Synergistic Effects of Hybrid Fillers on the Development of Thermally Conductive Polyphenylene Sulfide Composites

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ABSTRACT: The future of integrated circuits with three-dimensional chip architecture hinges on the development of practical solutions for the management of excessive amounts of heat generation. This requires new polymer–matrix composites (PMCs), with good processibility, high effective thermal conductivity (k_{eff}), and low but tailored electrical conductivity (σ). This article explores the synergy of hybrid fillers: (i) hexagonal boron nitride (hBN) platelets with different sizes and shapes; (ii) hBN platelets with carbon-based fillers promoting the k_{eff} of the polyphenylene sulfide (PPS) composites. It explores the promotion of interconnectivity among the fillers in the PPS matrix, leading to higher k_{eff}, by the uses of hybrid fillers. It discusses using carbon-based fillers as secondary fillers to tailor the PMCs' σ. Finally, it presents the effects of hybrid fillers on the PMCs' coefficient of thermal expansion. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Moore's law stating that the number of transistors on a chip will double about every 2 years has held for four decades, but the emerging three-dimensional (3D) chip architecture[1] offers an opportunity to take CMOS performance trends into the next decade. It can mitigate the interconnect problem inherent to modern microprocessor designs and enable a higher memory bandwidth for future 3D microprocessors. Recent progress in the fabrication of high-aspect-ratio vertical interconnects, called through-silicon vias (TSVs),[2–4] has opened the door for high density area array interconnects between a stacked processor and memory chips. When a very large system is integrated onto a Chip (SoC) in multiple tiers, the average distance between system components is reduced, leading to improved performance. However, the surging performance and enhanced chip functions come with a hidden cost—increased heat. The continuous increase in component densities being packed onto a chip means more electrical power is required to run it. A large amount of heat is generated during the operation of the components, leading to overheating. Overheating chips have reduced

reliability, potentially leading to computer crashes, mangled files, graphical glitches, even permanent damage. In other words, the future of 3D integrated circuits hinges on the development of practical solutions for heat removal. This prompts the development of advanced composite and monolithic materials tailored to meet the specific requirements of the electronic packaging or other heat management solutions.

In this context, thermally conductive but electrically insulating polymer composites become increasingly important. Various kinds of fillers, such as metal, metal oxide, carbon black, carbon fiber, carbon nanotube, ceramic, etc. have been studied extensively to determine if they are suitable for thermally conductive polymer composites. Previous studies have revealed that the effective thermal conductivities (k_{eff}) of polymer matrix composites (PMCs) are not as high as those of other advanced materials, such as metal matrix or ceramic matrix composites.[5] However, they have a number of advantages, including ease of fabrication, low density, and, for some materials, relative low material costs. A breakthrough that allows the fabrication of PMCs with dramatic improvement in k_{eff}, without

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compromising the electrical insulating property of polymers is vital to technological advancement in the heat management of electrical and electronic devices.

/PMCs with a high k_{eff} can be obtained by dispersing highly thermally conductive fillers in the polymer matrix. Bigg[6] has indicated that there is no additional improvement when the ratio of the filler's thermal conductivity to the matrix's thermal conductivity is over 100. Therefore, in the case of fillers with thermal conductivities equal to or greater than 100 times the polymeric matrices' thermal conductivities, the volume fraction becomes a critical factor in the composite's thermal conductivity. In general, composites with low loadings of filler particles allow the heat to flow uniformly through since all particles are well dispersed, but such low filler content limits the interconnection of filler particles. Increasing the filler content promotes the formation of preferential heat conducting paths to dissipate heat through the composite.[7,8]

Extensive studies have been conducted to promote PMC's k_{eff} using various kinds of fillers. For example, metal,[9–12] ceramics,[13–18] and carbonaceous fillers[19–22] have been applied to fabricate PMCs. k_{eff} of PMCs fabricated in these studies were in the range of 0.5–2.0 W mK^{-1} when the filler content was lower than 33.3 vol %. Although PMCs with k_{eff} (i.e., 5.0–32.5 W mK^{-1}) have been reported in the literature,[12–14] this requires either the addition of 60–90 vol % of thermally conductive fillers or the use of electrically conductive metal fillers, compromising either the processibility of the composites or the electrical insulating property of PMCs, two key benefits of PMCs in heat management applications. Previous studies also suggest that the development of thermally conductive networks hinges on the sizes and shapes,[8,23] the aspect ratios,[23,24] and the spatial and geometric arrangements[25] of the fillers. Experimental studies reveal that smaller filler particles result in lower composites' k_{eff} because of a larger interfacial area, causing phonon scattering and hindering phonon transport.[26] Furthermore, fillers with a high aspect ratio enhance the formation of heat conductive networks,[9,10] promoting the composites' thermal conductivities.

Various studies on thermally conductive PMCs filled with ceramic fillers have incorporated silicon carbide (SiC),[27] aluminum nitride (AlN),[15,28] or hexagonal boron nitride (hBN)[14,16–18] in polymer matrices. The high hardness of SiC and AlN is detrimental to the manufacturability of the composites. In contrast, hBN, which resembles the two-dimensional covalent network of graphite, has a low dielectric constant (i.e., ~ 4) and is lubricious. These intrinsic properties are consistent with the objectives of developing thermally conductive PMCs, including achieving high thermal conductivity, high electrical resistivity, and good processibility. While there are practical limits on the maximum amount of thermally conductive fillers that can be used without compromising processibility and mechanical performance,[29] strategies that can promote the formation of random bridges or networks would promote PMCs' k_{eff}. Some researchers have found that the addition of hybrid fillers of different shapes and/or sizes leads to a higher PMC k_{eff} due to the formation of effective thermal conductive path.[24,29–31] However, these studies focused on the effect of hybrid fillers on the

PMC's k_{eff}. In fact, the addition of a secondary filler not only promotes the k_{eff} of the PMCs but also tailors the electrical resistivity of the PMCs if it is electrically conductive. Thermally conductive PMCs with tailored electrical resistivity can be used for EMI shielding, capacitors, and electronic packaging materials. In light of this, this article investigates the synergistic effects of hybrid fillers, (i) hBNs of different sizes and shapes and (ii) hBN with another type of fibrous fillers, on promoting k_{eff} and tailoring the electrical conductivity of PMCs. It also considers the effects of hybrid fillers on the PMCs' coefficient of thermal expansion.

EXPERIMENTAL

Materials

Commercially available polyphenylene sulfide (PPS) (Ticona, Fortron 0203B6) was used as the matrix material in this work. The fillers used include two types of hBNs (Momentive Performance Materials, PolarTherm, PTX60 and PT110), pitch-based carbon fiber (CF) (Cytec Industries, ThermalGraph DXD), and multi-wall carbon nanotube (CNT) (Cheaptubes. com). The hBN fillers, PTX60, and PT110 have different shapes and sizes. PTX 60 particles are spherical agglomerates with mean diameters equal to 60 μm. PT110 are platelets whose mean particle sizes equal 45 μm. All hBN fillers were surface modified with amino silane (Struktol$^®$ SCA 1100) before being compounded with other fillers and the PPS matrix. PPS, CF, and CNT were used as received with no further modification. The physical properties of the polymers and fillers are summarized in Tables I through III.

PPS was chosen as the matrix material because of its high service temperature (200°C), which is required in various heat management applications. For the primary filler, hBN$_{PTX60}$ (i.e., spherical agglomerates) was chosen for several reasons: (i) it is electrically insulating; (ii) it resembles the layered structure of graphite, making it extremely soft and therefore more easily compounded at high loading; and (iii) its spherical geometry leads to isotropic filler properties. For the secondary fillers, hBN$_{PT110}$ (i.e., platelets), CF, and MWCNT were chosen because of their high aspect ratios and excellent thermal conductivities.

Surface Modification

Amino silane $((C_2H_5O)_3SiC_3H_6NH_2)$, a versatile coupling agent used to provide a superior bond between inorganic fillers and organic polymers, was used to modify the surface of hBN. Amino silane was first dispersed in a 50–50 ethanol–water solution. hBN powders were then added to the solution and mixed for 10 min by a magnetic stirrer. The samples were filtered and

Table I. Physical Properties of PPS

Physical properties	Values
Density (ρ)	1350 kg m^{-3}
Thermal conductivity (k)	0.22 W m-K^{-1}
Dielectric strength	22-28 kV mm^{-1}
Melting temperature (T_m)	280°C
Service T_{max}	200°C

Table II. Physical Properties of Various Grades of hBN

	PTX60	PT110
Density (ρ)	2280 kg m^{-3}	2280 kg m^{-3}
Thermal conductivity (k)	300+ W m-K^{-1}	300+ W m-K^{-1}
Dielectric strength	53 kV mm^{-1}	53 kV mm^{-1}
Shape	Spherical agglomerates	Platelets
Size	60 µm	45 µm

dried for over 12 h at ~ 60°C. For all the surface modifications of hBN, eight parts of amino silane were added to 100 parts of hBN as suggested by supplier of the silane.

Composite Preparation

PPS powders were dry-blended with the desired volume fractions and compositions of fillers, summarized in Tables IV–VI. All samples have 33.3 vol % of fillers. The mixtures were then melt-compounded in a micro-compounder (DSM Xplore 15) at 300°C and 50 rpm for 6 min. For the hBN$_{PTX60}$-MWCNT hybrid fillers, it was impossible to compound the mixture to create an hBN$_{PTX60}$-MWCNT ratio equal to 2 : 1 because of the mixture's high viscosity. The extruded composites were cooled in a water bath at room temperature. The extrudates were pelletized using a pelletizer and subsequently ground into fine powder by a mill freezer (SPEX CertiPrep Group, model 6850 Freezer/Mill).

Test Specimen Preparation

The melt-compounded composites were compression-molded, at 310°C, into disc-shaped samples of 20-mm diameter. Samples prepared for thermal conductivity measurements were 10-mm thick; those prepared for dielectric analyses were 2-mm thick. All samples prepared for thermal conductivity measurements were machined and ground to improve the surface smoothness to improve the accuracy of the measurements. Three 2-mm deep radial holes were drilled 1-mm below the top surface in the middle and 1-mm above the bottom surface of the samples for thermal conductivity measurements. Three thermocouples, with diameters of 0.076 mm, were pushed into the holes.

CHARACTERIZATION

The work studied surface modifications of hBN and the fillers morphologies of the composites. It investigated multifunctional properties and different characteristics of various samples, including the effective thermal conductivity (k_{eff}), electrical con-

Table III. Physical Properties of Various Grades of CF and MWCNT

	CF	MWCNT
Density (ρ)	2150 kg m^{-3}	2100 kg m^{-3}
Thermal conductivity (k)	400–650 W m-K^{-1}	3000 W m-K^{-1}
Electrical conductivity	>3300 S cm^{-1}	>100 S cm^{-1}
Shape	Fibrous	Hollow tubes
Length	200 µm	20–40 µm
Diameter	10 µm	20–40 nm

Table IV. Compositions of PPS-hBN Composites

Composite name	Vol. fraction of PPS	Vol. fraction of hBN$_{PTX60}$	Vol. fraction of hBN$_{PT110}$	Vol. ratio of hBN$_{PTX60}$: hBN$_{PT110}$
BN1	0.667	0.333	–	1 : 0
BN2	0.667	0.266	0.067	4 : 1
BN3	0.667	0.250	0.083	3 : 1
BN4	0.667	0.222	0.111	2 : 1
BN5	0.667	–	0.333	0 : 1

ductivity (σ), and the coefficient of thermal expansion (CTE) of all samples. All reported measurements were determined by analyzing three samples.

Surface Modifications of hBN

A thermogravimetric analyzer (TGA, TA Instruments, model Q50) was used to qualitatively investigate the amount of amino silane bonded to the hBN fillers' surfaces. Both hBN$_{PTX60}$ (i.e., spherical agglomerates) and hBN$_{PT110}$ (i.e., platelets), with or without surface modifications, were heated to 900°C at 20°C min^{-1} under nitrogen gas flow protection. The weight loss upon heating was recorded and analyzed.

Composite Morphologies

The dispersion of the filler systems in the compression-molded samples was examined using a scanning electron microscope (SEM, JEOL, model JSM6060) operated at 20 kV. Sample cross-sections were obtained by cooling and fracturing the composites in liquid nitrogen. The cross-sections were sputter coated with platinum prior to the SEM analyses.

Effective Thermal Conductivity (k_{eff})

A thermal conductivity analyzer (in accordance with ASTM E1225-04)[32] was used to measure k_{eff} at 150°C. The analyzer measures the sample's k_{eff} by comparing the temperature gradient across the sample to that across a pair of stainless steel 304 reference bars. A heat sink silicone compound was applied to the interfaces between the sample and the reference bars to enhance the thermal contact and reduce the thermal resistance.

Electrical Conductivity (σ)

The electrical conductivity (σ) of the composites were obtained by a dielectric/impedance analyzer (Novocontrol Technologies, model Alpha-N). A root-mean-square (rms) voltage of 1 V was applied over a frequency of 10^2 to 10^5 Hz. The measurements were used to determine if the electrical insulating properties of

Table V. Compositions of PPS-hBN-CF Composites

Composite name	Vol. fraction of PPS	Vol. fraction of hBN$_{PTX60}$	Vol. fraction of CF	Vol. ratio of hBN$_{PTX60}$: CF
BNCF1	0.667	0.266	0.067	4 : 1
BNCF2	0.667	0.250	0.083	3 : 1
BNCF3	0.667	0.222	0.111	2 : 1

Table VI. Compositions of PPS-hBN-MWCNT Composites

Composite name	Vol. fraction of PPS	Vol. fraction of hBN$_{PTX60}$	Vol. fraction of MWCNT	Vol. ratio of hBN$_{PTX60}$: MWCNT
BNCNT1	0.667	0.266	0.067	4 : 1
BNCNT2	0.667	0.250	0.083	3 : 1

the PPS had been suppressed by the inclusion of various filler systems.

Coefficient of Thermal Expansion (CTE)

The coefficient of thermal expansion (CTE) was measured using a thermomechanical analyzer (TMA, TA Instruments Q400). The composites were heated to 200°C at a rate of 5°C min^{-1}. The CTEs were determined from the slope of the plot at 50 and 150°C, depicting changes in dimension and temperature.

RESULTS AND DISCUSSION

Surface Modification of hBN

The fractional loss in weight of hBN$_{PTX60}$ and hBN$_{PT110}$, with and without surface modification by amino silane, is shown in Table VII. Because the organic coupling agent is volatile compared to hBN, the fractional loss in weight of the silane-treated hBN particles after heating to a high temperature indicates the amount of silane present. TGA results revealed that the amounts of volatile/decomposable materials on the as-received hBN particles were negligible. The weight loss of the silane-treated hBN$_{PTX60}$ particles was much higher. In contrast, the TGA data for treated hBN$_{PT110}$ showed negligible fractional weight loss. This indicates the silane treatment resulted in a coating on the hBN$_{PTX60}$ agglomerate but not on the hBN$_{PT110}$ platelet.

Effect of Hybrid Fillers on the PMC's Effective Thermal Conductivity (k_{eff})

Figure 1 shows the effect of filler compositions on the k_{eff} of the PPS-based composites filled with 33.3 vol % fillers. The k_{eff} PPS-hBN composites filled with either hBN$_{PTX60}$ only or hBN$_{PT110}$ only were increased from 0.22 W mK^{-1} of the neat PPS to 1.77 and 1.55 W mK^{-1}, respectively. SEM micrographs of PPS-hBN$_{PTX60}$ composite and PPS-hBN$_{PT110}$ composite are shown in Figure 2(a,b). Although hBN$_{PTX60}$ particles are 60-μm spherical agglomerates, Figure 2(a) reveals that the agglomerates had been broken down into very fine particles (i.e., <10 μm) during compounding and compression molding. The smaller hBN platelets in the PPS-hBN$_{PTX60}$ composite would result in a higher filler population density than the PPS-hBN$_{PTX60}$ com-

Table VII. Fractional Loss in Weight of hBN Particles Upon Heating to 900°C

hBN filler	Fraction weight loss
PTX60, as received	<0.05%
PTX60, surface modified	1.13%
PT110, as received	<0.05%
PT110, surface modified	<0.05%
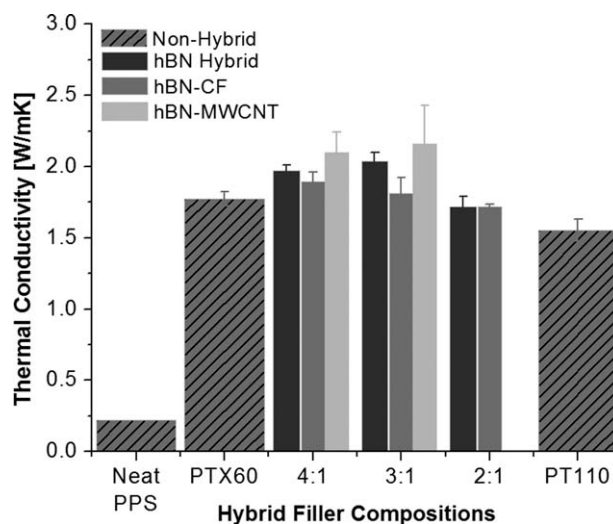
Figure 1. Effects of hybrid filler compositions on PMC's k_{eff}.

posite, enhancing the formation of a thermally conductive network in the PPS matrix and increasing the PMC's k_{eff}.

Figure 1 also reveals the synergistic effects of hybrid hBN fillers of two different sizes (hBN$_{PTX60}$ and hBN$_{PT110}$) on the k_{eff} of
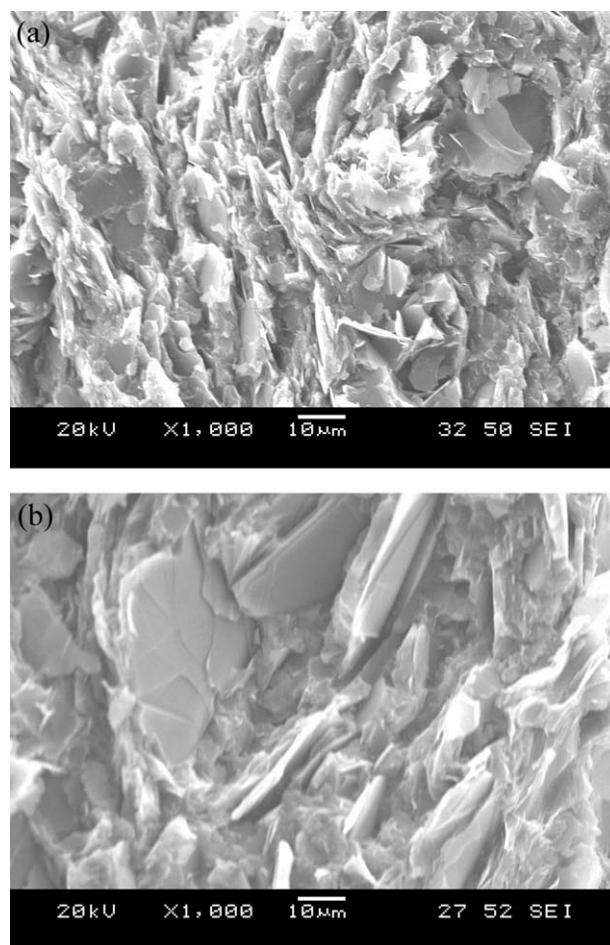
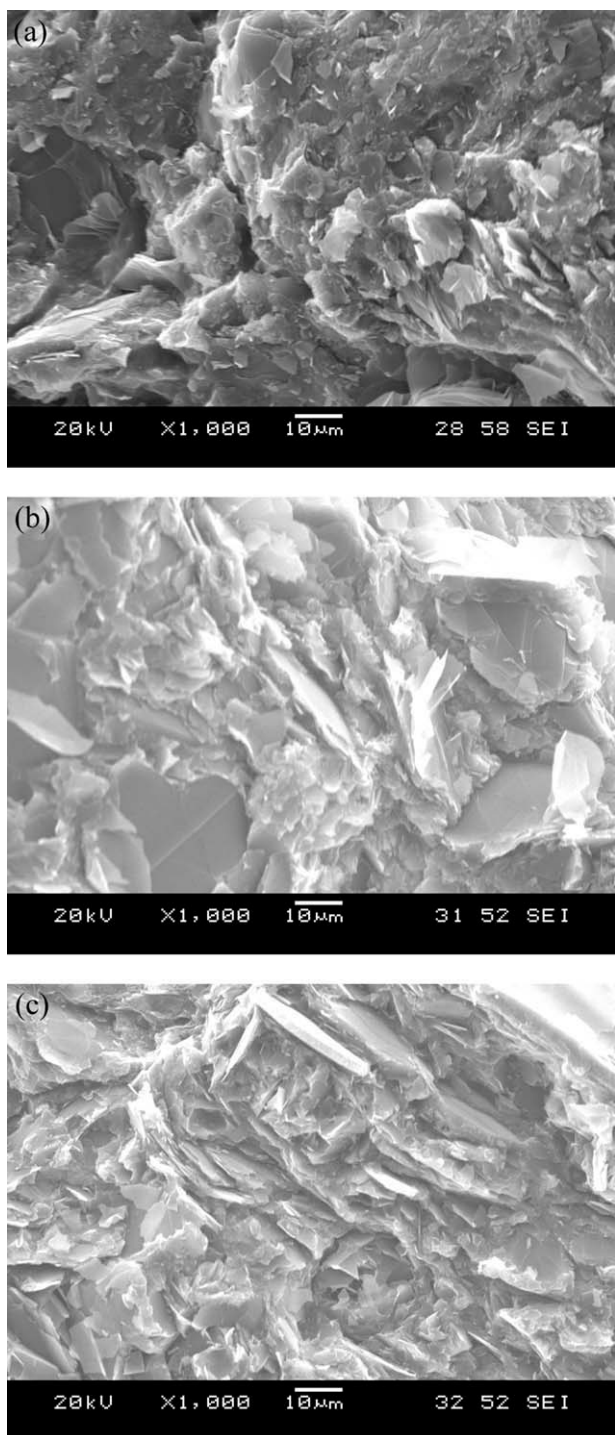**Figure 2.** SEM micrographs of (a) PPS-PTX60 and (b) PPS-PT110 composites with 33.3 vol % hBN.

Figure 3. SEM micrographs of PPS-PTX60 and PPS-PT110 composites with 33.3 vol % hBN_{PTX60}-hBN_{PT110} hybrid fillers with hBN_{PTX60}-to-hBN_{PT110} ratios of (a) 4 : 1; (b) 3 : 1; and (c) 2 : 1.

The SEM micrographs showed that the aspect ratios and the sizes of hBN_{PT110} platelets were higher than those of hBN_{PTX60} platelets. The larger hBN_{PT110} platelets seemed to serve as bridges, as indicated in Figures 3(a) through (c), interconnecting the individual hBN_{PTX60} fine platelets, and having a synergistic effect on the composite's k_{eff}. PMC's k_{eff} measurements
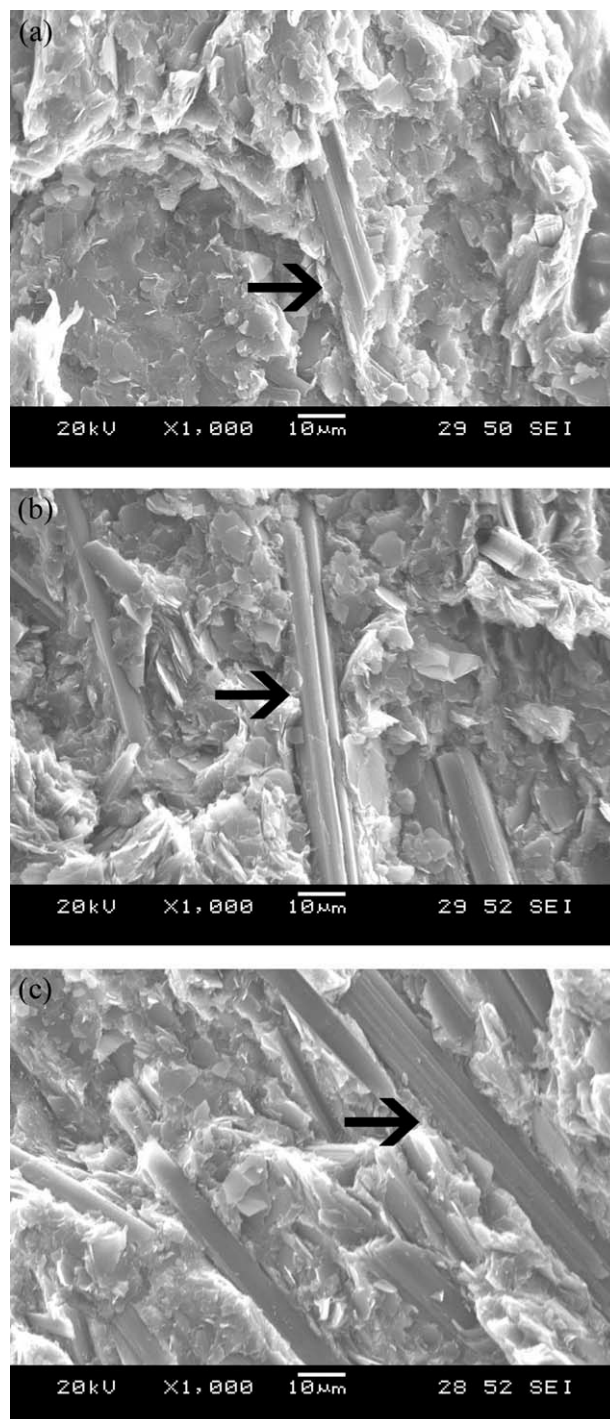

Figure 4. SEM micrographs of PPS-hBN-CF composites with 33.3 vol % hBN_{PTX60}-CF hybrid fillers with hBN_{PTX60}-to-CF ratios of (a) 4 : 1; (b) 3 : 1; and (c) 2 : 1.
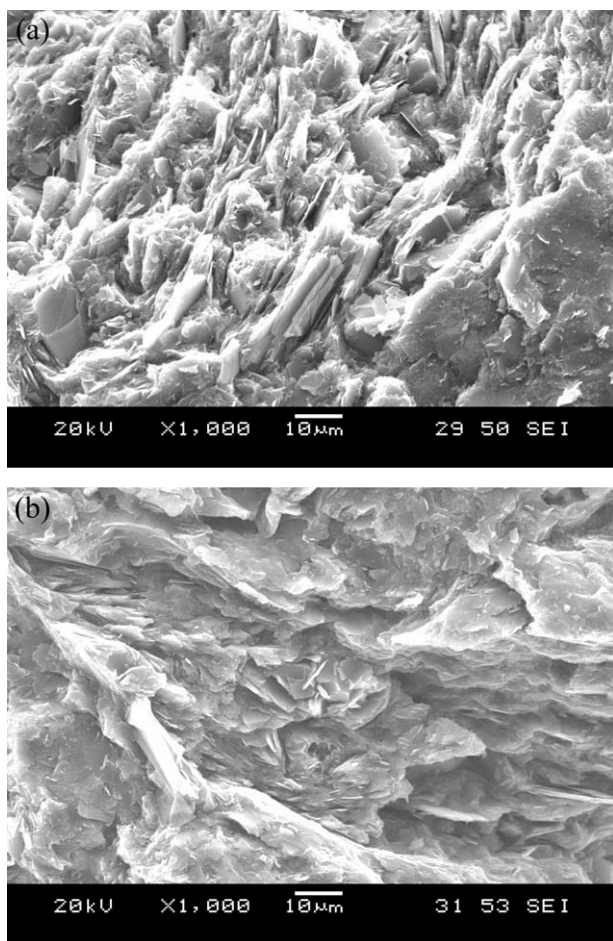
PPS-hBN composites. Measurements clearly indicated that hybriding hBN_{PTX60} with hBN_{PT110}, with the volume ratio of hBN_{PTX60} to hBN_{PT110} equal to 4 : 1 or 3 : 1, promoted the PMC's k_{eff} to 1.97 and 2.04 W mK^{-1}. Nevertheless, when the volume ratio of hBN_{PTX60} and hBN_{PT110} was 2 : 1, the PMC's k_{eff} is slightly lower than that filled with only one hBN_{BTX60}.

Figure 5. SEM micrographs of PPS-hBN-MWCNT composites with 33.3 vol % hBN_{PTX60}-MWCNT hybrid fillers with hBN_{PTX60}-to-MWCNT ratios of (a) 4 : 1 and (b) 3 : 1.

also indicated an optimal volume ratio between the smaller and larger hBN platelets (i.e., hBN_{PTX60} : hBN_{PT110} = 3 : 1), thereby maximizing the PMC's k_{eff} at a particular filler loading. When the volume ratio was higher, the PMC's k_{eff} was reduced because of the insufficient number of fine platelets dispersed in the PPS matrix for the large platelets to bridge. When the volume ratio was lower i, the smaller number of larger platelets limited the bridging among the fine platelets.

In addition to hybriding hBN fillers of different sizes, the study also investigated the effects of adding electrically conductive secondary fillers with high aspect ratios (i.e., CF or MWCNT) to the PPS-based composites filled with hBN_{PTX60} on k_{eff}. Figure 1 indicates that the inclusion of CF as secondary filler led to limited increases in the PMC's k_{eff} when hBN_{PTX60}-to-CF ratios were 4 : 1 and 3 : 1 despite the bridging of hBN fine platelets by CF as illustrated in Figures 4(a) through (c). It is believed that hBN_{PTX60} and CF is not an appropriate hybrid filler combination to promote PMC's k_{eff}. In contrast, k_{eff} measurements indicated that MWCNT was an effective secondary filler. As Figure 1 shows, PPS-based composites filled with hBN_{PTX60} and MWCNT exhibited substantial promotion in the composite's k_{eff}. Compared to the k_{eff} of 1.77 W mK^{-1} for the PPS-based

composites with single hBN_{PTX60} fillers, the values of k_{eff} for composites filled with 4 : 1 and 3 : 1 volume ratios of hBN_{PTX60} and MWCNT hybrid fillers were increased to 2.10 and 2.16 W mK^{-1}. Figures 5(a) through (b) illustrate the micrographs of these PPS-hBN-MWCNT composites.

When the three combinations of hybrid fillers, (i) hBN platelets of different sizes, (ii) hBN_{PTX60} with CF, and (iii) hBN_{PTX60} with MWCNT, were compared, the synergistic effects were found to be best for the composites with hBN with MWCNT, followed by those with hBN platelets of different sizes. However, hybriding hBN with CF showed limited improvement over composites filled with the same loading of single hBN fillers. Because the ratios of the filler's thermal conductivity to the matrix's thermal conductivity are over 100 for hBN, CF, and MWCNT, the additional improvement in the PMC's k_{eff} values for composites filled with hBN_{PTX60} with MWCNT is not likely caused by the higher k of MWCNT.[6] In contrast, the promotion of PMC's k_{eff} is believed to be attributable to the shapes and sizes of the secondary fillers. Among the three types of secondary fillers (hBN_{PT110}, CF, and MWCNT), MWCNT has the highest aspect ratio ($\sim$ 1000). hBN_{PT110} and CF have similar aspect ratios ($\sim$ 20); however, hBN_{PT110} platelets are smaller than CF, leading to a higher population density in the PMC. Using the dimensions of the fillers, the study estimated their population densities in the composites; the results appear in Figure 6. The figure confirms that for the same volume fraction of secondary fillers, MWCNT had the highest filler population density, followed by hBN_{PT110}, while CF had the lowest filler population density. This finding, along with the experimental measurements of PMC's k_{eff}, suggests that the effectiveness of secondary fillers to promote PMC's k_{eff} increased with higher aspect ratios and smaller filler sizes.

Effect of Hybrid Fillers on the PMC's Electrical Conductivity (σ)

The electrical conductivities (σ) of the PMCs filled with different hybrid filler systems were measured and the results plotted in Figures 7(a) through (c). Figure 7(a) shows that σ of PPS-
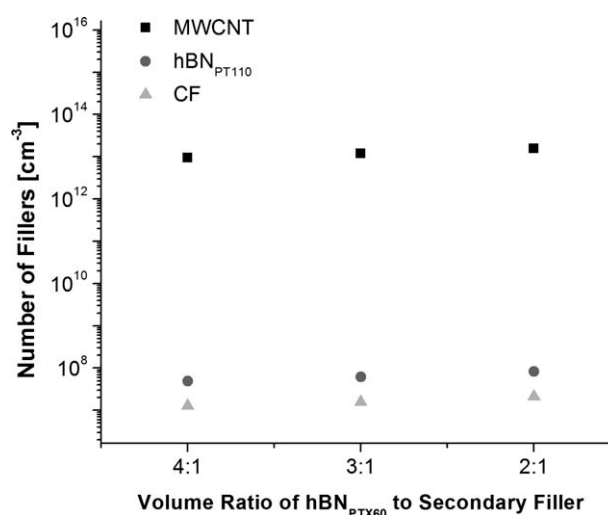

Figure 6. Population density of secondary fillers (filler content = 33.3 vol %).
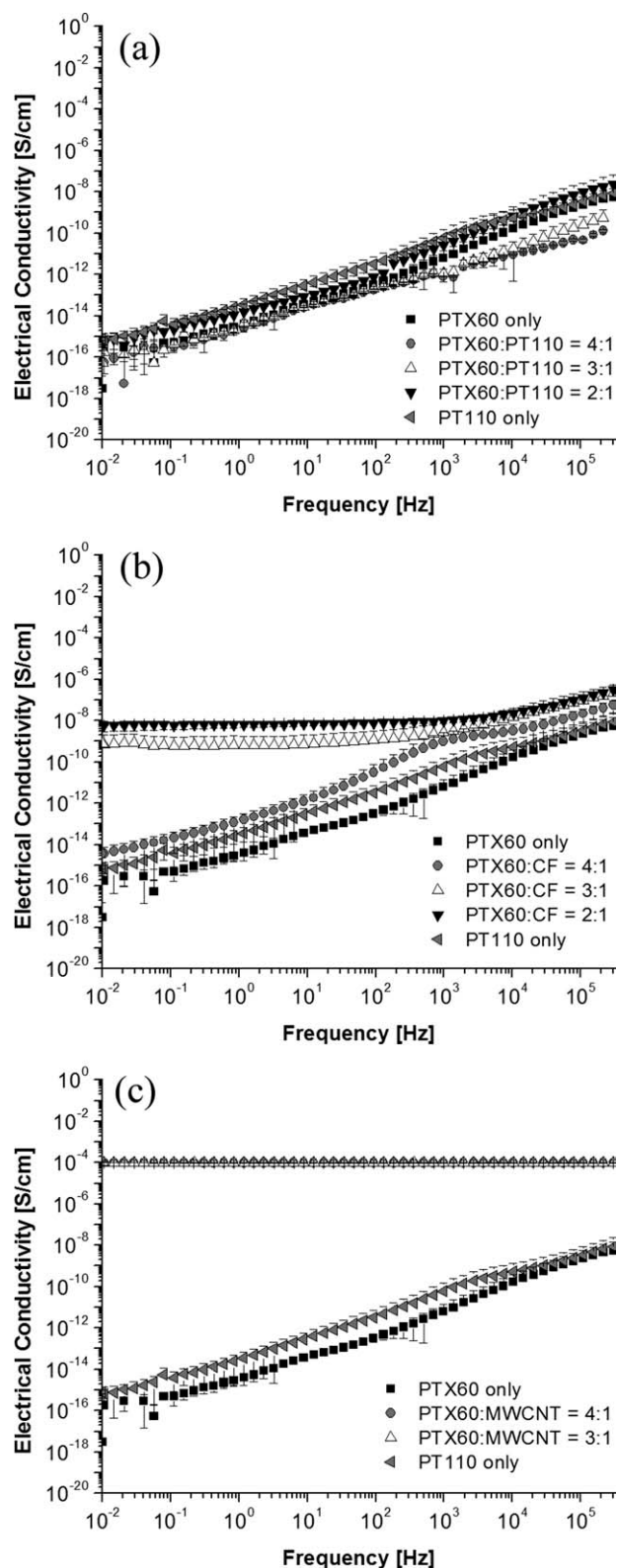
Figure 7. Effects of hybrid filler compositions on PMC's electrical conductivity for (a) PPS-hBN$_{PTX60}$-hBN$_{PT110}$ composites (b) PPS-hBN$_{PTX60}$-CF composites; and (c) PPS-hBN$_{PTX60}$-MWCNT composites.

based composites filled with only hBN remained low, regardless of whether the PMC consisted of single type fillers or hybrid fillers. In other words, the electrical insulating properties of PPS were not compromised with the addition of hBN. Figure 7(b) shows that when the hBN$_{PTX60}$ to CF volume ratios were 4 : 1 and 3 : 1, the impedance of the PPS-hBN$_{PTX60}$-CF composites was very similar to that of PPS-based composites filled with only hBN. However, when the hBN$_{PTX60}$ to CF volume ratio changed to 2 : 1, the PMC's σ increased significantly. At this filler composition, the volume fraction of CF was 11.1 vol %, higher than the percolation threshold (9.0 vol %) reported by Chingerman et al.,[33] resulting in the dramatic increase in the PMC's σ. Furthermore, for the two PMCs filled with hBN$_{PTX60}$ and MWCNT, the σ was significantly higher than for all other composites. The volume fractions of MWCNT in the PPS-hBN$_{PTX60}$-CF composites were 6.7 and 8.3 vol % when the hBN$_{PTX60}$ to MWCNT volume ratios were 4 : 1 and 3 : 1, respectively. Therefore, the MWCNT contents in both composites were significantly higher than the percolation threshold reported in the literature.[34] The frequency independent behavior of PPS-hBN-MWCNT composites' σ served as further evidence of the formation of continuous conductive pathways interconnecting the MWCNTs between the two electrodes in the dielectric analyzer. In short, the σ measurements of various hybrid filler systems suggest that the choice and amount of secondary fillers not only promote the PMC's k_{eff} but also serve as parameters to tailor its σ.

When the percolation threshold of MWCNT in the PPS-hBN$_{PTX60}$-MWCNT composites was overcome, this led to large increases in σ, but not in the PMC's k_{eff}. The interfiller contacts (hBN$_{PTX60}$-hBN$_{PTX60}$, MWCNT-MWCNT, and hBN$_{PTX60}$-MWCNT) might have considerable thermal contact resistance, suppressing the potential to significantly enhance PMC's k_{eff} with thermally conductive fillers. In other words, strategies to reduce such thermal contact resistance among embedded fillers would need to be investigated to realize the full potential of PMCs in the electronic packaging industry.
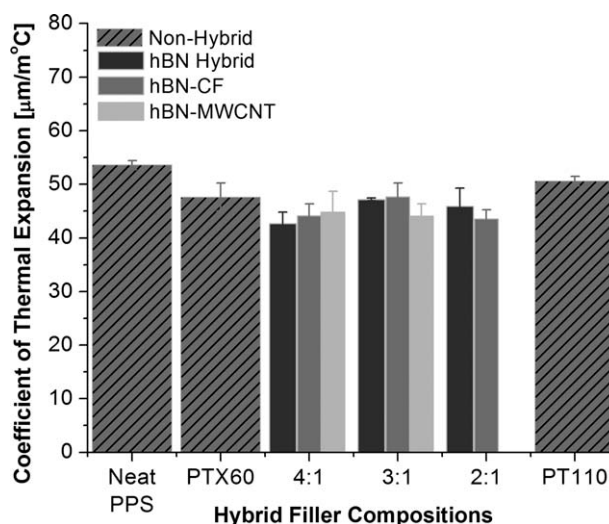

Figure 8. Effects of hybrid filler compositions on PMC's CTE (below the glass transition temperature of PPS).

Effect of Hybrid Fillers on the PMC's Coefficient of Thermal Expansion (CTE)

Figure 8 shows the effect of filler compositions on the PMC's coefficient of thermal expansion (CTE) below the glass transition temperature (T_g). In this study, the CTEs of all PMCs were lower than those of the neat PPS. The particle size distribution and size are reported as factors that might influence the CTE of the composite system.[35] The smaller platelet size for hBN_{PTX60} might explain why the CTE of the hBN_{PTX60}-filled composite was lower than that of the hBN_{PT110}-filled composite. Moreover, the hybrid fillers allowed more efficient packing of the fillers in the PPS matrix, leading to a slightly lower CTE. Nevertheless, since the total filler contents for all composites fabricated in this work were held constant (i.e., 33.3 vol %), their CTEs were very close.

CONCLUSIONS

Polyphenylene sulfide (PPS)-based composites filled with hybrid fillers, consisting of hexagonal boron nitride (hBN) platelets of different sizes or hBN with multi-walled carbon nanotube (MWCNT) were found to have enhanced effective thermal conductivity (k_{eff}), while composites filled with hBN and pitch-based carbon fiber (CF) had limited increase in k_{eff}. In the hybrid system, the secondary filler promoted the interconnection among the primary fillers through the formation of a structured network to facilitate heat conduction across the materials. For each combination of hybrid filler systems, there was an optimal volume ratio between the hybriding fillers. As an example, consider fine platelets of hBN_{PTX60} as the primary filler; if the volume ratio of the fine platelets to the larger secondary filler (i.e., hBN_{PT110}) is too high, the composite's k_{eff} is reduced because of the insufficient number of fine platelets dispersed in the PPS matrix for the larger secondary fillers to bridge. In contrast, if the volume ratio is too low, the limited number of larger secondary fillers restricts the degree of bridging among the fine platelets. Experimental results demonstrated secondary fillers with a higher aspect ratio and smaller size (e.g., MWCNT) to be more effective in promoting the composite's thermal conductivity.

When carbon-based secondary fillers (e.g., CF and MWCNT) were used, the composites' electrical conductivity (σ) increased significantly if the volume fractions of these electrically conductive fillers were over the percolation threshold. This phenomenon was caused by the formation of electrically conductive pathways through the composite samples. In other words, it would be possible to control the type and loading of an electrical conductive filler as the secondary filler to tailor the electrical conductivity of a polymer matrix composite (PMC).

Despite the significant increases in σ for PMCs filled with MWCNT as the secondary filler, their k_{eff} did not increase to the same degree. Such results suggest that considerable thermal contact resistance might also exist at the interfiller contacts. Future research should develop strategies to lower this resistance if the electronic packaging industry is to take full advantage of the potential of polymer PMCs.

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