Electric Properties of Carbon Black–Epoxy Resin Composites at Microwave Frequencies

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SYNOPSIS

This present paper is a study of the dielectric behavior of carbon black–epoxy resin composites at the microwave frequencies 9.5 and 35 GHz. The results of this research have shown that the complex propagation constant γ_g for these mediums depends on the frequency F, on the volume concentration ϕ of the conducting medium, and on the particle size. Numerical simulations allow us to fit the dependence of the measures upon the sample thickness, but we have to assign dielectric and diamagnetic properties of the heterogeneous medium. The permittivity and the permeability depend on the particle concentration, and the real part of the permeability is always smaller than unity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Electrical properties of a composite system consisting of conducting particles embedded in insulating matrix have been extensively studied in the past. The behavior of the effective conductivity and dielectric constant of these mediums are expected to be well predicted by the results of the percolation models in DC regime[1-4] as well as at low frequencies.[5-9] At high microwave, infrared, and optical frequencies, mixing laws[10-13] and effective medium theories[14,15] have been proposed for calculating the complex permittivity as a function of composition and constituent properties. For very low particle concentrations, these laws give identical results, often in agreement with experiments.[16-18] However, for concentrations higher than a few percent, they generally give different results, often in disagreement with experiments.[17-19] A modified effective medium theory, based on a probabilistic growth model introduced by Sheng, is found to predict the optical properties of W-Al_2O_3 and Au-SiO_2 composite films.[20] To the best of our knowledge, this model has not yet been applied to microwave experimental data.

In a recent paper,[21] we have showed experimentally that in carbon black–epoxy resin composite mediums there is a number of variables (volume concentration of carbon, particle size, and sample thickness) that affect the complex propagation constant at the microwave frequency 35 GHz. This result demonstrates that the proposed model for describing the electric behavior of such media must be necessarily related to these parameters. Propagation laws, taking into account the diffraction of the incident wave by the inclusions, lead to satisfactory results in case of particles with a diameter on the order of 1 mm.[22,23]

In this work, which is the continuation of that presented in ref. 21, we propose an experimental study on the dielectric behavior of two series of carbon black–epoxy resin composites at the microwave frequencies 9.5 and 35 GHz. First, we report the contribution of different parameters, such as the inclusion dimension, the frequency (F), and the concentration (ϕ), of the conducting medium on the complex propagation constant. Then we fit the experimental dependence on the sample thickness by

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a numerical simulation, which takes into account the dielectric and diamagnetic properties of the sample.

EXPERIMENTAL

Materials

The samples that have been examined consisted of small carbon black particles (produced by Cabbot Co.) randomly embedded in insulating epoxy resin matrix (ARALDITE D by Ciba Geigy Co.). Two types of carbon black have been used: Monarch 700 and Sterling, with respective diameters of 20 nm and 300 nm, and respective conductivity of 1500 $(\Omega m)^{-1}$ and 2200 $(\Omega m)^{-1}$. The two series of samples, Monarch-Epoxy and Sterling-Epoxy, used in this investigation are the same as in the previous study.[21] The samples are cut to appropriate dimensions so as to fill completely the waveguide sections, which are 10.86×22.16 mm^2 at 9.5 GHz and 7.11×3.56 mm^2 at 35 GHz.

DC Conductivity Measurements

DC conductivity measurements were carried out by two electrode cells using a Keithley electrometer (Model 617 from Hewlett Packard). The experiment involves the measurement of the samples' resistance to calculate DC conductivity.

Microwave Measurements

The complex propagation constant, $\gamma_g = \alpha_g + j\beta_g$, of the samples at 9.5 and 35 GHz can be calculated from the complex reflection and the transmission coefficients measured with impedance bridges using the classical results of the electromagnetic theory.[24,25] The two methods used for determining γ_g are recalled below.

(a) The waveguide is terminated by a sliding short situated behind the sample respective to the direction of the incident wave; the reflection coefficient in front of the sample is given by

$$\rho = \frac{\left(\gamma_0 - \frac{\gamma_g}{\mu^*}\right)\exp(\gamma_g d) + \left(\gamma_0 + \frac{\gamma_g}{\mu^*}\right)\rho_1 \exp(-\gamma_g d)}{\left(\gamma_0 + \frac{\gamma_g}{\mu^*}\right)\exp(\gamma_g d) + \left(\gamma_0 - \frac{\gamma_g}{\mu^*}\right)\rho_1 \exp(-\gamma_g d)} \tag{1}$$

where d is the sample thickness and γ_0 is the propagation constant in air; the complex propagation constant γ_g is expressed as

$$\gamma_g^2 = -\frac{4\pi^2}{\lambda_o^2}\left[\varepsilon^*\mu^* - \left(\frac{\lambda_o}{\lambda_c}\right)^2\right] \tag{2}$$

where $\varepsilon^* = \varepsilon' - j\varepsilon''$ and $\mu^* = \mu' - j\mu''$ are, respectively, the relative complex permittivity and permeability. λ_c is the cut-off wavelength of the particular waveguide, which is a function of the waveguide dimension, and λ_0 is the vacuum wavelength.

The reflection coefficient ρ_1 is obtained by

$$\rho_1 = -\frac{\left(\gamma_0 - \frac{\gamma_g}{\mu^*}\right)\exp(\gamma_0 \Delta) + \left(\gamma_0 + \frac{\gamma_g}{\mu^*}\right)\exp(-\gamma_0 \Delta)}{\left(\gamma_0 + \frac{\gamma_g}{\mu^*}\right)\exp(\gamma_0 \Delta) + \left(\gamma_0 - \frac{\gamma_g}{\mu^*}\right)\exp(-\gamma_0 \Delta)} \tag{3}$$

Δ is the distance between the sample and the movable short circuit. In the complex plane, ρ describes a circle, while Δ is varied from Δ_0 to $\Delta_0 + (\lambda_g/2)$ (λ_g is the wavelength in waveguide); $|\rho|$ undergoes successive extrema $|\rho_{\min}|$ and $|\rho_{\max}|$, which are obtained experimentally when the short circuit is moved along the waveguide. We define the attenuation

$$A_M = -10 \log|\rho_{\min}|, \quad \text{and} \quad A_m = -10 \log|\rho_{\max}|$$

which allow the computation of the propagation constant γ_g of the sample.

(b) The waveguide containing the sample is now terminated by low reflection load, and both reflection ρ and transmission τ coefficients of the sample are measured by means of adapted detectors. The coefficients ρ and τ are defined by the classical relations[26]

$$\rho = \left[\gamma_0^2 - \left(\frac{\gamma_g}{\mu^*}\right)^2\right] \frac{\exp(\gamma_g d) - \exp(-\gamma_g d)}{\left(\gamma_0 + \frac{\gamma_g}{\mu^*}\right)^2 \exp(\gamma_g d) - \left(\gamma_0 - \frac{\gamma_g}{\mu^*}\right)^2 \exp(-\gamma_g d)} \tag{4}$$

$$\tau = 4\,\frac{\gamma_g}{\mu^*}\,\gamma_0 \frac{\exp(-\gamma_g d)}{\left(\gamma_0 + \frac{\gamma_g}{\mu^*}\right)^2 \exp(\gamma_g d) - \left(\gamma_0 - \frac{\gamma_g}{\mu^*}\right)^2 \exp(-\gamma_g d)} \tag{5}$$

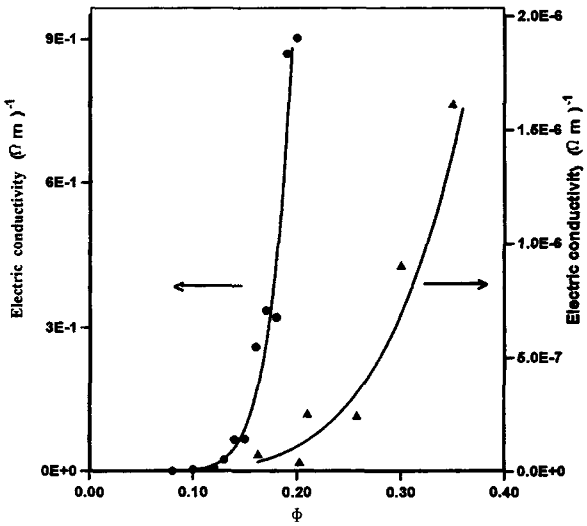

Figure 1 The variation of DC conductivity with volume concentration of carbon black for Monarch 700-Epoxy (●) and Sterling-Epoxy (▲).

By using attenuators, one determines the two attenuations: $A_R = -20 \log|\rho|$ and $A_T = -20 \log|\tau|$. From the knowledge of A_R and A_T, the propagation constant γ_g of the sample is computed.

RESULTS AND DISCUSSION

The DC electrical conductivity of a conductor–insulator composite vanishes below the percolation threshold; it is expressed theoretically as[27,28]

$$\sigma_{DC} \propto (\phi - \phi_c)^t \qquad (6)$$

where ϕ is the percentage of the conductor, ϕ_c is the percolation threshold, and t is the critical exponent. For carbon particles Raven 2000 in epoxy resin, the value of the exponent t is 2.0,[9] which is in good agreement with the literature.[3,6]

From eq. (6) it is clear that σ_{DC} becomes manifestly larger when ϕ is higher than ϕ_c. Figure 1 shows the composition dependence of DC conductivity for two series of samples, and ϕ_c can be estimated from the plots. These values of ϕ_c are, respectively, from 8% to 10% for the mixture Monarch-Epoxy, and from 15% to 17% for Sterling-Epoxy; the latter value is in good agreement with the theoretical threshold, which is equal to 17%.[29,30] Figure 1 suggests that predicted ϕ_c depends on the carbon particle size, and a composite with smaller carbon particles shows lower ϕ_c. This result is qualitatively similar to what has been observed by Nakamura et al.[31]

The coefficients α_g and β_g for both series of samples at the same thickness (10 mm at 9.5 GHz and 3.2 mm at 35 GHz) are calculated from the measured attenuations A_M and A_m, on the basis that the composite materials are assumed to be nonmagnetic ($\mu' = 1$ and $\mu'' = 0$). The attenuation A_R is also measured to avoid multiple determination in the calculations. The variations of α_g and β_g as functions of the carbon concentration ϕ are linear (Figs. 2(a) and 2(b)) for the two frequencies. By use of a least-square fit, we found that all linear correlation coefficients of

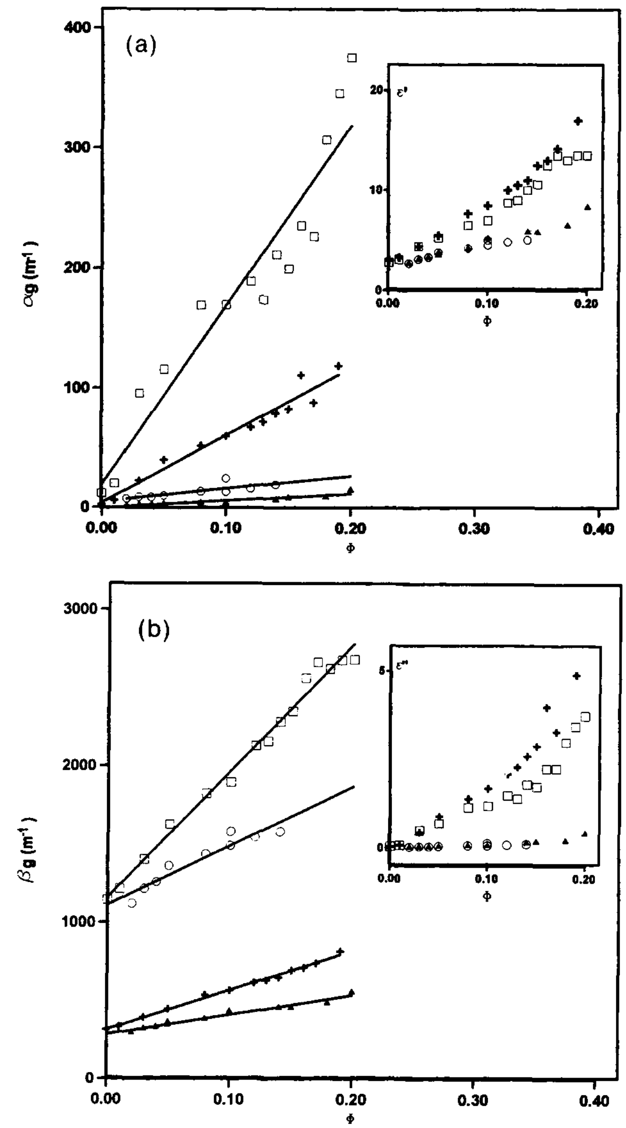

Figure 2 Dependence of the real part α_g (a) and the imaginary part β_g (b) of the propagation constant with the volume concentration ϕ of carbon black at 9.5 GHz (full symbol) and 35 GHz (open symbol) for two series of samples Monarch-Epoxy (+, □) and Sterling-Epoxy (▲, ○). The insets show the variation of ε' (a) and ε'' (b) vs. ϕ.

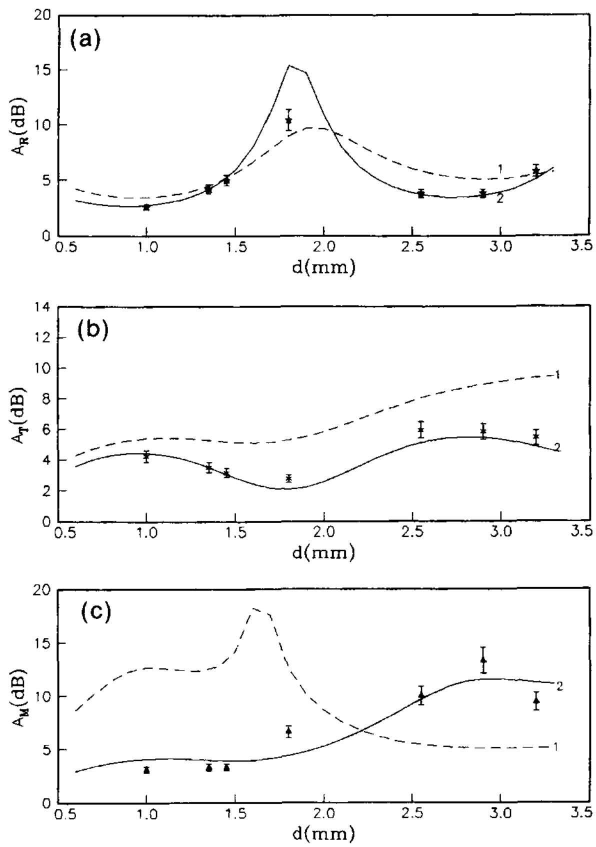

Figure 3 Variation of A_R (a), A_T (b) and A_M (c) with sample thickness d for Monarch 700-Epoxy composite (ϕ = 10%) at F = 35 GHz. The bars give the experimental uncertainty. The solid curves are the theoretical fits for (1) $\alpha_g = 37\ m^{-1}$, $\beta_g = 1186\ m^{-1}$,

$\varepsilon' = 5.00$, $\varepsilon'' = 1.50$, $\mu' = 1$, $\mu'' = 0$.

(2) $\alpha_g = 47\ m^{-1}$, $\beta_g = 1168\ m^{-1}$,

$\varepsilon' = 5.96$, $\varepsilon'' = 0.77$, $\mu' = 0.96$, $\mu'' = 0.03$.

different straight lines are higher than 0.9. On the other hand, the slope of the curve for Monarch-Epoxy is higher than that for Sterling-Epoxy at a given frequency. Moreover, the ratio β_g/F for each series of the samples does not depend on the frequency, and this allows the statement that for $\phi < 20\%$

$$\beta_g/F = (248\phi + 33)10^{-9} \quad \text{for Monarch-Epoxy}$$

$$\beta_g/F = (118\phi + 31)10^{-9} \quad \text{for Sterling-Epoxy}$$

For $\phi = 0\%$ (pure resin), the value of β_g (304.0 ± 9.5) m^{-1} at 9.5 GHz and (1120 ± 35) m^{-1} at 35 GHz.

Real and imaginary parts of the complex dielectric permittivity, ε' and ε'', were calculated from eq. (2) with $\mu' = 1$ and $\mu'' = 0$. The insets of Figures 2(a) and (b) are the respective plots of ε' and ε'', and as a function of ϕ at 9.5 and 35 GHz. These results show that a nondivergence of the dielectric constant was observed at the DC percolation threshold ϕ_c. Microwave measurements[32] showed that the anomaly in the dielectric constant is moved toward concentrations higher than ϕ_c, presumably due to dimensionality effect (small penetration of the microwave field).[21]

In the case of a homogeneous medium (resin epoxy), the measurements of the coefficients A_R, A_M, and A_T as a function of the thickness have shown complete agreement between the experimental and the calculated values.[21,24] However, for the heterogeneous medium Monarch-Epoxy, the experimental and calculated values coincide only for A_R. This special behavior of the conductor–insulator systems has been studied in our previous measurements on composite samples.[21,24] Figures 3(a–c) give the variations of the coefficients A_R, A_T, and A_M for a Monarch-Epoxy with a carbon concentration ϕ = 10%. In order to find a good agreement with the measured values of A_R, A_M, and A_T, we have considered the parameters α_g and β_g occurring in equations (1), (3), (4), and (5) as adjustable parameters. An iterative procedure is used until the departure of calculated values of A_R, A_M, and A_T from the measured values becomes as small as possible. In this procedure, the sample is assumed to be a homogeneous medium.

If the numerical simulation involves only the dielectric properties (the relative complex permeability is equal to unity) of the equivalent medium (curve 1 in Fig. 3(a–c), we never obtained a good fit. A better fit is obtained when we allot dielectric and magnetic properties to the equivalent medium with $\mu' < 1$ (curve 2 in Fig. 3(a–c).

The values of the permeability obtained at 35 GHz by this way for a few concentrations of the mixture Monarch-Epoxy resin are reported in Table I.

It is seen that the permeability decreases as a function of the volume concentration. This feature

Table I Dielectric and Magnetic Properties of the Samples Monarch-Epoxy at 35 GHz

ϕ (%)	ε'	ε''	μ'	μ''
5	4.11	0.15	0.96	0.02
10	5.96	0.77	0.96	0.03
13	8.75	1.20	0.92	0.02
15	10.50	2.10	0.97	0.02

of metal–insulator composites can be understood if we recall that when conducting particles are embedded in an insulating matrix, surface currents are created by the magnetic field of the electromagnetic wave. Each particle appears as a magnetic dipole, the whole medium becomes diamagnetic with a complex permeability μ^*, and absorption occurs by Joules effect.[33]

CONCLUSION

The results presented in this paper show that a heterogeneous medium made of conducting particles embedded in an insulating matrix has to be considered as a diamagnetic medium in the microwave range. A model that does not include that property must fail to fit experiments.

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