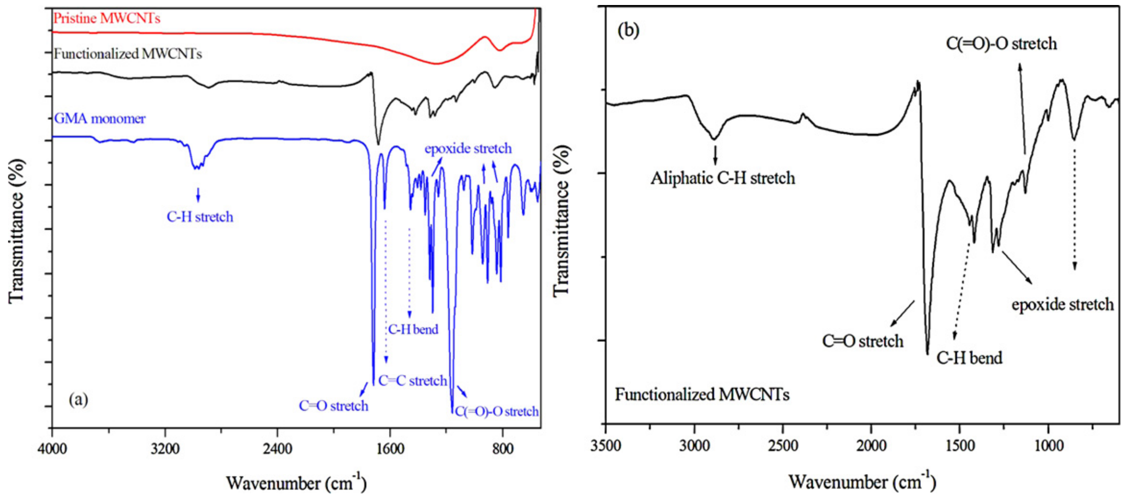

Fig. 3. FTIR spectra (a) of pristine MWCNTs, functionalized MWCNTs, and GMA monomer. FTIR spectra (b) of functionalized MWCNTs.

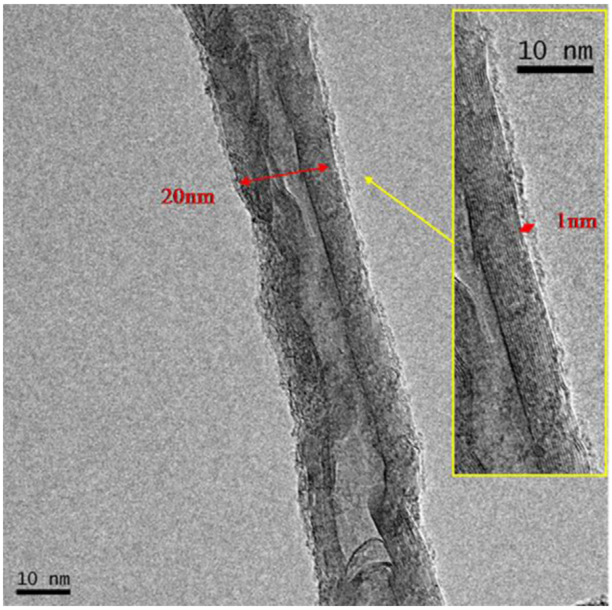

Fig. 4. TEM image of functionalized MWCNTs.

The treatment of MWCNTs by free radical polymerization is an effective method to graft polymer chain on MWCNT surface. The functionalized MWCNTs exhibited good dispersion and long term stability which implied that the effective dispersion of MWCNTs was achieved by covalently grafting GMA polymer chains on the MWCNT surface. FTIR spectra of pristine MWCNTs, functionalized MWCNTs and GMA monomer are shown in Fig. 3. After free radical polymerization, the addition absorbance at 2896 cm^{-1} and 1450 cm^{-1} appeared which indicated the C–H stretching and C–H bending of GMA polymer chains. The peak at 1687 cm^{-1} could attribute to C=O stretch of ester group; the peak at 1130 cm^{-1} indicates C(=O)–O stretch. In addition, three peaks at 1281, 992, and 864 cm^{-1} are attributed to the vibration of epoxide group. The presence and location of these bonds indicated that GMA polymer chain was grafted on MWCNTs.

3.2. The morphology of MWCNT and BN

This study also investigates the structures of functionalized MWCNT and BN using TEM (Fig. 4) and SEM (Fig. 5). These results clearly show that the nanotube was coated with GMA-grafting polymer. Moreover, a polymer shell appeared on the whole MWCNT sidewall. The average MWCNT diameter was estimated to be 15–30 nm. The surface of functionalized MWCNTs was rather rough, and the average thickness of the polymer shell was about 1 nm. Fig. 5 shows a typical SEM image of the BN powder, which exhibited a flake shape.

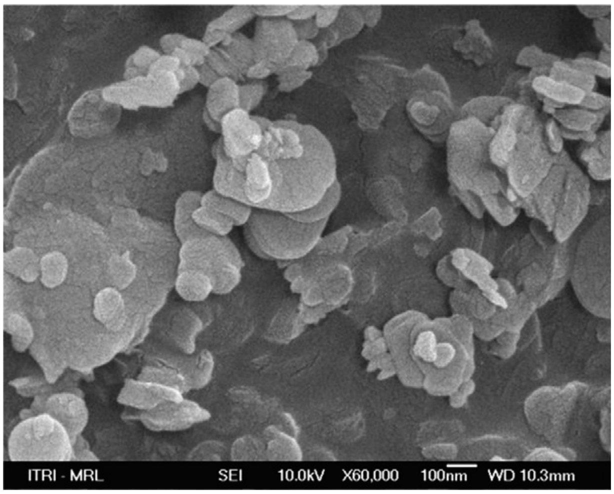

Fig. 5. SEM image of pristine BN.

3.3. The morphologies of BN/epoxy composites and hybrid filler/epoxy composites

Fig. 6(a) and (b) shows the fracture morphology of 25 vol% BN/epoxy composites. These figures clearly showed that the pristine BN was present mainly in the form of agglomerates. A poor interface appeared between epoxy and BN (Fig. 6(a)), whereas the functionalized BN was dispersed more uniformly and embedded in the epoxy, confirming a much superior interface adhesion with the BN in epoxy matrix (Fig. 6(b)). This phenomenon was due to the amine group of zirconate coupling agent grafted on the BN surface, which was attached to the epoxide group of epoxy by covalent bonding. Fig. 6(c)–(f) shows SEM images of the fracture surface of the hybrid filler/epoxy composites, which were prepared with various amounts of BN and 1 vol% MWCNTs. Fig. 6(c) and (e) shows epoxy composites containing 25 vol% pristine BN and 1 vol% pristine MWCNTs. The pristine MWCNTs were dispersed in the matrix as MWCNT bundles with a bundle diameter of about 1 μm. Most of the MWCNTs were pulled out from epoxy matrix, indicating an incomplete stress transfer from epoxy to MWCNTs. In contrast, Fig. 6(d) and (f) shows that the epoxy composites containing 25 vol% functionalized BN and 1 vol% functionalized MWCNTs showed a large number of white dots on the composite surfaces, indicating that the nanotubes were well embedded in the epoxy matrix.

3.4. Thermal conductivity of composites containing a single filler or hybrid filler

Fig. 7 illustrates the thermal conductivity of epoxy/MWCNT composites with pristine MWCNTs and functionalized MWCNTs. Huxtable et al. reported that the thermal conductivity of CNT/polymer composites was lower than the intrinsic thermal conductivity of CNTs, due to heat resistance caused by the CNT–polymer matrix interface [10]. The measurements of thermal conductivity for functionalized MWCNT/epoxy composites reveal a significant improvement in thermal conductivity compared to pristine CNTs. Specifically, thermal conductivity increases 135% by adding small quantity (0.76 vol%) of functionalized MWCNTs. The representative factor was proposed to demonstrate the enhancement of thermal conductivity. The GMA polymer chain relates MWCNTs to epoxy and provides good interface compatibility that reduces interfacial thermal resistance. However, adding 1.6 vol% MWCNTs decreases the thermal conductivity of MWCNT/epoxy composites with functionalized MWCNTs and pristine MWCNTs. Because an excessive amount of MWCNTs forms nanotube bundles, the phonon structure disperses nanotubes bundles into three dimensions by strong intertube coupling. This phenomenon prohibits the phonon transfer, preserving the heat at the intertube junction [11]. Accordingly, the optimum content of functionalized MWCNTs is 1 vol%.

Fig. 8 shows the thermal conductivity of BN/epoxy composite. The thermal conductivity of BN/epoxy increased with the BN content. With a low BN content, the BN was segregated around the epoxy matrix, and provided only a slight increase in thermal conductivity. The thermal conductivity of composites with a BN 25 vol% increased significantly because the amount of BN was sufficient to form the thermal network pathways. Composites containing

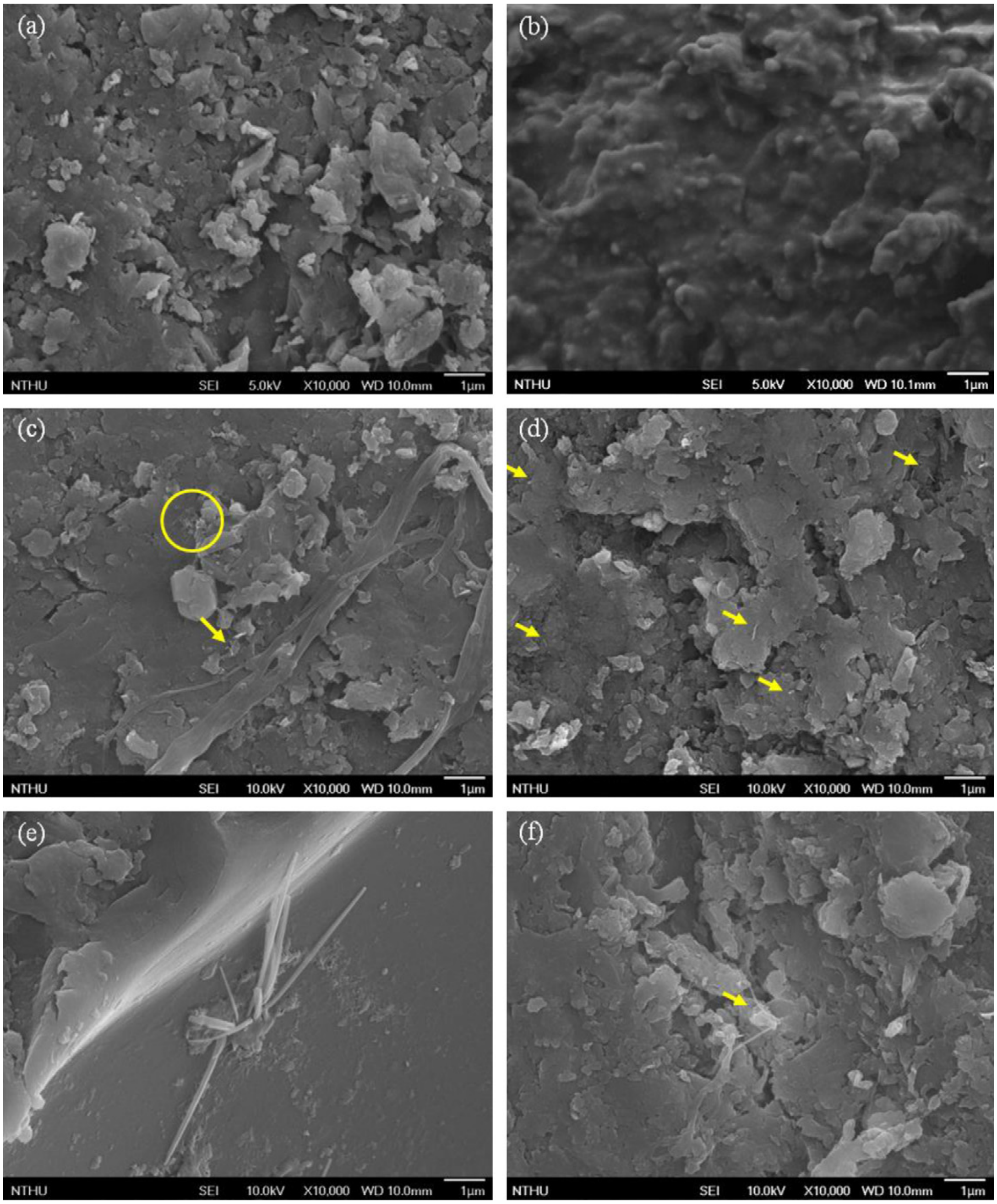

Fig. 6. SEM images of epoxy composites with (a) 25 vol% pristine BN, (b) 25 vol% functionalized BN, (c and e) 25 vol% pristine BN and 1 vol% pristine MWCNTs, (d and f) 25 vol% functionalized BN and 1 vol% functionalized MWCNTs.

functionalized BN possess better thermal conductivity than pristine BN. Functionalized BN exhibits better interfacial interaction in an epoxy matrix. In addition, the active organic monomolecular layer of BN reacts with epoxy through a crosslinking reaction, which forms chemical bonds between BN and epoxy and reduces the thermal interface resistance. The MWCNT/epoxy composites exhibited higher thermal conductivity than BN/epoxy composites with a low filler content, due to the fact that the inherent thermal conductivity of MWCNTs was higher than that of BN. Moreover, the high-aspect-ratio of MWCNTs formed heat conductive pathways in the epoxy matrix more easily than low-aspect-ratio BN, with an irregular flake shape.

A comparison of Fig. 7 with Fig. 9 shows that the thermal conductivity of epoxy composites with two kinds of hybrid filler system were higher than epoxy composites with a single filler. Furthermore, the thermal conductivity of BN/epoxy composites increased significantly when the BN loading exceeded 20 vol% BN (Fig. 8), whereas adding 10 vol% BN and 1 vol% MWCNTs of hybrid filler enhanced thermal conductivity (Fig. 9). Two factors were proposed to explain the enhancement of thermal conductivity. First, high thermal conductivity and aspect ratio of MWCNTs could easily form thermal transfer pathway. Second, those results in Figs. 7–9 pointed out that for adding 1 vol% functionalized MWCNTs, thermal conductivity enhancement ratio is 141.27%; for adding 25 vol% functionalized BN, thermal conductivity increased to 188.88%. Further, by adding both 25 vol% functionalized BN and 1 vol% functionalized MWCNTs together, thermal conductivity increased to 699.74%. Thermal conductivity of composites containing MWCNT and BN was existed to the synergistic effect. The hybrid filler system improved heat conduction with three-dimensional networks,

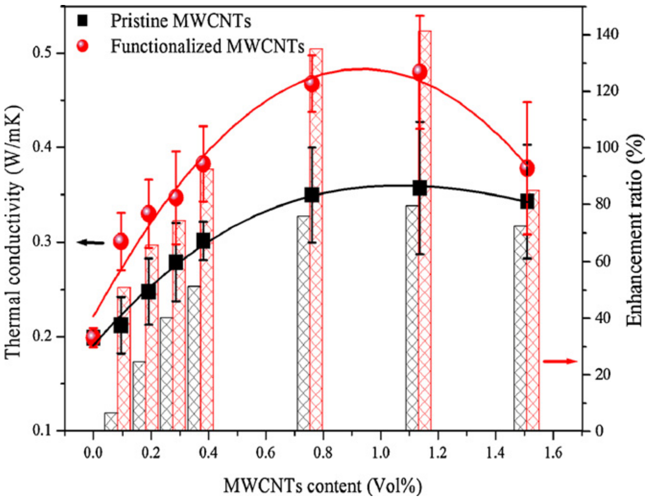

Fig. 7. Thermal conductivity of epoxy composites with various types of MWCNTs (the symbol represents the thermal conductivity; the bar represents the enhancement ratio).

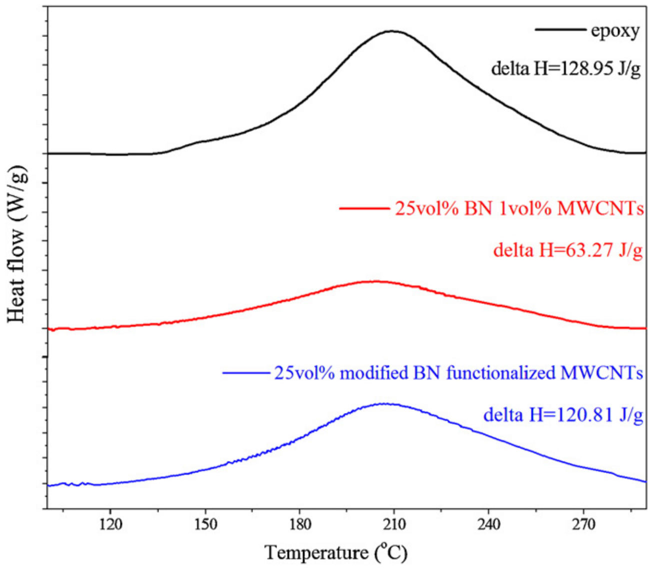

Fig. 10. The curing reaction of epoxy and epoxy composites by non-thermal DSC.

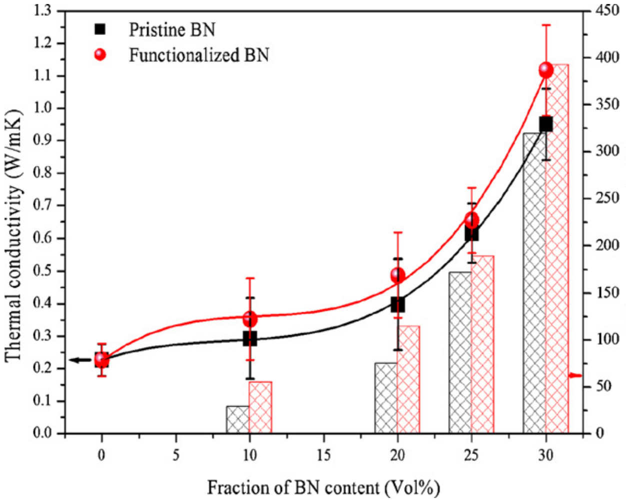

Fig. 8. Thermal conductivity of epoxy composites with various types of BN.

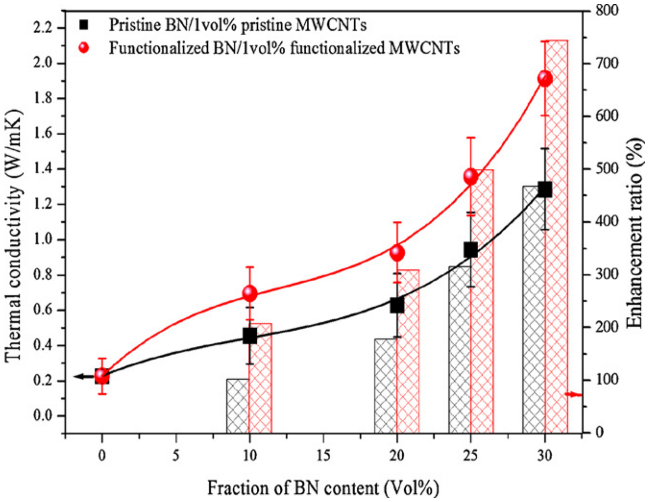

Fig. 9. Thermal conductivity of epoxy composites with various types of hybrid filler.

and shows a positive effect on the thermal conductivity of composites. In addition, it was postulated that the heat transfer network was the critical factor in the intrinsic thermal conductivity of filler and filler content [1]. Further, by increasing functionalized BN content to 20 vol% and 1 vol% functionalized CNT, the synergistic effect was obvious with an extra increase of 52.81% and a whooping 168.44% with 25 vol% functionalized BN and 1 vol% functionalized MWCNTs, which however increased to 165.40% for 30 vol% functionalized BN and 1 vol% functionalized MWCNTs. The synergistic effect of the hybrid filler produced high thermal conductivity in hybrid filler/epoxy composites, making it possible to reduce the volume of inorganic filler in the epoxy matrix. Fig. 9 indicates that the thermal conductivity of composites with functionalized hybrid filler is higher than that of composites with pristine hybrid filler.

This study utilized SEM (Fig. 6) and DSC (Fig. 10) to determine the improvement of interfacial interaction and wettability between filler and epoxy matrix, and dispersion of the filler. Comparing the DSC curves of epoxy composites with pristine hybrid filler and functionalized hybrid filler revealed that the enthalpy (ΔH) of the curing reaction of the pristine hybrid filler system was weaker than that of functionalized hybrid filler system. Moreover, the maximum curing temperature dropped with the addition of filler. These phenomena indicate the steric hindered effect of filler on epoxy curing. There is no covalent bonding between hybrid filler and epoxy, and the interfacial interaction between the hybrid filler and epoxy was weak. However, the reactive sites of the functionalized hybrid filler reacted with the epoxy during the curing process. This increased the ΔH of the functionalized hybrid filler system, and implied that adding functionalized hybrid filler decreased the free volume of composite material. Moreover, this factor also led to an effective reduction in the resistance of the thermal interface. The schematic chemical interactions of functionalized BN and MWCNTs/epoxy are illustrated in Fig. 11. Fig. 11(a) shows that the amine groups on the BN surface participate in the opening ring reaction with epoxy, leading to the formation of an ester and an OH group [12]. The epoxide rings of functionalized MWCNTs first reacted with amine curing agent, and then cross-linked with the other epoxy groups (Fig. 11(b)). Moreover, the amine group of BN and the epoxide group of MWCNTs had a possibility to react (Fig. 11(c)).

The findings from the thermal, FTIR, and morphology results above revealed the reasons for the improvement in the thermal

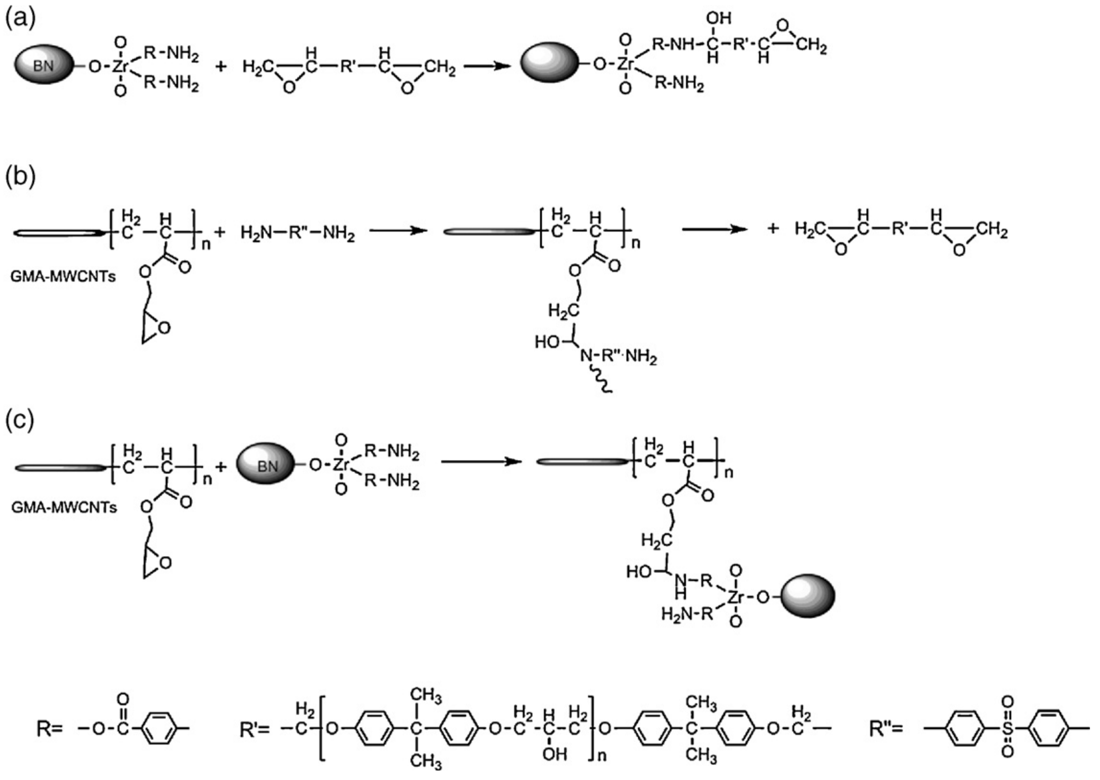

Fig. 11. Reaction scheme for functionalized BN and MWCNTs with epoxy matrix.

conductivity of composites containing hybrid filler, and illustrated how the chemical modification of the hybrid filler surface affected thermal conductivity. The surface functionalization of filler improved the dispersion and chemical bonding of epoxy matrix and filler, and was able to reduce the thermal interfacial resistance. Moreover, hybrid filler was easily able to form a thermal conductive network, which was a practical means to increase thermal conductivity.

4. Conclusions

This study used various inorganic fillers including BN and MWCNTs with surface functionalization, alone or in combination, to prepare epoxy composites. The surface of MWCNTs was functionalized by free radical polymerization of GMA, and BN was modified with a zirconate coupling agent to improve the interfacial interaction. Results showed that the thermal conductivity in the hybrid filler composites were higher than that of single filler composites, due to the synergistic effect of the hybrid filler. The thermal conductivity of epoxy composite containing 30 vol% modified BN and 1 vol% functionalized MWCNTs was 1.91 $\mathrm{W\,mK^{-1}}$, which was higher than that of epoxy composite with 30 vol% pristine BN (0.95 $\mathrm{W\,mK^{-1}}$), epoxy composite with 30 vol% pristine BN and 1 vol% pristine MWCNTs (1.12 $\mathrm{W\,mK^{-1}}$) and neat epoxy (0.18 $\mathrm{W\,mK^{-1}}$). DSC analysis confirmed the reaction conversion and molecular confinement between epoxy and filler. The ΔH of epoxy composites with 25 vol% pristine BN and 1 vol% MWCNTs (63.3 $\mathrm{J\,g^{-1}}$) was lower than that of neat epoxy (129.0 $\mathrm{J\,g^{-1}}$), because the presence of inorganic filler hindered the mobility of the reactive species. However, the ΔH of epoxy composites with 25 vol% modified BN and 1 vol% functionalized MWCNTs (120.8 $\mathrm{J\,g^{-1}}$) was comparable to that of neat epoxy, due to the fact that the reactive groups on the modified filler surface were able to bond chemically with the epoxy matrix, leading to a reduction in the thermal interfacial resistance.

References

[1] K. Yang, M. Gu, Compos. Part A: Appl. 41 (2010) 215–221.
[2] Y. Xu, D.D.L. Chung, C. Mroz, Compos. Part A: Appl. 32 (2001) 1749–1757.
[3] C.Y. Hsieh, S.L. Chung, J. Appl. Polym. Sci. 102 (2006) 4734–4740.
[4] H. Ishida, S. Rimdusit, Thermochim. Acta 320 (1998) 177–186.
[5] W. Zhou, D. Qi, H. Li, S. Shao, Thermochim. Acta 452 (2007) 36–42.
[6] T. Zhou, X. Wang, G.U. Mingyan, X. Liu, Polymer 49 (2008) 4666–4672.
[7] K. Naito, J.M. Yang, Y. Xu, Y. Kagawa, Carbon 48 (2010) 1849–1857.
[8] P. Kim, L. Shi, A. Majumdar, P.L. McEuen, Phys. Rev. Lett. 87 (2001), 215502-1.
[9] H. Zhu, M. Tan, G. Lian, X. Zhang, D. Cui, Q. Wang, Solid State Sci. 11 (2009) 1283–1287.
[10] S.T. Huxtable, D.G. Cahill, S. Shenogin, L. Xue, R. Ozisik, P. Barone, M. Usrey, M.S. Strano, G. Siddons, M. Shim, P. Keblinski, Nat. Mater. 2 (2003) 731–734.
[11] C.T. Hsu, W.K. Hsu, Appl. Phys. Lett. 90 (2007) 253104.
[12] M. Abdalla, D. Dean, P. Robinson, E. Nyairo, Polymer 49 (2008) 3310–3317.