Microwave Properties of Carbon Black–Epoxy Resin Composites and Their Simulation by Means of Mixture Laws

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ABSTRACT: This article reports on a study of the dielectric properties of carbon black dispersions in an insulating epoxy matrix at microwave frequencies. Measurements showed that the complex permittivity of the composites depends strongly on the nature and concentrations of the conducting medium. The experimental values of the complex permittivity were compared to those obtained by using different mixing laws. We show that effective medium theories correctly account for the experimental results at low conducting particle concentrations. At concentrations higher than a few percent, these laws fail to interpret experimental results and all tentative results must take into account parameters such as the particle size, their distribution, and the existence of agglomerates. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 969–973, 1999

Key words: microwave; mixture laws; composites; dielectric permittivity

INTRODUCTION

Permittivities of heterogeneous mixtures were investigated by different authors nearly one hundred years ago, and since that time, many theories were developed and various empirical formulas were proposed. These laws were generally applied to a mixture of dielectric[1] or pure conductors.[2] In the case of composite mediums consisting of conducting particles randomly dispersed in an insulating matrix, the dc[3,4] and the low frequency[5,8] electrical properties can be described by means of percolation theory. Effective medium theories were extensively used to describe optical and infrared properties of composite systems.[9–12] For very low particle concentration, all mixture laws give nearly the same results in frequent agreement with experiments. When concentrations are higher than a few percent, these mixture laws generally disagree with experimental results.

In two earlier publications,[13,14] we showed that at microwave frequencies of 9.5 and 35 GHz, the complex propagation constant γ_g for carbon black–epoxy resin composites depends on the frequency F, on the volume concentration Φ, and on the particle size of the conducting phase. Numerical simulations allowed us to fit the dependence of the measured reflection and transmission coefficients with sample thickness.

In this article, we present the results of an experimental study on the dielectric behavior of carbon black–epoxy resin composites at microwave frequencies. The experimental permittivity

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Table I Physical Properties of the Two Types of Carbon Black Used in This Study

Carbon Black Type	Diameter (nm)	Conductivity $(\Omega m)^{-1}$	Density (g/cm^3)
Monarch 700	20	1500	1.900
Sterling	300	2200	1.862

values will be compared with those obtained by different mixing laws.

EXPERIMENTAL

Sample Description

Samples investigated in this study are composed of nearly spherical carbon black particles (produced by Cabbot Co.) randomly dispersed, with a desired volume concentration Φ ($0 \le \Phi \le 0.20$), in an insulating epoxy resin matrix (diglycidyl ether of bisphenol A (DGEBA, Ciba Geigy Co.). The essential features of the two types of carbon black (Monarch 700 and Sterling) used for this study are summarized in Table I. The specific mass of the resin epoxy is 1.16 (g/cm^3) and its dc conductivity is $<10^{-13}$ $(\Omega m)^{-1}$. The preparation procedure was described earlier.[15] The two series of samples Monarch 700–Epoxy and Sterling–Epoxy have a static percolation threshold of 8 and 16%, respectively.

Microwave Measurements

The complex permittivity is defined as $\varepsilon^* = \varepsilon' - j\varepsilon''$, where ε' is the usual relative dielectric constant, and ε'' can be expressed as a sum of two terms $\varepsilon'' = \varepsilon''_{\text{relax}} + \sigma/\varepsilon_0\omega$, where σ is the dc electric conductivity, ε_0 is the vacuum permittivity, and $\omega = 2\pi F$ is the pulsation. $\varepsilon''_{\text{relax}}$ represents the contribution, to the imaginary part, of an eventual relaxation phenomenon. Since the dielectric and conductivity losses cannot in practice be separated, those are usually combined in ε''.

The complex permittivity ε^* of the samples is calculated from the reflection and transmission coefficients measured, at microwave frequencies, with an impedance bridge,[13,14] by applying the classical results of electromagnetic theory.[16]

Mixture Laws

In a review article about dielectric properties of heterogeneous mixtures, Van Beek[17] discusses a number of equations for the permittivity. Let us consider an inhomogeneous medium consisting of a random dispersion of small conducting spheres with complex permittivity $\varepsilon_c^* = \varepsilon_c' - j\varepsilon_c''$, with a volume concentration Φ, dispersed randomly in a continuous medium with complex permittivity $\varepsilon_m^* = \varepsilon_m' - j\varepsilon_m''$. We present the different laws used for the modelization of the dielectric behavior for the conductor–insulator composite medium. To explain the dielectric loss due to the interfacial polarization of a binary mixtures, when the volume fraction Φ of the dispersion is small, Maxwell-Garnett gives the following equation[18]:

$$\varepsilon^* = \varepsilon_m^* \frac{\varepsilon_c^*(1 + 2\Phi) + 2\varepsilon_m^*(1 - \Phi)}{\varepsilon_c^*(1 - \Phi) + \varepsilon_m^*(2 + \Phi)} \qquad (1)$$

Bruggeman's symmetrical equation applicable to conductivities as well as to the complex permittivity, is expressed for the permittivity by[19]:

$$\Phi \frac{\varepsilon^* - \varepsilon_c^*}{2\varepsilon^* + \varepsilon_c^*} + (1 - \Phi) \frac{\varepsilon^* - \varepsilon_m^*}{2\varepsilon^* + \varepsilon_m^*} = 0 \qquad (2)$$

By applying the Onsager model to the case of a mixture of spherical particles, Böttcher obtained the formula[20]:

$$\frac{\varepsilon^* - \varepsilon_m^*}{3\varepsilon^*} = \Phi \frac{\varepsilon_c^* - \varepsilon_m^*}{\varepsilon_c^* + 2\varepsilon_m^*} \qquad (3)$$

An empirical equation was established by Lichtenecker[21]:

$$\ln(\varepsilon^*) = \Phi \ln(\varepsilon_c^*) + (1 - \Phi)\ln(\varepsilon_m^*) \qquad (4)$$

Another expression, based on a mathematical hypothesis, was proposed by Lichtenecker and Rother.[22] The expression has the following form:

$$(\varepsilon^*)^k = \Phi(\varepsilon_c^*)^k + (1 - \Phi)(\varepsilon_m^*)^k \qquad (5)$$

in which k is a nonvanishing constant. For $k = \pm 1$, one recovers the two Wiener's limits,[23] and for $k = \frac{1}{3}$, the Looyenga's formula is found.[24]

Recently, S. Stölzle et al.[25] established an expression strongly similar to eq. (5) to account for the effect of particle interaction with increasing volume concentration by introducing the exponent k as a function of Φ. This parameter k was deduced by numerical simulation:

$$k(\Phi) = (1.65 \pm 0.05)\Phi + (0.265 \pm 0.005)$$

For conducting dispersed particles, approximate equations can be derived from the formulas for composite permittivities when ε_c^* tends to infinity. With this assumption, the well-known expressions are:

Bruggeman's formula[26]:

$$\varepsilon^* = \frac{\varepsilon_m^*}{(1 - \Phi)^3} \tag{6}$$

Corkum's equation[27]:

$$\varepsilon^* = \varepsilon_m^* \frac{(1 + 2\Phi)}{(1 - \Phi)} \tag{7}$$

and the recent equation established by Shin et al.[28]:

$$(\varepsilon^*)^\alpha = \frac{(1 - \Phi)(\varepsilon_m^*)^\alpha}{\left(1 - \dfrac{\Phi}{\Phi_c}\right)} \tag{8}$$

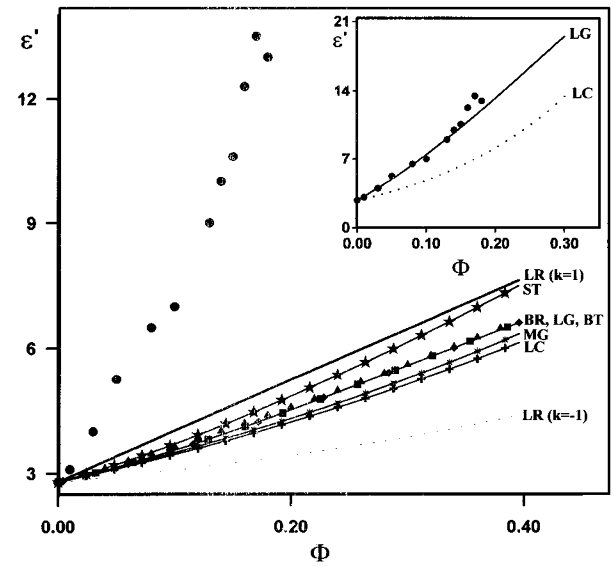
in which Φ_c is the percolation threshold and α is a positive constant.

RESULTS AND DISCUSSION

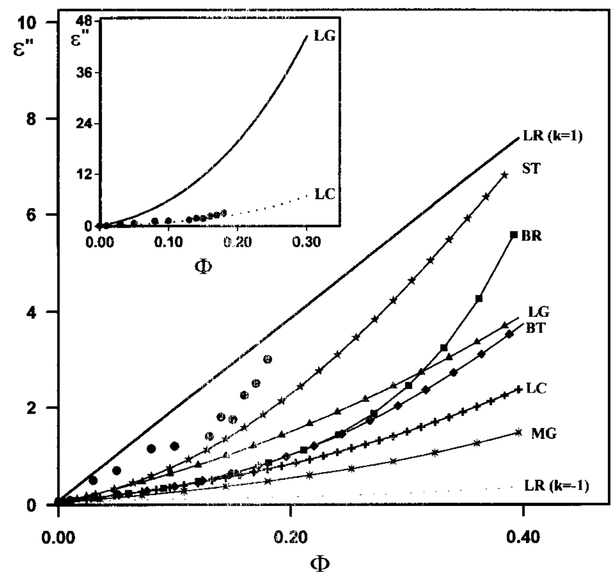
We expect from any of these equations, which are supposed to be applied to conductor–insulator composites, to account for both the real and the imaginary parts of the complex permittivity over the entire range of volume fraction Φ, at a given frequency.

For both frequencies of 9.5 and 35 GHz, the experimental variations of ε^* versus Φ are represented by full circles. The predicted results of the various equations from (1) to (5) are identified as follows: Maxwell-Garnett (MG), Bruggeman (BR), Böttcher (BT), Lichtenecker (LC), Lichtenecker–Rother (LR), Looyenga (LG), Stölzle et al. (ST), and Shin et al. (SH).

Figure 1(a, b) reports, respectively, the experimental and the calculated values of ε' and ε'' of the Monarch 700–Epoxy resin composites at a frequency of 35 GHz. The respective permittivity of components used in the calculation are $\varepsilon_c^* = 15 - j19$, and $\varepsilon_m^* = 2.8 - j0.08$ for the unloaded resin epoxy.



(a)



(b)

Figure 1 The real part, ε' (a), and the imaginary part, ε'' (b), of the complex permittivity of the Monarch 700–Epoxy resin composites as a function of the volume concentration Φ at 35 GHz. Full circles are the measured values. Solid and dashed lines are calculated, respectively, by means of the various equations (see text).

We note that for ε', the predicted values are situated between the two Wiener's limits of the LR equation [Fig. 1(a)]. However, the experimental data are larger than the calculated ones, and the difference between them increases with increasing volume concentration. For example, the

LR equation gives a deviation about 61% below the experimental value at $\Phi = 0.20$.

Concerning ε'', the best results can be taken from the more recent ST form and the upper limit of the LR equation [Fig. 1(b)]. The value used of the complex permittivity of carbon black was estimated from measurements on a compressed powder by the impedance bridge method. The uncertainty is large due to the difficult estimation of the packing fraction of the conducting powder as confirmed by Yadav and Gandhi[29] (ratio of the density of the powder and the density of the solid bulk). According to these authors, ε' and ε'' of a powder increase with increasing packing fraction. Furthermore, the carbon complex permittivity is computed from the measured reflection and transmission coefficients, assuming that carbon thickness is smaller than the wavelength. Significant error can also arise from the effect of small penetration of the electromagnetic wave through the conducting particles (the skin depth of the Monarch 700 is about 7×10^{-2} mm at 35 GHz and the sample thickness is in the order of 1 mm).

To circumvent this problem, we tentatively assumed the complex permittivity of carbon black to be of the form $\varepsilon_c^* = \varepsilon_c' - j(\sigma_c/\varepsilon_0\omega)$, in which σ_c is the dc electrical conductivity [$\sigma_c = 1500\ (\Omega\mathrm{m})^{-1}$, so $\varepsilon_c'' = 771$; ε_c' being an adjustable parameter]. Calculations are made up by the use of the iterative procedure. The insets of Figure 1(a, b) report the results of best fits of eqs. (4) and (5), respectively, to ε' and ε''; it is clear that neither relations fit both ε' and ε''.

We attempt to fit the electric behavior of these mediums by using eqs. (6)–(8), which characterize the conducting particles with an infinite complex permittivity. Calculations are compared to experimental data at a frequency of 9.5 GHz and for two series of samples: the Monarch 700–Epoxy and Sterling–Epoxy. Figure 2(a, b) shows that the disagreement with experiments is also important, except for eq. (8), which is valid for concentrations below the percolation threshold. This equation gives good conformity when α is taken as an adjustable parameter (best fit gives $\alpha = 1.42$ for the series Monarch 700–Epoxy and $\alpha = 1.91$ for the series Sterling–Epoxy).

All mixture laws discussed above fail to interpret the dielectric behavior of conductor–insulator composite medium. There are large discrepancies between observation and prediction. This disagreement seems to originate from the assumption that effective medium theories do not take into account the particle size or the occurrence of particles clustering. By studying a dispersion of carbon black particles in a nitrile rubber matrix, at microwave frequencies (1.7–18

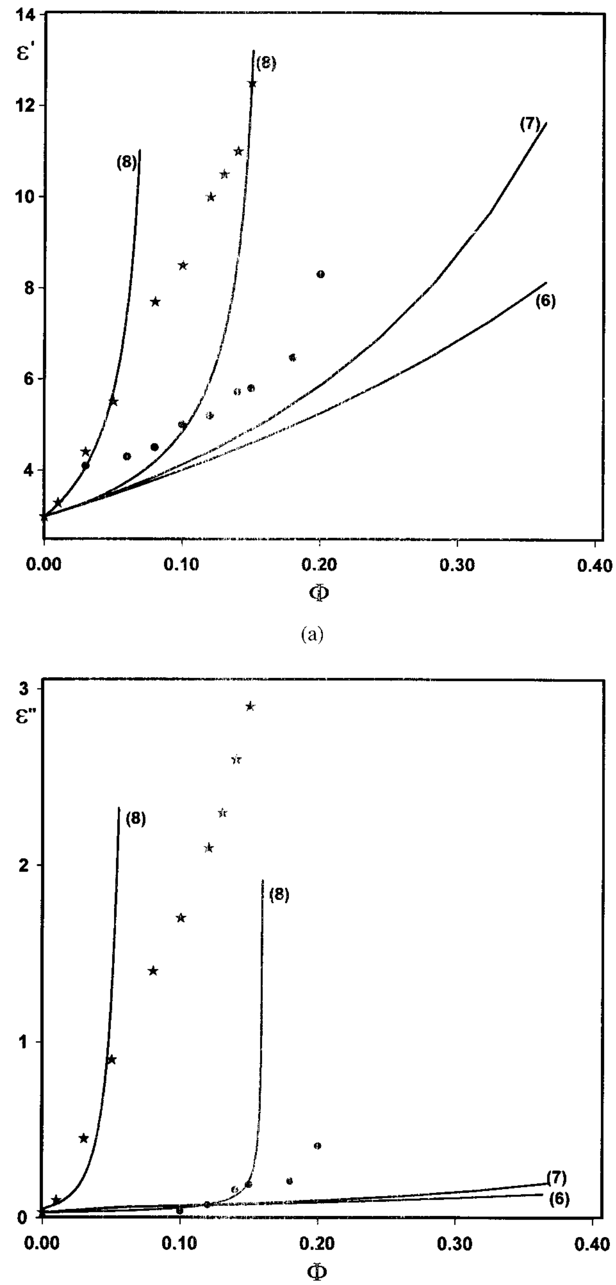


Figure 2 The real part, ε' (a), and the imaginary part, ε'' (b), of the complex permittivity of carbon black–epoxy resin composites as a function of the volume concentration Φ at 9.5 GHz. Symbols indicate the measurements, (★) Monarch 700–Epoxy, and (●) Sterling–Epoxy. Solid lines show theoretical values referred to by the numbers of equations with $\varepsilon_m^* = 3 - j0.05$.

GHz), Kaiser[30] showed that the electric properties of composites are dominated by those of the adsorbate phase connecting the carbon black cores of the filler particles in contact. On other hand, we showed in a previous work[13] that when three types of carbon black particles were used, the microwave complex permittivity decreases with increasing particle size. Furthermore, no exact theoretical or empirical methods exist, including effects of agglomerated particles. The sufficient resolution of calculation is based on an experimental determination of the microstructure. This will be possible using advanced X-ray microtomography.[31]

CONCLUSIONS

Different mixture laws were used to describe the dielectric behavior of composite mediums consisting of a random dispersion of conducting carbon black particles in a resin epoxy matrix at microwave frequencies. All these laws do not agree with experiments. This discrepancy seems to be the result of ignoring the parameters such as the particle size, the distribution, and the existence of agglomerates. A modified effective medium theory is found to include the size parameter.[32] This model, which is available when the particle radius is less than a tenth of a wavelength in the material, was not yet applied to our microwave experimental data. However, by using ε'_c as an adjustable parameter, we found that the best fits can be obtained separately by using the LG equation for ε' and LC equation for ε''. Unfortunately, no universally known equation exists to appropriately describe the carbon black–epoxy medium at high concentration.

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