

# High Thermal Conductive Epoxy Molding Compound with Thermal Conductive Pathway

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**ABSTRACT:** The epoxy molding compound (EMC) with thermal conductive pathways was developed by structure designing. Three kinds of EMCs with different thermal conductivities were used in this investigation, specifically epoxy filled with  $\text{Si}_3\text{N}_4$ , filled with hybrid  $\text{Si}_3\text{N}_4/\text{SiO}_2$ , and filled with  $\text{SiO}_2$ . Improved thermal conductivity was achieved by constructing thermal conductive pathways using high thermal conductivity EMC ( $\text{Si}_3\text{N}_4$ ) in low thermal conductivity EMC ( $\text{SiO}_2$ ). The morphology and microstructure of the top of EMC indicate that continuous network is formed by the filler which anticipates heat conductivity. The highest thermal conductivity of the EMC was 2.5 W/m K, reached when the volume fraction of EMC ( $\text{Si}_3\text{N}_4$ ) is 80% (to compare with hybrid  $\text{Si}_3\text{N}_4/\text{SiO}_2$  filled-EMC, the content of total fillers in the EMC was kept at 60 vol %). For a given volume fraction of EMC ( $\text{Si}_3\text{N}_4$ ) in the

EMC system, thermal conductivity values increase according to the order EMC ( $\text{Si}_3\text{N}_4$ ) particles filled-EMC, hybrid  $\text{Si}_3\text{N}_4/\text{SiO}_2$  filled-EMC, and EMC( $\text{SiO}_2$ ) particles filled-EMC. The coefficient of thermal expansion (CTE) decreases with increasing  $\text{Si}_3\text{N}_4$  content in the whole filler. The values of CTE ranged between  $23 \times 10^{-6}$  and  $30 \times 10^{-6} \text{ K}^{-1}$ . The investigated EMC samples have a flexural strength of about 36–39 MPa. The dielectric constant increases with  $\text{Si}_3\text{N}_4$  content but generally remains at a low level (<6, at 1 MHz). The average electrical volume resistivity of the EMC samples are higher than  $1.4 \times 10^{10} \Omega \text{ m}$ , the average electrical surface resistivity of the EMC samples are higher than  $6.7 \times 10^{14} \Omega$ . © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2117–2125, 2009

**Key words:** thermal properties; structure; dielectric properties; networks; morphology

## INTRODUCTION

Thermal conductive and electrical insulating polymer composites are extensively used in electronic packaging. Owing to the tendency of developing denser and faster electronic circuits systems, heat dissipation in microelectronic packaging becomes an increasingly important issue.<sup>1,2</sup> The next generation packaging materials is expected to possess higher heat dissipation capability, lower coefficient of thermal expansion (CTE) and lower signal transmission speed delay. The accumulated heat from electronic devices should be removed by increasing heat dissipation capability of packaging materials.<sup>3,4</sup> Polymer composites filled with high thermal conductive filler emerge themselves as a cost effective and feasible way to resolve the thermal dissipation problem.

The intrinsic thermal conductivity of polymers is too low for being suitable for electronic packaging. For example, the thermal conductivity of epoxy is

only about 0.15–0.25 W/m K.<sup>5</sup> An effective and feasible way to achieve higher thermal conductivity is to fill the polymers with high thermal conductive ceramic material, such as AlN,  $\text{Si}_3\text{N}_4$  (>150 W/m K)<sup>6,7</sup>. Many composite systems have been investigated including different kinds of polymers (such as epoxy,<sup>4,8–12</sup> polystyrene,<sup>13,14</sup> HDPE,<sup>15,16</sup> polyimide,<sup>17</sup> polyurethane,<sup>18</sup> polybenzoxazine,<sup>19</sup> polyvinylidene fluoride<sup>20</sup>) and different ceramic fillers (such as AlN,<sup>4,9,10,12,15,17,20</sup> BN,<sup>8,9,15,16,19</sup>  $\text{Al}_2\text{O}_3$ ,<sup>8,10,18</sup>  $\text{SiO}_2$ ,<sup>8,10</sup> SiC,<sup>15,20</sup>  $\text{Si}_3\text{N}_4$ ,<sup>11,14</sup> diamond<sup>8</sup>). The focus has been centered at considering the effect of polymer type, filler category, volume fraction, shape, size distribution, and surface treatment of filler. In industry, epoxy molding compound (EMC), which consists of 30–45 vol % epoxy and 55–70 vol % fused silica, is currently used as typical encapsulant for large size chips and small package devices.<sup>21</sup> This cost effective encapsulant exhibits suitable CTE, high moisture resistance and relatively high mechanical strength, but poor heat dissipation capability because of the low intrinsic thermal conductivities of epoxy and fused silica. The demand for heat dissipation points new fillers such as high performance AlN,  $\text{Si}_3\text{N}_4$ , BN, etc. However, addition of such fillers in large amounts is quite expensive. The development of high thermal

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conductive polymer composites in a proper and cost effective way, using ceramic filler, has been extensively studied.<sup>13–15</sup>

Dispersion of different ingredients in composites influences the bulk properties.<sup>11,12,14,16,20</sup> Conventionally, the EMC microstructure consists of continuous polymer matrix and uniformly distributed hybrid filler.<sup>3,15</sup> High thermal conductivity requires high content of filler. Yu has proposed a new filler distributed structure in polymer matrix.<sup>13</sup> Using sphere-like polystyrene as matrix and AlN powders as filler, the ceramic filler surrounding polymer formed high thermal conductive pathway. This is an effective way to prepare polymer composites with very good thermal conductive performance. Based on Yu's research, we have investigated the performance of PS/Si<sub>3</sub>N<sub>4</sub> composite with similar structure.<sup>14</sup> That study has proven that heat flow can be well oriented by the thermal conductive network formed by the filler. However, that structural distribution rather worsens the mechanical properties of the composites. Our preliminary studies have shown that the EMC using pre-cured EMC (Si<sub>3</sub>N<sub>4</sub>) particles with pure epoxy resin can be effective for increasing the EMC thermal conductivity with lower filler volume fraction.<sup>11</sup> In this work, we developed a novel feasible and cost effective microstructure design of such composites, which consists of both the high thermal conductive Si<sub>3</sub>N<sub>4</sub> and the conventional SiO<sub>2</sub> as filler, to achieve an optimum thermal conductive pathway in the resultant composite.

In the present study, composites with three different kinds of microstructure (A, B, and C) were fabricated through material and structure design. Epoxy resin and multi-fillers of Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> were used as the matrix and filler, respectively. To compare the thermal conductivity of three kinds of EMC designed structure, the total content of fillers of the prepared samples was kept constant at 60 vol %. That is: Si<sub>3</sub>N<sub>4</sub> content in EMC (Si<sub>3</sub>N<sub>4</sub>) particles or in EMC (Si<sub>3</sub>N<sub>4</sub>) powders, SiO<sub>2</sub> content in EMC (SiO<sub>2</sub>) particles or in EMC (SiO<sub>2</sub>) powders (as mentioned below) were all kept constant, 60 vol %. The sample A was prepared in two steps: Firstly, Si<sub>3</sub>N<sub>4</sub> filler was mixed with epoxy resin, curing agent and additives in a mixer. The mixture was then put into a mold and hot pressed at 175°C and under a pressure of 50 MPa pressure for 5 min for pre-curing. The pre-cured sample with Si<sub>3</sub>N<sub>4</sub> filler was crushed into particles (sieved through 18 mesh sieve), named as EMC (Si<sub>3</sub>N<sub>4</sub>) particles. Meanwhile, SiO<sub>2</sub> filler was mixed with epoxy resin, curing agent and additives to prepare EMC (SiO<sub>2</sub>) powders. Then, the EMC (Si<sub>3</sub>N<sub>4</sub>) particles were added in the EMC (SiO<sub>2</sub>) powders and both were cured to obtain the final samples. EMC (SiO<sub>2</sub>) powders formed a continuous network in that sample. The sample B was also pre-

pared with two steps like sample A, the difference was that EMC (SiO<sub>2</sub>) particles (the pre-cured sample with SiO<sub>2</sub> filler was crushed into particles) were added in the EMC (Si<sub>3</sub>N<sub>4</sub>) powders (Si<sub>3</sub>N<sub>4</sub> filler was mixed with epoxy resin, curing agent, and additives without pre-curing). EMC (Si<sub>3</sub>N<sub>4</sub>) powders formed a continuous network with high thermal conductivity. The advantage is that expensive Si<sub>3</sub>N<sub>4</sub> filler can be saved. For the sample C, named as EMC (Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>), both fillers were added at the same time during mixing with epoxy resin, curing agent and additives in the mixer. The EMC (Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub>) sample was then cured at 175°C and 50 MPa pressure in the mold. Morphology, microstructure, thermal conductivity, CTE, mechanical properties, dielectric constant, electrical volume resistivity, and electrical surface resistivity of the produced EMC samples were experimentally determined.

## EXPERIMENTAL SECTION

### Materials and surface treatment of filler

Novolac epoxy resin, the molecular weight of which was 653 g/mol, was used as matrix resin and linear phenolic resin as curing agent (supplied by Bluestar New Chemical Materials, Wuxi, China). The weight ratio of epoxy to linear phenolic resin was 5/3. Accelerator (2-methylimidazole, 1 wt % of EMC), flame retardant (Sb<sub>2</sub>O<sub>3</sub>, 1 wt % of EMC), and UV absorber (carbon black, 0.8 wt % of EMC) were also used (as additives). Fillers used were Si<sub>3</sub>N<sub>4</sub> powders (supplied by Fujian Sinocera Advanced Materials, Fuzhou, China, average size of 5 μm) and crystalline silica SiO<sub>2</sub> (average size of 4 μm). Figure 1(a,b) shows the morphologies of the two fillers; it can be seen that Si<sub>3</sub>N<sub>4</sub> had a rod-like shape, while SiO<sub>2</sub> was irregular in shape. The physical properties of fillers and the epoxy resin are shown in Table I.

To secure a good dispersion and a strong filler/matrix interface, a silane (KH550, NH<sub>2</sub>—(CH<sub>2</sub>)<sub>3</sub>Si—(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) was used as the surface treatment agent of the filler. First, Si<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub> filler was mixed with the silane coupling agent (1 wt % of filler) in alcohol by stirring for 2 h; then, a vacuum drying process at 60°C for 24 h was carried out to remove alcohol. The surface treated filler was sieved through a 200 mesh sieve and stored in a vacuum oven at 60°C to prevent moisture absorption on the surface of the filler.

### Sample preparation

#### Preparation of pre-cured EMC particles

The epoxy resin and curing agent in the weight ratio of 5/3 was thoroughly mixed via stirring. The additives (i.e. accelerator, flame retardant, UV absorber)

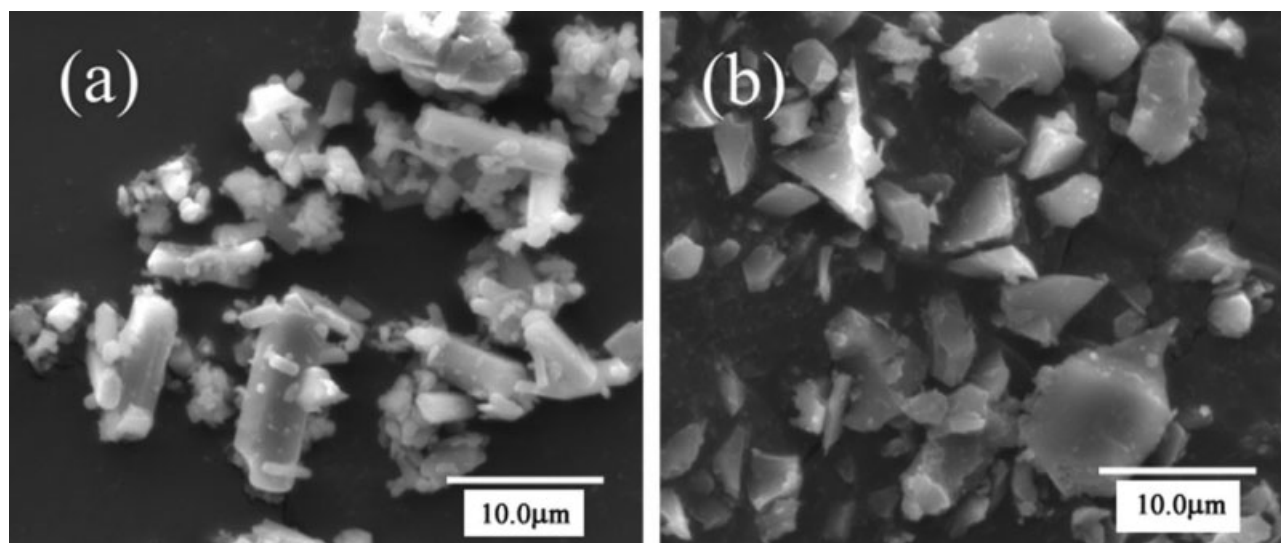


Figure 1 Morphology of filler powders (a)  $\text{Si}_3\text{N}_4$  (b)  $\text{SiO}_2$ .

were then added and the mixture was further stirred for 2 h until the additives were fully dispersed. Mixtures of different proportions of filler ( $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$ ) with the above polymer mixture were mixed in a mixer for 2 h. The mixtures were then degassed in a vacuum oven for 1 h.

The mixture containing sole filler ( $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$ ) was put into a mold and hot pressed at  $175^\circ\text{C}$ , under a pressure of 50 MPa for 5 min as pre-curing. When the mold was heated to  $175^\circ\text{C}$ , the mixture was put in and a 50 MPa pressure was applied. The epoxy used had a softening point of only  $65^\circ\text{C}$ , under such high temperature, epoxy soon began to melt. With the existence of accelerator 2-methylimidazole, cross-linking reaction between epoxy and phenolic resin began. Furthermore, under the condition we investigated, a viscosity of lower than 1 Pa s could be expected,<sup>22,23</sup> this viscosity was low enough to achieve good wet-out of the filler, void formation could also be prevented. EMC filled with sole  $\text{Si}_3\text{N}_4$  filler, as reported,<sup>11</sup> 50 vol % content of the filler had already formed thermal conductive pathway, so pathway formed by adding 60 vol %  $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$  filler could be expected. After cooling down to room temperature, the pre-cured EMC ( $\text{Si}_3\text{N}_4$ ) or EMC ( $\text{SiO}_2$ ) were crushed into particles and sieved through an 18 mesh sieve. Then the pre-cured EMC particles were prepared. The flow chart of preparation of the pre-cured EMC particles was shown in Figure 2(a). It should be mentioned that 5 min was not long enough for the cross-linking reaction to reach a 100% conversion.<sup>24</sup> So during the sample preparing process mentioned below, unreacted epoxy and phenolic resin would react in the pre-cured particles and at the surface of the particles with melted EMC powders to get a strong interface.

#### Preparation of EMC

Preparation of EMC powders was shown in the flow chart in Figure 2(b).

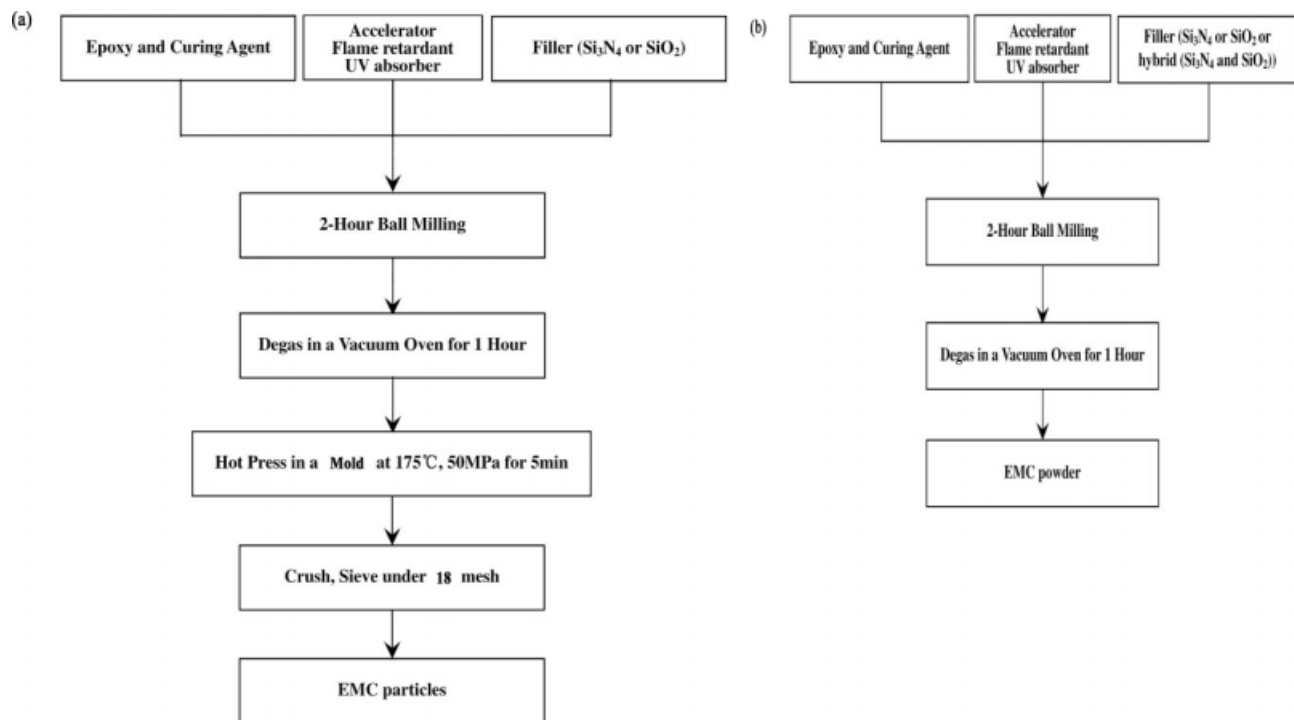
To prepare the sample A and the sample B, EMC ( $\text{Si}_3\text{N}_4$ ) or EMC ( $\text{SiO}_2$ ) particles were used. For sample A, EMC ( $\text{Si}_3\text{N}_4$ ) particles were mixed with the required amount of EMC ( $\text{SiO}_2$ ) powders in a mixer for 2 h. Then the mixture was degassed in a vacuum oven for 1 h, and the mixture was put into a mold and hot pressed at  $175^\circ\text{C}$  under a pressure of 50 MPa for 5 min. Post-curing process was carried out at  $175^\circ\text{C}$  for 4 h. For sample B, mixing, hot pressing and post-curing processes were followed similar to sample A preparation. The difference was that EMC ( $\text{SiO}_2$ ) particles were added into EMC ( $\text{Si}_3\text{N}_4$ ) powders.

The sample C was prepared in one step. Epoxy resin and curing agent were mixed together with the additives. The  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  filler were then added in different volume ratios and mixed in a mixer for 2 h. After degassing in a vacuum oven for 1 h, the EMC ( $\text{Si}_3\text{N}_4/\text{SiO}_2$ ) powders were put into a mold and hot pressed at  $175^\circ\text{C}$  under a pressure of 50 MPa for 5 min.

The pre-cured samples were then post-cured at  $175^\circ\text{C}$  for 4 h. All the samples were cooled down

TABLE I  
Physical Property of Epoxy Resin and Filler

Materials	Thermal conductivity (W/m K)	CTE ( $10^{-6}/\text{K}$ )	Dielectric constant	Density ( $\text{g}/\text{cm}^3$ )
Epoxy	0.15–0.25	50–90	6–8	1.2
Crystalline silica	14	15	3.8–5.4	2.64
$\text{Si}_3\text{N}_4$	>150	3	8	3.2



**Figure 2** Flow chart of sample preparation (a) preparation of pre-cured EMC particles (b) preparation of EMC powders.

to room temperature and machined to get the required dimensions for characterization using a diamond saw.

### Characterization

All samples were dried for 2 days in a vacuum oven before characterization. Thermal conductivity of samples was calculated by eq. (1)

$$\lambda = C_p \times \rho \times \alpha \quad (1)$$

where  $\lambda$  is the thermal conductivity,  $C_p$  is the specific heat capacity,  $\rho$  is the density and  $\alpha$  is the thermal diffusivity. Specific heat capacity measurements of the EMC samples were performed on a calibrated differential scanning calorimeter (DSC, CDR-4P, CANY Precision Instruments, Shanghai, China) from  $-10^\circ\text{C}$  to  $50^\circ\text{C}$ , with a heating rate of  $5^\circ\text{C}/\text{min}$ , using alumina as standard sample. The density was determined by Archimedes' principle of immersion. Weight and buoyancy measurements were made with an electronic balance (FA1004N, CANY Precision Instruments, Shanghai, China), using distilled water as a liquid. The thermal diffusivity was determined by a laser-flash method. The measurements were made with a Netzsch system (LFA 427, German) at room temperature. Samples used were 12.6 mm in diameter and 2 mm in thickness with a polished surface. Before the tests, samples were coated with colloidal carbon to prevent penetration of the laser beam in samples.

To investigate the dispersion state of pre-cured particles and filler in EMC, the morphology of samples was recorded using digital microscope (KH-7700, Hirox, Japan). Microstructure of samples was observed using a scanning electron microscope (SEM, Quanta 200, FEI).

CTEs were measured with a linear dilatometer (PCY-II, Huaifeng Instrument Manufacturing, Xiangtan, China) from room temperature to  $120^\circ\text{C}$ , using bar-shaped samples ( $6 \times 6 \times 50 \text{ mm}^3$ ) with a heating rate of  $5^\circ\text{C}/\text{min}$ . CTE values were calculated with eq. (2)

$$\alpha = \frac{\Delta L}{L_0} \times \frac{1}{\Delta T} \quad (2)$$

where  $\alpha$  is the CTE,  $\Delta L/L_0$  is the relevant expansion of samples and  $\Delta T$  is the difference of temperature.

The flexural properties of the EMC samples were determined according to ISO 178. The apparatus used was an Electro-mechanical Universal Test Machine (CMT5504, SANS Testing Machine, Shenzhen, China) with a three-point bend jig. The loading rate was applied according to the specimen dimension as defined in ISO 178.

Dielectric constant of the EMC samples was measured with a high frequency Q measurement system (QBG -3D, AIYI Electronic Equipment, Shanghai, China). The testing frequency was set at 1 MHz. The measurements were performed with samples of 26 mm in diameter and about 4 mm in thickness. Electrical volume resistivity and electrical surface

resistivity of the EMC samples were measured with an insulation resistivity tester (DZ2631, Dazhan Electro-mechanical Technology Research Institute, Nanjing, China) at 100 V DC after charged for 60 s according to IEC 60,093.

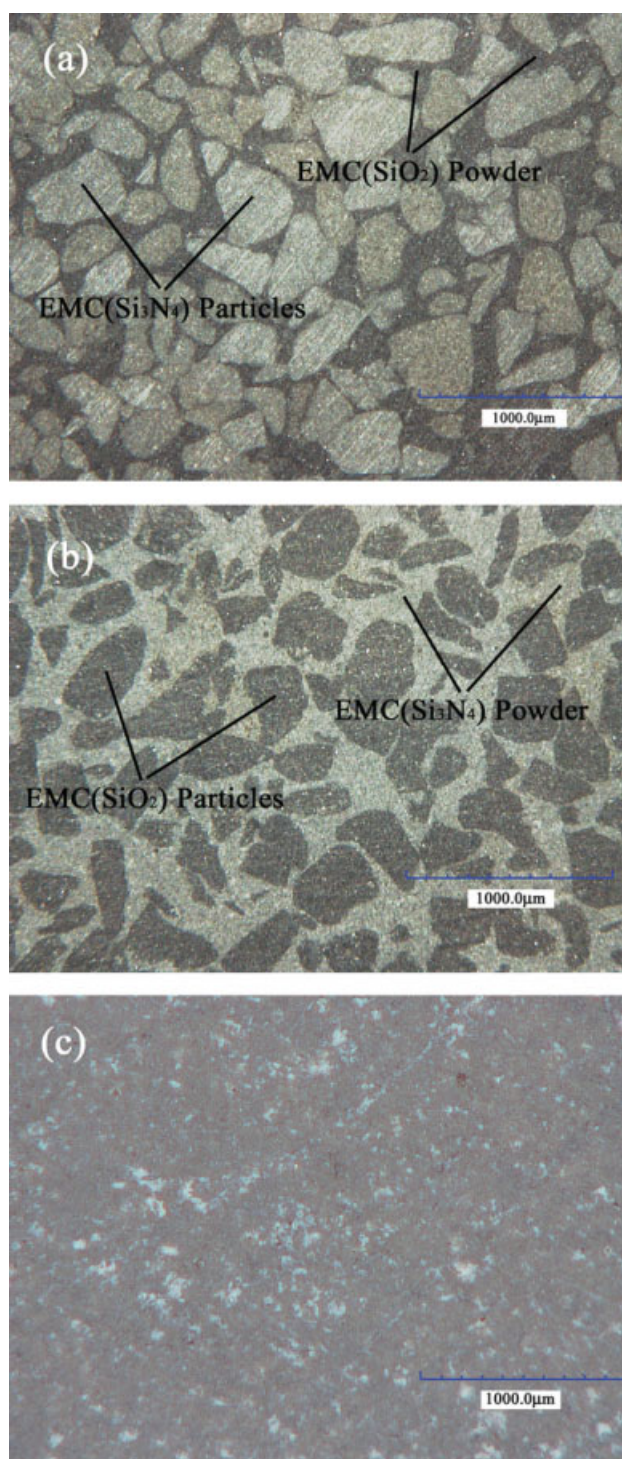
The presenting values are the average of three different independent measurements.

## RESULTS AND DISCUSSION

### Microstructure

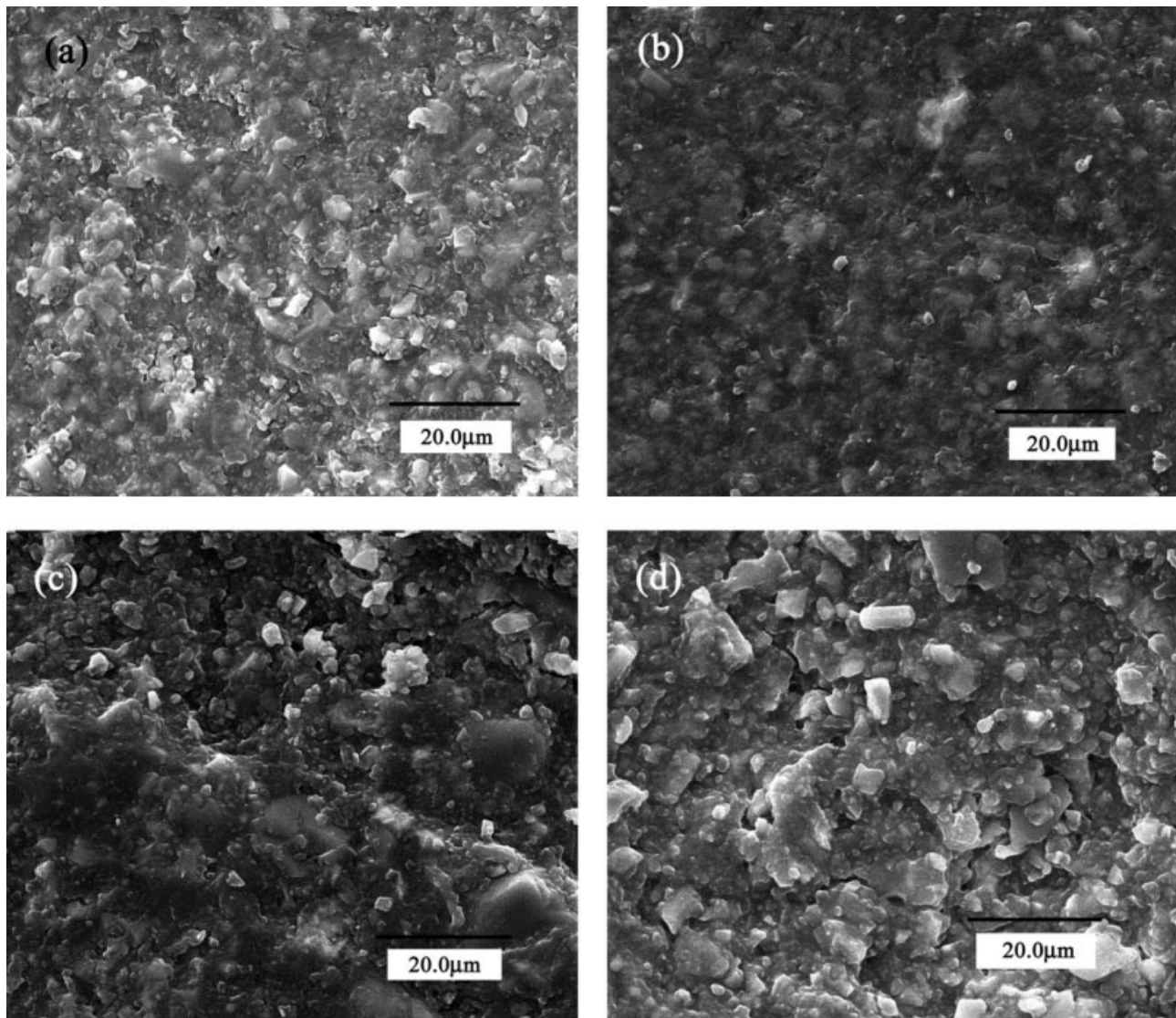
Figure 3 shows the typical top morphology of the EMC samples observed with a digital optical microscope. In Figure 3(a), showing sample A, the whole EMC ( $\text{Si}_3\text{N}_4$ ) particles filled-EMC ( $\text{SiO}_2$ ) powders and the particles occupy the 60% of the total area (consequently corresponding to 60% of the volume). The volume fraction of  $\text{Si}_3\text{N}_4$  in EMC ( $\text{Si}_3\text{N}_4$ ) particle is 60%, that is similar (i.e. 60%) to volume fraction of  $\text{SiO}_2$  in EMC ( $\text{SiO}_2$ ). It can be seen that the EMC ( $\text{Si}_3\text{N}_4$ ) particles are surrounded by the EMC ( $\text{SiO}_2$ ). Some connectivity among adjacent EMC ( $\text{Si}_3\text{N}_4$ ) particles in small regions can be also observed. In this structure, the performance of EMC ( $\text{Si}_3\text{N}_4$ ) particles with higher thermal conductivity may be obstructed by the EMC ( $\text{SiO}_2$ ) surroundings. In Figure 3(b) of sample B, the morphology of EMC is shown where the EMC ( $\text{Si}_3\text{N}_4$ ) powders are filled with EMC ( $\text{SiO}_2$ ) particles. The volume fraction of  $\text{SiO}_2$  in the EMC ( $\text{SiO}_2$ ) particles,  $\text{Si}_3\text{N}_4$  in the EMC ( $\text{Si}_3\text{N}_4$ ) powders and the particles in the whole EMC sample is 60% in all cases. The EMC ( $\text{SiO}_2$ ) particles are surrounded by the EMC ( $\text{Si}_3\text{N}_4$ ) powders with some connectivity in small regions among adjacent EMC ( $\text{SiO}_2$ ) particles. In Figure 3(c), showing sample C, the EMC sample was filled with  $\text{Si}_3\text{N}_4/\text{SiO}_2$  hybrid filler. The volume fraction of the whole filler content reaches 60%. In this structure, all fillers have been merged in the polymer matrix. The structure design of sample B mostly aimed at utilizing the higher thermal conductivity of the EMC ( $\text{Si}_3\text{N}_4$ ) powders to form thermal conductive pathway in the whole EMC. The low thermal conductive EMC ( $\text{SiO}_2$ ) particles are isolated in this structure. Therefore, thermal conducting effect can be completed by the continuous EMC ( $\text{Si}_3\text{N}_4$ ) parts. In EMC filled with sole  $\text{Si}_3\text{N}_4$  filler, as reported in an earlier study,<sup>11</sup> 50 vol % content of filler is enough to form a thermal conductive network. Hence, it is expected that a network should form by adding 60 vol %  $\text{Si}_3\text{N}_4$  filler and most heat should be conducted via that thermal conductive pathway. Moreover, this structure aims at saving the expensive  $\text{Si}_3\text{N}_4$ .

Figure 4 shows SEM images of the microstructure and the dispersion of the filler in EMC ( $\text{Si}_3\text{N}_4$ ) composites, EMC ( $\text{SiO}_2$ ) composites and the EMC



**Figure 3** Digital microscope images of EMC samples (a) Sample A (b) Sample B (c) Sample C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

( $\text{Si}_3\text{N}_4/\text{SiO}_2$ ) sample. Figure 4(a) shows the microstructure of EMC ( $\text{Si}_3\text{N}_4$ ) particles [it is the same sample in Fig. 3(a)]. The image of Figure 4(b) corresponds to the EMC ( $\text{SiO}_2$ ) particles, also shown in Figure 3(b). In both Figure 4(a,b), it can be seen that the  $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$  fillers are homogeneously

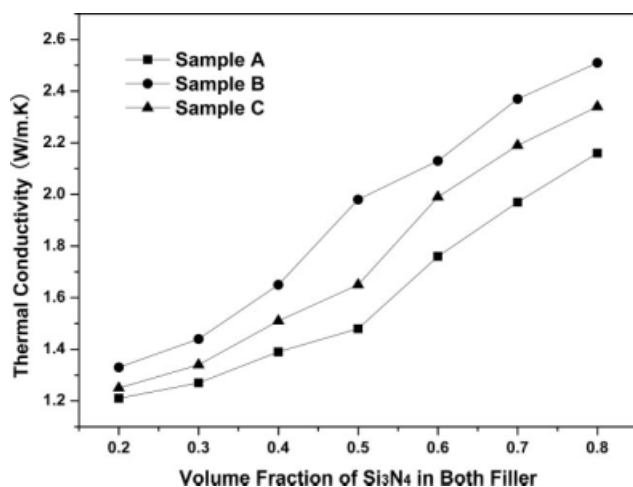


**Figure 4** SEM images of the microstructure and the dispersion of the filler (a)  $\text{Si}_3\text{N}_4$  in EMC ( $\text{Si}_3\text{N}_4$ ) particles (b)  $\text{SiO}_2$  in EMC ( $\text{SiO}_2$ ) particles (c) combination between EMC ( $\text{SiO}_2$ ) particles and EMC ( $\text{Si}_3\text{N}_4$ ) powders (d)  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  dispersion in sample of EMC ( $\text{Si}_3\text{N}_4/\text{SiO}_2$ ).

dispersed in the epoxy resin matrix. There are a few clusters likely occurred owing to the large filling content of filler. Figure 4(c) shows the combination between EMC ( $\text{SiO}_2$ ) particles and EMC ( $\text{Si}_3\text{N}_4$ ) powders. There is no obvious interface between EMC ( $\text{SiO}_2$ ) and EMC ( $\text{Si}_3\text{N}_4$ ). So it can be concluded that the EMC ( $\text{SiO}_2$ ) and the EMC ( $\text{Si}_3\text{N}_4$ ) combine very well in the boundary area. This is most likely due to the cross-linking reaction of the continuous epoxy matrix that takes place at a high temperature and under a high molding pressure. Figure 4(d) shows the microstructure of the EMC ( $\text{Si}_3\text{N}_4/\text{SiO}_2$ ) sample which corresponds to the sample of Figure 3(c). The dispersion regime of both fillers is basically the same. The fillers homogeneously disperse in the epoxy resin with some clusters observed, as well.

### Thermal conductivity

Figure 5 shows the results of experimental thermal conductivity for the three investigated samples. Provided that the content of fillers was up to 60 vol %, the variation of  $\text{Si}_3\text{N}_4$  was realized by changing the proportion of either EMC ( $\text{Si}_3\text{N}_4$ ) or EMC ( $\text{SiO}_2$ ) particles, or  $\text{Si}_3\text{N}_4$  filler in sample C. Moreover,  $\text{Si}_3\text{N}_4$  content in EMC ( $\text{Si}_3\text{N}_4$ ) particles or in EMC ( $\text{Si}_3\text{N}_4$ ) powders,  $\text{SiO}_2$  content in EMC ( $\text{SiO}_2$ ) particles or in EMC ( $\text{SiO}_2$ ) powders were also kept constant, 60 vol %. It can be seen that the increase in the volume fraction of  $\text{Si}_3\text{N}_4$  causes an enhancement of thermal conductivity. The highest conductivity of 2.51 W/m K was achieved for 80% volume fraction of  $\text{Si}_3\text{N}_4$  in the whole filler (the fraction of  $\text{Si}_3\text{N}_4$  in the EMC sample is only 48 vol % indeed), while  $\text{SiO}_2$  has a



**Figure 5** Thermal conductivities of the three investigated EMC with different thermal conductive structure designs as a function of the volume fraction of Si<sub>3</sub>N<sub>4</sub> in both fillers.

proportion of 20 vol %. That is about 10 times bigger than the intrinsic conductivity of the epoxy (0.15–0.25 W/m K<sup>5</sup>). The thermal conductivity of Si<sub>3</sub>N<sub>4</sub> (>150 W/m K<sup>6,7</sup>) is higher than that of crystalline silica (14 W/m K<sup>25</sup>), but in the EMC, the epoxy matrix in the space among fillers acts as thermal barrier. Thus, the thermal conductivity of the EMC does not dramatically increase, compared with the filler itself.

For sample C, thermal conductivity remarkably increases when the content of Si<sub>3</sub>N<sub>4</sub> in both fillers exceeds 50 vol %. This value of filler content can be considered as a threshold, because the fillers start to form thermal conductive clusters in EMC.<sup>12</sup> Furthermore, rod-like Si<sub>3</sub>N<sub>4</sub> powders grains are adjoined with each other more easily. For sample A, thermal conductivity also increases when the content of Si<sub>3</sub>N<sub>4</sub> in both fillers exceeds 50 vol %. Apparently, at that content, the EMC (Si<sub>3</sub>N<sub>4</sub>) particles start to contact with each other, forming thermal conductive pathways. For the structure of EMC (SiO<sub>2</sub>) particles filling the EMC (Si<sub>3</sub>N<sub>4</sub>) powders, abrupt increasing was not observed. In this case, the thermal conductivity should be mainly performed via the EMC (Si<sub>3</sub>N<sub>4</sub>) pathways, but not via the EMC (SiO<sub>2</sub>) particles. Therefore, the thermal conductive pathway formed is a key parameter. The maximizing of volume fraction of filler and the optimization of the microstructures are also important factors for enhancing thermal conductivity of EMC.

Figure 5 allows the comparison of thermal conductivity of the three investigated EMC samples. Although the volume fractions of the two fillers are the same, different structures result in different thermal conductivities. For a given volume fraction of Si<sub>3</sub>N<sub>4</sub>, thermal conductivity of sample B is higher

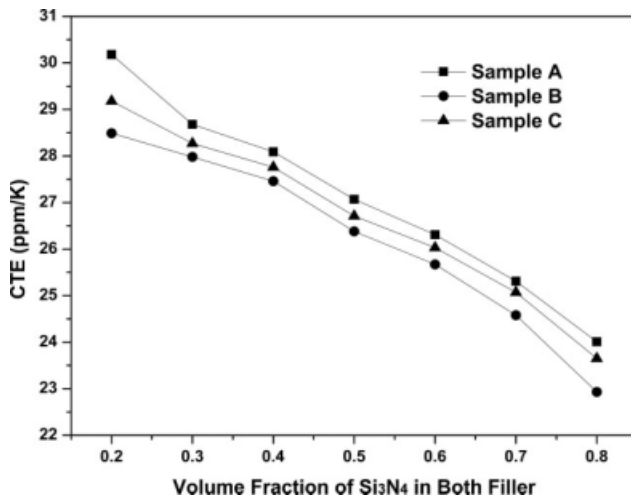
than that of sample C, while that of sample A is the lowest one. Sample B exhibits the highest thermal conductivity because Si<sub>3</sub>N<sub>4</sub> is not dispersed as much as in sample C, considering that the heat is mainly conducted by the Si<sub>3</sub>N<sub>4</sub>, which forms conductive pathway. Sample A shows lower thermal conductivity than sample C because the high thermal conductive EMC (Si<sub>3</sub>N<sub>4</sub>) particles are separated by EMC (SiO<sub>2</sub>) powders. By the way, as pre-cured particles used in sample A and sample B were cured to some extent, the interface among pre-cured particles and EMC powders will lower the density of cross-linking network, and thermal conductivity may be lowered, because heat cannot transfer through molecular bonds as much as in sample C, and interface does not allow the transfer of heat energy by means of phonon. Thermal conductivity of sample A and sample B can be better improved if the density of cross-linking network is higher. These results suggest that the design of EMC (SiO<sub>2</sub>) particles filled-EMC (Si<sub>3</sub>N<sub>4</sub>) powders is the most effective method. They also indicate that this structure design is feasible for expensive Si<sub>3</sub>N<sub>4</sub> filler saving. In this structure, the effective conductive paths are formed by the Si<sub>3</sub>N<sub>4</sub> filler, while the SiO<sub>2</sub> filler only plays a role of volume addition. Hence, EMC designed as above anticipates both better thermal conductivity and cost reduction.

### CTE and flexural properties

With regard to stability and reliability of the interfaces under thermal-fatigue, high thermal stresses are built up if large difference exists between the CTE values of the contacting materials. In the light of the use in electronic packaging, the EMCs are expected to have low compatible CTE with the silicon chip ( $2.616 \times 10^{-6} \text{ K}^{-1}$  at 300 K<sup>23</sup>), solder bumps or substrate to avoid pronounced thermal expansion mismatch. Polymers have expansion coefficient many times larger than the chips. Therefore, fillers with lower expansion are added into the system.

Figure 6 shows the dependence of CTE of the investigated EMC samples, measured from room temperature to 120°C. It is seen that the CTE decreases with increasing volume fraction of Si<sub>3</sub>N<sub>4</sub>. The CTE of Si<sub>3</sub>N<sub>4</sub> is lower than that of SiO<sub>2</sub>. Therefore, for a given filler content, the CTE value of EMC lowers over increasing the content of Si<sub>3</sub>N<sub>4</sub> filler. It is noticed that the investigated EMC samples have low CTE values (between  $23 \times 10^{-6}$  and  $30 \times 10^{-6} \text{ K}^{-1}$ ).

At a given volume fraction of Si<sub>3</sub>N<sub>4</sub>, the CTE values of sample B are lower than that of sample C, while those of sample A are the highest ones. The property of CTE is sensitive to dispersion state of fillers in the composites. In sample A, the EMC (SiO<sub>2</sub>) network mainly contributes to the thermal



**Figure 6** CTE of the three investigated EMCs with different thermal conductive structure designs as a function of the volume fraction of Si<sub>3</sub>N<sub>4</sub> in both fillers.

expansion because most heat is conducted by the EMC (SiO<sub>2</sub>) part. In sample B, the CTE values are lower than those of sample A because the CTE of SiO<sub>2</sub> is higher than that of Si<sub>3</sub>N<sub>4</sub>. The CTE values of sample A are higher than those of sample C because the SiO<sub>2</sub> filler contributes more pronouncedly in the thermal expansion of the former system (sample A).

The averages of flexural strength and averages of flexural modulus of the three investigated EMCs are presented in Table II. Sample A and sample B have similar flexural strengths, while that of sample C are the highest. The total content of fillers of sample A and sample B is kept constant at 60 vol % and the structure design methods are similar, therefore, these two EMC samples have similar flexural strength. Sample C has the highest flexural strength because they were cured in one time. Pre-cured particles used in sample A and sample B were cured to some extent, and the interface among pre-cured particles and EMC powders will lower the density of cross-linking network, comparing with that of EMC powders. Therefore, flexural strength decreases when pre-cured particles are used.

### Electrical properties

Dielectric constant of packaging materials has a great impact on device performance. In general,

**TABLE II**  
Average Flexural Strengths of the Three EMC Samples

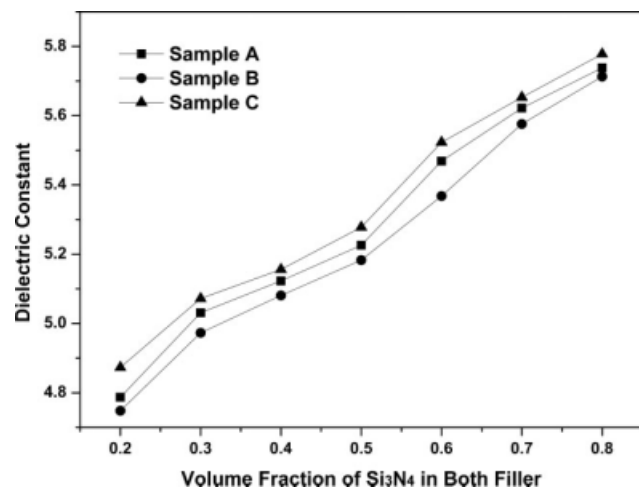
	Average flexural strength (MPa)	Average flexural modulus (MPa)
Sample A	36.5	2887.2
Sample B	36.6	2902.1
Sample C	38.8	3068.4

packaging materials with low dielectric constant are needed to minimize signal delay.<sup>4</sup>

Figure 7 shows the plots of the dielectric constant versus the content of Si<sub>3</sub>N<sub>4</sub> in all EMC samples filled with Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> with the three different structures. Accordingly, dielectric constant of EMC increases with increasing of volume fraction of Si<sub>3</sub>N<sub>4</sub>, but all the values are maintained at a relatively low level (<6, at the test frequency of 1 MHz). Dielectric constant of composites can be calculated using eq. (3)

$$\varepsilon^{\kappa} = \alpha_1 \varepsilon_1^{\kappa} + (1 - \alpha_1) \varepsilon_2^{\kappa} \quad (3)$$

where  $\varepsilon$ ,  $\varepsilon_1$ ,  $\varepsilon_2$  are the dielectric constants of composite, filler, and matrix, respectively,  $\alpha_1$  is the volume fraction of the filler, and  $\kappa$  is a constant determined by the dispersion of the two phases of the composite. According to eq. (3), dielectric constant of EMC increases with the increasing volume fraction of Si<sub>3</sub>N<sub>4</sub> filler, because the dielectric constant of Si<sub>3</sub>N<sub>4</sub> filler ( $\varepsilon_1$ ) is higher than that of epoxy and SiO<sub>2</sub>. However, eq. (3) does not take into account the effect of interfacial polarization. Interfacial polarization also causes increasing of dielectric constant. As filler is surface treated, stronger interface is realized among epoxy resin and filler than among the fillers. Therefore, stronger interfacial polarization among resin and filler can be expected than among fillers. Moreover, filler in sample A and sample B touch the adjacent ones to form conductive pathway, so there are more interface areas among resin and filler in sample C. As a result, highest dielectric constant is realized in sample C for a given content of Si<sub>3</sub>N<sub>4</sub> filler. For a given content of Si<sub>3</sub>N<sub>4</sub>, dielectric constants of sample B are found to be higher than those of sample A, which may be because that interfacial



**Figure 7** Dielectric constant of the three investigated EMC with different thermal conductive structure designs as a function of the volume fraction of Si<sub>3</sub>N<sub>4</sub> in both fillers.



**TABLE III**  
Average Electrical Resistivity of the Three EMC Samples

	Average Electrical Volume Resistivity ( $10^{10}\Omega\text{ m}$ )	Average Electrical Surface Resistivity ( $10^{14}\Omega$ )
Sample A	1.44	6.71
Sample B	1.46	6.74
Sample C	1.43	6.73

polarization among  $\text{Si}_3\text{N}_4$  filler is stronger than among  $\text{SiO}_2$  filler.

The averages of electrical volume resistivity and electrical surface resistivity of the three investigated EMCs are presented in Table III. All the three EMCs with different thermal conductive structure designs have similar electrical resistivities, because the materials used are the same. Electrical resistivity of  $\text{Si}_3\text{N}_4$  is bigger than  $10^{12}\Omega\text{ m}$  at room temperature.<sup>26</sup>  $\text{SiO}_2$  is also not a conductor. Therefore, the addition of the two fillers in epoxy resin will increase the electrical resistivity of EMC. The electrical resistivities of the three EMCs shown in Table III also indicate their usefulness as good insulating materials for packaging applications.

### CONCLUSIONS

EMCs were fabricated using novolac epoxy resin as matrix,  $\text{Si}_3\text{N}_4$ , and  $\text{SiO}_2$  powders as multi-fillers. A high thermal conductive pathway was achieved in a novel structure design of the composites. In the three structures, sample B (EMC ( $\text{SiO}_2$ ) particles filled-EMC ( $\text{Si}_3\text{N}_4$ ) powders) was proved to be the most effective one in thermal conductivity enhancement and cost reduction, a highest thermal conductivity of 2.51 W/m K was achieved with 80 vol % of EMC ( $\text{Si}_3\text{N}_4$ ) in samples (content of the whole filler in all samples is 60 vol %). For a given volume fraction of  $\text{Si}_3\text{N}_4$  in the whole filler, thermal conductivity values increase in the order of EMC ( $\text{Si}_3\text{N}_4$ ) particles filled-, hybrid  $\text{Si}_3\text{N}_4/\text{SiO}_2$  filled-, and EMC ( $\text{SiO}_2$ ) particles filled-EMC samples. CTE decreases with  $\text{Si}_3\text{N}_4$  content in the whole filler increasing, and CTE values of all samples are between  $23 \times 10^{-6}$  and  $30 \times 10^{-6} \text{ K}^{-1}$ . The investigated EMC samples have a flexural strength of about 36–39 MPa. The dielectric

constant increases with  $\text{Si}_3\text{N}_4$  content increase, however, it remains at a comparatively low level (<6, at 1 MHz). Dielectric properties are also affected by the dispersion state of the filler in the composites of different structures. The electrical resistivity of the investigated EMCs indicates their usefulness as good insulating materials for packaging applications.

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