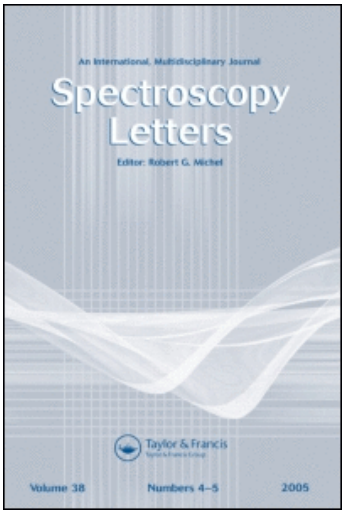

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ABSTRACT Dielectric properties of carbon black–epoxy resin composites were studied in the frequency range between 100 Hz and 15 MHz and over a temperature range 23–98°C. The results show that the composites exhibit, below the critical concentration, a dielectric relaxation phenomenon due to dipolar groups of epoxy resin and to interfacial polarization. This relaxation phenomenon was modeled by the Cole–Cole model.

KEYWORDS composites, dielectric properties, dielectric relaxation, heterogeneous systems

1. INTRODUCTION

The physical properties of composites based on a dispersion of conducting particles within an insulating matrix have been extensively studied over the past decades.[1–3] The electrical properties of such media are dependent on the properties of each component, the degree of dispersion, the interaction between components, and on the volume fraction ϕ of the filler.[4] The filler concentration dependence of the electrical conductivity is characterized by an insulator-to-conductor transition at a critical volume concentration, the conducting threshold ϕ_c. In agreement with percolation theory, various electrical properties may exhibit power law behavior versus $(\phi - \phi_c)$ in the neighborhood of ϕ_c.[5] Carbon black–polymer composites are the most extensively used systems. In previous works,[6–8] these materials have been studied, at ambient temperature, and for various volume concentrations of carbon black, at low and microwave frequencies. The parameters investigated were the volume concentration, the size of the carbon black inclusions, and the frequency of the applied field. In this previous works, we have shown that these critical exponents describing the conductivity and dielectric constant, obtained near the percolation threshold, are in good agreement with published values. Besides, we have found that dielectric behavior of these composites can be described by the universal dielectric response.

The purpose of this paper is to study the effect of temperature on the dielectric properties of a dispersion of carbon black particles in an epoxy matrix over the frequency range 100 Hz to 15 MHz for various temperatures in the range 23–98°C, and for volume concentrations below the conductivity threshold. The data give evidence of relaxation phenomena for which we have determined the dielectric parameters: the relaxation frequencies, the loss peak maximum, and the activation energy.

1.1. The Cole–Cole Model

The dielectric relaxation can be characterized by a Cole–Cole response function of dipolar elements:[9]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{\beta_\alpha}} \quad (1)$$

where ε_s is the static relative permittivity at zero frequency, ε_∞ is the relative permittivity at infinite frequency, τ is the average value of relaxation times distribution, ω is the angular frequency ($\omega = 2 \cdot \pi F$), and $\beta_{cc} = 1 - \alpha_{cc}$ is an empirical parameter taking values in the range (0–1) and whose physical significance is a related to the width at half-height of the distribution of relaxation times function.[10] The limiting cases $\alpha_{cc} = 0$ corresponds with the ideal relative complex permittivity of Debye.[11] From equation (1), the dielectric relaxation is of the Cole–Cole type if the Argand representation in the complex plane [$\varepsilon'' = \varepsilon''$ (ε')] is a semicircle tilted respective to the real axis by an angle $\alpha_{cc}\pi/2$, its center having the following coordinates:

$$(\varepsilon'_c, \varepsilon''_c) = \left[\frac{\varepsilon_s + \varepsilon_\infty}{2}, -\frac{(\varepsilon_s - \varepsilon_\infty)}{2} tg \frac{(\alpha_{cc}\pi)}{2}\right] \quad (2)$$

2. MATERIALS AND METHODS

2.1. Sample Description

The samples investigated in this study are carbon black particles Monarch 1100 (Cabot Co., USA) with a diameter of 14 nm and a static electrical conductivity $\sigma_{DC} = 1.7\ (\Omega\ \text{cm})^{-1}$, dispersed in an insulating epoxy resin matrix DGEBF (diglycidylic ether of bisphenol F) having conductivity of the order $\sigma_{DC} = 1.40 \times 10^{-16}$ $(\Omega\ \text{cm})^{-1}$ with the glass transition temperature $T_g \approx 80°\text{C}$. Several samples consisting of an epoxy polymer matrix charged with different carbon black proportions have been used. Carbon black volume fractions of the samples used are 0.5%, 2%, 3%, 5% and 7% (apart from epoxy resin matrix sample). More details about the samples preparation are given in Ref. [12]. As a characterization of these series of samples, we performed electrical resistance measurements. A conductivity threshold was evidenced and the critical concentration $\phi_c = 8\%$ was determined.

2.2. Dielectric Measurements

The complex permittivity function $\varepsilon^* = \varepsilon' - \varepsilon''$ was measured by using a Hewlett Packard Network Analyzer (model 4194A) interfaced with a microcomputer.[8] The relative permittivity ε' and the loss factor ε'' of the sample were deduced from the capacitance and the conductance, respectively. The samples were cut into cylindrical shapes 3 mm thick and with a diameter of 12 mm. Each of both circular surfaces were polished and covered with a thin layer of silver to serve as electrode. The measurements were performed, in the frequency range 100 Hz to 15 MHz, under isothermal conditions for temperatures included in the range 23–98°C. The precision of temperature control was $\pm 0.5°\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Epoxy Matrix

Polymeric materials present more than one loss peak, and it is usual to refer to them as α, β, or γ relaxations.[13] The α relaxation is possible only around and above the glass transition temperature T_g, the β relaxation is observed at low temperature, and the relaxation γ is a superposition of the α and β processes.

In Figure 1, the variation of ε'' as a function of ε' is reported for the unloaded epoxy resin matrix at different temperatures. As mentioned above, we observe at low temperature the existence of a single relaxation peak, which is identified to the β process that is caused by the reorientation of the polar entities present in the matrix, like residual amines (–NH_2 and–NH–), epoxy and hydroxyl formed from the ring-opening of epoxides by amines. In the neighborhood of the glass transition temperature, a second relaxation peak appears at a lower frequency F = 13 KHz that is probably due the microbrownian motion in the polymer matrix. Actually, above T_g the polymer is no longer in the glassy state, so local motions of short-chain segments are possible.[14] The variations

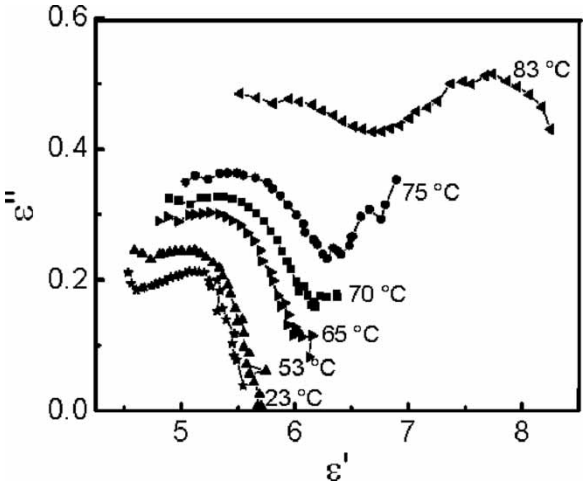

FIGURE 1 Loss Factor ε'' as a Function of Permittivity ε' for Epoxy Polymer at the Various Temperatures Reported on Each Curve.

of ε'' versus ε' also display an abrupt increase close to the temperature T_g.

From equation (1), we have established a calculation program for the fit of the Cole–Cole model to the experimental data. The fitting parameters are the radius of the semicircle and the center coordinates. Figure 2 represents the experimental and calculated complex permittivities at different temperatures, in Argand diagram. We have reported in Table 1 the values of the relaxation frequency $F_{\max}$ ($2\pi \cdot F_{\max}$ $\tau = 1$) and of the fitting parameters (α_{cc}, ε_s, ε_∞) obtained for the different temperatures.

Besides, we have deduced the activation energy, E_a, of the epoxy polymer from the Arrhenius plot:

$$F_{\max} = F_0 \cdot \exp(-E_a/kT), \tag{3}$$

where k Boltzmann's constant, F_0 the pre-exponential constant, and T the absolute temperature. The activation energy for this process is calculated from the slope of the least-squares fit line to the plot of log $F_{\max}$ versus temperature $1/T$. This plot (Fig. 3) is linear, and the activation energy is $E_a = 0.20$ eV, with a linear correlation coefficient 0.91. The value of energy can be attributed to the motion of the

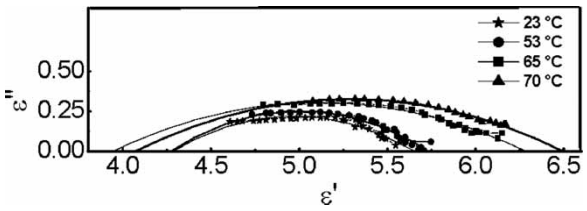

FIGURE 2 Cole–Cole Simulating Curves and Experimental Data for Epoxy Resin Matrix at Several Temperatures.

TABLE 1 Values of the Parameters According to the Cole–Cole Distribution for Epoxy Resin Matrix at Several Temperatures

T (°C)	ε_∞	$\varepsilon_s - \varepsilon_\infty$	$F_{\max}$ (kHz)	τ (s)	$\beta_{cc} = 1 - \alpha_{cc}$
23	4.29	1.25	282	5.65×10^{-7}	0.43
53	4.33	1.37	520	3.06×10^{-7}	0.52
65	4.23	1.96	2400	6.63×10^{-8}	0.38
70	4.29	2.07	3250	4.90×10^{-8}	0.39

polymer chains segments. This value is in good agreement with the result obtained by El Moznine et al. on the composite materials based on epoxy resins filled with alumina.[15] The energy due to interfacial polarization is then weak. Similar results have been obtained by Sreehari Sastry on epoxy resin composites containing fillers like glass, ferrite, and carbon.[16]

3.2. Carbon Black–Epoxy Resin Composites

Figure 4 is a plot of ε'' as a function of ε' for various carbon black concentrations at room temperature. When $\phi < \phi_c = 8\%$, it evidences a relaxation peak whose height increases with the concentration. The relaxation phenomena is probably the result of the combination of two polarization mechanisms:[17] the first one issued from the dipolar origin of the polymer and the other one from the presence of the carbon. The second polarization mechanism causes a virtual electric charge concentrated at the interface of the heterogeneous system components that have different dielectric properties. This gives rises to the

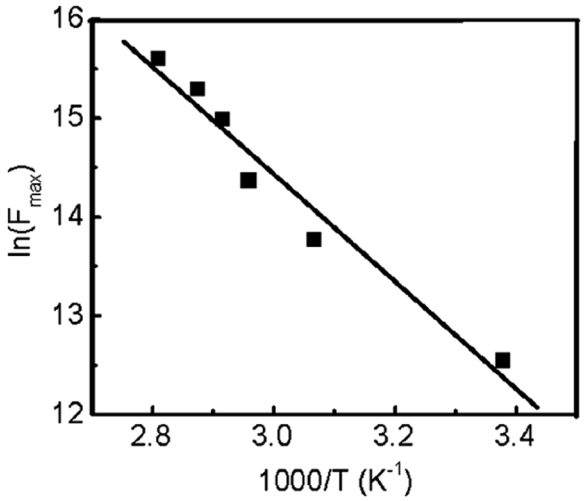

FIGURE 3 Arrhenius Plots for Epoxy Resin Polymer.

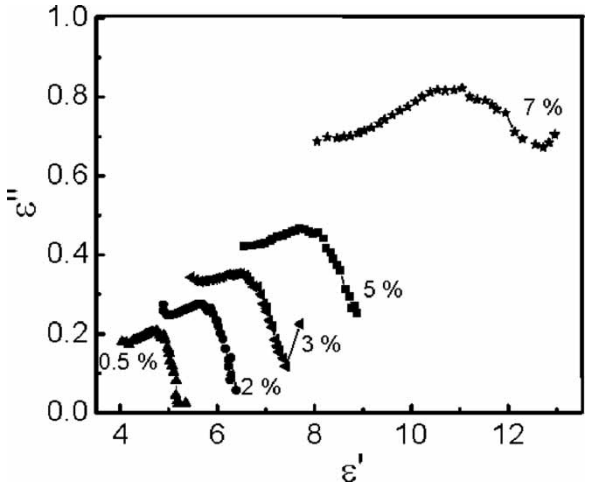

FIGURE 4 Loss Factor ε'' as a Function of Permittivity ε' of Carbon Black–Epoxy Resin Composites at the Room Temperature for Different Values of Carbon Concentrations.

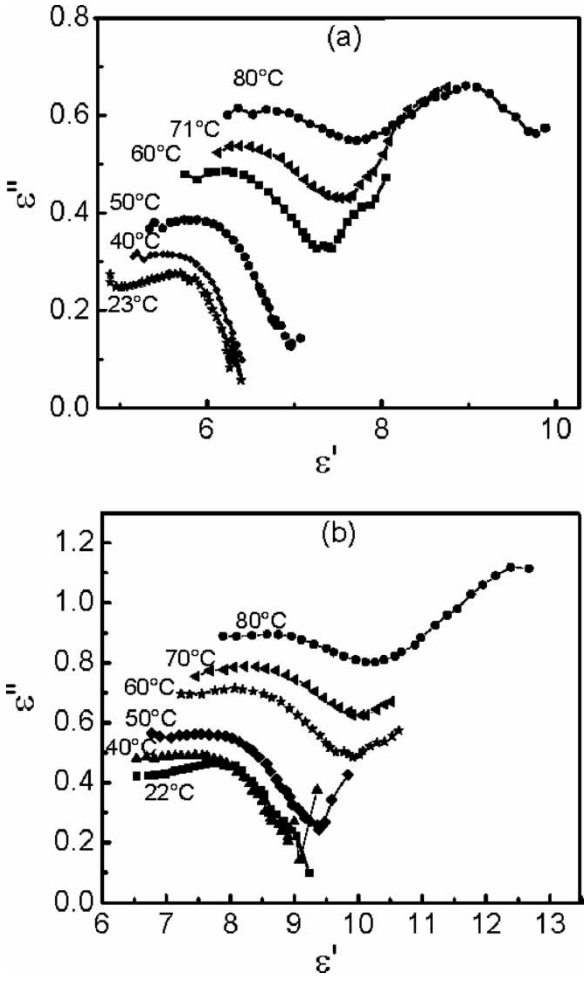

FIGURE 5 Loss Factor ε'' as a Function of Permittivity ε' for Carbon Black–Epoxy Resin Composites (a: ϕ = 2% and b = 5%) at Several Temperatures.

polarization effect known as Maxwell–Wagner–Sillars (M-W-S) polarization.[18] It is apparent that the locations of the loss peak are not affected by the carbon concentration in matrix, contrary to its peak intensity. In Table 2, we summarize the results of the calculated dielectric properties of the composite with several concentrations of carbon particles at 23°C. A study carried out on another series of samples (Raven 7000-DGEBF) showed that the relaxation peak vanishes for the volume concentrations above threshold, and the dielectric behavior of the materials is no more of Cole–Cole type;[6] experimental results obtained appear to be in qualitative agreement with the dielectric universal response laws proposed by Jonscher.[19,20]

The coordinates of the centers of the half circles of Cole–Cole, for various carbon concentrations, defined by the relation (2) are connected by the line of equation: $\varepsilon''_{cc} = -2.30\ \varepsilon'_{cc} + 10.90$ with a coefficient of correlation 0.99. A similar result was found by Helsen et al. on mixtures made up of carbon black dispersion in mineral oil.[21]

The variations of ε'' versus ε' for the concentrations ($\phi = 2\%$ and $\phi = 5\%$) at different temperatures are plotted in Figure 5a and 5b. These curves show that the height of the relaxation peak increases with temperature. Close to the glass transition temperature T_g, one can note the appearance of a second relaxation peak, which is due to the microbrownian motion inside the solid. For the two concentrations $\phi = 2\%$ and $\phi = 5\%$, one observes the first peak in the interval of temperature 23–70°C, the second peak appears in the vicinity of temperature 80°C. The characteristic parameters of this distribution are reported in Table 3.

From the values reported in Table 3, we note that all parameters increase with temperature; except for exponent $(1 - \alpha_{cc})$ that decreases as the temperature

TABLE 2 Values of the Parameters According to the Cole–Cole Distribution for Composite Materials at Ambient Temperature

ϕ (%)	ε_∞	$\varepsilon_s - \varepsilon_\infty$	F_{max} (kHz)	τ (s)	$\beta_{cc} = 1 - \alpha_{cc}$
0.50	4.10	1.60	200	7.96×10^{-7}	0.36
2.00	4.45	1.97	113	1.41×10^{-6}	0.35
3.00	4.66	3.24	113	1.41×10^{-6}	0.31
5.00	5.05	4.60	113	1.41×10^{-6}	0.25
7.00	5.76	9.47	113	1.41×10^{-6}	0.21

TABLE 3 Parameters of the Cole–Cole DIstribution for Carbon Black–Epoxy Resin Composites (ϕ = 2 and 5%) at Several Temperatures

ϕ (%)	T (°C)	ε_∞	$\varepsilon_s - \varepsilon_\infty$	F_{max} (kHz)	τ (s)	$\beta_{cc} = 1 - \alpha_{cc}$
2	23	4.65	1.79	153	1.04×10^{-6}	0.39
	40	4.61	1.92	3250	4.90×10^{-8}	0.41
	50	4.58	2.50	3250	4.90×10^{-8}	0.38
	60	4.57	3.27	3250	4.90×10^{-8}	0.36
5	23	5.90	3.45	153	1.04×10^{-6}	0.31
	40	5.31	4.02	1300	1.22×10^{-7}	0.34
	50	5.33	4.43	1300	1.22×10^{-7}	0.32
	60	5.17	5.72	3250	4.90×10^{-8}	0.31

rises. According to the significance of α_{cc}, while the temperature is high enough, the Cole–Cole distribution of relaxation times tends to a delta-Dirac distribution and the composite shows a Debye-like dielectric behavior characterized by a single relaxation time. Figure 6 is a plot of $\log(F_{max})$ versus $1/T$ for four concentrations: $\phi = 0.5\%$, 2%, 3%, and 5%. By means of a least-squares fit of our data, we obtain the slope of an Arrhenius plot with a linear correlation coefficient r_{co} higher than 0.90. The values of the activation energy for various carbon black concentrations are reported in Table 4. These values did not change much when carbon black is present inside the epoxy polymer matrix, which means that the carbon black particles do not interact or only weakly with the chain segments of the macromolecules in the epoxy resin polymer. Further, it gives us an understanding that there is a poor bonding between the polymer matrix and the carbon particles.

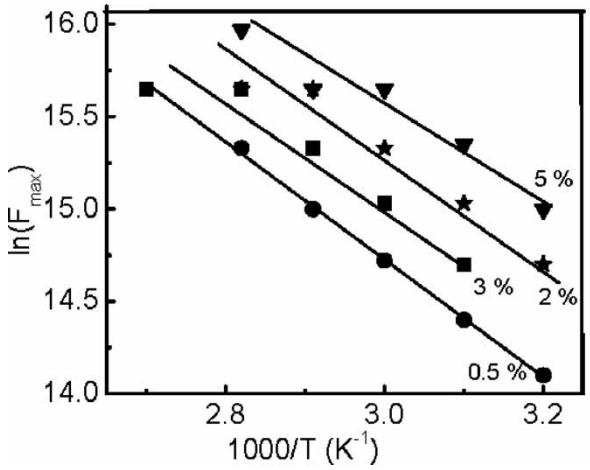

FIGURE 6 Arrhenius Plots for Carbon Black-epoxy Resin Composites. The Solid Lines Represent a Linear Regression Analysis of the Experimental Data Points.

TABLE 4 Carbon Black Concentration Dependence of the Activation Energy

ϕ (%)	0.50	2.00	3.00	5.00
E_a (eV)	0.29	0.23	0.25	0.20
r_{co}	0.99	0.96	0.95	0.95

4. CONCLUSIONS

Electrical measurements have been carried out on carbon black–epoxy resin composites in the frequency range between 100 Hz and 15 MHz and over a temperature range of 23–98°C for the concentrations of carbon black below the conductivity threshold. The dielectric relaxation phenomenon is observed, for all volume concentrations, which is attributed to dipolar groups of epoxy polymer and to interfacial polarization. The Cole–Cole empirical model gives a good modeling of the experimental dielectric results. Improvements in the knowledge of the dielectric properties of the composite materials involve complementary studies above the concentration threshold that are in progress and should be published.

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