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Chemically modified boron nitride-epoxy terminated dimethylsiloxane composite for improving the thermal conductivity

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Abstract

The thermal conductivities of composites with an epoxy-terminated dimethylsiloxane (ETDS) matrix and boron nitride (BN) powder fillers were investigated. Two surface curing agents, 3-glycidoxypropyltrimethoxysilane (KBM-403) and 3-chloropropyltrimethoxysilane (KBM-703), were doped onto the surfaces of hydroxyl-functionalized boron nitride using a simple sol–gel process to act as fillers in the thermally conducting composites. These synthesized materials were embedded in epoxy resin via a solvent casting method. The surface modification had an appreciable effect on the thermal conductivity resulting in increased thermal conductivity up to 70 wt%. The thermal conductivities of the composites containing 70 wt% BN particles treated with the KBM-403 and KBM-703 curing agents were 4.11 and 3.88 W/mK, respectively, compared to 2.92 W/mK for the composite without surface treatment.

Keywords: B. Composites; C. Thermal conductivity; D. Nitrides; Surface treatment

1. Introduction

Demands for the miniaturization and continuous performance improvements of electronic packages have led to the development of new microelectronic packaging techniques. The typical characteristics of future microelectronic packaging include high density, high frequency, and high speed [1–3]. It is well known that the reliability of an electronic device is exponentially dependent on the operating temperature of the junction, whereby a small difference of the operation temperature can result in a two-fold reduction of the lifespan of a device [4]. Improvements of size and performance are likely to result in the generation of a greater amount of heat in a smaller volume of space. To ensure proper device operation, the unwanted heat must be removed as quickly and effectively as possible to maintain the operation temperature, suggesting that the packaging materials of the product needs to have good thermal conductivity [5,6].

Epoxy resin has been widely applied in electronics, paints, electrical insulators, printed circuit boards, and packaging materials as a matrix [7,8]. Unfortunately, epoxy used alone as an electronic packaging material cannot effectively dissipate the heat generated from high packing and power-density devices, given the relatively low thermal conductivity range of epoxy of 0.1–0.3 W/mK. Several studies have been conducted to improve the thermal conductivity of epoxy. For example, polymers filled with thermally conductive fillers are emerging as a cost-effective means of coping with thermal management issues.

Many researchers have investigated the thermal conductivity enhancement of composite materials including oxides (Al_2O_3, SiO_2, ZnO) [9–11], carbide (SiC) [12], and nitrides (AlN, BN, Si_3N_4) [13,14]. The properties of these epoxy/inorganic filler composites depend on the nature of the inorganic filler including their chemical and physical composition, size, shape and dispersion in the epoxy matrix. Thermally conductive fillers, like those mentioned above, have attracted attention due to their high thermal and low electrical conductivities, while metallic particles have high thermal and electrical conductivities. Among the fillers, boron nitride has been considered as

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an attractive candidate due to its significantly high thermal conductivity (~300 W/mK), lack of toxicity, superior chemical stability, electrical insulation properties, and relatively low cost.

In order to obtain a higher thermal conductivity while maintaining the existing properties, filler loadings of 60 wt% or higher have traditionally been incorporated to form a heat conduction path in the matrix that is as continuous as possible. However, a high filler content becomes rather inflexible with voids and cracks forming between fillers. Moreover, the BN/epoxy slurry has a relatively low viscosity before drying, which facilitates the sedimentation of the BN filler. As a result, BN fillers settle to the bottom of the composite film, the heat-conductive path is cut off, and the thermal conductivity decreases. In response to this issue, many studies have suggested fabrication of a surface-modified BN particle to prevent filler sedimentation [15,16].

Recently, BN has been coated with a surface-curing agent to further enhance the thermal conductivity of polymer composites, resulting in a reduction of sedimentation due to the lone-pair electron interaction of particle surfaces into the matrix. Gu et al. achieved a thermal conductivity of 1.052 W/mK using a hot disk instrument for epoxy filled with silane-modified BN at a solid loading of 60 wt% [17]. Yung et al. reported the effect of multi-modal particle size mixing on the formation of a thermally conductive network [18]. Unfortunately, these previous experiments used nano-scale BN particles (~1 μm). Due to the small size of the filler-contained film, heat passing through the boundary of the particles is more frequently the main cause of the phonon scattering. The diffuse boundary scattering due to the short wavelength in comparison to interface roughness of dominant phonon heat carriers not only reduces the phonon mean free path, but can also destroy the coherence of the phonons [19]. Thermal resistance at particle junctions known as thermal boundary resistance or Kapitza resistance is one of the primary causes of heat transfer property reduction. In the presence of a heat flux across the boundary, this thermal resistance causes a temperature discontinuity at the boundary. Due to the differences of the electronic and vibrational properties of various materials, an energy carrier will scatter when attempting to traverse the interface [20–22].

It is known that hexagonal BN particles have a plate-like shape with flat surfaces corresponding to the basal planes of the hexagonal crystal structure. The basal plane of BN is molecularly smooth and has no surface functional groups available for chemical bonding or interactions. In contrast, the edge planes of the platelets have functional groups such as hydroxyl and amino groups. These functional groups allow the BN filler to disperse in an organic solvent and chemically bond with other molecules. Large BN particles are significantly decreased in the edge plane areas, resulting in difficulty obtaining uniform dispersion and chemical bonding. To this end, Sato et al. employed 0.7 μm BN particles as a thermal conductive filler on polyimide resin [23,24]. For the effective use of micro-scale BN as a filler, another surface treatment is necessary to make the reaction site of the particle surface.

In this study, a polymer matrix, dimethyl siloxane-based epoxy, was employed to fabricate a thermally conductive composite and a 12 μm BN particle was adopted as a composite filler to reduce phonon scattering and improve the thermal conductivity. To increase the affinity and dispersibility of the filler in the epoxy matrix, which is expected to provide a good thermal conductivity, two types of surface curing agents were employed. The resulting surface curing agent-coated BN possessed electrical insulating properties in addition to enhanced thermal conductivity due to reduced thermal resistance at the junction. The mechanical properties of the fabricated composites were measured and the data demonstrates that a small amount of surface curing agent enhances the thermal and mechanical properties.

2. Experimental

2.1. Synthesis of ETDS

The epoxy-terminated dimethysiloxane (ETDS) oligomer was obtained from Shin-Etsu silicon (KF-105, equivalent weight (E.E.W)=490 g/eq, density=0.99 g/cm^3). In our previous study, the weight ratio of the epoxy to the curing agent was determined to provide efficient flexibility of the matrix. In this study, the equivalent weight ratio of ETDS to DDM (4.4′-diamino diphenylmethane) was 1:2. 1.9 g of DDM was placed in a four-neck round flask equipped with a reflux condenser and was preheated to 363 K. 9.5 g of the ETDS resin was added and heated in an oil bath at 363 K for 1 h under a N_2 atmosphere. The bubbles in the mixture were removed by placing the mixture in a vacuum oven for 30 min at room temperature. The mixture was then placed in an oil bath at 323 K for 10 min in a N_2 atmosphere. The final degassing was performed in a vacuum oven for 1 h at room temperature to remove air bubbles [25].

2.2. Surface modification of BN

The detailed synthesis procedure is shown in Fig. 1. First, micro-BN particles were suspended in a 5 M sodium hydroxide solution at 110 °C for 18 h to attach more hydroxide ions onto the surfaces. Because micro-BN particles have few functional groups, surface treatment is necessary to facilitate chemical bonding with the surface curing agent. After base solution dipping, the particles were rinsed with D.I. water and filtered several times to adjust the pH from basic to neutral. The micro-BN hydroxide particles were left in the furnace at 80 °C for 5 h, cooled to room temperature, and then stored in desiccators.

The BN particles were modified with two surface curing agents, KBM-403 and KBM-703, obtained from Shin-Etsu Silicon by a sol-gel reaction. An appropriate amount of 3-glycidoxypropyltrimethoxysilane (KBM-403; 3–5% based on the weight of the micro-BN particles) and 3-chloropropyltrimethoxysilane (KBM-703) were added to D.I. water and stirred at 50 °C for 30 min to achieve hydrolysis. The micro-BN hydroxide particles were then dipped into the

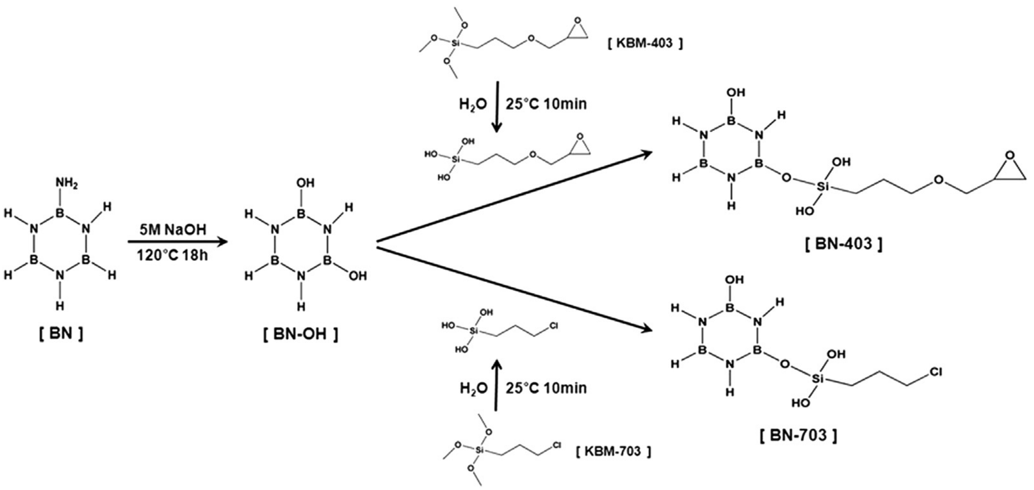

Fig. 1. Reaction scheme for the preparation of surface curing agent treated BN particle (BN-403, BN-703).

resulting solution and stirred at 70 °C for 1 h, followed by rinsing with D.I. water and filtering three times. The particles were then vacuum dried at 80 °C for 5 h to remove the solvent. The amount of the coating solution necessary is preferably 0.05–10% by weight, based on the weight of the particles. When the amount of the coating solution is less than 0.05% by weight, there is a tendency for insufficient and non-uniform particle coating to occur. When the amount of the coating solution exceeds 10% by weight, the obtained particles may possess excessive thermal resistance, thereby causing a decrease of the thermal conductivity of the composite films [26].

2.3. Preparation of the BN/epoxy composites

The composites were prepared by solution blending and a casting method consisting of (a) adding surface curing agent-coated micro-BN to the ETDS epoxy resin (50, 60, 70 wt%) for approximately 3 h in N,N-dimethylformamide (DMF) until the synthesized materials were completely mixed, (b) fabricating the composite films to a uniform thickness via a doctor blade on the Teflon mold, (c) pre-curing the films at 150 °C for 3 h until no air bubbles appeared on the surface followed by post-curing at 180 °C for 5 h, and (d) cooling to room temperature.

2.4. Characterization

Fourier transform infrared (FT-IR; Parkin-Elmer Spectrum One) spectroscopy and X-ray photoelectron spectroscopy (XPS; VG-Microtech, ESCA2000) were employed to analyze the surface curing agent-coated BN. For FT-IR spectroscopy, the ATR mode was used to avoid the influences of moisture adsorbed on the potassium bromide (KBr) particles and the scans were performed using radiation in the frequency range of 400–4000 cm^{-1}. In the XPS analysis, a monochromatic Mg Kα X-ray source was used at 1253.6 eV and the Gaussian peak widths obtained by curve fitting were constant in each spectrum. Thermogravimetric analysis (TGA; TGA-2050, TA instrument) of the samples was carried out to examine the thermal degradation of BN, BN-403, and BN-703. 4 mg of the samples were heated to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Field emission scanning electron microscopy (FE-SEM; Sigma, Carl Zeiss) was carried out to confirm the cross-sections of the component films before and after the silane treatment. The samples were sputtered with a thin layer of platinum to avoid the accumulation of charge before the FE-SEM observations. The thermal diffusivity (δ, mm^2 s^{-1}) at room temperature was measured on disk samples using a laser flash method (Netzsch Instruments Co., Nanoflash LFA 447 System). The specific heat (C, J g^{-1} K^{-1}) at room temperature was measured on disk samples via differential scanning calorimetry (DSC; Perkin-Elmer Co., DSC-7 System) and the bulk density (ρ_{comp}, g cm^{-3}) of the specimens was measured using the water displacement method. The thermal conductivity (Φ, W mK^{-1}) was calculated using the following equation:

$$\Phi = \delta C \rho_{\text{comp}}$$

To study the mechanical properties of the composite materials, mechanical analysis (DMA; Triton Instrument, Triton DMTA) was carried out. The storage modulus of the solid films was measured at a frequency of 1 Hz. The temperature range was −180 to 180 °C with cooling and heating rates of 10 °C/min.

3. Results and discussion

3.1. Structure analysis

The chemical structures of the surface-modified BN were determined using Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Fig. 2(a–c) shows the FT-IR spectra of pristine BN, BN-403, and BN-703, respectively. For pristine BN, the bands at 1400 and 800 cm^{-1} indicate stretching vibration in the hexagonal BN. The absorption band of pristine BN at 2300–2380 cm^{-1} represents absorbed CO_2.

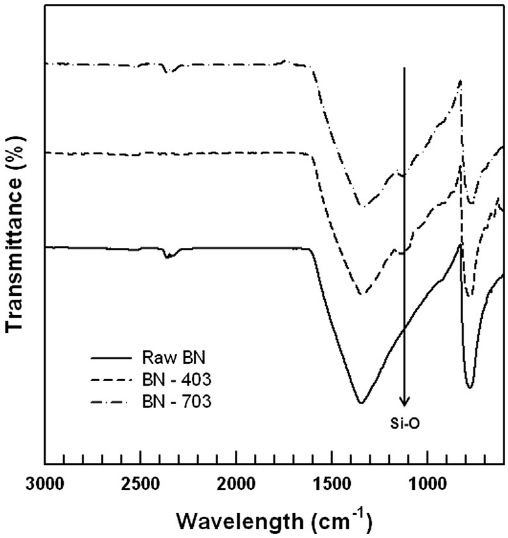

Fig. 2. FT-IR spectra of (a) raw BN, (b) BN-403 and (c) BN-703.

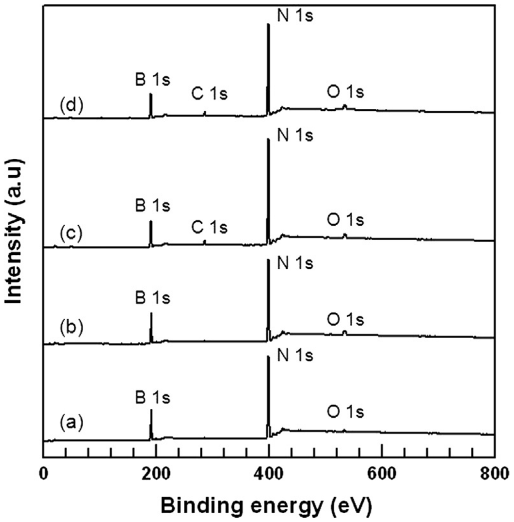

Fig. 3. X-ray photoelectron spectroscopy survey scans of (1) raw BN, (b) BN-OH, (c) BN-403, and (d) BN-703.

Comparing the pristine BN and the surface curing agent-treated BN (BN-403 and BN-703), the new band at 1100 cm^{-1} corresponds to stretching of the Si–O bonds, which existed in the pure surface curing agent.

Detailed surface information of pristine BN, BN–OH, BN-403, and BN-703 was collected by X-ray photoelectron spectroscopy (XPS) and the corresponding results are presented in Fig. 3. In the spectrum of pristine BN, there are only two elements of B and N. However, the O 1s signal emerges in the spectrum of BN–OH. This result implies that the hydroxyl groups were effectively introduced on the BN surfaces and edges via the sodium hydroxide treatment. These hydroxyl groups, acting as anchor sites, enabled attachment between the BN particles and surface curing agent. Moreover, the new peaks of C 1s and Si 2p can be assigned in the spectra of both BN-403 and BN-703, indicating that both surface curing agents, 403 and 703, were successfully attached to the surface and edges of pristine BN particles.

The detailed chemical bonding of fabricated, surface-treated BN particles was confirmed from the de-convoluted B 1s, Si 2p, and C 1s spectra, the results of which are shown in Fig. 4. Fig. 4(a and b) show the de-convoluted B 1s spectra of BN-403 and BN-703, respectively. The B 1s spectra of both BN-403 and BN-703 showed a strong binding energy peak for the B–N bond and a weak binding energy peak for the B–OH bond at 190.4 eV and 192 eV, respectively [27,28]. The B–OH peak resulted from the introduction of a hydroxyl group by the base treatment. In order to provide clearer evidence of chemical bonding between the BN particles and the silane curing agent, the Si 2p peak of these synthesized materials can be fitted by a curve with several component peaks. Fig. 4(c and d) shows the de-convoluted Si 2p spectra of BN-403 and BN-703, respectively. In the spectra of both BN-403 and BN-703, the strong peak at the binding energy of 102.1 eV represents the bond between silicon and oxygen originating from the BN particles (B–O–Si), indicating that the surface curing agent and BN particles are connected through the hydroxyl groups. The peak at 103.3 eV is attributed to siloxane (Si–O–Si) resulting from the partial hydrolysis of the silane curing agent molecules during the silanization reaction. Moreover, the peak at 100.8 eV is attributed to Si–C bonding in the silane curing agent molecules. These results are in agreement with the reaction mechanism of silane, including the hydrolysis of –OCH_3, condensation to oligomers, hydrogen bonds between oligomer and hydroxyl groups on the substrate, and the formation of the covalent linkage between silane and the substrate. The peak at 102.5 eV is attributed to Si–OH bonding, indicating that some hydroxyl groups did not hydrolyze and a small amount of hydroxyl group remained [29,30]. This implies that the amount of hydroxyl groups on the BN surface was not sufficient to make a uniform siloxane network and some hydroxyl groups in the surface curing agent were not hydrolyzed. This is due to the basal plane of the boron nitride particle surface having no functional groups. In addition, the silane coupling agent does not coat the surface uniformly such that the hydroxyl groups of the surface curing agent remained. The C 1s spectra of both BN-403 and BN-703 were de-convoluted to compare the structural differences of the two silane curing agents and the results are shown in Fig. 4(e and f), respectively. In the spectra of both BN-403 and BN-703, the strong peak at a binding energy of 284.7 eV indicates the C–C bond and the weak peak at the binding energy of 283.44 eV represents the C–Si bond, which exists in the surface curing agent structure. The primary difference between KBM-403 and KBM-703 is that KBM-403 has ether and epoxide groups, whereas KBM-703 has a chloride atom at the end of the carbon chain. In the C 1s spectrum of BN-403, C–O bonding is observed at a binding energy of 286.2 eV, which originates from the ether and epoxide groups. However, in the case of BN-703, the peak at 285.9 eV is attributed to C–Cl bonding, which can be explained by the existence of a chloride atom at the end of the carbon chain [31]. Based on these results, it can be concluded that the silane treatment can effectively introduce the surface curing agent onto the surface of BN.

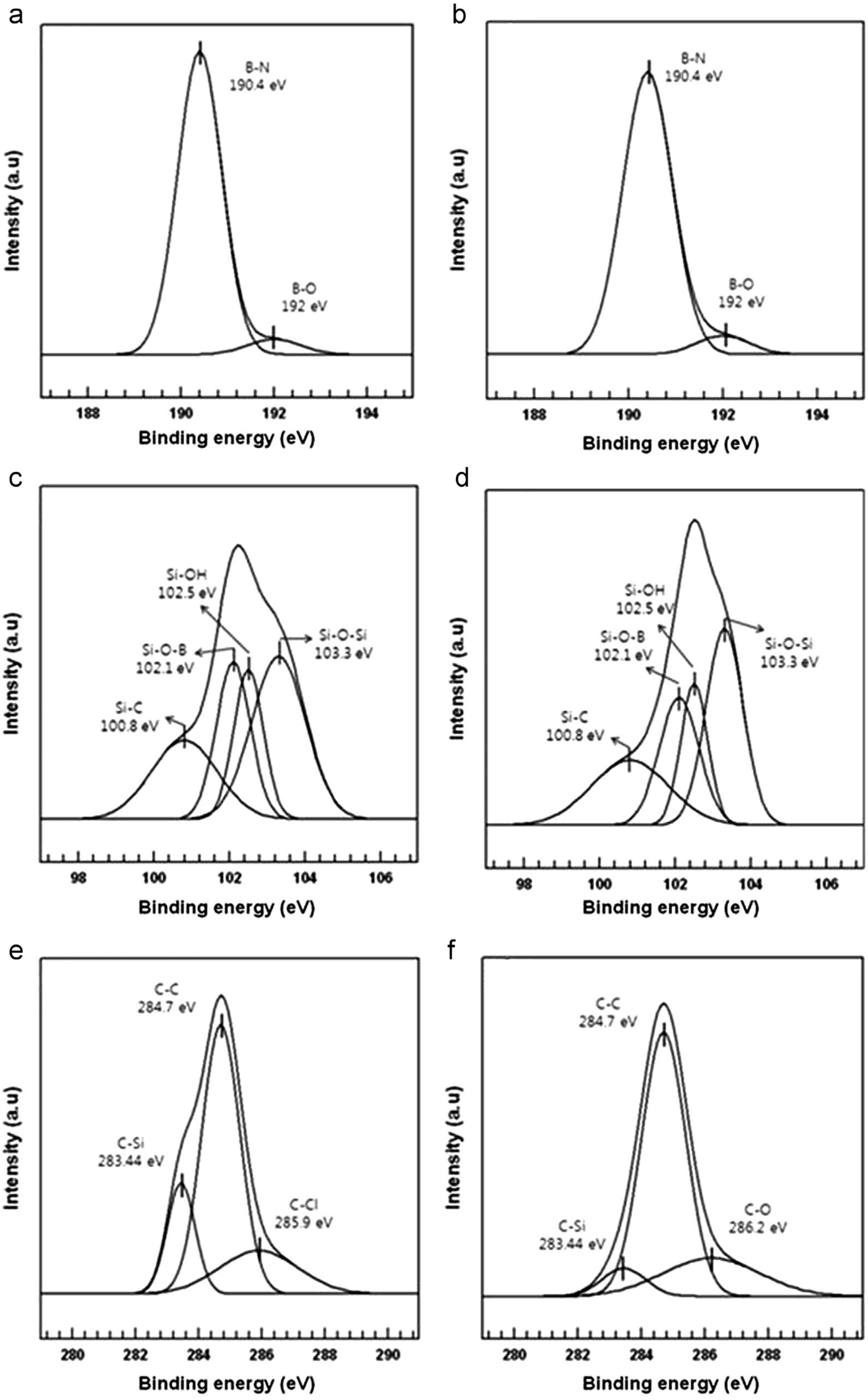

Fig. 4. XPS spectra of BN-403 and BN-703. (a) XPS B 1s spectrum of BN-403: (b) XPS B 1s spectrum of BN-703: (c) XPS Si 2p spectrum of BN-403: (d) XPS Si 2p spectrum of BN-703; (e) XPS C 1s spectrum of BN-403: (f) XPS C 1s spectrum of BN-703.

The compositions of the as-prepared BN, BN-403, and BN-703 composites were further investigated via TGA (Fig. 5). The experiments were performed up to 800 °C in air at a heating rate of 10 °C min^{-1}. Under these conditions, weight loss was not observed up to 800 °C for pristine BN, whereas weight losses of about 4% and 3.6% were observed for BN-403 and BN-703, respectively, due to thermal decomposition of the surface curing agents attached to the BN. The mass ratios of KBM-403/BN and KBM-703/BN for BN-403 and BN-703 were calculated to be 0.042/1 and 0.037/1, respectively. Moreover, these ratios between BN and the surface curing agent are optimal to mix the surface curing agent-treated BN as a filler and the silane-based epoxy as a matrix [32]. As reported by Itoh et al., the surface curing agent is poorly dispersed in the particles when too little is added and the desired effect of improved crack formation resistance in the cured resin composition cannot be achieved [33]. An excess of surface curing agent in the resin composition leads to a decreased thermal conductivity. This is because the redundant coupling agent causes phonon scattering and gives rise to a decreased thermal conductivity of the composites, resulting in low thermal conductivity materials.

3.2. Thermal properties

The thermal conductivity of the composites is controlled by the intrinsic conductivities of the filler and matrix as well as the shape, size, and loading level of the filler. Table 1 shows the variations of the thermal conductivity of the BN/ETDS composites with nano-BN (~1 μm), micro-BN (8 μm, 12 μm), and a filler content ranging from 50 to 70 wt%. The thermal conductivity of pristine ETDS is approximately 0.2 W/mK. It can be seen that as the weight fraction of these fillers increased, the thermal conductivity also increased considerably. With 12 μm particles at loadings of 50 wt%, 60 wt%, and 70 wt%, the thermal conductivity increased by factors of 11.1, 13.35, and 14.58, respectively, compared to the pure resin (~0.2 W/mK). As shown for the three types of particles, the thermal conductivity is also a function of the particle size, where the results parallel the effect of the particle type. The highest thermal conductivity values were obtained from the 12 μm particle-filled composites at all filler loading levels. This result can be explained by the thermal interface resistance caused by phonon boundary scattering. In theory, the scattering of phonons in composite materials is primarily due to the existence of an interfacial thermal barrier from acoustic mismatch or damage of the surface layer between the filler and the matrix. Large particles tend to form fewer thermally resistant polymer-layer junctions than small particles at the same filler content. Large particles are therefore used as a thermal conducting filler because of their negligible phonon scattering effect and excellent thermal conductivity [34,35].

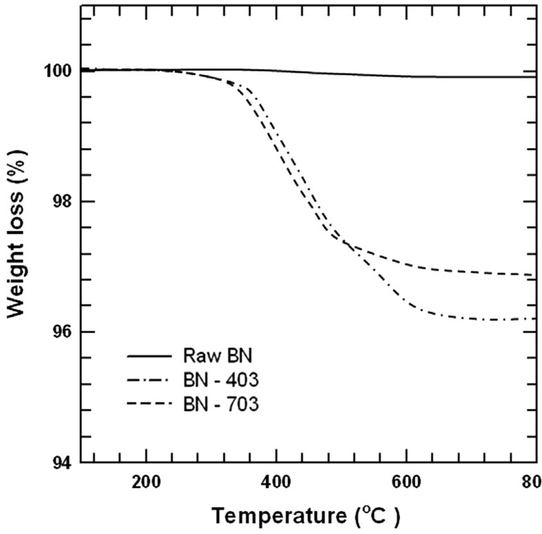

Fig. 5. TGA thermograms of pristine BN, BN-403 and BN-703.

In this paper, the use of a micro-filler to improve the thermal conductivity of composites was studied. The influence of the BN concentration and surface treatment on the thermal conductivity of BN/ETDS composites is presented in Fig. 6. It can be seen that as the weight fraction of these synthesized materials increased, the calculated thermal conductivity of all of the investigated composites increased considerably. The use of surface curing agents clearly improved the thermal conductivities of the composites. At 12 μm BN particle loadings of 50, 60, and 70 wt%, the thermal conductivities of the KBM-403- and KBM-703-treated BN/ETDS composites increased by factors of 1.17, 1.23, and 1.41 and 1.15, 1.19, and 1.33 compared to the untreated BN/ETDS composite, respectively. This effect could be explained by the enhanced dispersibility of particles in the composite caused by the surface curing agent. The two surface curing agents used contain an epoxide group and chloride functional groups that interact with the active groups of the epoxy matrix. Thus, the organic active groups or long molecular chains on the surface of the modified BN either react or entangle with the reactive groups of the epoxy matrix. The addition of surface curing agents to the

Table 1
Thermal conductivity of various particle size and filler contents (W/mK).

Size of BN particles	Thermal conductivity at various filler concentration [W/mK]		
	50 wt%	60 wt%	70 wt%
~1 μm	1.49	1.67	2.15
8 μm	2.16	2.35	2.77
12 μm	2.32	2.73	2.92

epoxy matrix therefore improves the interface bonding between the BN particles and matrix, leading to an enhanced thermal conductivity. In addition, this result could be explained by the reduction of the phonon diffuse boundary scattering that constitutes a significant part of the thermal resistance accompanying an imposed temperature gradient. The phonon scattering at interfaces, both for free surfaces and those bonded to other materials, observed for most real interfaces has yet to be quantitatively explained. The boundary resistance between two carefully bonded solids appears to be satisfactorily described by the acoustic impedance mismatch between the two media. The silane coupling agents acted as phonon transfer bridges between the polymer and the ceramic filler, which reduced the phonon boundary scattering and improved the thermal conductivity at low concentrations.

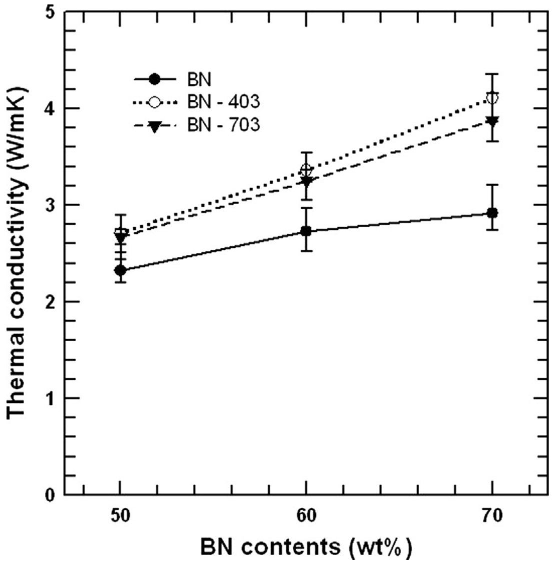

Fig. 6. Effect of surface treatment of BN particles on the thermal conductivity of BN/ETDS composites at various filler concentration.

As demonstrated in this study, the KBM-403 treatment was more effective than KBM-703 in enhancing the thermal conductivity. This can be explained by the ETDS/DDM polymerization mechanism. When the composite curing was performed at high temperature, epoxide groups in the ETDS react with DDM, and the ring opening and polymerization reactions proceed continuously. Similarly, epoxide groups in KBM-403 react with DDM and are polymerized with ETDS. As a result, the boron nitride filler linked with the matrix through covalent bonding. However, KBM-703 has a chloride group that instead forms non-covalent bonding, a dipole-dipole interaction, with the ETDS matrix. Therefore, KBM-403-

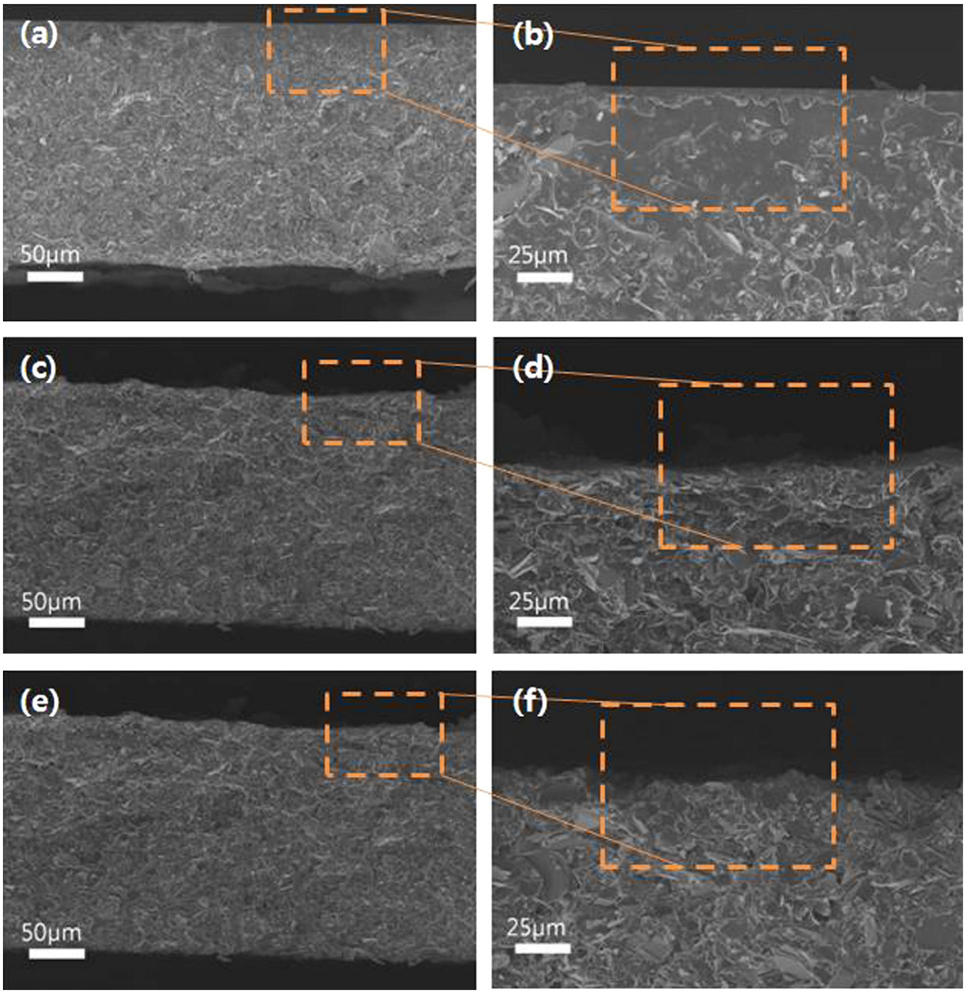

Fig. 7. SEM cross section image of (a)–(b) BN/ETDS, (c)–(d) BN-403/ETDS and (e)–(f) BN-703/ETDS composites with 50 wt% filler concentration.

treated BN has a stronger interaction with the ETDS matrix along with good dispersibility and a higher thermal conductivity than the KBM-703-treated BN composite.

The differences in the cross-sectional images of each composite can be correlated to the existence of a silane coupling agent. Fig. 7 shows FE-SEM images of the cross-sections of 50 wt% BN/ETDS and two kinds of surface coupling agent-treated BN/ETDS composite films. As observed in Fig. 7(a, c and e), all of the composite films appear to be homogeneously distributed. However, when the BN/epoxy composite film is observed at higher magnification (Fig. 7(b)), it can be seen that the BN filler settled to the bottom and a non-uniform distribution can be observed in the top of the film. This phenomenon is due to sedimentation of the filler, which is an endemic problem of the casting method. BN fillers were well mixed for a sufficient time with the epoxy resin, maintaining good fluidity at the high temperature, but sedimentation of the filler progressed in the post curing step. On the other hand, the images in Fig. 7(d and e) show a uniform cross-section of the silane coupling agent-treated BN, which was dispersed more uniformly and embedded in the epoxy, creating superior interface adhesion with the BN in the epoxy matrix. Uniform distribution of BN particles develops in the conduction carrier path. Moreover, BN has an idiopathic high surface energy, indicating that the phase interaction force between the epoxy and BN particles is very weak and suggesting that a low energy is needed to pull BN particles out from the matrix [36]. The images in Fig. 7(d and f) show an enhanced homogeneous distribution of BN particles throughout and a decrease of cracks and voids between the BN particles. This is further evidence that the surface curing agent enhanced the BN particle affinity with the matrix.

Fig. 7 shows that the use of surface coupling agents effectively improves the homogeneous dispersion of BN particles in the epoxy, eliminates the agglomeration of filler, and decreases the void content and defects in the composites, resulting in an increased thermal conductivity.

3.3. Mechanical properties

The mechanical properties of the composites with enhanced thermal conductivities were also measured by dynamic mechanical analysis (DMA). This was carried out to determine the improvement of the mechanical properties after the surface modification of the boron nitride particles in the polymer matrix. Since the operation temperature of the electronic package is generally about 150 °C, the stability of the composites was examined up to this temperature. The storage modulus of composite films with a filler content of 70 wt% is displayed in Fig. 8 as a function of temperature. As expected, the slopes of the curves tended to decrease near the glass temperature (T_g). It can be clearly seen that the storage modulus of the composites increased with filler surface modification, which is due to the mechanical reinforcement resulting from the strong interactions between BN and the ETDS matrix. As mentioned above, silane coupling agents improved the adhesive property between the filler and matrix, as the stress is not well transferred when the same force is applied to the composite. The KBM-403 in the composites prevented efficient treeing of the propagation of stress and, as a result, the storage modulus could be improved where the modulus of the KBM-403 treated with the BN composite was higher than that of the KBM-703-treated BN composite.

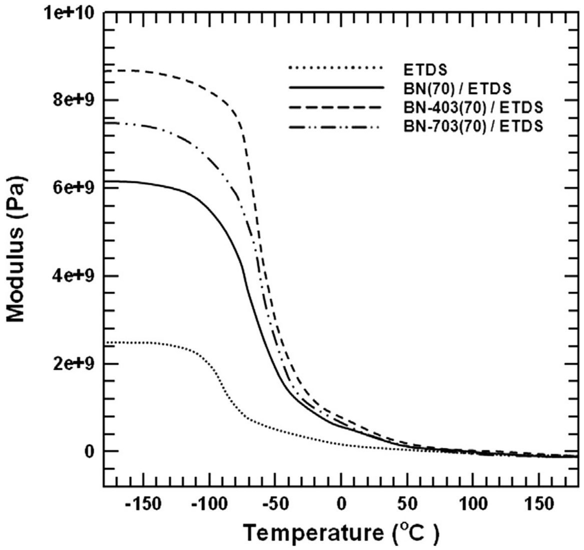

Fig. 8. Storage modulus of ETDS and ETDS composites with 70 wt% filler concentration.

The tan δ peak position, which is a measure of the glass transition temperature (T_g), shifted to higher temperatures with surface modification. The peak height was reduced when compared to that of the surface-untreated BN composite because the well dispersed filler and sufficient incorporation of epoxy restricted the mobility of the epoxy chains, resulting in the higher mechanical properties observed for the surface-treated BN composites.

4. Conclusion

BN/epoxy composite films with different BN particle sizes and contents were successfully fabricated with a surface curing agent using a solvent casting method. The thermal conductivities of polymer composites filled with various types of particles were evaluated and the thermal interface resistance theory was applied. Various particle to filler ratios were tested and the 12 μm filler demonstrated a higher performance, in the range of 136–149%, than the nano-size filler (∼1 μm). Furthermore, by applying micro-sized particles, the formation of conductive networks was maximized while minimizing the thermal interface resistance along the heat flow path. This thermal interface resistance is caused by phonon scattering in the interface of materials, which is the primary cause of decreased thermal conductivity.

Silane pretreatment followed by a surface curing agent addition resulted in improved dispersibility and adhesive properties of BN particles in epoxy resin as well as a higher thermal conductivity at the same filler content than the untreated composite. The highest thermal conductivity of 4.11 W/mK was obtained for the surface-treated ETDS composite loaded with 70 wt% 12 μm BN, representing a value 20.5 times higher than the value obtained from pure ETDS. It was concluded that enhancing the adhesion filler with a matrix in order to reduce voids and cracks in the sample is an appropriate method to obtain a high thermal conductivity. Moreover, because of the variation of the structures between the two kinds of surface curing agents, the distinct thermal properties were caused by the formation of different chemical interactions.

In further studies, we advise that additional research be performed regarding the micro-size filler distribution and the limitations of the ratio of the filler size and composite film thickness.

Acknowledgments

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