Thermal Conductive Performance of Organosoluble Polyimide/BN and Polyimide/(BN + AlN) Composite Films Fabricated by a Solution-Cast Method

D.H. Kuo,[1]* C.Y. Lin,[1] Y.C. Jhou,[1] J.Y. Cheng,[1] G.S. Liou[2]*
[1]*Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan*

[2]*Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan*

Organosoluble polyimide (PI)/ceramic composite films with different BN or (BN + AlN) contents were under investigation for their thermal conductive performances. The chosen polyimide constituted by 4,4′-oxydiphthalic dianhydride/2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane could be dissolved and cast into thin films at room temperature. The commercially available BN and AlN fillers up to a volume ratio of 0.6 were added to the polyimide and their thermal conductive performances were measured. BN powders needed a surface precoating treatment to avoid sedimentation. The dense and flexible PI/BN composite films, after a drying treatment at 200°C, showed high thermal conductivity of 2.3 W/m·K^{-1} at a BN volume ratio of 0.6, as compared with 0.13 W/m·K^{-1} for pristine polyimide. However, in the case of PI/(BN + AlN) composite films, thermal conductive performance degraded because the films became highly porous at the higher AlN content. POLYM. COMPOS., 34:252–258, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Organic-inorganic composites have gained wide applications in composite industry and for flexible electronics, because they can display better mechanical and functional properties than their individual component [1, 2]. As an example, polymers used as electronic packaging materials alone cannot effectively dissipate heat generated from high packing and power-density devices, because they have relatively low thermal conductivity (κ) ranging 0.1–0.5 W/m·K^{-1} [3]. To solve the problem of heat dissipation, thermally conductive, and electronically insulating ceramic fillers of alumina (Al_2O_3), boron nitride (BN), aluminum nitride (AlN), silicon nitride (Si_3N_4), etc., have been added to form hybrid composites [4–7].

Aromatic polyimides (PIs) are one kind of high-performance polymers that have been widely used as substrates for flexible electronic devices because of their outstanding performance in thermal, mechanical, and optic-electrical properties [8–10]. There are two main methods for preparing PIs. One is a two-step process, by which a diamine first reacts with a tetracarboxylic dianhydride in a polar aprotic solvent at ambient condition to form a poly (amic acid) (PAA) intermediate, followed by dehydration and cyclization at ∼300 °C. Although this approach has advantages of using less toxic solvent and directly forming final products after thermal imidization, it has the drawbacks of the instability in the PAA precursor, the liberation of water during imidization, and the difficulty in the control of imidization. The second method is a one-step process, by which a diamine directly reacts with a tetracarboxylic dianhydride at 190–210°C with a solvent having a high boiling point [11]. The advantages of this one-step approach are the lower imidization temperature to form PI with higher molecular weights and the feasibility of utilizing monomers with lower reactivity.

Composites with BN or AlN as a filler have been widely fabricated in the polymer matrices of epoxy, high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), poly(butylene terephthalate) (PBT), polystyrene (PS) etc. Young et al. had demonstrated κ of 19.0 W/m·K by a laser flash technique for epoxy filled with silane-modified BN at a solid loading of 26.5 vol% [12]. Powder-mixed and melt-mixed HDPE/BN composites with a BN content of 35 vol% had κ values of 1.24 and 1.04 W/m·K^{-1}, respectively, after measurements with a hot-disk thermal analyzer [13]. LLDPE/(30 vol% AlN) composites with titanate coupling reagent-modified fillers showed κ of 1.08 W/m·K^{-1}, as determined by a hot disk method [14]. Injection molded

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PBT/(22 vol% BN) composites displayed κ of 1.1 W/m·K^{-1} by a laser flash instrument [15]. PS/(20 vol% AlN) composites with κ of 0.75 W/m·K^{-1} had a five-time increase in thermal conduction, as compare to the pristine matrix [16]. Due to the different measurement methods, the comparisons in κ need to be cautious.

The investigations on the PI-based composites containing the important thermal-conducting fillers of BN and AlN are limited. Due to the large differences in measuring κ value, the following literature surveys focus on those reports involving a hot-disk method. Xie et al. studied the preparation and thermal conduction of PI/AlN composites. They found that AlN powders treated with silane coupling agents could improve the compatibility between PI and AlN and their κ values increased from 0.02 W/m·K^{-1} for pure PI to 0.8 W/m·K^{-1} for a composite with 33 vol% AlN [17]. Li et al. prepared PI/BN composites by adding 3-mercaptopropionic acid (MPA)-modified fillers with different particle sizes. Their PI/(30 wt% BN) composites with the microsized and nanosized fillers at a weight proportion of 7:3 exhibited a high κ value of 1.2 W/m·K^{-1}, which was attributed to the formation of a filler network [18]. PI/(60 vol% BN) composite with a κ value of 7 W/m·K^{-1} was fabricated by tuning the hetero-interface without surface modification [19]. For the above-mentioned studies, polyimide used in the composite was all fabricated by a two-step approach.

In this study, our PI/ceramic composite films were prepared by mixing the one-step polyimide and BN or (BN + AlN) in tetrahydrofuran (THF) to form a suspension, followed by casting to develop composite films. The organosoluble PI with hydroxyl groups was synthesized from 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-OH diamine) and 4,4'-oxydiphthalic dianhydride (ODPA) [9].

The improvements in phase segregation and particle sedimentation during solution coating were investigated. The effect of different filler contents on κ of composites was also studied.

EXPERIMENTAL

Materials

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-OH diamine, 98%) was purchased from Alfa Aesar and recrystallized from methanol after refluxing at 60–65°C with the addition of small amount of distilled water. The precipitated crystal was dried in oven at 90°C for 2 days. ODPA (98%) received from TCI America was purified by refluxing in acetic anhydride (99%, Aldrich, MO) at 140°C for 3 h under the nitrogen (99.9%) atmosphere, followed by fast precipitation in an ice bath for 1 h. The precipitated crystal was filtered and washed with toluene (99.5%, Avantor Performance Materials, PA), followed by drying in oven at 90°C for 2 h. m-Cresol (99%, Alfa Aesar) used as a solvent was dehydrated by phosphorus pentaoxide (99.9%, Sigma-Aldrich). Our polyimide was

synthesized by a one-step polycondensation reaction between 6F-OH diamine and ODPA in m-cresol with isoquinoline (95%, TCI America, OR) as a catalyst. The imidization reaction was executed at 200°C for 15 h, after that PI fiber was precipitated from methanol and dried at 90°C for 24 h [9, 20].

### Organosoluble PI/Ceramic Composite Films

Flexible and thermally conductive polyimide/ceramic composite films were prepared by solution blending of ceramics and organosoluble PI in THF, followed by cast coating to form films at room temperature. The chosen ceramic fillers include precoated BN and AlN powders. BN and AlN were purchased from Sigma-Aldrich LLC. Precoated BN powders were prepared by dispersing BN powders in a THF-based polyimide solution with the aid of ultrasonication for 1 min in the presence of 1-methoxy-2-propyl-acetate (MPA), and casting to form a film. Then, the mortar-pestle milling was used to mill the resulting film into PI-coated BN powders. Ceramic-filled polyimide composites in this study involved two systems of the PI/BN and PI/(BN + AlN). Scheme 1 shows the illustrative process procedures for preparing PI/BN composite films with a solution method. The PI/BN composite films were fabricated by mixing precoated BN powders with a PI solution to form composites with different BN/(BN + PI) volume ratios of 0.3, 0.4, 0.5, and 0.6. The PI/(BN + AlN) system was constituted with the 40% PI/60 vol% ceramic composites, in which the ceramics of AlN and BN had the AlN/(AlN + BN) volume ratios of 0, 0.3, 0.7, and 1. Table 1 shows compositions of PI/(BN + AlN) composite films. This system was fabricated by mixing precoated BN powders and un-coated AlN powders with an MPA-containing PI solution to form slurry, followed by casting into films. The cast composite films for both of the systems were dried at 160, 200, and 250°C for 10 h.

Characterization

Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F) was used to observe the as-received ceramic powders, surface morphology, and cross-section of our composite films. The actual ceramic contents in different composite films were determined by the thermogravimetric analysis (TGA, TA Instruments Q500), which was executed from 30 to 800°C at a heating rate of 20°C min^{-1} and a mixed (95% nitrogen/5% oxygen) flow rate of 20 cm^3/min^{-1}. Thermal conductivity measurements of our composite films were performed on a hot-disk thermal analyzer (TechMark TPS 2500) at 25°C.

RESULTS AND DISCUSSION

Figure 1 shows FE-SEM images of commercially available (a) BN and (b) AlN powders. The BN particle
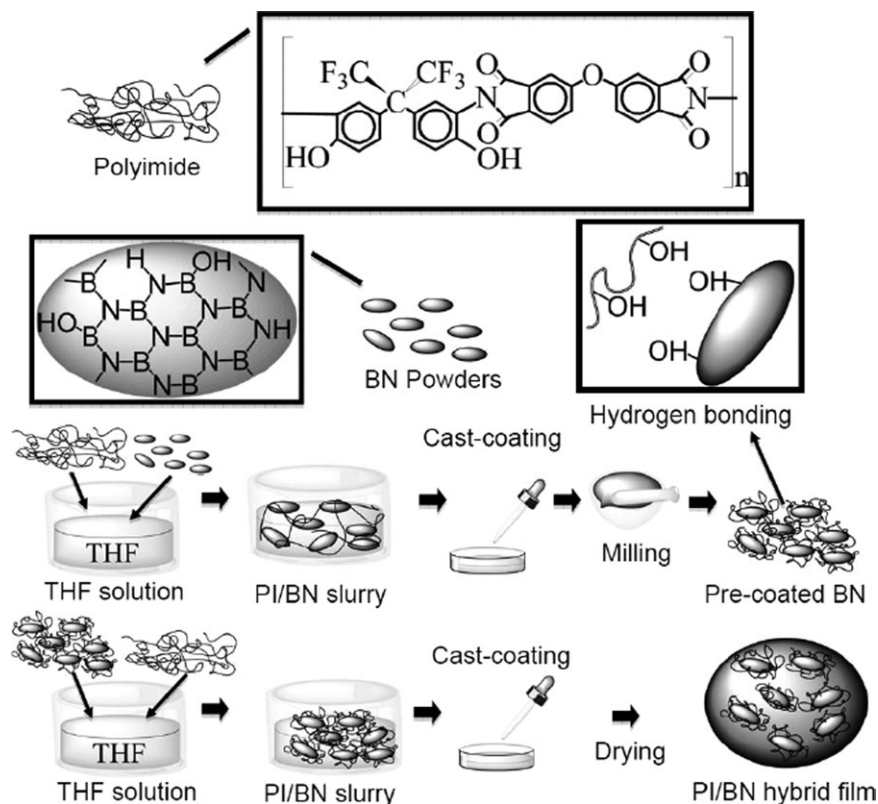
SCHEME 1. Illustrative process procedures for preparing PI/BN composite films by a solution-cast method.

exhibited uniform plate-like shape with particle size of ~0.5 μm, while AlN powder revealed irregular shapes and a wide distribution of 0.4–2.4 μm in particle size. It is known that BN with a small size has hydroxyl and amino groups on the edge planes of the platelets and these functional groups can allow the BN powders to disperse in a solvent [21]. Therefore, we prepared PI/BN composite films by mixing BN powders and PI in a solution with the utilization of the functional groups on BN. However, the (BN + PI) slurry using the one-step PI has low viscosity, as compared with the paste formed by mixing viscous PAA with fillers in a two-step process. The low-viscosity slurry facilitates the sedimentation of the ceramic fillers. The cross-sectional FE-SEM image of the PI/60 vol% BN composite film with uncoated filler is displayed in Fig. 2. The film had a nonuniform cross section and most of BN fillers settled to the bottom of composite film. The sedimentation is the major disadvantage of using our one-step PI to prepare the solution-cast composite films containing fillers with a relatively large particle size. Even though a surfactant of MPA had been tried to solve the sedimentation problem, it was not successful.

To overcome the sedimentation problem of BN particles, a precoated technique was applied. That is, BN particles were precoated with a PI solution through a solution process, followed by adding the dried PI-coated BN particles into a second PI solution and then casting the slurry into a composite film. The advantage of precoating BN with PI is the formation of polymer tangling

between the precoated PI and the second PI solution, which can prevent the sedimentation of BN particles before drying. Figure 3 shows (a) surface and (b) cross-sectional FE-SEM images of PI/BN composite films fabricated by a precoating technique with filler volume ratios of (1) 0.3, (2) 0.4, and (3) 0.6. From Fig. 3b, it is obvious that BN platelets are trapped in the PI matrix and prefer to form horizontally regular stacking at a higher BN content. The insets in Fig. 3b are the FE-SEM images under a lower magnification to show the uniformity of filler distribution. These uniform PI/BN composite films are flexible, even though the BN filler content has reached a volume ratio of 0.6. The inset images in Fig. 3a exhibit their optical photographs in a bending state to demonstrate their flexibility.

Figure 4 displays thermogravimetric analyses of PI/BN composite films at different filler contents. It was found that the decomposition temperature (T_d) at 10% weight loss was 515°C for pure PI. The T_d values of PI/BN

TABLE 1. Compositions of PI/(BN + AlN) composite films.

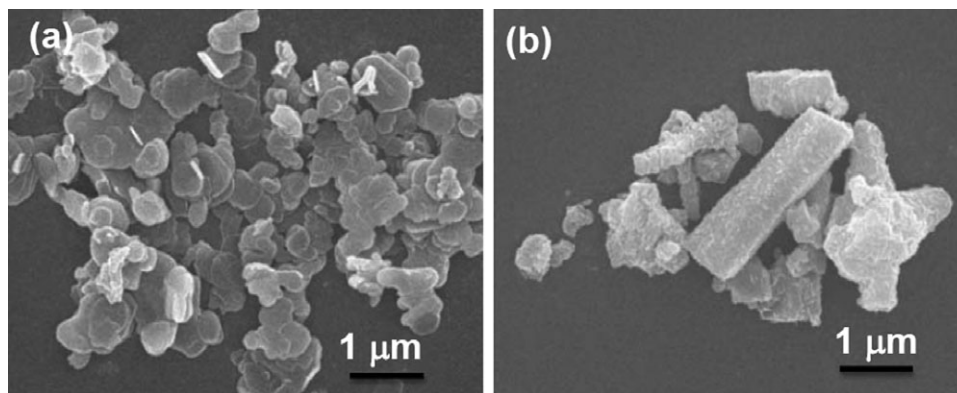| Sample	BN/(BN + AlN) Volume ratio	Filler volume ratio		
		BN	AlN	PI
PI/60 vol% ceramic	0	0	0.6	0.4
composite films	0.3	0.18	0.42	0.4
	0.7	0.42	0.18	0.4
	1	0.6	0	0.4

FIG. 1.   FE-SEM images of commercially available (a) BN and (b) AlN powders.

composite films increased from 541 to 566, as the BN content increased from 30 to 60%. The TGA curves slightly shifted toward higher temperatures with increasing the filler content, which indicated that BN filler could improve the thermal stability of PI matrix. In addition, the total weights of the residues after TGA tests were 0.3, 34.8, 44.7, 52.4, and 63.7 wt% for films with BN volume ratios of 0, 0.3, 0.4, 0.5, and 0.6, respectively. These weight ratios of residues were in agreement with the mass fraction of BN originally added in the PI matrix.

Figure 5a shows thermal conduction analyses of PI/BN composites at different filler contents and drying temperatures. Pristine PI had relatively low κ value of 0.13 W/m·K^{-1}. After embedding with the BN particles, the κ values of composite films gradually increased. When the BN loading reached a high volume ratio of 0.6 and the drying treatment was at 160°C, the κ value of this composite film reached 0.7 W/m·K^{-1}. The reason for increasing κ with the increase in the filler content is due to the reduced distance between the BN particles for the enhanced phonon interaction. For the purposes of improving the interfacial compatibility and reducing the thermal

FIG. 2.   Cross-sectional FE-SEM image of PI/BN composite films with uncoated filler at a volume fraction of 0.6.

conductive resistance between the filler and PI matrix, we had dried composite films at temperatures of 160, 200, and 250°C to remove completely the residual solvent. The result showed that the highest κ value was 2.3 W/m·K^{-1} for the composite films with BN volume ratio of 0.6 after a drying process at and above 200°C. This value of 2.3 W/m·K^{-1} measured with a hot-disk technique for PI-based composite films is only inferior to the two-step result reported by Sato etc. and is much improved as compared with others involving with the hot-disk measurement. The high κ value for PI/BN composites using a two-step PI is attributed to the thermal imidization at 300°C under warm pressing to form a thin plate. Under this pressing, hexagonal BN plates in a viscous PAA medium will be aligned and PAA will be squeezed out of gaps between BN plates. The aligned BN particles might form a conduction path through contacts. Our experiment was in a different way. The solution-cast method is a simple technique without applying loading. Our results, after treating at different drying temperatures, indicate κ is strongly dependent upon the moisture. The moisture surrounding the thermally conductive fillers can interrupt the thermal conductive path for phonon propagation. This moisture problem has not been observed for PI-based composites using a two-step polyimide [22].

AlN is the second candidate for our ceramic fillers because of their attractive properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, etc. The reported κ value for AlN was close to 260 W/m·K^{-1} at ambient temperature, as compared with 300 W/m·K^{-1} for BN [23]. Figure 6 shows (a) surface and (b) cross-sectional FE-SEM images of PI/60% ceramic composite films with the AlN/(AlN + BN) volume ratios of (1) 0.3, (2) 0.7, and (3) 1. As the AlN content increased, the amount of voids increased. The insets in Fig. 6b are the cross-sectional FE-SEM images under a lower magnification to show the porosity problem. The formation of voids at higher AlN content is caused by the difficulty in packing the large and irregular AlN fillers. Although composite films were porous, they retained some flexibility, as shown in the insets of
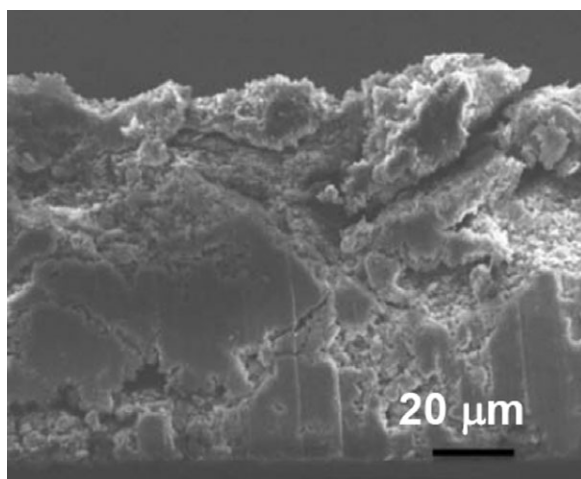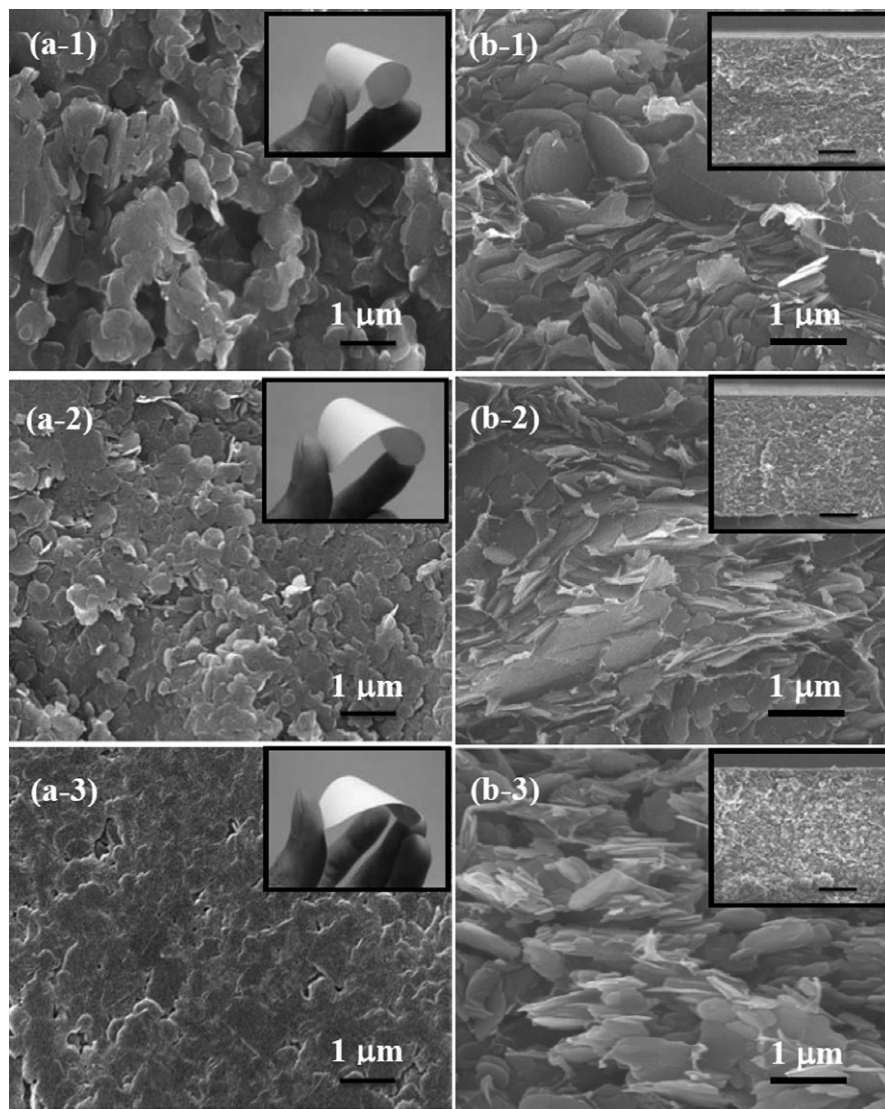
FIG. 3. (a) Surface and (b) cross-sectional FE-SEM images of PI/BN composite films with filler volume ratios of (1) 0.3, (2) 0.4, and (3) 0.6. The optical images in the insets of (a) demonstrate the flexibility of PI/60% ceramic composite films. The insets in (b) are the cross-sectional FE-SEM images under a lower magnification with a scale bar for 20 μm.

Fig. 6a. However, the packing could be improved and the porosity could also be reduced by using the intermixing of finer BN particles with the large AlN particles. Figure 5b shows the variation of the κ values of PI/60% ceramic composite films with the AlN/(AlN + BN) volume ratio. The κ values of PI/60 vol% (BN + AlN) composite films reduced from 2.3 to 0.29 W/m·K, as the AlN/(AlN + BN) ratio increased from 0 to 1. Although AlN possesses high κ, the drop in κ of composite film can be attributed to porosity, which is related to the difficulties in packing and alignment of the irregular AlN fillers in polyimide matrix. The warm pressing used by the two-step PAA approach can solve the packing problem.

The improvements in κ of polyimide by introducing the thermally conductive and electrically insulating fillers of BN and AlN are demonstrated by using a solution-cast method. With this approach, a PI instead of viscous PAA
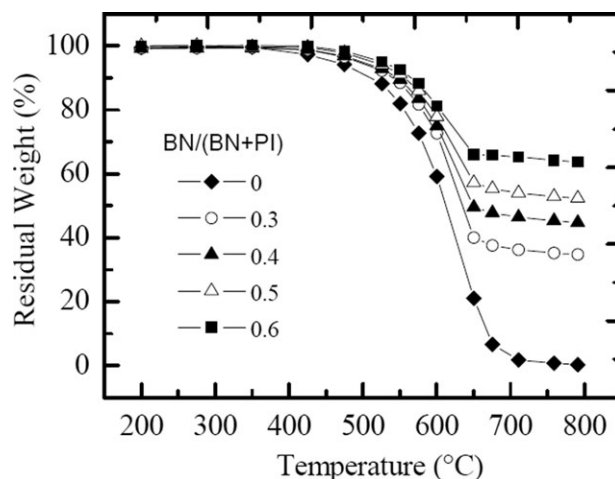

FIG. 4. TGA thermogravimetric analyses of PI/BN composite films at different filler contents.
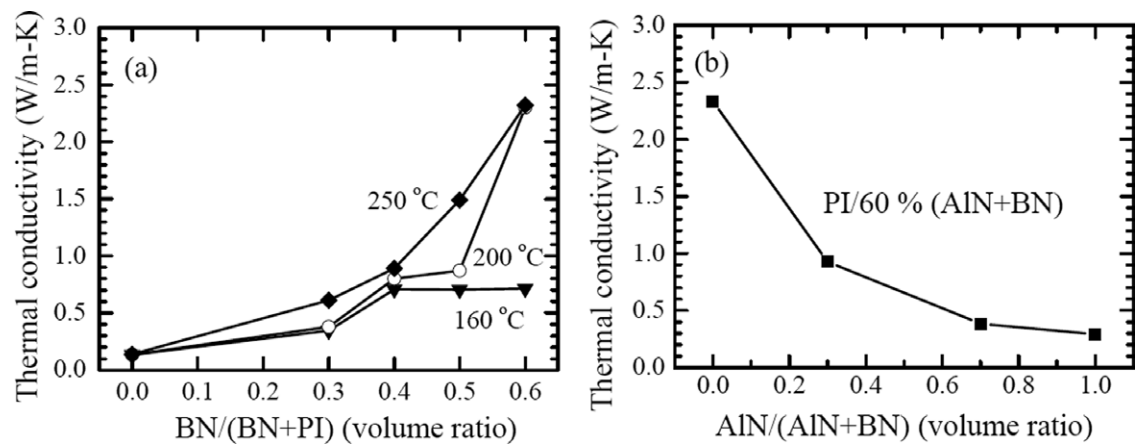
FIG. 5. (a) Thermal conduction analyses of PI/BN composite films at different filler contents and drying temperatures. (b) Variation of the thermal conductivity of PI/60% ceramic composite films with the AlN/(AlN + BN) volume ratio.
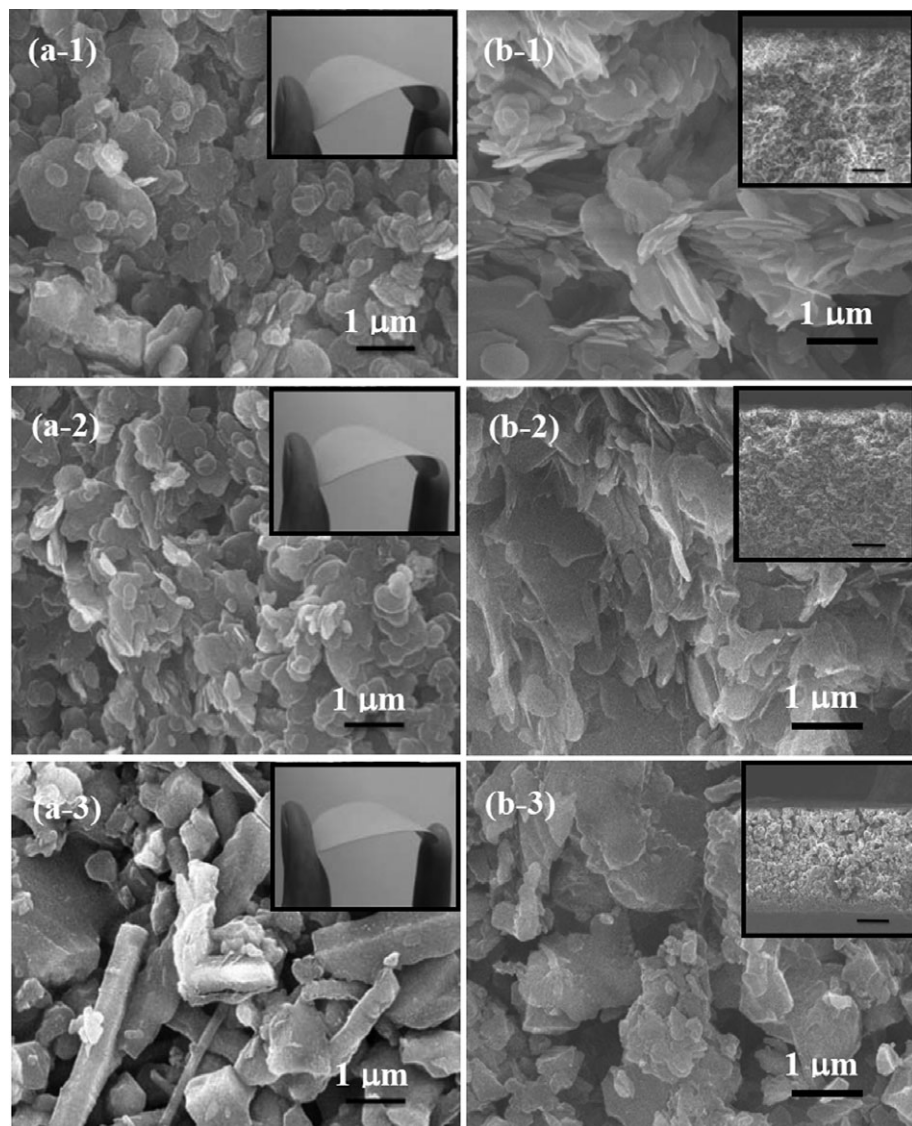

FIG. 6. (a) Surface and (b) cross-sectional FE-SEM images of PI/60% ceramic composite films with the AlN/(AlN + BN) volume ratios of (1) 0.3, (2) 0.7, and (3) 1. The optical images in the insets of (a) demonstrate the flexibility of PI/60% ceramic composite films. The insets in (b) are the cross-sectional FE-SEM images under a lower magnification with a scale bar for 20 μm.

is used. This method can fabricate thin composite layers using casting, spin coating, screen printing etc., which provide the advantage to integrate with the thin film technology and the processes used for flexible electronics. Although the moisture from the solvent results in a serious problem in thermal conductivity of solution-cast composites, further improvements can be made by using a vacuum evaporator to dry the composite films because of the low boiling temperature of 66°C for tetrahydrofuran.

CONCLUSIONS

Polyimide/ceramic composite films with different BN or (BN + AlN) contents have been successfully fabricated with a precoating technique. Because the resulting composite films were derived from the organosoluble PI as a matrix using low boiling point solvent such as THF, therefore these composite films can be fabricated at room temperature instead of 300°C by using a PAA route. This low-temperature process can afford PI/BN or PI/(BN + AlN) films suitable for flexible substrates with improved heat-dissipating capacity. The precoating technique was used to prevent the fast sedimentation of ceramic fillers during solution-cast process by forming tangling bonding between the precoated solid PI and the solution-cast PI. These uniform and flexible PI/BN composite films, after a drying treatment at 200°C, show high κ value of 2.3 W/m·K^{-1} at a BN volume ratio of 0.6, which is a seventeen-fold increase as compared with the pristine polyimide. The reasons for much higher κ value of PI/BN films are related to the ordered stacking, the formation of continuous contacts at a higher BN content, and the low moisture from the cast solvent. The relatively low κ value of PI/(BN + AlN) at the AlN/(AlN + BN) ratio of 1 is attributed to the introduction of voids by the large and irregular AlN particles and without applying an external pressing force.

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