Thermal and Dielectric Properties of the Aluminum Particle/Epoxy Resin Composites

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Received 8 October 2009; accepted 14 March 2010
DOI 10.1002/app.32442
Published online 9 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Microsized aluminum/epoxy resin composites were prepared, and the thermal and dielectric properties of the composites were investigated in terms of composition, aluminum particle sizes, frequency, and temperature. The results showed that the introduction of aluminum particles to the composites hardly influenced the thermal stability behavior, and decreased T_g of the epoxy resin; moreover, the size, concentration, and surface modification of aluminum particles had an effect on their thermal conductivity and dielectric properties. The dielectric permittivity increased smoothly with a rise of aluminum particle content, as well as with a decrease in frequency at high loading with aluminum particles. While the dissipation factor value increased slightly with an increase in frequency, it still remained at a low level. The dielectric permittivity and loss increased with temperature, owing to the segmental mobility of the polymer molecules. We found that the aluminum/epoxy composite containing 48 vol % aluminum-particle content possessed a high thermal conductivity and a high dielectric permittivity, but a low loss factor, a low electric conductivity, and a higher breakdown voltage. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3156–3166, 2010

Key words: thermal properties; dielectric properties; fillers; composites

INTRODUCTION

In recent years, size reduction of high-performance electrical devices has required a high integration of passive components such as resistors, capacitors, and inductors, which outnumber active integrated circuit (IC) elements and occupy more than 70% of the space of a substrate.[1–3] The continuous IC miniaturization trend calls for replacing discrete passive components with embedded passives, a technology in which passive components are buried as a layer in an organic substrate. Among passive components, special interest is focused on capacitors because they are used for various functions, such as decoupling, bypassing, filtering, and timing. They're also capable of enhancing the electrical performance and reducing the size and cost of an electronic system.[4–6] The emerging embedded-capacitor technology is important because it will enable significant performance and functionality improvement of future electronic devices.[5] Embedded capacitors are specially printed portions of printed circuit board (PCB) laminates that perform the charge-storing function but do not require space on the PCB surface. One major technical challenge to the implementation of this technology is the development of appropriate dielectric materials with good electric and mechanical properties, as current PCB manufacturing methodologies cannot apply traditional ceramic dielectrics.[5]

The rapid development of electronic technology has created a demand for materials with good physical and mechanical properties.[2] Functional polymer composites have the ability to meet these needs, and the use of various conductive fillers-such as metallic powders (such as Au, Ag, Cu, Al),[4,5,7,8] carbon (carbon black, carbon nano-tube, carbon fiber and graphite),[9–12] and ceramic particles (i.e., $BaTiO_3$, PMN-PT, CdO, WO_2)[1,3,6,13,14] have been extensively explored and shown to improve the polymer's conductivity and dielectric properties. Until now, extensive attention was given to the preparation of a polymeric composite with a high dielectric constant, low dielectric loss, and good processability for the applications in embedded capacitors and substrates; however, the thermal conductivity of these dielectric materials has been seldom investigated and reported.

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Contract grant sponsor: China Postdoctoral Science Foundation; contract grant numbers: 20070421113, 200801434.

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Despite the increasing miniaturization of IC,[15–17] the subsequent integration of transistors leads to an escalation of power dissipation as well as an increase in heat flux when the device is working at high frequency. As such, the heat dissipation problem is of great importance to the lifespan of high-performance electronic devices.[18,19] Therefore, it is crucial that the heat generated from these devices be dissipated as quickly and as effectively as possible, maintaining the device's desired operating temperature.[20–22] Developing a polymer composite that possesses a high thermal conductivity and dielectric constant but a low dielectric loss is very important, as high thermal conductivity prolongs the lifespan of polymer dielectrics.[18]

Significant changes in the conductivity and dielectric constant of a composite can be observed around the percolation threshold. This is due to the formation of a conductive network, whereas thermal conductivity only depends on the number of heat conductive pathways or networks formed from conductive filler particles in the matrix.[18] At low filler content, the thermal conductivity increases rather slowly; when the loading of filler particles is greater than the percolation threshold, both the thermal conductivity and dielectric constant begin to increase obviously. However, the dielectric loss rise significantly.

To meet the requirements above, a surface-passivated aluminum particle having a core-shell structure was used as filler.[4] The core is metallic aluminum, and the nanoscale shell (about 2–8 nm) is insulating aluminum oxide (alumina). Such core-shell-structured aluminum particles give their composite a high dielectric constant as a percolative system because of their metallic core. At the same time-due to the insulating alumina ceramic shell-they offer a low dielectric loss, comparable to that of a neat epoxy resin.[4]

Due to the abrupt variation of dialectic constant and loss near the threshold, it is risky to prepare percolative dielectrics with a threshold composition. Because of its percolative nature, the high dielectric constant percolative composite requires a uniform dispersion and a precise control of the loading filler.[5] On the other hand, polymer composites with ceramic fillers often suffer a relatively low dielectric constant even with a very high filler loading (greater than 60 vol %). However, aluminum/polymer composites have the combined advantages of a percolative composite and a ceramics/polymer system, showing a high dielectric constant and a low dielectric loss.[4] Furthermore, the aluminum/polymer composite shows high thermal conductivity at a filler loading greater than the percolative threshold point due to the high thermal conductivity of aluminum (270 W/m K) and alumina (33 W/m K) compared to polymer and some ferroelectric ceramics. To investigate the effect of aluminum size on the thermal conductivity and dielectric properties of filled polymer composites, we employed two different-sized particles-2 μm and 40 μm-in this study.

The aim of this article is to prepare a high thermal conductive polymer composite with a high dielectric constant but a low dissipation factor. Epoxy resin was selected as the matrix resin in this study due to its good mechanical properties, including low water uptake and coefficient of thermal expansion, easy processing, and excellent chemical resistance. To obtain a good dispersion of high-content aluminum particles and form better, more homogeneous packaging resulting in a higher composite dielectric constant, an epoxy-functionalized silane coupling agent was applied to functionalize the surface of aluminum particles. This improved the particles' interfacial adherence and processibility, further enhancing the dielectric and thermal conductive properties of the aluminum/epoxy composite.

EXPERIMENTAL

Materials

The polymer matrix used in this study was a diglycidyl ether of bisphenol A-type epoxy resin (D.E.R-331, Dow Corp.) with an epoxy value of 0.52–0.54. A flexible epoxy resin (Long chain polyglycol di-epoxide liquid resin, D.E.R-732, Dow Corp.) was used as a reactive toughening agent to overcome the brittleness of the matrix. The curing agent was methyl hexahydrophthalic anhydride (MeHHPA) from Shanghai Shengyuan, China, and the cure accelerator was 2,4,6-tri(dimethylaminomethyl) phenol (DMP-30) from Shanghai Haitai, China. The aluminum particles, with an average diameter of 2 and 40 μm, respectively, were purchased from Yuanyang Aluminum, Henan. The silane coupler used was γ–glycidoxypropyl-trimethoxysilane, which had an epoxide as one of its end group, provided by Nanjing Xiangfei Chemical, China.

Samples preparation

Surface modification of aluminum particles

Surface treatment for aluminum particles using the silane coupler γ–glycidoxypropyl-trimethoxysilane involved the following steps: (a) making an ethanol aqueous solution at a 95 wt % concentration; (b) adding the silane coupling agent (1.0% of the aluminum mass) to the solution and stirring for 15 min in a flask with reflux setting, adjusting the ethanol aqueous solution pH to 3–5 using diluted hydrochloric acid and stirring for 20 minutes; (c) adding aluminum particles to the solution made in (b) and

stirring while ultrasonicating for 60 minutes; (d) heating to 80°C and refluxing for 6 h while stirring and then cooling to room temperature, letting it set for 2 hours; (e) rinsing with ethanol by filtration at least three times; and (f) drying the mixture at 110°C for 10 h.

Preparation of the aluminum/epoxy composites

The epoxy resin (D.E.R-331) was blended with the flexible epoxy D.E.R-732, the curing agent, aluminum particles, and accelerator according to the designed mass-fraction ratio (as shown in Table I). Then, the blend was stirred vigorously for 1 h, and the obtained homogeneous mixture was degassed for about 30 min in a vacuum to get rid of bubbles. After that, the liquid mixture was poured into a clean glass plate mold kept at 80°C, and was cured in an oven at 100°C for 1 h and 150°C for 5 h. Afterwards, the cured sample was left to cool down slowly to room temperature. Thus, the epoxy-based composites with aluminum powder concentrations ranging from 0 to 48 vol % were prepared.

Characterization

We used the differential scanning calorimeter (DSC) (Model, DSC 200PC, Netzsh Corp., Selb, Germany) to analyze the influence of the aluminum content on the glass transmission temperature of the epoxy samples (5 ~ 10 mg) directly cut from the molded sheet. Measurements were conducted in a nitrogen atmosphere, from 20 to 200°C, at a heating rate of 10°C/min.

Weight loss of the samples (5–10 mg) upon heating was measured using a thermogravimetric analyzer (model: SDTA851, Swiss). Measurements were conducted in a nitrogen atmosphere, from 25 to 600°C, at a heating rate of 15°C/min. The observed weight loss was analyzed.

A Hot Disk thermal analyzer (Hot Disk AB, Uppsala/Sweden) measured the thermal conductivity of the samples, using the transient place source (TPS) method, which is based on a transient technique depicted by Saxena.[23] According to this method, a disk-shaped TPS sensor with a diameter of 7 mm and a thickness of 0.07 mm is placed between two circular sample pieces with diameters of 20 mm and thicknesses of ~ 2 mm. After achieving isothermal conditions in the sample, a constant pulse current is passed through the heating sensor. Resistance and temperature of the sensor are recorded simultaneously by measuring the sensor's voltage increase.

Morphological observation on the samples was performed using a scanning electron microscope (SEM) (model: JSM-7000F, JEOL, Japan). The observation was carried out on the cross-sections of samples to study filler distribution.

TABLE I
Formulation of Al/Epoxy Composite

Raw materials	Content
Epoxy (331)/g	70
Epoxy (732)/g	30
MeHHPA/g	90
DMP-30/g	1
Aluminum/g	Variant

The dielectric measurement was performed on a broadband dielectric spectrometer (Novocontrol Technology Company, Germany) with an Alpha-A high-performance frequency analyzer. The measurement was carried out in the frequency range of 10^{-1} to 10^{7} Hz below room temperature and at the −20 to 200°C range to investigate the dielectric property's dependence upon temperature. The specimens for dielectric measurement were made as circular discs about ~ 1 mm in thickness and 20 mm in diameter. At least two samples were tested to check reproducibility. All measurements were carried out in the cryostat to avoid possible surrounding effects.

The dielectric breakdown strength of the samples was measured using a ball–rod electrode arrangement under a continuous AC voltage loading supplied by a 50 kV, 50 Hz transformer. The arrangement and sample were immerged in insulated oil to prevent surface discharges and flashovers. The test for each sample was performed at room temperature; the sample was placed directly between two copper-ball electrodes opposing each other. The lower electrode was connected to the earth, and an increasing AC voltage with a rate of 2 kV/s was applied to the upper electrode until the sample failed. When the test finished, the ultimate breakdown voltage was recorded. The dielectric breakdown strength of each sample was determined as the average of six tests. The specimens for dielectric breakdown strength were about 1 mm thick.[24]

RESULTS AND DISCUSSION

Thermal properties

DSC analyses of the cured neat epoxy and the epoxy composites containing different aluminum content are depicted in Figure 1. Data obtained from the DSC curves are summarized in Table II. Table II reflects that the glass transition peak temperature (T_g) of cured pure epoxy resin is 70.1. As the volume fraction of aluminum particles (2 μm) increases, the T_g shows corresponding changes. With an increase in the aluminum loading, the T_g of the composites decreased first when the content of aluminum particles was 9 vol %, and then increased; when the filler concentration was greater than 21 vol % the T_g decreased second. The existence of aluminum

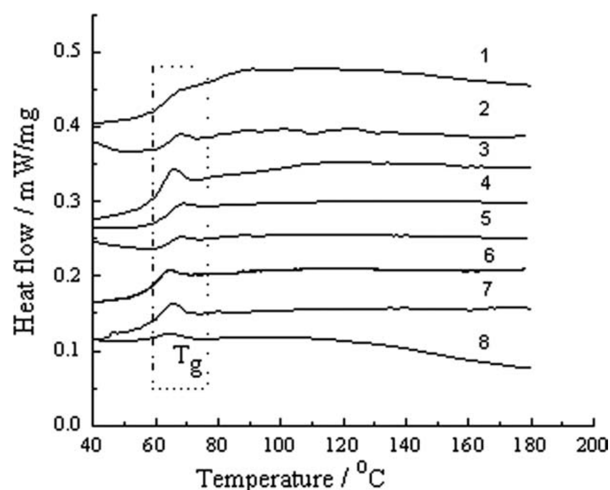

Figure 1 DSC of (1) cured neat epoxy and the cured epoxy composite with 2 μm aluminum particles (2, 3, 4, 5, 6, 7, 8) at 4, 9, 14, 21, 28, 37, 48 vol %, respectively.

particles in the epoxy resin reduced the degree of cross linking and improved the mobility of the chain segment due to the interfacial action between aluminum particles and the epoxy matrix. Therefore, the T_g decreased due to the cured epoxy network's better molecular mobility, especially when the volume fraction of the aluminum content was 0.09, 0.28, 0.37, and 0.48, respectively. The slight increase in T_g values of the composites when Al content lies in between 9–21 vol % might be ascribed to the reason that the filler particles reinforced the molecule chains of epoxy resin, and compensated some defects existing in the cured networks, thus resulting in a slight decrease in the motion of epoxy chains.

The composite with aluminum at 48 vol % contained only a little epoxy and could potentially form several small, aggregated, filler cluster structures; thus, the T_g decreased as a result of the appearance of voids.[2] The DSC results suggest that the incorporation of aluminum particles into the epoxy composites would change the mobility of the epoxy molecules, and therefore, we could observe a decrease of T_g in the composites.[2]

TG analyses of the cured pure epoxy and the epoxy composites with different aluminum content are illustrated in Figure 2. As the figure shows, the introduction of aluminum particles to the composites hardly influences the thermal stability behavior of the epoxy resin; in another words, the thermal stability of pure epoxy is similar to that of the epoxy composites containing aluminum content.

At low aluminum content such as 9–14 vol %, the composite showed a slight drop in thermal stability. However, further increasing the filler concentration of the composite resulted in an improved thermal stability—that is, a slightly higher degradation onset temperature, compared to pure epoxy. This may be ascribed to the lower heat capacity (0.88 Jg^{-1} $°C^{-1)}$ and much higher thermal conductivity (270 W/m K) of aluminum as compared to 1.1 Jg^{-1} $°C^{-1}$ and 0.22 W/m K of epoxy resin. With a high aluminum content, the epoxy composite obtains a higher thermal conductivity, which will cause it to preferably absorb the heat, resulting in epoxy chains starting to degrade at higher temperatures.[25] However, with a low aluminum concentration, the thermal conductivity of the composite is not obviously improved as compared to pure epoxy. This will result in a decrease in the onset degradation temperature of epoxy.

The thermal conductivity of aluminum-epoxy composites at various levels of filler loading is plotted in Figure 3. It suggests that thermal conductivity increased as aluminum content increased, due to the high thermal conductivity of aluminum particles. At low aluminum content, the thermal conductivity increased rather slowly, whereas, at high filler loading, the thermal conductivity obviously increased. This is because the heat-conductive aluminum particles surrounded or encapsulated by a polymer matrix cannot touch one another at a low loading. The result is low thermal conductivity due to the high interfacial thermal contact resistance between filler

TABLE II
Data Obtained From the DSC Curves

Sample no.	Aluminum (vol %)	T_g (°C)
1	0	70.1
2	4	68.1
3	9	65.7
4	14	69.0
5	21	68.7
6	28	64.5
7	37	65.4
8	48	63.8

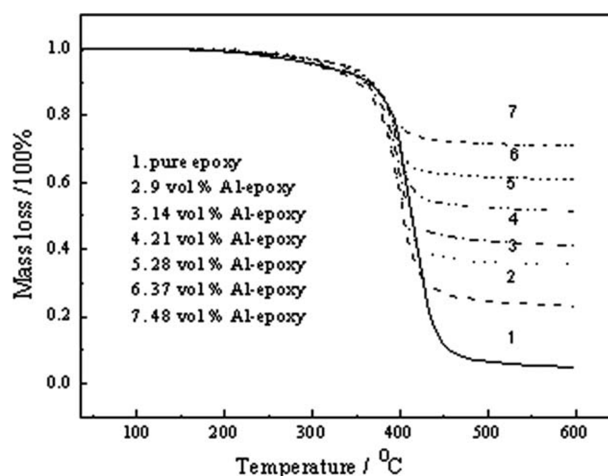

Figure 2 TGA curves of epoxy and its aluminum particles composites.

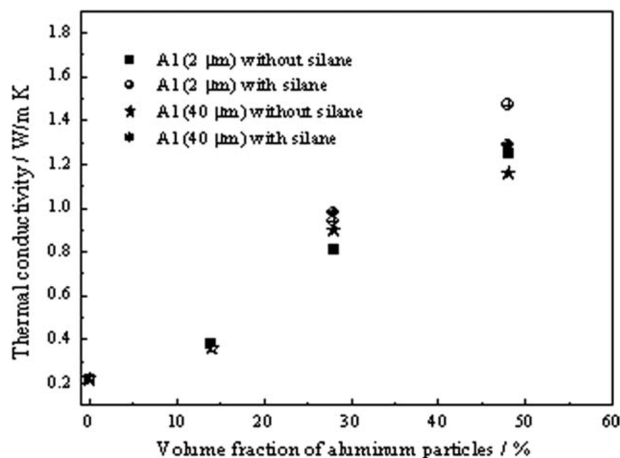

Figure 3 Thermal conductivities of the composites as a function of aluminum content.

particles and the polymer matrix. On the other hand, at a high filler loading, the filler particles begin to touch one another and form particle clusters or a more compact packing structure within the matrix. This leads to improved thermal conductivity because of the decreased interfacial thermal contact resistance.[18,26] Figure 4 shows the microstructure of aluminum/epoxy composites, in which aluminum particles are homogeneously dispersed in the epoxy matrix. The uniform dispersion of aluminum particles eliminated the agglomerate of filler, decreased the air voids ($k_{air} = 0.0024$ W/mK) and defects between filler particles. Therefore, it decreased the thermal contact resistance, facilitating improved thermal conductivity.

The aluminum particle size also affects the thermal conductivity of filled epoxy composites. Figure 3 demonstrates that the thermal conductivities of the composites with aluminum (2 μm) are 0.81 and 1.25 W/m K at 28 and 48 vol % filler content, respectively, corresponding to 0.9 and 1.16 W/m K of those with aluminum (40 μm).

At 28 vol % aluminum-particle content, larger-sized particles with lower specific surface areas are desired to minimize the scattering of phonons; moreover, larger-sized particles tend to form fewer thermally resistant junctions in the epoxy matrix layer than the smaller-sized particles with the same filler content.[26,27] Therefore, the composites containing larger-sized particles exhibited slightly higher thermal conductivity than those with smaller particles. However, at a concentration of 48 vol % aluminum particle-concentration, the smaller filler particles formed a much denser packing structure in the matrix than the larger ones. This is because there is a larger number of smaller particles, and heat conduction pathways which result in a higher thermal conductivity.

Figure 3 also shows that the use of a coupling agent improved thermal conductivity. The thermal conductivities of the composite at 28 and 48 vol % aluminum particles (2 μm) with a surface treatment of 0.94 and 1.47 W/m K, respectively, corresponded to the 0.81 and 1.25 W/m K of those without surface treatment; this thermal conductivity improvement also holds true for the aluminum-filled (40 μm) epoxy composite. As we know, various phonon-scattering processes cause thermal resistance, and the interfacial thermal barriers in composites are mainly due to phonons scattering as a result of an acoustic mismatch and the flaws associated with the matrix–filler interface. Adding the coupling agent to the epoxy could improve the interface between the filler particles and the matrix, increasing thermal conductivity.[26,28]

To predict the thermal conductivity of composites as a function of filler content, many theoretical models concerning the thermal conductivity of composites have been published.[29,30] Among them the Maxwell-Eucken, Bruggeman, and Neilsen models, etc, were used here to evaluate the thermal conductivity of Al/epoxy composites.

Maxwell-Eucken model

$$k_c = k_m \frac{2k_m + k_f + 2V_f(k_f - k_m)}{2k_m + k_f - V_f(k_f - k_m)} \tag{1}$$

Bruggeman model

$$1 - V_f = \frac{k_f - k_c}{k_f - k_m}\left(\frac{k_m}{k_c}\right)^{1/3} \tag{2}$$

Neilsen model

$$k_c = \frac{1 + ABV_f}{1 - B\psi V_f} \quad B = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + A}, \psi = 1 + \frac{V_f^2(1 - V_m)}{V_m^2} \tag{3}$$

Zhou model

$$k_c = k_m\left[1 + \frac{V_f(k_f - k_m)}{k_f - V_f^{1/3}(k_f - k_m)}\right] \tag{4}$$

where k_c, k_m, and k_f are the thermal conductivity of composites, polymer and filler, respectively; V_f is the volume fraction of filler.

In Figure 5, the thermal conductivity values obtained from the experimental study for the composites are compared with several thermal conductivity models. As seen from this figure, all models predicate fairly well thermal conductivity values up to 20 vol % filler loading, whereas beyond 20 vol % filler content Maxwell and Zhou models obviously underestimate the thermal conductivity of the composites, and Bruggeman and Nielsen models are

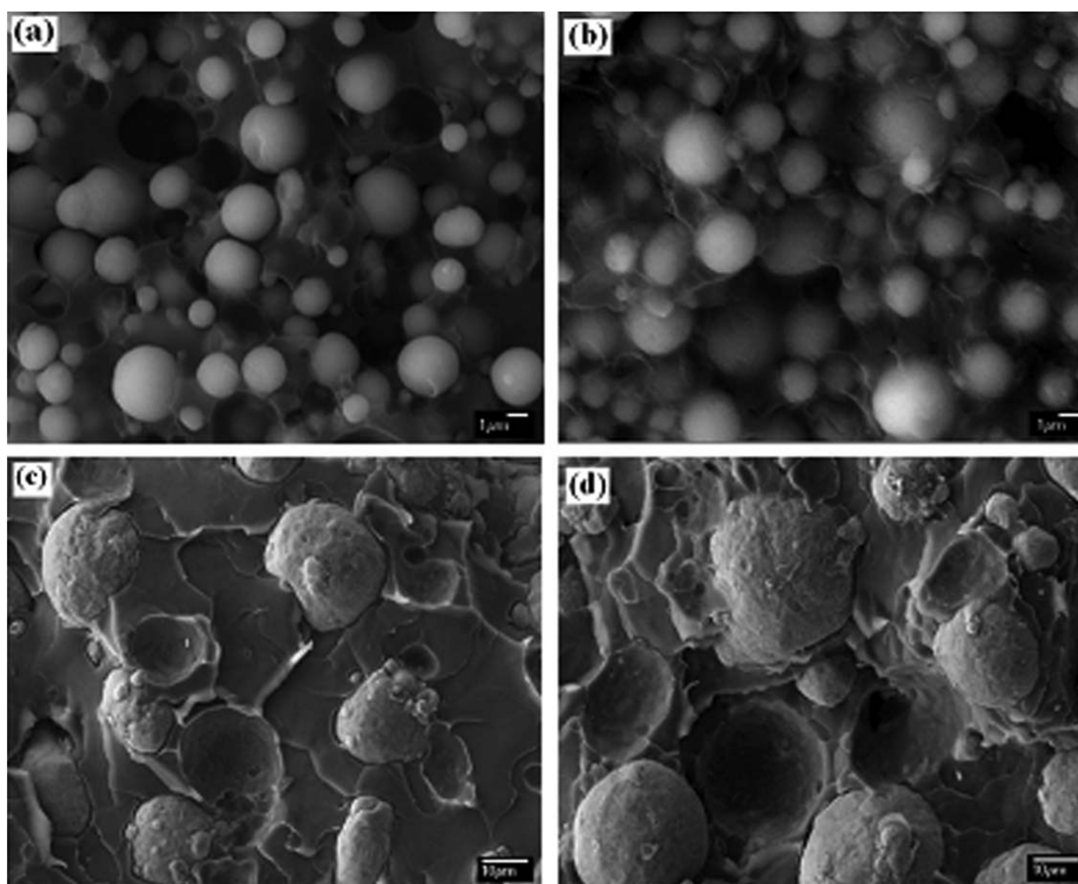

Figure 4 Microstructures of fractured surface of the epoxy composites loading (a, b) 2 μm and (c, d) 40 μm aluminum at (a, c) 28 vol % and (b, d) 48 vol %.

basically suitable for predicting the thermal conductivity of the composites. That is because that both Maxwell and Zhou models are valid only if the filler concentration is less than 20 vol %.

Dielectric properties

The effects of aluminum content, particle size, frequency, and temperature on the dielectric properties of the aluminum/epoxy composites are illustrated in Figures 6–9. These figures show that, as more aluminum particles were added to the epoxy, the dielectric constant and dissipation factor showed an increase in aluminum content as well as an increase in temperature.

Aluminum is a self-passivation metal, which leads it to the formation of a core-shell (nanoscale aluminum oxide insulating shell and metallic aluminum core) structure in aluminum particles. The core-shell-structured aluminum particles provide their composites with a high dielectric constant but a low dielectric loss, comparable to that of a neat epoxy.[4] Such a frequency independence behavior is consistent with the properties of the insulating ceramic.[4]

From Figure 6, we can see that the dielectric permittivity obviously increased with increasing aluminum content, and the dielectric permittivity of the epoxy containing 48 vol % of 2 μm and 40 μm aluminum particles at 10^3 Hz were 34 and 29, respectively, which is 7–8 times higher than that

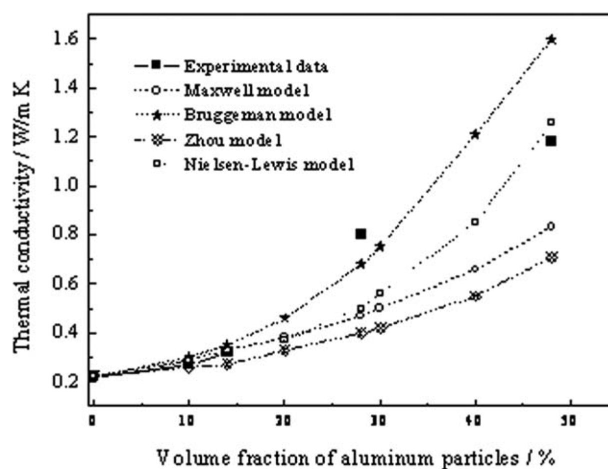

Figure 5 Comparison of thermal conductivity data for Al/epoxy composites with theoretical models.

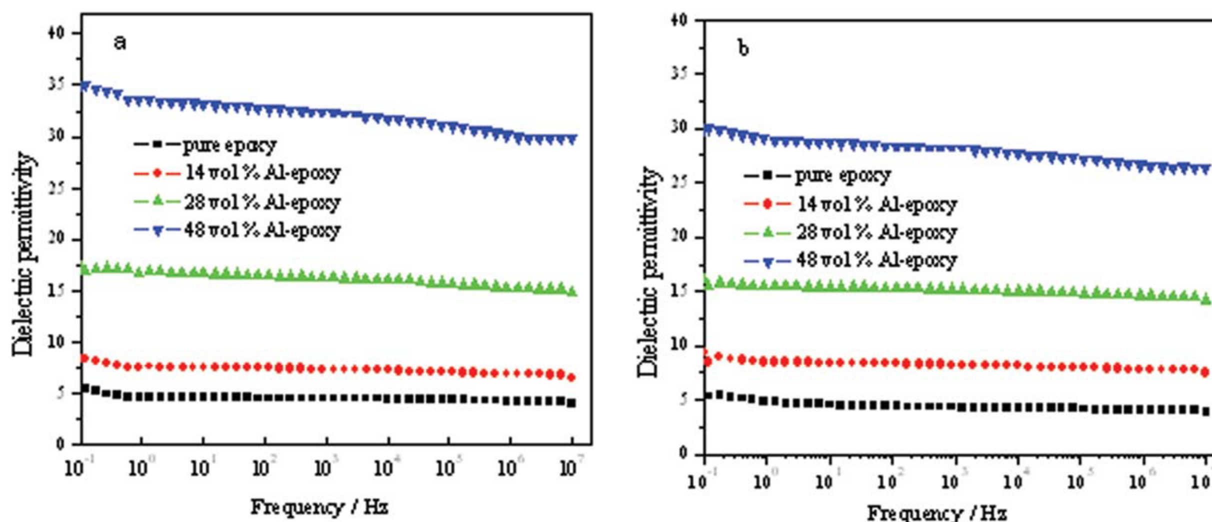

Figure 6 Effect of frequency on the dielectric permittivity of aluminum/epoxy composites at various filler content (a) 2 μm and (b) 40 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the neat epoxy. The dielectric permittivity enhancement can be ascribed to interfacial polarization, also referred to as the Maxwell-Wagner-Sillars (MWS) effect, a phenomenon that appears in heterogeneous media consisting of phases with different dielectric permittivity and conductivity, attributed to the accumulation of charges at the interfaces. In the present case, when the aluminum content is low they are isolated, that is, placed so far apart that there is no interaction between them. As the aluminum concentration is raised, clusters of metal particles are formed. A cluster may be considered as a region in the epoxy where aluminum particles are in contact or very close to each other (as seen in Fig. 4). The average polarization associated with a cluster is larger than that of an individual particle because of an increase in the dimensions of the metallic inclusion and, hence, greater interfacial area,[7] which leads to greater average polarization and thus a greater contribution to dielectric permittivity.

It is also seen from Figure 6 that for a given loading of aluminum the dielectric permittivity shows nearly frequency independent, and the dielectric permittivity versus frequency curves is parallel to the frequency axis in the log scale for lower volume fractions of aluminum. Additionally, the frequency independence behavior can be ascribed to the balanced dispersion of aluminum particles in the epoxy matrix as shown in Figure 4. The frequency-independent behavior of the aluminum/epoxy composites indicate that the major polarization mechanisms contributing to their dielectric constants do not change over the measured range. Moreover, the slope of the line slightly increased with an increase in the aluminum content (i.e., 48 vol % Al). For the 48 vol % Al-epoxy system, the slight decrease in the dielectric constant with a frequency increase is ascribed to the interfacial dipoles having less time to orient themselves in the direction of the alternating field. So, Figure 6 illustrates the Al/epoxy composite possesses high dielectric permittivity with frequency independence.

Figure 7 compares the composition dependency of dielectric permittivity of Al-epoxy composites with some theoretical predictions[7,31] about the dielectric permittivity of composite materials.

Logarithms mixing model

$$\log \varepsilon_c = \log \varepsilon_m + V_f \log \frac{\varepsilon_f}{\varepsilon_m} \tag{5}$$

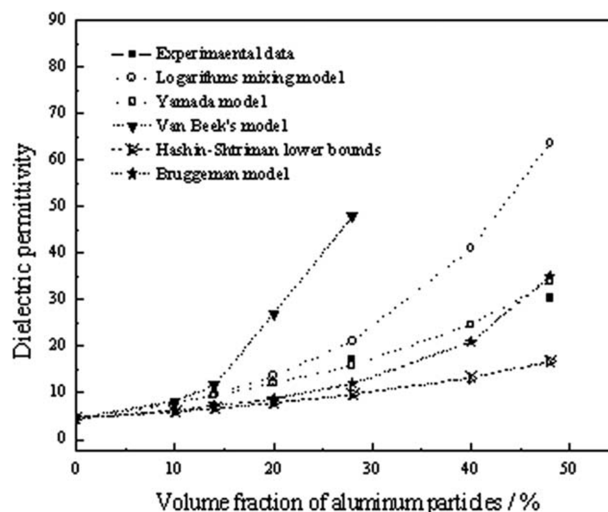

Figure 7 Comparison of dielectric permittivity data for Al/epoxy composites with theoretical models.

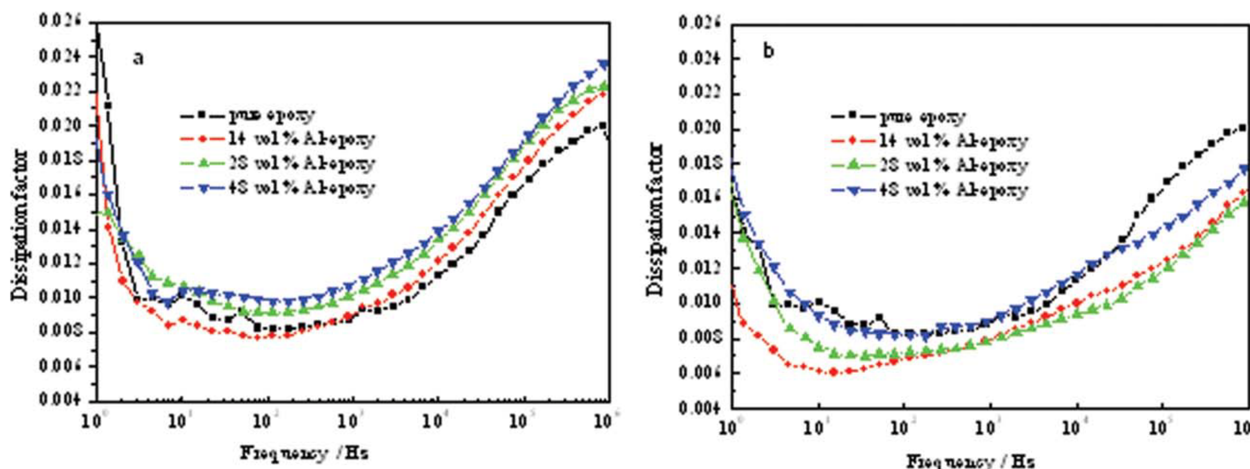

Figure 8 Loss tangent' frequency dependency of the composites at various filler content (a) 2 μm and (b) 40 μm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Yamada model

$$\varepsilon_c = \varepsilon_m \left[1 + \frac{nV_f(\varepsilon_f - \varepsilon_m)}{n\varepsilon_m + (1 - V_f)(\varepsilon_f - \varepsilon_m)}\right] \tag{6}$$

Van Beek's model

$$\varepsilon_c = \varepsilon_m \frac{(1 + V_f)}{(1 - 4V_f)} \tag{7}$$

Hashin-Shtriman lower bounds

$$\varepsilon_c = \varepsilon_m + \frac{V_f}{1/(\varepsilon_f - \varepsilon_m) + (1 - V_f)/3\varepsilon_m} \tag{8}$$

Bruggeman model

$$\varepsilon_c = \varepsilon_m/(1 - V_f)^3 \tag{9}$$

where ε_c, ε_m, and ε_f are the dielectric permittivity of composites, polymer and filler, respectively; V_f is the volume fraction of filler.

As can be seen from Figure 7, none of the theoretic equations agrees well with the experimental values for the entire content range. Compared to other various theoretic models, the Yamada model gives a better fit. The discrepancy between the experimental and theoretic values can be ascribed to the inherent weakness of these equations. They were derived on the assumption that the dispersed particles are spherical and that the volume fraction is low. However, in real system, the dispersed particles are not completely spherical. Also by assuming that the dispersed phase volume fraction is low, these equations were considering only dipole interactions. It was pointed out that multipole interactions become important when particles approach contact.[32] In random or disordered distributions, cluster

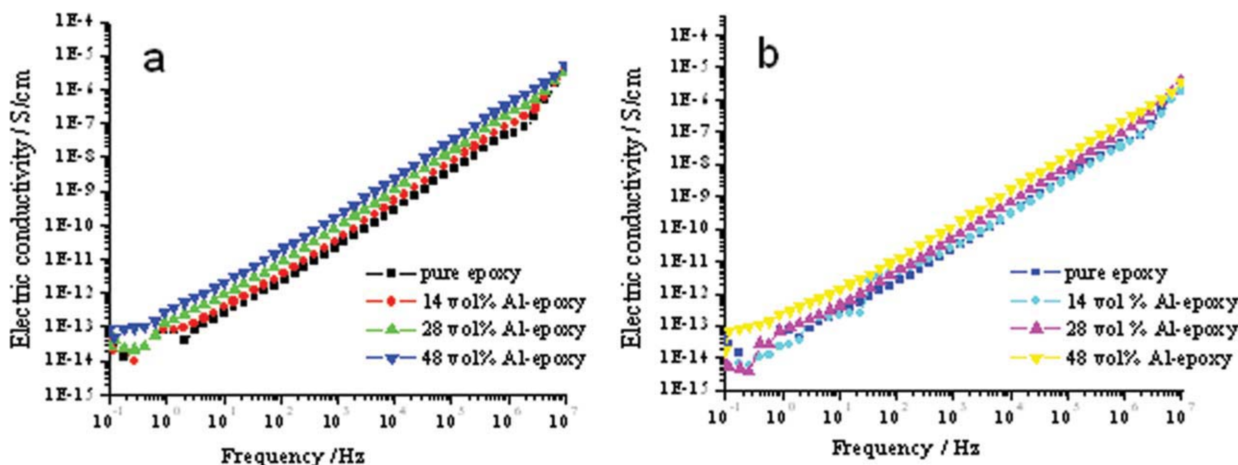

Figure 9 Electric conductivity' frequency dependency of the composites with aluminum (a) 2 μm and (b) 40 μm at various contents. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

formation and thus close encounters between particles can take place at any volume loading.[7]

Figure 8 shows the dielectric loss factor of the neat epoxy and the aluminum/epoxy composites under various applied sweep frequencies. The dissipation factor of the samples all exhibited initial very slight decreases with increasing frequency, followed by an increase to a certain frequency 10^6 Hz. The first increase in the dissipation factor at low frequency can be attributed to dipole polarization,[33] since dipoles have less time to orient themselves in the direction of the alternating field with increasing frequency. So, as the frequency increased further, the dipole polarization effects reduced obviously, and the value of the dissipation factor declined accordingly. Xu[4] also observed that the dissipation factor increased remarkably as the frequency decreased below 1 Hz for nano-aluminum/epoxy composites, and he considered electrode polarization as the main reason in the low frequency range, which may influence the dissipation factor much more than the dielectric constant. Additionally, at low frequency, the decrease in dissipation factor also can be due to the dc conductivity. However, the dielectric loss tangent tends to increase when the frequency is above 1.0 kHz, and a peak of dielectric loss tangent appears at about 10^6 Hz for the composites, this is an obvious relaxation loss process related to the epoxy resin.

In the frequency range of 1–10^6 Hz, we observed that the dissipation factor of the composites is still at a low level (generally less than 0.0264) at 10^6 Hz for both aluminum/epoxy composites because of the nano-scale insulating alumina ceramic shell, which satisfied the need for a low loss value in a practical engineering application.

The particle size of aluminum has an effect on the dielectric properties of the composites. As shown in Figure 6, the dielectric constant of the epoxy composites with 2 μm aluminum particles at 28 and 48 vol % exhibited higher values than the composites with 40 μm aluminum particles. We can see from Figure 4 that the epoxy resin is self-connected into a continuous phase, while aluminum particles are randomly dispersed in the matrix, and the filler particles are surrounded by the matrix. We assumed that there was a higher chance for aluminum particles to form a continuous, random cluster with a decrease in particle size. Moreover, the smaller aluminum particles/epoxy composite showed a stronger interfacial polarization effect, compared to a larger specific surface area. From Figure 8 the dielectric loss factor of the epoxy composites with 2 μm aluminum particles exhibited slightly higher values than the composites with 40 μm aluminum particles, the reason might be associated with the discrepancy in interfacial polarization effect resulted from different particle sizes.

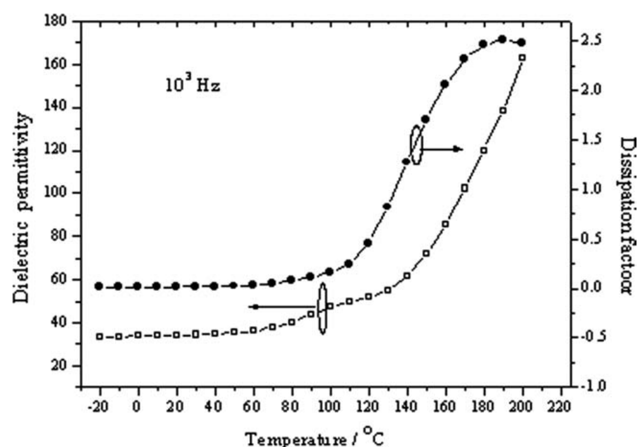

Figure 10 Dielectric property' temperature dependence of the composites with 48 vol % aluminum (2 μm) at 10^3 Hz.

The AC electric conductivity, which we obtained from the dielectric measurements for an epoxy composite with 2 and 40 μm aluminum particles, is presented in Figure 9. Figure 9 reveals that the electric conductivity showed independence of the particle size of aluminum, and gently increased with an increase in aluminum concentration and frequency. For the 48 vol % aluminum-epoxy composites, the electric conductivity increased from 4.9×10^{-14} S/cm at 0.1 Hz to 3.1×10^{-6} at 10^6 Hz. At lower frequencies, the aluminum-epoxy composites exhibited a low electric conductivity because of the insulating aluminum oxide shell as an interlayer between the aluminum cores.

From the discussion above, we found that the epoxy composite with 48 vol % aluminum particles (2 μm) shows higher thermal conductivity and dielectric permittivity than that with aluminum (40 μm). So we selected the former and further investigated the dielectric property's dependence on temperature, and the dielectric strength for its dielectric applications.

Figure 10 depicts the temperature dependence of dielectric permittivity and loss tangent of the composites with aluminum (2 μm) at 48 vol % and 10^3 Hz. Both dielectric permittivity and loss tangent increased with the temperature when it was greater than 60–70°C. Figure 10 suggests that the temperature, especially within the aforementioned range, plays a key role in determining the dielectric property of the composites. According to the DSC results, at a temperature near T_g, the dipoles might begin to have enough mobility to contribute to the loss tangent and dielectric permittivity.

The change of dielectric property in the composites includes three competitive mechanisms: (1) the secondary relaxations or increased mobility of segments of polymer molecules at elevated temperatures below the glass transition temperature; (2)

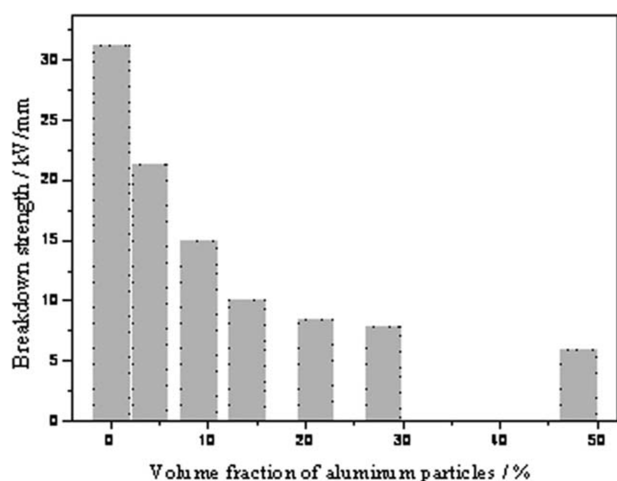

Figure 11 Effect of aluminum (2 μm) content on the electrical breakdown strength of the aluminum/epoxy composites at room temperature.

thermal expansion of resin that disrupts the aluminum particles' chains of contact; (3) the structure of aluminum particles changing with increased temperatures, which could generate a modification in the filler's dielectric response.[2] The increased segmental mobility of polymer facilitates the orientation of dipoles, thereby leading to an increase in the dielectric constant. On the other hand, the differential thermal expansion of the epoxy and the aluminum can disrupt the cluster of aluminum particles, which results in a decrease in the dielectric constant due to a decrease in the size of conductive inclusion. In the present case, the dielectric constant shows an increase in the considered temperature range, so we can assert that segmental mobility is the dominating mechanism.[7]

For a dielectric application, the dielectric strength's ability to withstand a high electric field should be considered. Figure 11 presents dielectric strength's dependence on the aluminum loading. One can see that the dielectric strength remarkably decreased as the aluminum loading increased, although the aluminum loading remained within a comparatively low range. But as the aluminum concentration increased further, the dielectric strength slowly decreased. For example, the dielectric strength decreased from 31.2 to 10 kV/mm as the aluminum concentration increased from 0 to 30 vol %; whereas, at 48 vol % aluminum-powder content, the dielectric strength reached 6.0 kV/mm. Spatial charges generated at the aluminum and epoxy interface under the applied electric field may cause the dielectric strength decrease. At high aluminum content such as 48 vol %, the composite still possessed a high dielectric strength of 6.0 kV/mm, compared to other commonly used metals/polymers. The reasons may be attributed to the following factors: (1) the used aluminum particle has a passivated oxide layer (a kind of insulating layer) around its aluminum core, which can act as an electrical barrier governing the tunneling current between the neighboring aluminum cores and (2) the apparent contact resistance may be found between aluminum particles at high content because of undesirable voids that make it impossible for complete contact between the particles to be realized.[34] Additionally, the highest aluminum content in this study still did not reach the percolative threshold point because of no dielectric singularity observed in this study. As seen in the SEM observation from Figure 4 that even at 48 vol % high content of aluminum, the microstructure consists of isolated aluminum particles separated by layers of insulating polymer; that is, no formation of continuous network or chains of aluminum has occurred.

It is worth noting that the aluminum/epoxy composites at 48 vol % aluminum content still possessed good dielectric breakdown strength characteristics, which is of a great significance for practical application.[34]

CONCLUSION

The prepared aluminum/epoxy composites simultaneously possessed a high thermal conductivity and a high dielectric permittivity but a low loss factor due to the uniform dispersion of aluminum particles in the matrix, as well as the low electric conductivity and higher breakdown voltage at 48 vol % aluminum content.

The incorporation of aluminum particles into the epoxy composites decreased the T_g of the composites. The use of aluminum particles has little effect on the thermal stability of the composites.

Thermal conductivity increased with an increase in aluminum concentration. This is due to the partial network of aluminum in the epoxy and the surface modification of aluminum by silane. Furthermore, the aluminum particle size has an effect on the thermal conductivity and dielectric permittivity at a higher filler loading.

Several theoretical models were employed to predict the thermal conductivity and dielectric permittivity of the composites. The results suggest that, although none of the theoretical curves agreed well with the experimental values, the Bruggeman and Yamada models are basically suitable for predicting the thermal conductivity and dielectric permittivity of the composites, respectively.

The dielectric permittivity of the aluminum/epoxy composites basically showed frequency independence, increasing with an aluminum content increase because of interfacial polarization, in which the dissipation factor increased with rising frequency at a

higher frequency. No dielectric singularity was observed in the relationship between the dielectric constant and the maximum aluminum loading used in this study, which was attributed to the absence of a continuous network of aluminum in the epoxy matrix. Both dielectric permittivity and the dissipation factor increased with the temperature due to the segmental mobility of the polymer molecules.

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