

Interfacial relaxation phenomena in particulate composites of epoxy resin with copper or iron particles

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Abstract

Interfacial dielectric relaxations have been studied in composites made with epoxy resin and copper or iron particles. Over the temperature range reported (20–160 °C) relaxation peaks are formed in the 10–10³ Hz frequency range. They are attributed to the Maxwell–Wagner–Sillars (MWS), or interfacial, polarization effect, created in heterogeneous dielectrics. The observed MWS loss peaks shift to lower frequencies if the content of the composites in the metal particles is increased. From the temperature dependence of relaxation frequency, the activation energy for the process is estimated to be 45 kJ mol⁻¹ (0.4 eV). Dielectric losses of the composites in the 10–10³ Hz frequency range can be regarded as the sum of losses from a Debye-type relaxation and of the conductivity term σ/ω . Interfacial dielectric losses are insignificant at high frequencies.

Keywords: Composites; Dielectrics; Interfacial phenomena; Metal fillers; Relaxation

1. Introduction

Conductive particles can be dispersed in an insulative polymer matrix [1] and the resulting composites are used in a variety of applications, e.g., EMI shields [2], static dissipative plastics [3], radar absorbing materials [4], conductive coatings [5], and coatings on metal surfaces exhibit protective characteristics against corrosion [6,7].

Epoxy resins are widely used as suitable matrices, besides their other applications in modern technology, because they offer versatility, low shrinkage, chemical resistance, and outstanding adhesion [8–10].

Conductive fillers can greatly alter the conductivity and dielectric characteristics of the polymeric medium in which they are dispersed [11]. They can create interfacial phenomena because of the heterogeneity of the constituents in the composite matrix. The most remarkable effect is expected from the Maxwell–Wagner–Sillars (MWS) [12–14] polarization which always develops in heterogeneous dielectrics.

In this work, the interfacial relaxation phenomena of some particulate composites, prepared by dispersing copper or iron particles in an epoxy resin, are analysed and studied. An effort is made to interpret these phenomena through existing equations, in spite of the inherent difficulties associated with the nature of the composites.

The role of the metal powders in the dielectric behaviour of the composites is also investigated.

2. Experimental

A commercially available bisphenol-A-type epoxy resin (DER 324, Dow Chemical Co.) was used as a prepolymer with an epoxide equivalent weight 197–206, a molecular weight 378, a viscosity 600–800 mPa s at 25 °C, and a density 1.11 g ml⁻¹ at 25 °C. As a curing agent, a cycloaliphatic amine (product XZ87706.05 of the Dow Chemical Co.) was used. The resin/curing agent ratio was stoichiometric according to the manufacturer's data sheets. The above system was used either in this formulation, or filled with powdered metals in different proportions. Metal powders of copper

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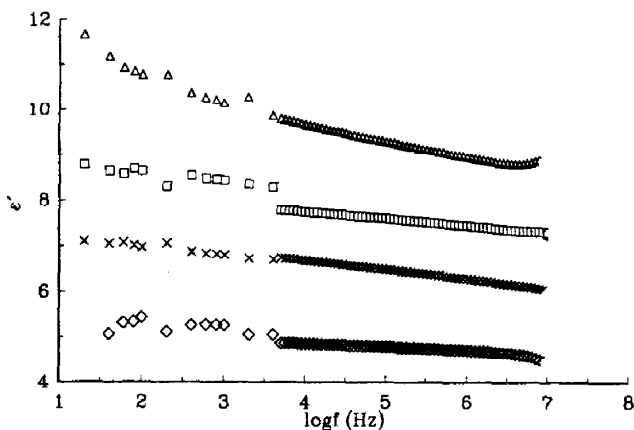


Fig. 1. Dielectric permittivity of composites with copper particles versus frequency, at a temperature of 60 °C (◇, epoxy matrix; ×, 20%; □, 30%; △, 40% w/w in copper).

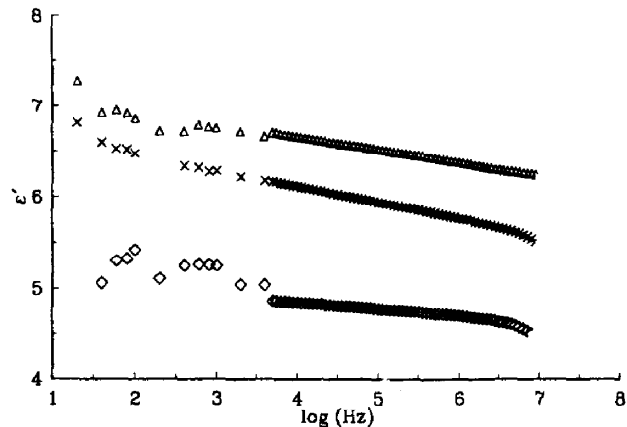


Fig. 3. Dielectric permittivity of composites with iron particles versus frequency, at a temperature of 60 °C (◇, epoxy matrix; ×, 20%; □, 30%; △, 40% w/w in copper).

(Merck) and iron (Ferak lab.) were used. The grain size was lower than 40 μm for iron and 63 μm for copper.

The mixture, after being stirred thoroughly, was put in a vacuum chamber for about 15 min for degassing. In the sequence, it was poured into suitable cylindrical moulds which were sealed and rotated to prevent the metal powder from settling. Initial curing was carried out at ambient for 24 h followed by post-curing at 40 °C for 48 h. Specimens in a circular disk form, 60 mm diameter and 3 mm thickness, were produced by machining from the original castings. All samples were stored in a vacuum desiccator in the presence of silica gel for at least 5 days before measurement to avoid any influence of moisture. Dielectric measurements were performed by means of a Video bridge T-2100 (Electro-Scientific Industries Inc.), in the frequency range of 20 Hz–5 kHz, and by an impedance analyser LF 3192A (Hewlett Packard), in the frequency range 5 kHz–13 MHz. Each value was the mean value of five mea-

surements in a logarithmic sweep of the frequencies (20 points per logarithmic unit). The test cell was a three terminal guarded system constructed according to ASTM D150-92 and D257-91 specifications [15]. Temperature was varied from ambient to 160 °C.

3. Results

The dielectric permittivity of the composites with copper particles at temperatures of 60 °C and 120 °C versus frequency is shown in Figs. 1 and 2, together with the permittivity of the pure matrix. Permittivity increases with increasing filler content and is high in the low frequency range, but diminishes as the frequency increases. At a temperature of 120 °C all samples have greater values of dielectric permittivity compared with their values at 60 °C, especially in the low frequency range. Composites filled with iron particles exhibit the

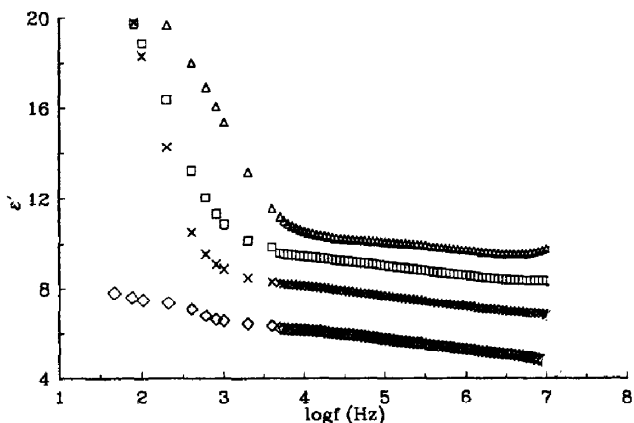


Fig. 2. Dielectric permittivity of composites with copper particles versus frequency, at a temperature of 120 °C (◇, epoxy matrix; ×, 20%; □, 30%; △, 40% w/w in copper).

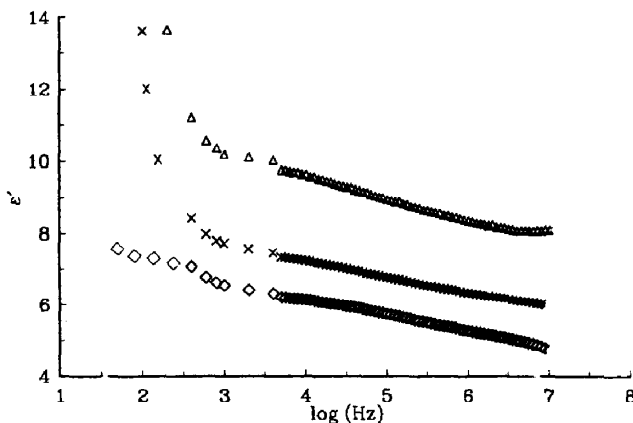


Fig. 4. Dielectric permittivity of composites with iron particles versus frequency, at a temperature of 120 °C (◇, epoxy matrix; ×, 20%; □, 30%; △, 40% w/w in copper).

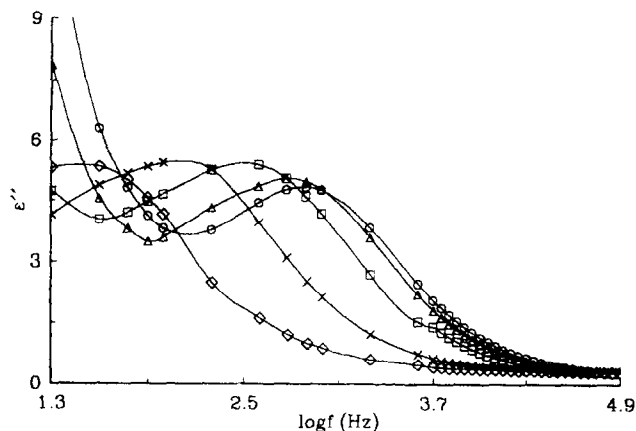


Fig. 5. Dielectric loss of composites with 20% w/w in copper particles versus frequency, at different temperatures (\diamond , 100 °C; \times , 120 °C; \square , 140 °C; \triangle , 145 °C; \circ , 150 °C).

same behaviour (Figs. 3 and 4) shown by the composites with copper particles.

Figs. 5 and 6 show the dielectric loss versus frequency, at different temperatures, of the composites with copper particles. Fig. 5 refers to the composite with 20% w/w in copper particles, while Fig. 6 to that with 30% w/w. In both cases, considerable losses appear in the low frequency range and the relaxation peaks shift to higher frequencies as the temperature is increased. It can also be seen that composites having a greater loading in conductive particles show a higher loss at lower frequencies. The Arrhenius plots derived from Figs. 5 and 6, for the composites with 20% and 30% w/w in copper particles, are shown in Fig. 10. The slope is almost the same for both composites.

Dielectric loss versus temperature for the pure epoxy resin and the composites with copper particles at a frequency of 1 kHz is shown in Fig. 11. As temperature is increased towards the glass transition temperature

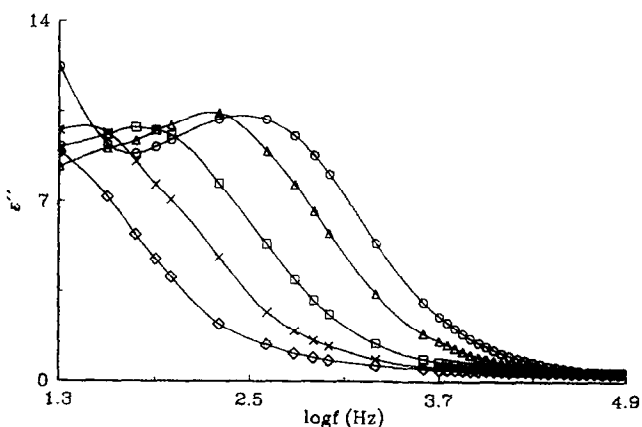


Fig. 6. Dielectric loss of composites with 30% w/w in copper particles versus frequency, at different temperatures (\diamond , 100 °C; \times , 120 °C; \square , 140 °C; \triangle , 145 °C; \circ , 150 °C).

(T_g) of the pure epoxy (≈ 180 °C), dielectric loss increases for every sample, including that of the pure resin. Different loading in conductive particles does not influence the glass transition temperature of the polymeric matrix. The same behaviour is also exhibited by the composites with iron particles. Their dielectric loss versus temperature at a frequency of 1 kHz is shown in Fig. 12, together with that of the pure epoxy resin.

4. Discussion

The dielectric permittivity of metal–insulator composites is greatly influenced by the presence of metal particles. An abundance of formulae has been proposed for the prediction of the permittivity of dielectric mixtures [16]. Some of these formulations can be transformed to be used for metal inclusions in insulative matrices [17,18]. When the conductive component in the dielectric mixture is increased, the permittivity increases as expected by theory [19,20], and found by many workers [15,21,22].

This behaviour is clearly seen in Figs. 1–4 for composites with increasing copper or iron content. High values of permittivity, observed in the low frequency range, are attributed to the process of interfacial polarization existing in heterogeneous dielectrics, and produced by travelling charge carriers. The piling of charges at the interfaces causes large-scale field distortions, in contrast to the other types of polarization (atomic, electronic, dipolar) which are produced by the displacement, or orientation, of bound charge carriers.

The theoretical approach to the situation [12–14] leads to a Debye-type relaxation process described by the following equations [23]:

$$\varepsilon^* = \varepsilon'_x + \frac{\varepsilon'_s - \varepsilon'_x}{1 + j\omega\tau} - j \frac{\sigma}{\omega} \quad (1)$$

$$\varepsilon' = \varepsilon'_x + \frac{\varepsilon'_s - \varepsilon'_x}{1 + \omega^2\tau^2} \quad (2)$$

$$\varepsilon'' = \frac{(\varepsilon'_s - \varepsilon'_x)\omega\tau}{1 + \omega^2\tau^2} + \frac{\sigma}{\omega} \quad (3)$$

Here, ε' , ε'' are the real and imaginary parts of the complex permittivity ε^* of the heterogeneous dielectric, and ε'_s , ε'_x the values of ε' when $\omega \rightarrow 0$ and $\omega \rightarrow \infty$; σ represents the conductivity of the dielectric; ε'_s , ε'_x , σ depend on the conductivities and permittivities of the constituents, and on their volume fractions present in the composite material.

In the case of spheroidal particles (ε_2 , σ_2) dispersed in a medium (ε_1 , σ_1), the limiting permittivities ε'_s , ε'_x and the relaxation time τ are also functions of the axial ratio (a/b) of the spheroids. Their expressions are the following [24]:

$$\begin{aligned} \epsilon'_s &= \epsilon_1 \frac{\sigma_1 + [A_\alpha(1 - \phi_2) + \phi_2](\sigma_2 - \sigma_1)}{\sigma_1 + A_\alpha(1 - \phi_2)(\sigma_2 - \sigma_1)} + \phi_2 \sigma_1 \\ &\times \frac{\sigma_1 + A_\alpha(\sigma_2 - \sigma_1)(\epsilon_2 - \epsilon_1) - [\epsilon_1 + A_\alpha(\epsilon_2 - \epsilon_1)](\sigma_2 - \sigma_1)}{[\sigma_1 + A_\alpha(1 - \phi_2)(\sigma_2 - \sigma_1)]^2} \end{aligned} \quad (4)$$

$$\epsilon'_\infty = \epsilon_1 \frac{\epsilon_1 + [A_\alpha(1 - \phi_2) + \phi_2](\epsilon_2 - \epsilon_1)}{\epsilon_1 + A_\alpha(1 - \phi_2)(\epsilon_2 - \epsilon_1)} \quad (5)$$

$$\tau = \frac{\epsilon_1 + A_\alpha(1 - \phi_2)(\epsilon_2 - \epsilon_1)}{\sigma_1 + A_\alpha(1 - \phi_2)(\sigma_2 - \sigma_1)} \quad (6)$$

The factor A_α in Eqs. (4)–(6) is the depolarizing factor along the α -axis and is a function of the axial ratio (a/b) of the particles; ϕ_2 is the volume fraction of the dispersed phase. For practical calculations, the following expressions of A_α can be used [25]:

$$\text{for } \alpha > b \quad A_\alpha = \frac{\ln(2\alpha/b) - 1}{(b/\alpha)^2}$$

$$\text{for } \alpha < b \quad A_\alpha \rightarrow 1$$

$$\text{for } \alpha = b \quad A_\alpha = 1/3$$

In this study, relaxation peaks of dielectric losses presented in Figs. 5 and 6 exhibit high values, and are formed in the low frequency range, as expected from the change in permittivity (Figs. 1–4) in this range. When the frequency is increased, the dielectric loss decreases quickly, because the term σ/ω of Eq. (3) becomes insignificant. It can be seen by comparing Figs. 5 and 6 that an increase in the filler content shifts the relaxation peaks to lower frequencies with a simultaneous increase in their abscissa. Eq. (6) justifies this behaviour, because, as the conductivity σ_1 of the matrix is very small and can be neglected, an increase in the volume fraction ϕ_2 leads to an increase in the relaxation time τ , with the consequent movement of the relaxation peak to lower frequencies. On the other hand, a higher filler content increases heterogeneity, produces extended interfaces, and results in increased conductivity and higher losses.

Eq. (3) predicts that dielectric loss consists of two distinct parts, one of which is due to a Debye-type relaxation, and the other results from the conductivity of the material. The superposition of these effects produces the curves of Figs. 5 and 6. To investigate this assumption, one of the curves of Fig. 5, representing the dielectric loss versus frequency at a temperature of 150 °C of the composite with 20% w/w copper loading, is isolated and further analysed. The symmetric nature of the curve implies that the Cole–Cole [26] distribution can be used:

$$\epsilon^* = \epsilon'_\infty + \frac{\epsilon'_s - \epsilon'_\infty}{1 + (j\omega\tau)^{1-\alpha}}$$

where α is a measure of the distribution of relaxation times present, with $\alpha = 1$ corresponding to the perfect

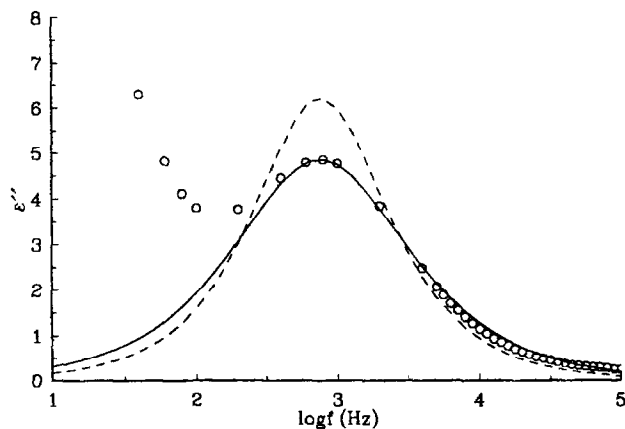


Fig. 7. Dielectric loss of the composite with 20% w/w in copper particles versus frequency, at a temperature of 150 °C (○, experimental points, solid line (—), Cole–Cole equation with $\alpha = 0.156$; and the dashed line (---) represents the theoretical Debye relaxation with a single relaxation time.

Debye process. In the present case, if $\alpha = 0.156$ the experimental relaxation curve fits to the Cole–Cole equation. Fig. 7 represents this situation. Experimental points are shown by the circles, and the solid line is drawn using the Cole–Cole equation with $\alpha = 0.156$. The dashed line represents a Debye relaxation with a single relaxation time.

The small value of α in the Cole–Cole equation is indicative of a system with a narrow distribution of relaxation times. The presence of metal particles, which also have a narrow distribution of their sizes, is responsible for this behaviour. Cole–Cole plots shown in Fig. 8 further support the evidence for a narrow distribution of relaxation times. From these plots, the values of $\epsilon'_\infty = 8.1$, $\epsilon'_s = 20.5$ and $\tau = 2.1 \times 10^{-4}$ s can be obtained.

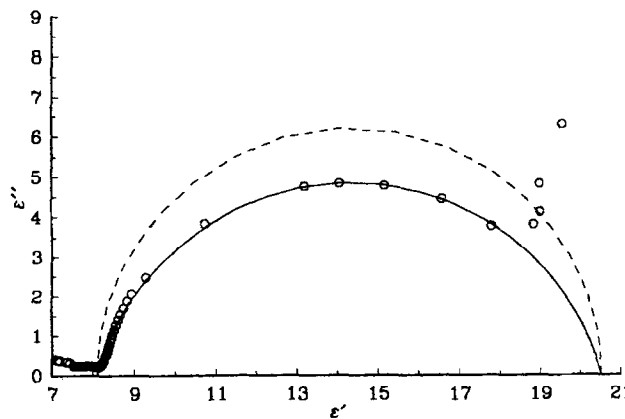


Fig. 8. Cole–Cole plots of the composite with 20% w/w in copper particles, at a temperature of 150 °C (○, experimental points; solid line (—), Cole–Cole equation with $\alpha = 0.156$; and the dashed line (---) represents the theoretical Debye relaxation with a single relaxation time.

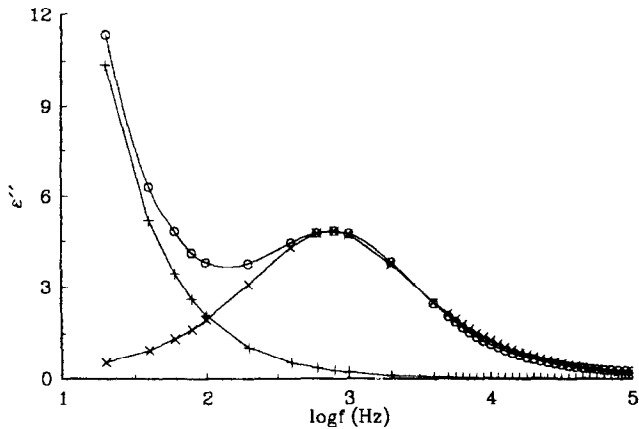


Fig. 9. Dielectric loss of the composite with 20% w/w in copper particles versus frequency, as the sum of two distinct parts; one results from the Debye relaxation with $\alpha = 0.156$ (points marked \times), and the other from the conductivity term σ/ω (points marked $+$).

It is not plausible, using Eqs. (4)–(9), to calculate ϵ'_{∞} , ϵ'_s and τ and then ϵ' , ϵ'' through Eqs. (2) and (3). The reason is that, in the composites tested, the second constituent is a metal and, apparently, there would be no physical meaning to attribute to it any value of dielectric permittivity. The logarithmic law of mixtures [27] is not applicable and existing modifications [28,29], for the case of a conductive constituent, are not suitable since the frequency of the applied field is not included as a variable. However, even though Eqs. (1)–(9) cannot be used for the calculation of parameters related to the phenomenon of interfacial polarization in the composites tested in this work, they can provide general trends concerning the dependence of permittivity on different variables.

The conductivity term σ/ω of Eq. (3) can be found by subtracting values of the curve representing the Cole–Cole relaxation with $\alpha = 0.156$ from the experi-

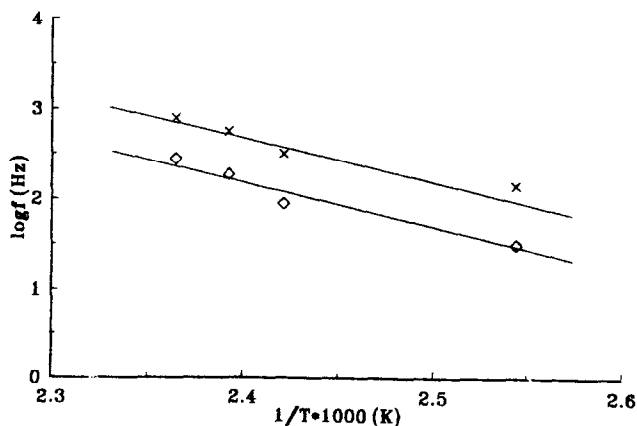


Fig. 10. Arrhenius plots of the loss peak locations versus $1/T$ for the composites with 30% w/w (\times) and 40% w/w (\diamond) in copper particles.

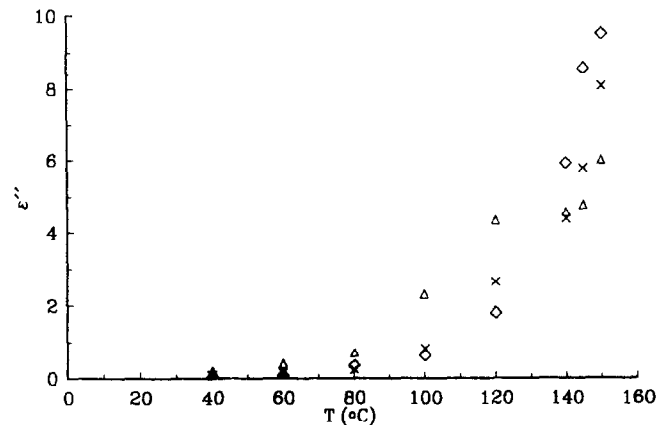


Fig. 11. Dielectric losses versus temperature at a frequency of 1 kHz for the composites with copper particles (\diamond , epoxy matrix; \times , 20%; \triangle , 40% w/w in copper).

mental values. In Fig. 9, the experimental points are again represented. It can be clearly seen that the conductivity is high in the low frequency range, and diminishes as the frequency is increased. Electron transport through metallic microcontacts and migration of ionic impurities must be responsible for the accumulation of charges at the interfaces, and the resulting conductivity in the low frequency range.

Fig. 10 demonstrates the Arrhenius plot of the loss peak locations versus $1/T$. Data for composites with 20% or 30% w/w in copper lie almost on parallel lines. An activation energy of about 45 kJ mol^{-1} (0.47 eV) is obtained for this MWS relaxation process.

Examining the dielectric losses ϵ'' as a function of temperature at a frequency of 1 kHz (Figs. 11 and 12), it can be seen that the pure matrix exhibits a maximum at high temperatures which correlates [30] with the

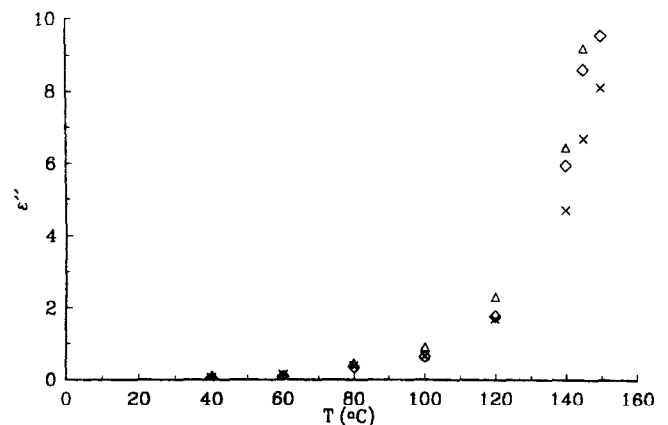


Fig. 12. Dielectric losses versus temperature at a frequency of 1 kHz for the composites with iron particles (\diamond , epoxy matrix; \times , 20%; \triangle , 40% w/w in iron).

glass transition temperature, is attributed to a relaxation process connected with the motion of large parts of the polymer molecules, and is characterized by the α -relaxation process [31]. For filled specimens, either with copper or iron, this maximum is unaffected by the filler [15]. The same behaviour has been found for all measured frequencies.

5. Conclusions

Interfacial polarization, or the MWS effect, is clearly evidenced in polymeric composites containing metal particles. The existence of interfaces produces high dielectric losses in the low frequency range, accompanied by relaxation phenomena which can be described using the Debye approach and the Cole–Cole distribution of relaxation times.

Dielectric losses can be considered as the sum of losses from a Debye-type relaxation, and of the conductivity term σ/ω . At higher frequencies, interfacial polarization losses become insignificant and the dielectric behaviour of these particulate composites is governed by the behaviour of the polymeric matrix.

For the interpretation of the interfacial dielectric phenomena, existing equations are considered inadequate because of difficulties associated with the conductive nature of the composites.

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