

Dielectric Properties of Aluminum–Epoxy Composites

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ABSTRACT: Dielectric properties of Al–epoxy composites were characterized as a function of composition, frequency, and temperature. The dielectric constant increased smoothly with an increase in the concentration of aluminum. An increase in dielectric constant was also observed with an increase in temperature as well as with a decrease in frequency. In general, dissipation factor values for composites with higher concentrations of aluminum were greater than those with lower volume content of aluminum. Also, the dissipation factor showed an increase both with a decrease in frequency and an increase in temperature. The increase in values of dielectric constant and dissipation fac-

tor with an increase in concentration of aluminum was attributed to interfacial polarization. The absence of any discontinuity in the plot of dielectric constant versus composition was ascribed to the absence of continuous aluminum chains in the composition range investigated. The increase in dielectric constant with a rise in temperature was attributed to the segmental mobility of the polymer molecules. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3602–3608, 2003

Key words: composites; dielectric properties; interfacial polarization; metal–polymer complexes; microstructure

INTRODUCTION

Composite materials, which are usually fabricated with an emphasis on properties such as mechanical strength, have also been used in electronic applications. One such class of composite materials is particulate-filled conductive polymer matrix composites. These composites consist of a polymer matrix in which a second phase, which is usually either a metal or a carbon-based filler, is dispersed, usually by conventional methods of polymer processing, for example, injection molding and extrusion. Conductive polymer composites, which are lightweight materials and combine the inherent processibility of polymers with the electrical conductivity of metals, have been used in a number of applications such as electromagnetic frequency interference (EMI) shields, antistatic devices, thermistors, and conducting coatings.^{1–3} Because of the technological importance of these composites, their electrical properties have been widely studied.^{1–15} However, most of these studies are related to the dc electrical conductivity of these composites; not much attention seems to have been paid to their dielectric properties. This is especially the case with metal–polymer composites. Conductor–polymer systems containing carbon-based fillers, on the other hand, have been more thoroughly investigated. As a consequence, information on the dielectric properties

of particulate-filled composites, especially metal–polymer composites, is scarce. The present study is devoted mainly to the synthesis and evaluation of the dielectric properties of aluminum–epoxy (Al–epoxy) composites as a function of composition, frequency, and temperature.

A well-known fact about conductor–insulator systems is the drastic change in the electrical conductivity of these composites in a narrow range of concentration of the conducting phase. This sudden change in the relationship between electrical conductivity and filler concentration is attributed to the formation of continuous chains or network of the conducting phase that spans throughout the insulating matrix. This phenomenon involving the change in the dispersion state of the conducting phase is usually explained by percolation theory and is known as percolation. The minimum volume content of the conducting filler at which the drastic change in electrical conductivity begins is referred to as the percolation threshold. According to the percolation model,^{16,17} the electrical properties such as electrical conductivity and dielectric constant of conductor–insulator systems should exhibit a power law dependency on the magnitude of the difference ($P - P_c$), where P denotes the volume fraction of the conducting phase and P_c stands for the percolation threshold. It has also been shown that the dielectric constant of metal–insulator systems might exhibit divergent behavior near the percolation threshold.¹⁸ Grannann et al.¹⁹ reported a “singularity” in dielectric constant in the case of a random metal–insulator composite below the percolation threshold.

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Thus, for a conductor-insulator system, the presence or absence of a dielectric singularity may be taken as an indication of either the presence or the absence of continuous chains of conducting phase in the polymer matrix.

EXPERIMENTAL

The starting materials for the preparation of composite samples were Al powder (Metal Powder Co., Madurai, India) and an epoxy (Araldite, Hindustan Ciba Geigy Ltd., Mumbai, India). The epoxy consisted of two parts, resin and hardener, which need to be mixed in equal volumes to form the epoxy polymer. For preparing composite samples, a weighed quantity of aluminum powder was first thoroughly mixed with a measured volume of epoxy resin. Then an equal volume of hardener was added and the resultant mixture was well mixed so as to obtain a uniform composition. The composite mixture thus obtained was pressed in a die at 40 MPa and at a temperature of 120°C; the pressure was maintained for about 0.5 h. A series of Al-epoxy samples with Al varying from 0 to 50 vol % was prepared.

The samples for dielectric measurements were made in the form of circular discs and polished on emery papers containing successively finer abrasives to achieve perfectly parallel and smooth surfaces. Both sides of the disks were suitably painted with a high-purity silver paint to improve electrical contact. The sample was kept properly in the test fixture, which was placed in a furnace and connected to an impedance analyzer (Model 4192; Hewlett-Packard, Palo Alto, CA) by insulated shielded cables. The test fixture, a three-terminal guarded system, was constructed in accordance with the specifications of ASTM, to avoid errors arising from the stray capacitance.²⁰ Measurements were made in the temperature range 30–130°C, maintaining a temperature rise of 1°C/min. Values of capacitance and dissipation factor ($\tan \delta$) were noted at temperature intervals of 5°C and in the frequency range 10 kHz–1 MHz.

RESULTS AND DISCUSSION

Concentration dependency of dielectric constant

The variation of dielectric constant as a function of composition at three different frequencies is shown in Figure 1. The following observations can be made from this figure:

1. The dielectric constant increases as the volume content of the aluminum in the polymer matrix is increased.

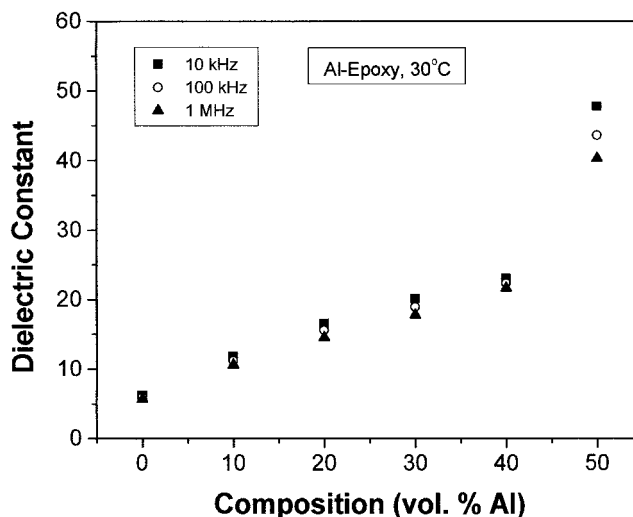


Figure 1 Variation of dielectric constant as a function of composition at three different frequencies.

2. The increase in dielectric constant is fairly smooth with no “dielectric singularity” in the concentration range studied.

The increase in dielectric constant with increase in metal content in metal-polymer systems has been observed by a number of investigators^{22–26} and also by the authors for Al-poly(methyl methacrylate) composites.¹⁵ This permittivity enhancement is attributed to interfacial polarization, also referred to as the Maxwell-Wagner-Sillars (MWS) effect or polarization, 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.^{27–29} In the present case, the system under investigation is a heterogeneous one, that is, Al-epoxy composites with different concentrations of aluminum particles dispersed in the epoxy resin. Epoxy has a lacunar structure with microspherical voids and consequently consists of two phases: air and polymeric matter.²⁵ It becomes more heterogeneous as filler is added to it because of the formation of interfaces between the dispersed phase and the epoxy matrix. When the aluminum content is low, the metal particles are isolated, that is, placed so far apart that there is no interaction between them. As the aluminum content is raised, clusters of metal particles are formed. A cluster may be considered as a region in the polymer matrix where metal particles are in physical contact or very close to each other. 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.²³

In view of the above, the following explanation for the variation of the dielectric constant as a function of

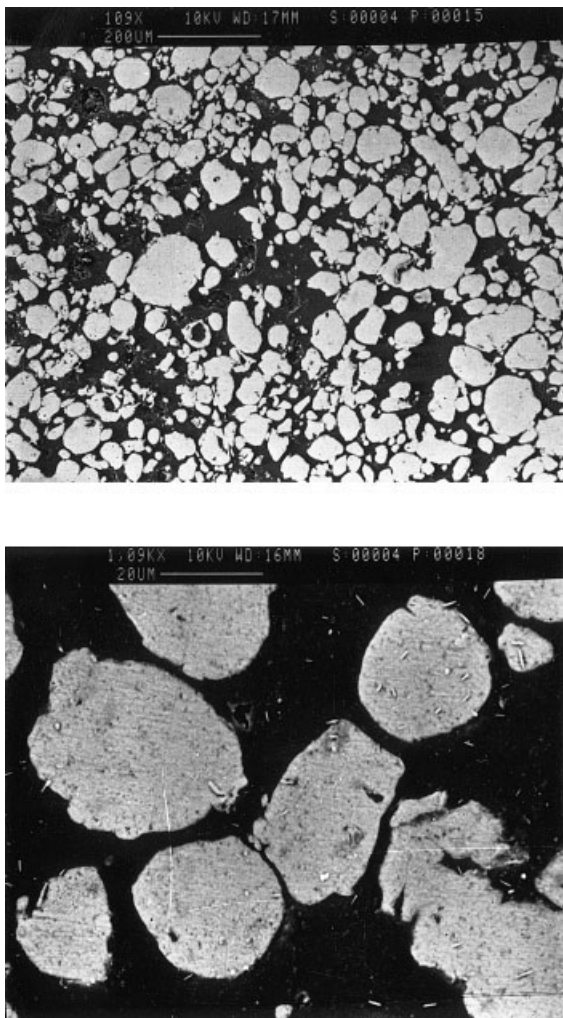


Figure 2 SEM micrographs of Al-epoxy composite containing 50 vol % Al.

concentration of aluminum can be given. Compared to pure epoxy, the dielectric constant of Al-epoxy composites is greater for all filler concentrations because the system becomes more heterogeneous than the pure epoxy as more metal is added to it. The increase in dielectric constant with increase in aluminum is attributed to the formation of clusters, which leads to greater average polarization and thus a greater contribution to dielectric constant.

As noted above, the dielectric constant shows a smooth rise with an increase in aluminum concentration. It has been shown that for conductor-insulator systems, the dielectric constant versus composition plot diverges near the percolation threshold, which has also been referred to as dielectric singularity.¹⁹ Because no such divergence behavior was observed in the composition range under study, it can be concluded that for the present system, the percolation threshold may possibly be observed at some concentration greater than 50 vol % of aluminum. It may be

noted that this value is much higher than the theoretical value of percolation threshold for metal-polymer systems. According to Miyasaka et al.,²¹ the critical concentration may be related to the surface tension of the polymer matrix; they showed that for composites of carbon black and some polymers the greater the surface tension of the polymer, the larger the critical volume of the conducting phase. Thus the absence of a critical concentration in the composition range under study is possibly attributable to good adhesion of aluminum particles by the epoxy resin. Typical micrographs of Al-epoxy composites containing 50 vol % aluminum are shown in Figure 2. It is seen from these figures that even at such high concentration 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.

Figure 3 compares the composition dependency of dielectric constant of Al-epoxy composites with some theoretical predictions about the dielectric constant of composite materials. Van Beek³⁰ reviewed equations or formulae that have been proposed to predict the dielectric constant of conductor-insulator systems. Some of them are: Bruggman's formula: $\epsilon^* = [\epsilon_2 / (1 - v_1)^3]$; Bottcher's formula: $\epsilon^* = \epsilon_2 / (1 - 3v_1)$; and Van Beek's formula: $\epsilon^* = \{[\epsilon_2(1 + v_1)] / (1 - 4v_1)\}$, where ϵ^* , ϵ_1 , and ϵ_2 represent the dielectric constant of the composite, the dispersed phase, and the matrix, respectively; and v_1 denotes the volume fraction of the dispersed phase. These formulae were derived by taking the dielectric constant of the conducting phase to be

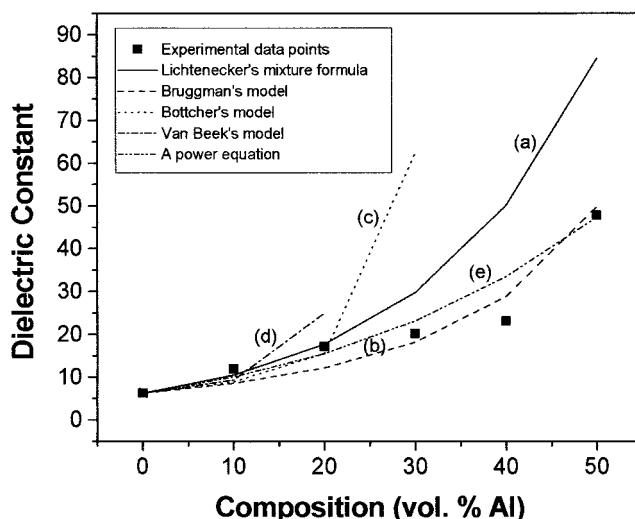
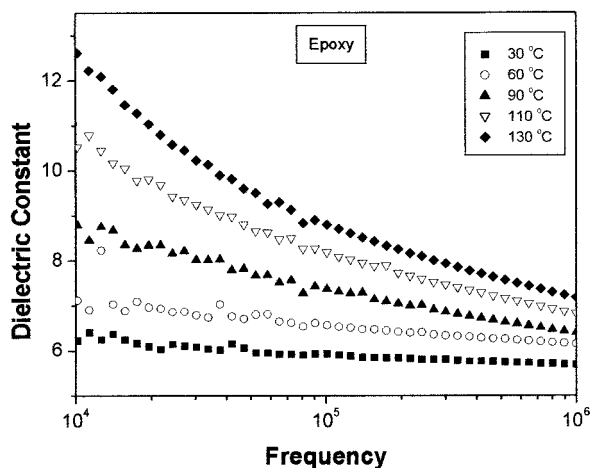
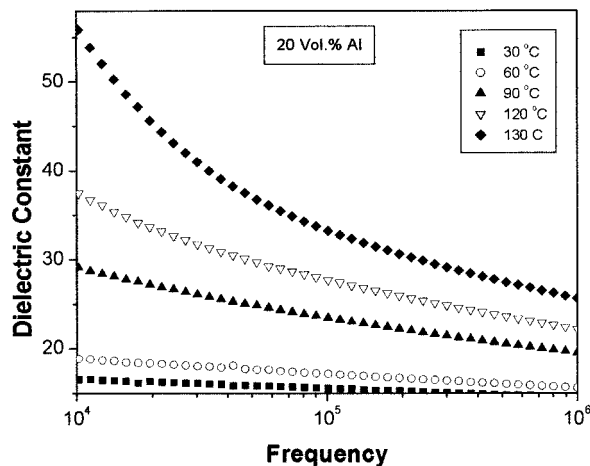


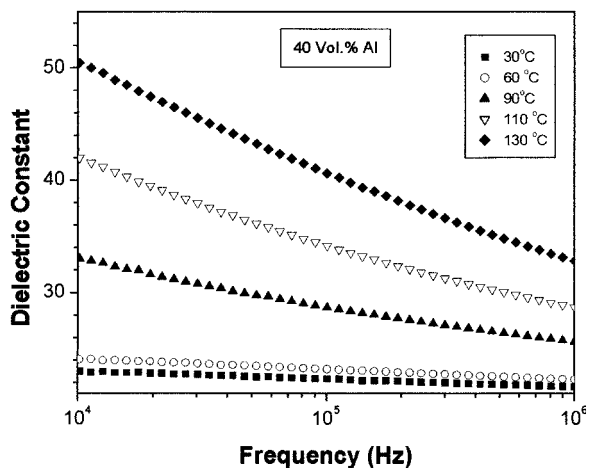
Figure 3 Comparison of permittivity data for Al-epoxy composites with theoretical models: (a) Lichtenecker's mixture formula with $\epsilon_1 = 1145$ and $\epsilon_2 = 6.22$; (b) Bruggman's formula: $\epsilon^* = [\epsilon_2 / (1 - v_1)^3]$; (c) Bottcher's formula: $\epsilon^* = \epsilon_2 / (1 - 3v_1)$; (d) Van Beek's formula: $\epsilon^* = \{[\epsilon_2(1 + v_1)] / (1 - 4v_1)\}$; and (e) a power equation: $\epsilon^* = \epsilon_2(1 + v_1)^5$, proposed by Baziard et al.²⁵ In the above equations, $\epsilon_2 = 6.22$.



(A) Pure Epoxy



(B) Al-Epoxy Composite with 20 Vol. % Al



(C) Al-Epoxy Composite with 40 Vol. % Al

Figure 4 Variation of dielectric constant as a function of frequency for Al-epoxy composites with different concentrations of Al at room temperature.

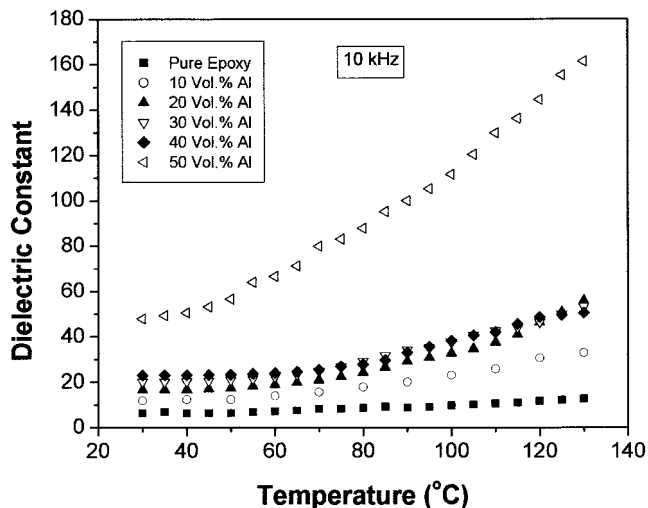


Figure 5 Variation of dielectric constant as a function of temperature for Al-epoxy composites with different concentrations of Al at 10 kHz.

infinite. In the present work, the experimental value of the dielectric constant of matrix (epoxy), ϵ_2 , was 6.22. As can be seen from Figure 3, none of the theoretical equations approximates the experimental values for the entire concentration range.

According to Lichtenecker,³¹ for a composite system consisting of a phase dispersed in another continuous matrix, the effective permittivity is given by the following formula, also referred to as “logarithmic law of mixtures”:

$$\log(\epsilon^*) = v_1 \log(\epsilon_1) + v_2 \log(\epsilon_2)$$

where v_2 denotes the volume fraction of the matrix and other symbols have the same meaning as before.

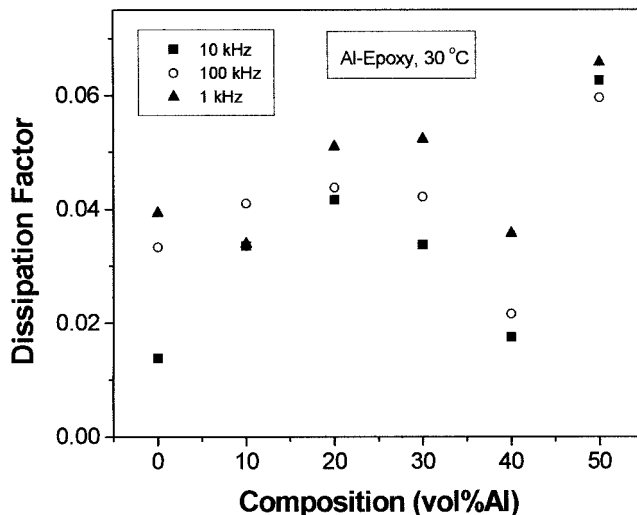
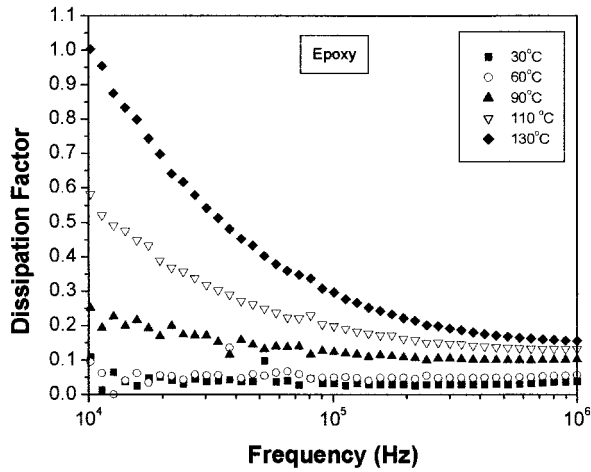
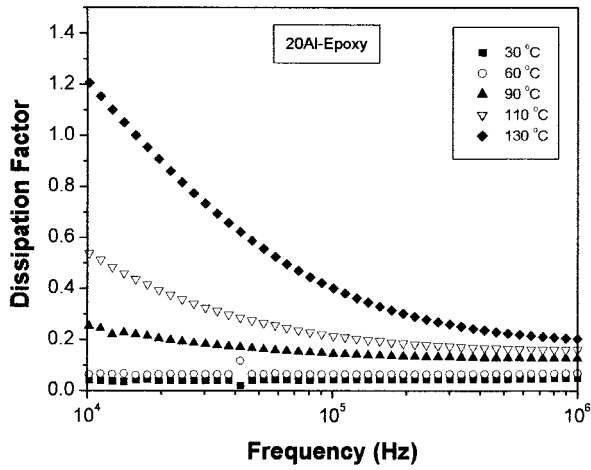


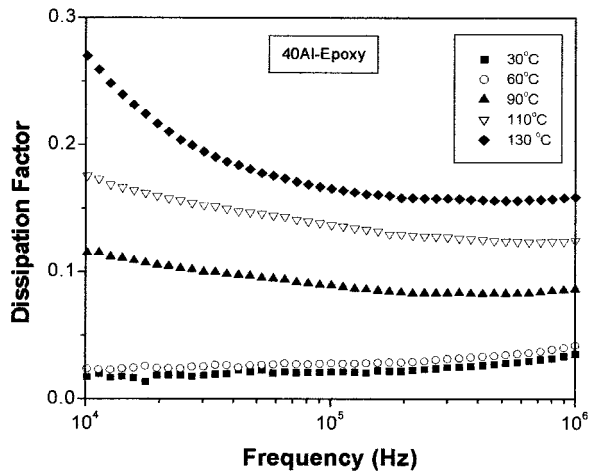
Figure 6 Variation of dissipation factor as a function of composition.



(A) Pure Epoxy



(B) Al-Epoxy Composite with 20 Vol. % Al



(C) Al-Epoxy Composite with 40 Vol. % Al

Figure 7 Variation of dissipation factor as function of frequency for some Al-epoxy composites.

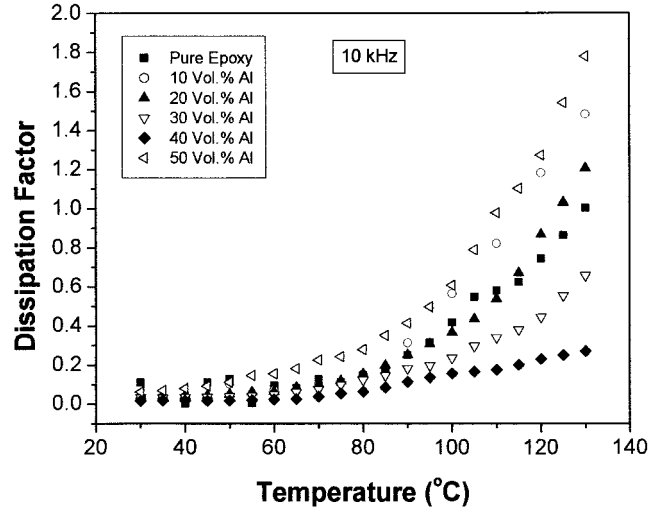


Figure 8 Variation of dissipation factor as a function of temperature for Al-epoxy composites at 10 kHz.

For a conducting material, the concept of dielectric constant is not valid. However, one can still apply the above equation as follows: (1) for each composition point, determine the value of ϵ_1 such that the value of composite permittivity obtained using the above equation is equal to the experimental value and then (2) take the average of the values of ϵ_1 found at various composition points. In the present case, the average value of ϵ_1 was found to be 1145. In Figure 3, the Lichtenecker curve is plotted along with the experimental curve. For Al-epoxy composites, such an analysis was performed by Paipetis and Tsangaris²⁴ and Baziard et al.²⁵ They found the value of the "dielectric constant of metal" to be 165 and 404, respectively. It should be noted that such values might be used only to express the effect of the metal filler on the dielectric constant of the polymer matrix, given that the concept of dielectric constant for a conducting material is not defined.²⁴

Figure 3 also compares the experimental values with an empirical power equation, $\epsilon^* = \epsilon_2(1 + v_1)^5$, proposed by Baziard et al.²⁵ Compared to various theoretical models, the empirical equation proposed by Baziard gives a better fit. The discrepancy between the experimental and theoretical values is attributed to the inherent weakness of these equations. They were derived on the assumption that the dispersed particles are spherical and that the volume fraction of the dispersed phase is low. However, in real systems, the dispersed particles are not always spherical, and it has been shown³² that the dielectric constant increases with an increase in aspect ratio. Also, by assuming that the dispersed phase volume fraction is low, these equations were considering only dipole interactions. It was pointed out by Doyle and Jacobs³³ that multipole interactions become important when particles ap-

proach contact. In random or disordered distributions, cluster formation and thus close encounters between particles can take place at any volume loading.

Frequency dependency of dielectric constant

Variations of dielectric constant with increase in frequency for pure epoxy and some Al-epoxy composites at different concentrations of aluminum are shown in Figure 4. As can be seen from these figures, the dielectric constant decreases as the frequency is increased. The decrease in the dielectric constant with increase in frequency is explained by the fact that as the frequency is raised, the interfacial dipoles have less time to orient themselves in the direction of the alternating field.

Temperature dependency of dielectric constant

Figure 5 depicts the variation of dielectric constant of pure epoxy and Al-epoxy composites at various concentrations of Al. It can be seen that in all cases the dielectric constant increases as the temperature is increased. Two competing mechanisms¹⁰ occur in metal-polymer system when its temperature is raised: first, the secondary relaxations or increased mobility of segments of polymer molecules at elevated temperatures below the glass-transition temperature; second, the differential thermal expansion of the resin and metal (the thermal expansion coefficient of resin is greater than that of aluminum). The increased segmental mobility of polymer facilitates the orientation of dipoles, thereby leading to an increase in dielectric constant. On the other hand, the differential thermal expansion of the resin and metal can disrupt the clusters of metal particles, which results in a decrease in dielectric constant resulting from a decrease in the size of conductive inclusion. Given that, in the present case, the dielectric constant shows an increase in the temperature range considered, it can be said that the segmental mobility is the dominant mechanism.

Dissipation factor

Figures 6 through 8 illustrate the variation of dissipation factor as a function of volume content of aluminum, frequency, and temperature, respectively. It can be seen from these figures that as more aluminum is added to the epoxy, the dissipation factor, in general, shows an increase, and the dissipation factor increases with a decrease in frequency as well as an increase in temperature. The increase in dissipation factor with increase in aluminum concentration, which is also shown by several other conductor-insulator systems, is considered a consequence of interfacial polarization.³⁰

CONCLUSIONS

1. Both dielectric constant and dissipation factor of Al-epoxy composites increased with an increase in volume content of aluminum, which has been attributed to interfacial polarization.
2. No dielectric singularity was observed in the relationship between dielectric constant and composition in the concentration range under study, which was ascribed to the absence of a continuous network of aluminum in the epoxy matrix.
3. Both dielectric constant and dissipation factor of Al-epoxy composites decreased with an increase in frequency.
4. A comparison of dielectric constant values of Al-epoxy composites with some theoretical models and an empirical power equation showed that, although none of the theoretical curves agreed with the experimental values, the power equation $\epsilon^{\text{Al-epoxy}} = \epsilon_{\text{epoxy}}(1 + v_{\text{Al}})^5$ showed good agreement with experimental points.
5. The dielectric constant of the Al-epoxy composites increased with an increase in temperature, attributed to the segmental mobility of the polymer molecules.

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