Simulation Method for Complex Permittivities of Carbon Black/Epoxy Composites at Microwave Frequency Band

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ABSTRACT: This paper studied the permittivity of carbon black/epoxy composites at microwave frequencies. The measurements were performed for permittivity at a frequency band of 0.5–18 GHz and for DC conductivity to find the percolation threshold of composite samples of 0.0–1.5 wt % of carbon black in epoxy resin. The experimental results show that the complex permittivity of the composite depends strongly on the nature and concentration of the carbon black dispersion. The frequency spectrums of dielectric constants and AC conductivities of composites were investigated by using the descriptions found in percolation theory. A new model, that is a branch of Lichtenecker–Rother formula, is proposed to obtain a rule of mixture to describe the complex permittivity of the composite as function of frequency and concentration of carbon black. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2189–2195, 2006

Key words: composites; computer modeling; carbon black; dielectric properties; microwave

INTRODUCTION

As a means to increase the complex permittivity of polymeric materials, composites containing conductive fillers such as carbon black, carbon fiber, metallic powders are widely used.[1] Carbon black is one of the most popular fillers. Conduction of polymeric materials mixed with carbon black is induced by the strong electric field effect between the conductive particles or by the movement of electrons through direct contact of particles. In the former case, processes such as tunneling, field emission, and space charge limited transport should be considered; whereas, in the latter case, resistive (ohmic) relation between the current and voltage generated through a consistent conductive network formed by the direct contact between carbon black particles should be considered. Thus, because of these variable phenomena mentioned earlier, it is apparent that the mathematical models describing the properties of electroconductive composite materials tend to be very complicated.[2] The dielectric constant and ac conductivity of a composite material are related to anomalous diffusion within each cluster and the depolarization effect between the clusters composed of conductive fillers inside the composite. These phenomena also cause the dielectric constant and electric conductivity of a composite material to become a function of all frequencies.[3,4]

The following are three different factors to determine the dielectric constant and conductivity of a composite material:

1. Material characteristics of each component of the composite.
2. Spatial dispersion form of components within the composite.
3. Surface resistant characteristics between conductive powders.

From a microscopic point of view, the same values of dielectric constants and conductivities will be obtained from the composites having the aforementioned factors.[2,3]

Percolation theory, a representative approach of the macroscopic point of view, is typical for simulating dielectric constants and conductivities of composites at a relatively low-frequency band including DC.[5,6] The description based on percolation theory for the dielectric constant and conductivity of a composite as a function of the overall range of frequency and filler concentration needs some semiempirical curve fittings and complex mathematical assumptions; they are not so simple to use intuitively.[3–9] Laibowitz et al. in 1984 observed that correlation length of a microscopic structure can be used to express the AC conductivity in the broad frequency band.[3] Benaboud et al. in 1998

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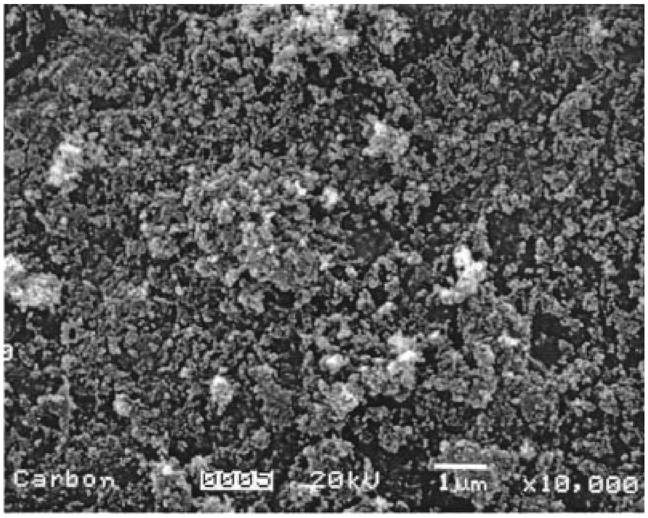

Figure 1 Scanning electron microscope photo of the carbon black.

had some experimental results that showed that as the frequency goes up, the rates of dielectric constants decrease and the rates of AC conductivities of composites increase around those of the percolation threshold itself.[7] Ezquerra et al. found the critical frequency; below that frequency, AC conductivity is constant to the frequency. They proposed a model based on the observation of Laibowitz et al. that the AC conductivities of composites are able to be expressed as a function in the overall range of the frequency for any filler concentration.[8,9]

In this study, we show the experimental value of complex permittivity of carbon black/epoxy composites at a microwave frequency band of 0.5–18 GHz. The characteristics of complex permittivity of composites were investigated by using percolation theory, and by using a newly proposed simulation method based on rule of mixture.

EXPERIMENTAL

Manufacture of specimens

Composite materials used in this study were manufactured using compounds which are composed of 4 wt % of carbon black of XE2 grade from DEGUSSA and 96 wt % of YD115 epoxy resin from KUKDO Chemicals, mixed by a three-roll mill. Composites with a variety of carbon black weight contents were manufactured by diluting the compound with YD115 and KBH1089, hardener from KUKDO Chemicals. A mixture (weight) ratio of YD115 and KBH1089 in epoxy used was 10:9. Figure 1 shows the SEM photograph of carbon black used, and its material specifications are presented in Table I.

The mixture was diluted by stirring at 1500 rpm for 30 min. After extracting the vapors from the material at vacuum condition, the diluted mixtures were poured into the mold at atmospheric pressure to make 2-mm thick composite plates. The composite plates were cured at a temperature of 120°C for over 2 h. Table II presents carbon black concentration, P, of the fabricated composites, where the concentration was calculated using the densities of epoxy resin (1.2 g/cm^3) and carbon black (1.87 g/cm^3), and the weight content of carbon black within the composite.

TABLE I
Carbon Black Specification

Density	1.87 g/cm^3
DBP absorption	420 ml/100g
Size of particle	25 nm
Shape of particle	Porous aggregate
Dielectric constant	2.5–3.0

Measurement of DC conductivity

The percolation threshold can be found by measuring the dc conductivities (σ_{DC}) of the composites. It is well known that there is a jump of DC conductivity around of the percolation threshold, so that a simple test method of measuring volume resistance values of square-shaped samples was used to obtain the dc conductivity. The samples were precisely cut to squares of 15 mm and covered with the conductive silver paint on both opposite surfaces. The measurement device for the conductivity was HP3458A Digital Multimeter. The device can measure the resistance in the range of 10 Ω–1 GΩ. Considering the shape of the specimens, the lower limit of the conductivity measurement was about 10^{-12} S/cm.

Figure 2 shows the DC conductivity obtained from the experiment. The DC conductivity of epoxy resin itself is below the limit of measuring. The solid line is the case in which the percolation threshold is assumed to be 0.04%. The percolation threshold may vary according to the manufacturing method of the composites, even if the polymeric matrix material and filler are the same. The research result of Schueler et al. in

TABLE II
Volume Fraction of Components in Composites

Material name	Weight fraction of carbon black (wt %)	Concentration (%) of carbon black (p)	Concentration of epoxy resin (%)
CB00	0.0	0.000	100.000
CB01	0.1	0.064	99.936
CB02	0.2	0.128	99.872
CB05	0.5	0.321	99.679
CB07	0.7	0.450	99.550
CB10	1.0	0.644	99.356
CB15	1.5	0.968	99.032

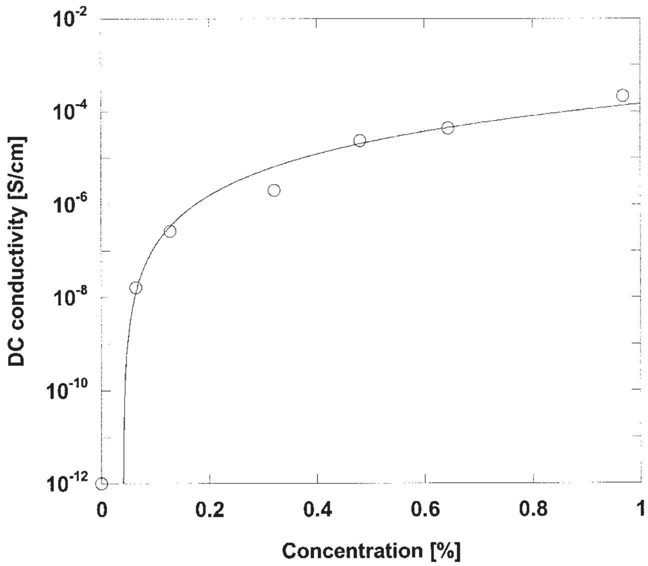

Figure 2 The DC conductivity of carbon black/epoxy composites. The solid line is the case that the percolation threshold (p_c) is assumed to be 0.04%.

1996 shows that fact clearly.[10] In this study, the percolation threshold is in a very low concentration range below 0.064%.

Measurement of complex permittivity

Complex permittivity is expressed simply by $\varepsilon^* = \varepsilon' - j\varepsilon''$, where $\varepsilon'$is dielectric constant and $\varepsilon''$is lossy term that is related with the electric conductivity (σ) of the material. The relationship between ε'' and σ takes the form of $\sigma = \omega\varepsilon_0\varepsilon''$.

Figure 3 shows the real and imaginary parts of complex permittivity obtained from the experiment. Both real and imaginary parts increase as the carbon black concentration increases. It was observed that, as compared with the real part, the imaginary part increases much more rapidly as the carbon black concentration increases.

To measure the complex permittivity at the microwave frequency band, Agilent N5230A (PNA-L Vector Network Analyzer) and 7-mm coaxial airline with Agilent N3696A (Electrical Calibration Module) were used. The specimens used for the complex permittivity measurements were machined out of composite plates so that the specimen could be inserted into the coaxial airline. The complex permittivity was obtained using Agilent 85071E (Material Measurement Software), in which the Nicolson–Ross–Weir method is implicated, from scattering parameters for reflected and transmitted TEM microwaves, which were continuously measured from 0.5 to 18 GHz.[11]

THEORIES AND RESULTS

Percolation theory

As to the electric conductivity at a low frequency or DC of composites, percolation theory was introduced by Kirkpatrick's resistance network model. Percolation theory says, percolation threshold (p_c), that if the concentration of a conductive filler at which the composite transforms from an insulating material into a conductive material at DC or low frequency AC current exists, and if the concentration of a filler is greater than the percolation threshold ($p > p_c$), there exists a fixed relationship between conductivity and concentration.[5]

Bergman and Imry noted the conductivity (σ_{DC}) takes the form $\sigma_{DC} \sim (p_c - p)^{-s}$, if $p < p_c$ and $\sigma_{DC} \sim (p$

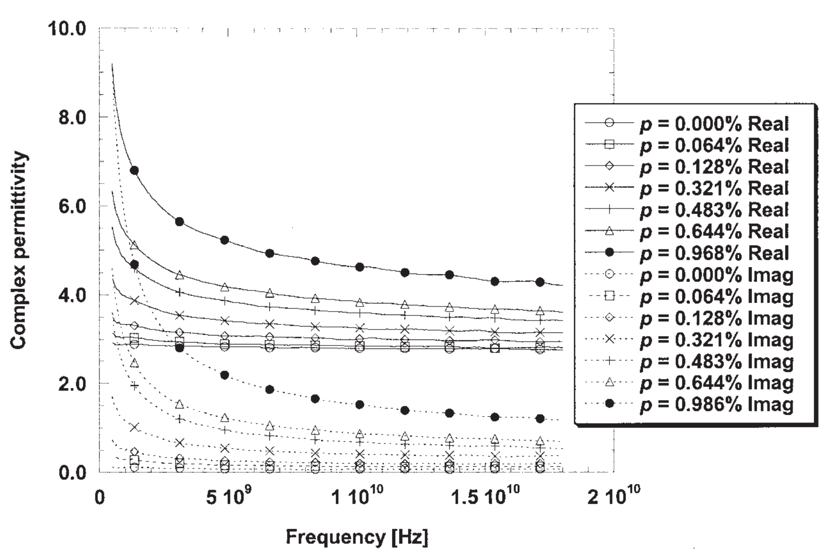

Figure 3 The complex permittivity of carbon black/epoxy composites.

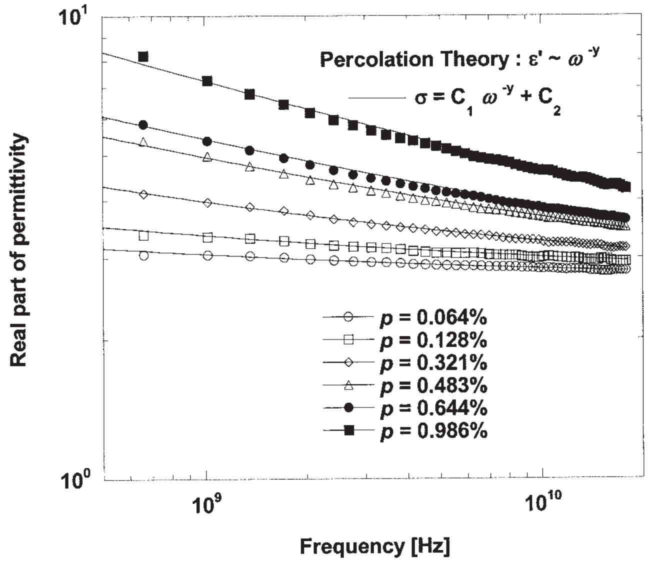

Figure 4 The frequency spectrums of the dielectric constants of carbon black/epoxy composites; curves are for the equation $\varepsilon'(\omega) \sim \omega^{-y}$ in percolation theory.

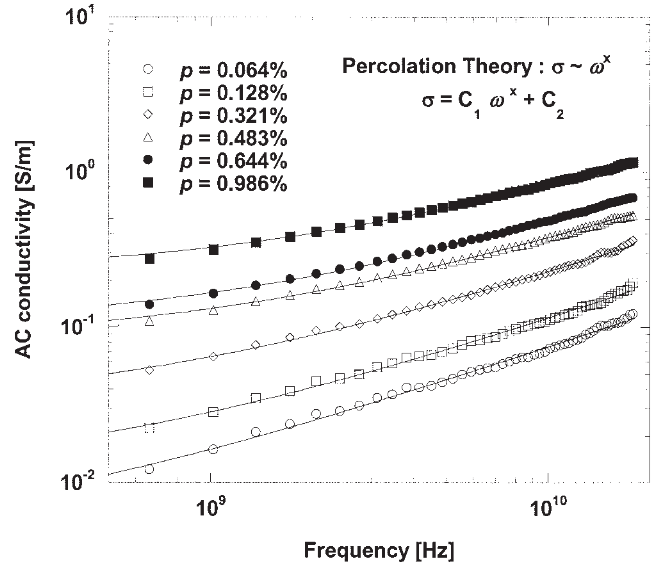

Figure 5 The frequency spectrums of the AC electrical conductivities of carbon black/epoxy composites; curves are for the equation $\sigma(\omega) \sim \omega^{x}$ in percolation theory.

$- p_c)^{t,}$ if $p < p_c$ where s and t are universal exponents indicating the characteristics of a composite.[6] The static dielectric constant of a composite, $\varepsilon_s = \varepsilon'(\omega \rightarrow 0)$, is expressed in the form $\varepsilon_s \sim\ p - p_c{}^{-s}$ in both cases $p < p_c$ and $p > p_c$.[6] To analyze the dielectric constants and conductivities of composites at lower frequency bands by applying the percolation theory, a number of studies were performed to determine the universal exponents.[1–7]

The frequency dependency of dielectric constant and conductivity around the percolation threshold can be expressed as $\sigma(\omega) \sim \omega^{x}$ and $\varepsilon'(\omega) \sim \omega^{-y}$, respectively, where $x = t/s + t$ and $y = s/s + t$.[6] From above relationships, an equation expressed as $x + y = 1$ can be obtained. It is called the general scaling relation.

The observation of Ezquerra et al. presents that, if p p_c, the conductivity can be expressed with a form $\log(\sigma/\sigma_{DC}) \sim \log(a_p f)$, where a_p can be obtained from the critical frequency (f_c) of the composites. The critical frequency (f_c) can be expressed as a function of filler concentration (p) with the form $\log f_c \sim \log(p - p_c)$.[8,9]

Figures 4 and 5 show the dielectric constants and conductivities as a function of frequency for various carbon black concentrations. In Figure 4, the curve fit equations for the experimental data are $\varepsilon' = C_1\ \omega^{-y} + C_2$. In Figure 5, the curve fit equations for the experimental data are $\sigma = C_1\omega^{x} + C_2$. The constants C_1 and C_2 are different for every composite. Table III shows that the values of exponents x and y are all about 0.75 and 0.25; moreover, the values are constant to the carbon black concentration. They show an obvious trend, in the wide range of concentration over percolation threshold, the dielectric constant and the AC conductivity can be expressed as $\sigma(\omega) \sim \omega^{x}$ and $\varepsilon'(\omega) \sim \omega^{-y}$. The summation of exponents x and y is 1 in the concentration range of this study. All the measured conductivities have continuous increments in the frequency range of this study, so that we can be sure that all the data are above the critical frequency.[8,9]

Figures 6 and 7 show the dielectric constants and conductivities as a function of carbon black concentration at various frequencies. In Figures 6 and 7, we can see that the simple curve fit equations $\varepsilon' = C_1p^{\eta} + C_2$ and $\sigma' = C_1p^{k} + C_2$ can be successfully used, where the exponents η, k, and the constants C_1, C_2 are different at every frequency. The result in Figure 7 agrees well with the observation from Bergman and Imry to Ezquerra et al. for the filler concentration dependency of AC conductivity.[6,8,9]

Lichtenecker–Rother theory

A representative equation to simulate dielectric constants of composites containing the fillers, with very high dielectric constant value and without any loss,

TABLE III
The Exponents x and y for the Composites

Concentration (%) of carbon black (p)	Exponent (x) for AC conductivity	Exponent (y) for real part of permittivity
0.064	0.75576	0.26276
0.128	0.76879	0.26258
0.321	0.74515	0.26517
0.450	0.74535	0.24853
0.644	0.75063	0.24503
0.968	0.75474	0.25345

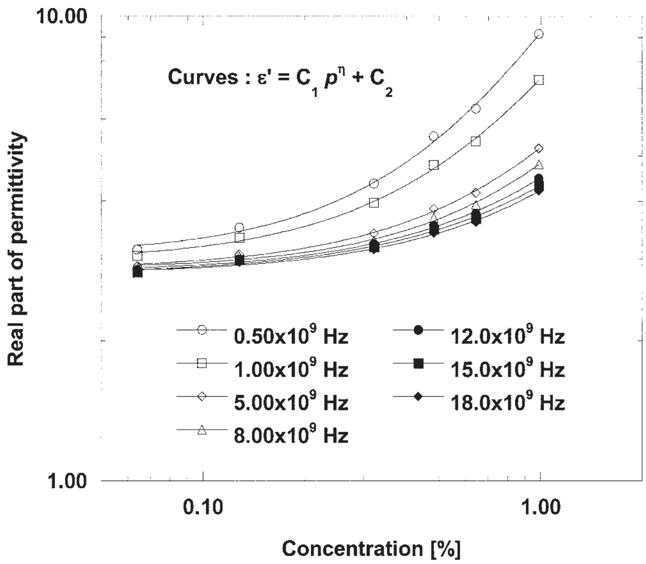

Figure 6 The carbon black concentration dependency of the dielectric constants of carbon black/epoxy composites; curves are for the equation $\varepsilon'(p) \sim p^{\eta}$.

has been proposed by Lichtenecker and Rother, as shown in the following equation[12]:

$$(\varepsilon_c')^k = p(\varepsilon_f')^k + (1 - p)(\varepsilon_m')^k \quad (1)$$

In eq. (1), ε_c', ε_f', and ε_m' are dielectric constants of a composite, pure dielectric filler, and polymer matrix material, respectively. Exponent k is a constant determined by the mechanism of wave propagating through the fillers contained in an insulating medium. It is known that $k = 1$ when the filler distribution is serial to the direction of wave propagation, whereas $k = -1$ when the filler distribution is parallel to the direction of wave propagation.[13] It is also known that $k = 1/3$ when the fillers are randomly distributed at low concentrations.[14] The filler distribution state in the medium has enough possibility to be changed as the filler concentration increases. In 1992, Stölzle et al. have expressed the exponent k of the Lichtenecker–Rother equation as a first-order equation of filler concentration p, so that the change of filler distribution state caused by the increase of filler concentration can be considered.[15] The constants of function of $k(p)$ are material constants determined for the composite material.

Applying the Lichtenecker–Rother theory to composites containing conductive fillers, the physical meaning of exponent k becomes different from the cases of applying composites containing pure dielectric fillers. It can be a determinant of the effects of the dielectric constant of epoxy resin and the conductivity of fillers on the real and imaginary parts of complex permittivity for composites. The shape of carbon black, agglomeration with irregularity of porosity, is not a perfect sphere and may affect the characteristics of composites as well.[3–4,13] In this study, this effect can be implemented by applying a correction factor, z, into eq. (1). So, a new modified equation can be proposed in the following form

$$(\varepsilon_c^*)^k = zp(\varepsilon_f^*)^k + (1 - zp)(\varepsilon_m^*)^k \quad (2)$$

where ε_c^*, ε_f^*, and ε_m^* are the complex permittivity of a composite, filler, and polymer matrix material, respectively. Exponent k is expressed as $k = Ap + B$ where A, B, and z can be obtained numerically from the experimental values. These three values are defined as functions of frequency.

Pantea et al.[16] compressed the same carbon black used herein, measuring dc conductivity as a function of concentration of carbon black, and observed a linear relation between the filler concentration and conductivity until reaching 3% of filler concentration. The conductivity of the carbon black used in this study was found to be 4100 S/m through extrapolation of the results. The dielectric constant of the carbon black is 2.75 which is the static value for most common kinds of carbon black.

Figure 8 shows frequency spectrums of A, B, and z obtained using the experimental complex permittivity of the composites. The frequency spectrums of A, B, and z can be expressed below in the overall frequency range of this study:

$$z = 3.230f^{0.0416} - 6.481 \quad (3)$$

$$A = 11.00f^{0.0208} - 14.748 \quad (4)$$

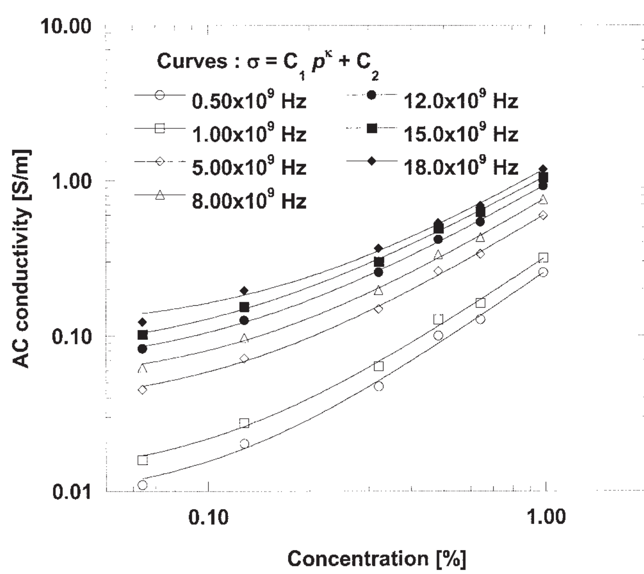

Figure 7 The carbon black concentration dependency of the ac electrical conductivities of carbon black/epoxy composites; curves are for the equation $\sigma(p) \sim p^{k}$.

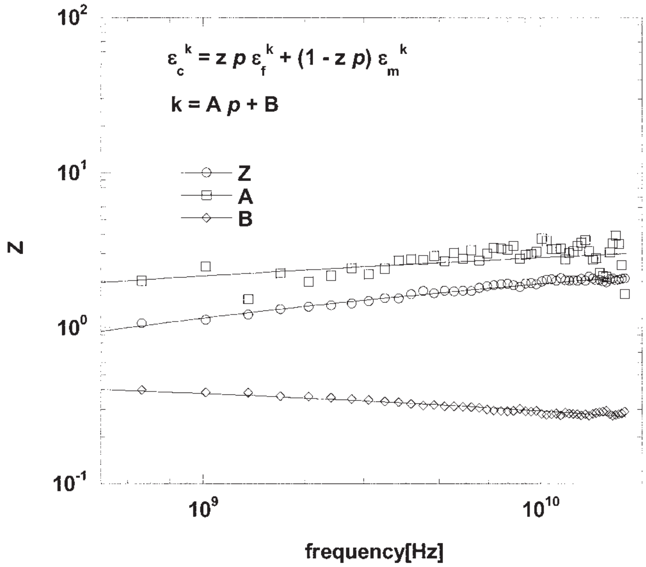

Figure 8 The frequency spectrums of constants: *A*, *B*, and *z*.

$$B = -0.220f^{0.0537} + 1.0582 \quad (5)$$

Figures 9 and 10 present the frequency tendency of dielectric constants and conductivities obtained from the represented model and the experiment. The results from the experiments agreed well with those simulated by the model.

Figures 11 and 12 show the characteristics of dielectric constants and conductivities from the presented model and experiment as functions of concentration of carbon black. They prove that the proposed model simulates the experimental results well.

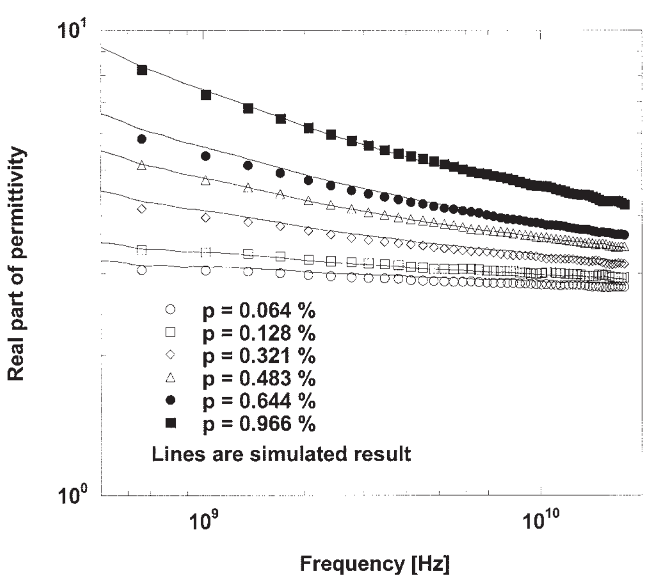

Figure 9 The comparison of the frequency spectrums of the dielectric constants of carbon black/epoxy composites from experimental values and simulated results of eq. (2).

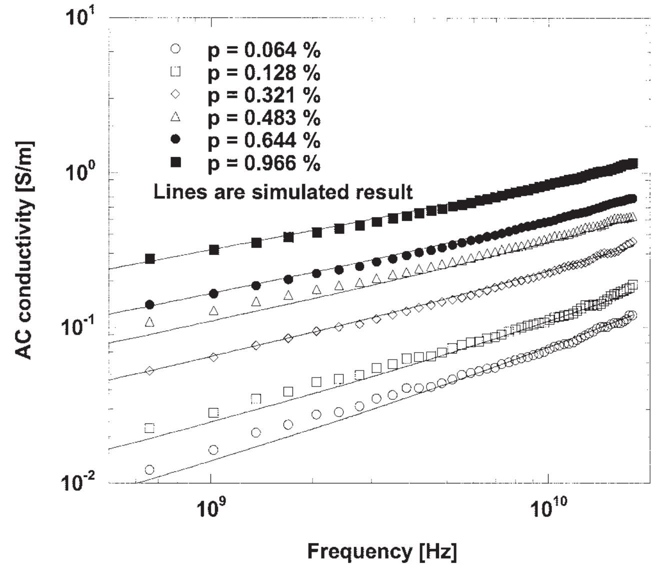

Figure 10 The comparison of the frequency spectrums of the ac electrical conductivities of carbon black/epoxy composites from experimental values and simulated results of eq. (2).

CONCLUSIONS

1. Composite materials with various carbon black contents from 0.0 to 1.5 wt % were manufactured, and the measurements of DC conductivity were performed. The percolation threshold was obtained through the dc conductivity.
2. The complex permittivities of composites were measured at a microwave frequency band from

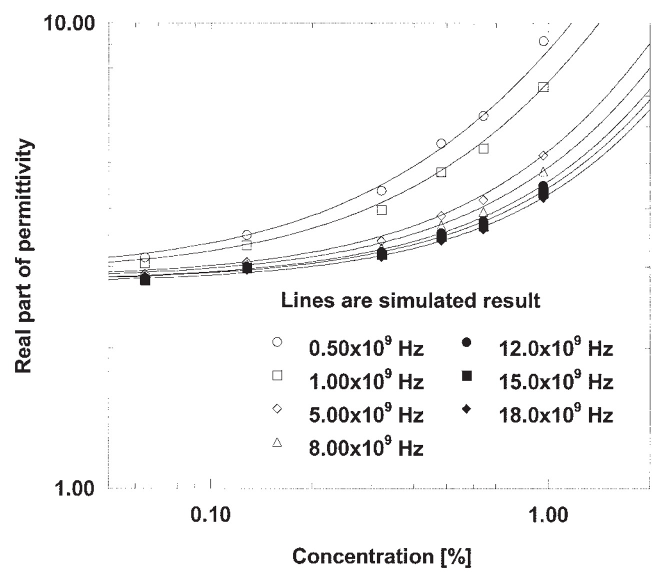

Figure 11 The comparison of the carbon black concentration dependency of the dielectric constants of carbon black/epoxy composites from experimental values and simulated results of eq. (2).

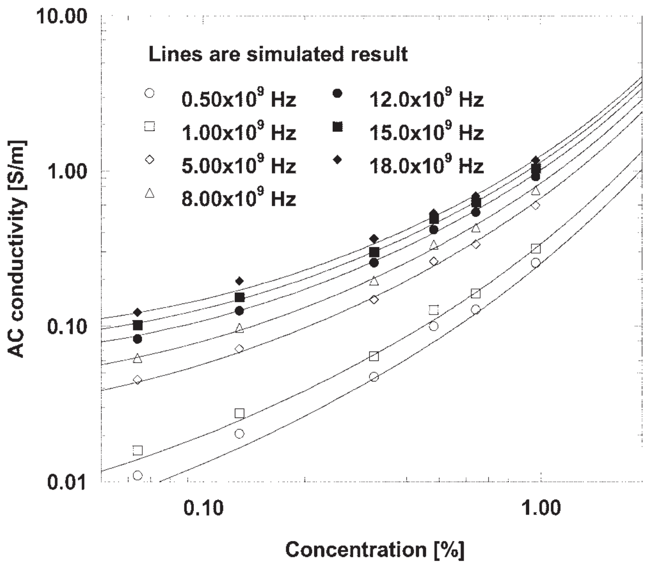

Figure 12 The comparison of the carbon black concentration dependency of the ac electrical conductivities of carbon black/epoxy composites from experimental values and simulated results of eq. (2).

0.5 to 18 GHz. The induced exponents $x = 0.75$ and $y = 0.25$ are constants with regard to the carbon black concentration. We can see an obvious trend that, in the wide range of concentration over the percolation threshold, the dielectric constant and the AC conductivity can be expressed as $\sigma(\omega) \sim \omega^x$ and $\varepsilon'(\omega) \sim \omega^{-y}$. The summation of exponents x and y is 1 in the concentration range of this study.

3. We can see the simple equations $\varepsilon' \sim p^\eta$ and $\sigma \sim p^\kappa$ can be successfully used for curve fits for the dielectric constants and conductivities as a function of carbon black concentration at various frequencies.
4. A new simulation method, which satisfies both frequency spectrum at the microwave frequency band and carbon black concentration dependency of dielectric constants and conductivities of the composites, was presented, and was compared with the experimental values, showing good agreement.

NOMENCLATURE

p = Concentration of carbon black in composites
ε' = Dielectric constant
ε'' = Lossy term of relative permittivity
σ = Conductivity
f = Frequency of wave
ω = Angular velocity of wave ($\omega = 2\pi f$)
ε_0 = Absolute dielectric value in the vacuum or in the air
p_c = Percolation threshold of conductive filler
σ_{DC} = DC conductivity
ε_s = Static dielectric constant
x, y = Universal exponents
$\varepsilon_c{}'$ = Dielectric constant of composite
$\varepsilon_f{}'$ = Dielectric constant of filler
$\varepsilon_m{}'$ = Dielectric constant of matrix
ε_c^* = Complex permittivity of composite
ε_f^* = Complex permittivity of filler
ε_m^* = Complex permittivity of matrix
z = Form factor for filler
k = Exponent for Lichtenecker–Rother formula
A, B = Constants for the exponent, k

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