Frequency Dispersion Characteristics of the Complex Permittivity of the Epoxy–Carbon Black Composites

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Received 19 November 1996; accepted 1 July 1997

ABSTRACT: The effects of frequency, volume fraction of carbon black, and porosity on the complex permittivity of the epoxy–carbon black composites were investigated and the frequency dispersion behavior model for the complex permittivity was proposed. In the epoxy–carbon black composites, the frequency dispersion behaviors of the complex permittivity changed from relaxation spectrum to resonance spectrum with increasing the amount of carbon black. The complex permittivity of the composites increased with decreasing the porosity. Comparing the complex permittivity of the composites filled with 2 vol % of carbon black with the values obtained from three types of previously reported model equations, the relaxation behavior coincided with the Havriliak–Negami model. The damping and asymmetrical factor values were increased with increasing porosity in the composites. The empirical equation proposed here was useful in describing the complex permittivity of the composites of >3 vol % carbon black with resonance type. The damping factor (γ) decreased as the filler content increased, but the asymmetrical factor (κ) increased reversely. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 363–369, 1998

Key words: complex permittivity; composite; frequency dispersion behavior

INTRODUCTION

An electromagnetic wave absorber can be divided into three categories: the absorber using ohmic lossy, dielectric lossy, and magnetic lossy materials. The electromagnetic wave absorber by the dielectric loss has often made use of the composites adding carbon to the polymer and acts as a wave absorber in high frequency bands.[1] The attenuation characteristics of electromagnetic wave absorbers are influenced by composition of materials, frequency, thickness, complex permeability, and complex permittivity.[2] It is very important to analyze the electromagnetic properties in manufacturing an electromagnetic wave absorber because the change of electromagnetic properties is closely related to electromagnetic wave absorbing characteristics. The complex permeability of epoxy–carbon black composites is independent of the frequency, but the complex permittivity has frequency dispersion characteristics.[3]

In this article, the epoxy–carbon black composites were used to study the effects of the volume fraction of carbon black and the porosity of composites on the frequency dispersion characteristics of complex permittivity. Also, the frequency dispersion behavior model for the complex permittivity of the epoxy–carbon black composites was evaluated in terms of the relaxation type and resonance type, respectively. In the case of the complex permittivity exhibiting a relaxation behavior, the experimental results were compared with the calculated values from prereported models. The complex permittivity of resonance type composites was compared with the calculated values of the empirical model proposed in this article.

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Journal of Applied Polymer Science, Vol. 67, 363–369 (1998)
 CCC 0021-8995/98/020363-07

Table I General Properties of Carbon Black (Ketjen EC)

Properties	Ketjen EC
Surface area (BET) (m^2/g)	1000
Particle size (nm)	37
Volatiles (%)	0.5
Pore volume DBP (mL/100g)	360

The factors affecting the damping and asymmetrical factor in relaxation and resonance equations were also investigated.

EXPERIMENTAL

Materials

The epoxy resin used in the experiment was polyglycidyl ether of *o*-cresol formaldehyde novolac (ESCN 195-6, Sumitomo Chemicals Co.) and the curing agent was phenol formaldehyde novolac resin (Tamanol 758, Arakawa Co.). Ketjen EC (AKZO Co.), whose general properties are shown in Table I, was used as conductive carbon black. After removing the moisture at 80°C for 48 h, the carbon black surface was treated with silane coupling agent, A-1120 (γ-aminopropyltrimethoxysilane, Union Carbide Co.), prior to mixing into the resins. A small amount of carnauba wax and catalyst was added in order to improve the dispersion of the carbon black and accelerate the polymerization, respectively.

Sample Preparations

Each component was weighed out and mixed together by the dry mixer to obtain powder mixture. The compositions of the epoxy and curing agent were controlled to be reacted stoichiometrically, one epoxy with one hydroxyl group. The powder mixtures having carbon black of 2 to 10 volume percents were kneaded by the double-shaft roll mill heated at 80–90°C for $\sim$ 5 min, then cooled and pulverized. These compounds were molded by compression molding at 175°C for 10 min to form a coaxial-shaped specimen 3 mm in inner and 7 mm in outer diameters, respectively, and the samples were finally obtained by postcuring at 180°C for 5 h.

Measurements

The complex permittivity of composites in the frequency range of 50 MHz to 10 GHz was measured by using a network analyzer (HP8719A) and coaxial air line (HP85051-60007).[4]

The apparent density, ρ_a (g/cm^3), and porosity, $\%P$, of the specimen were measured by the Archimedes method (ASTM C20-87) and were expressed as follows

$$\rho_a = \frac{W_d \times \rho_w}{W_d - W_{ss}} \tag{1}$$

$$\%P = \frac{W_s - W_d}{W_s - W_{ss}} \times 100 \tag{2}$$

where W_d, W_s, and W_{ss} represent the dry weight, saturation weight, and suspension weight, respectively. ρ_w is the density of water.

RESULTS AND DISCUSSION

Complex Permittivity of Composites

Effects of Carbon Black Content

Figure 1(a) shows the frequency dispersion behaviors of the complex permittivity of composites as a function of volume percent of carbon black. The real part of the permittivity increased with increasing the carbon black content. The imaginary values of the permittivity seemed to be independent of the carbon black content up to 1 GHz, but the maximum peak height of the imaginary part increased above 1 GHz. Since the imaginary values of permittivity are proportional to the conductivity of the composites, the increase of the peak value in the imaginary part results from the increased conductivity of the composites with the carbon black. It should be noted that the frequency dispersion spectra of complex permittivity changed from resonance type to relaxation type with decreasing the amount of carbon black.[5] The resonance spectrum can be found in the composites of more than 5 vol % carbon black and the relaxation spectrum in the composite of 2 vol % carbon black. It may be difficult to determine whether the dispersion behavior of the composite of 5 vol % carbon black is the resonance type or relaxation type in Figure 1(a). This could be easily understood by Figure 1(b), which shows the real values against the imaginary ones of permittivity. If the imaginary value, ε'', is larger than zero when the real value, ε', is zero, or if the curve exhibits a spiral type, the dispersion behavior of a composite shows the resonance type. On the other hand, if ε' has two distinct positive values when ε'' is zero, it shows the relaxation type. Therefore,

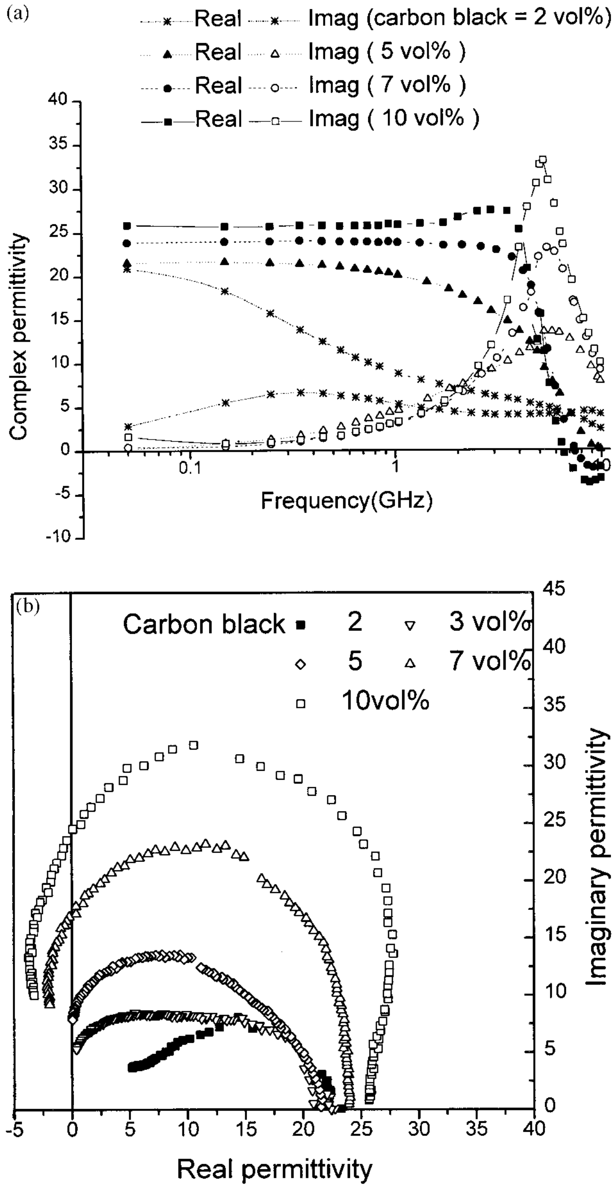

Figure 1 (a) The complex permittivity of epoxy–carbon black composites for various carbon black contents. (b) The Cole–Cole plot for the composites with various carbon black volume fractions.

the complex permittivity of the composite filled with 5 vol % carbon black could be regarded as a resonance type. The maximum peak of imaginary curves showing the resonance spectra slightly moved toward the low frequency range as the volume percent of carbon black was increased. The frequencies of maximum peak corresponding to 3, 5, 7, and 10 vol % of carbon black were 5.912, 5.789, 5.492, and 5.296 GHz, respectively. Thus, the maximum peak for the composite of 2 vol % of carbon black may be thought to emerge at higher frequency than that of the other composites, but the peak appeared at lower frequency, 0.296 GHz, as shown in Figure 1(a). This is due to the frequency dispersion transition from the resonance to the relaxation.

Effects of Porosity

Figure 2(a,b) show the change of the complex permittivity of the composites of 10 and 2 vol % carbon black as a function of the porosity, respectively. As the density of composites increased, the real part of the permittivity and the maximum peak value of the imaginary part increased in Figure 2(a). This may be due to the effect of the pores within a composite. The porosity was 1.58, 1.72, and 1.94, respectively, when the density of

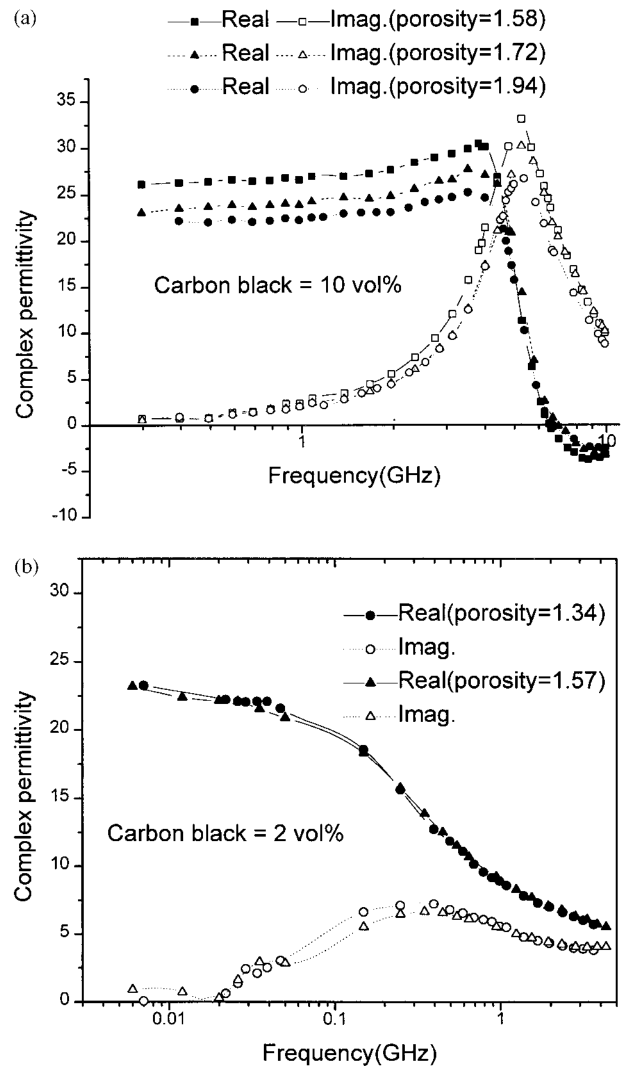

Figure 2 (a) The complex permittivity of the composites for various porosities at carbon black 10 vol %. (b) The complex permittivity of the composites for various porosities at carbon black 2 vol %.

the specimen, filled with 10 vol % carbon black, varied from 1.2552 to 1.2516 to 1.2491. However, the resonance frequency, at which the imaginary value of permittivity reaches its maximum, was unchanged because of the same content of carbon black. As shown in Figure 2(b), the relaxation curve of the composite filled with 2 vol % carbon black became broad and flat as the porosity increased.

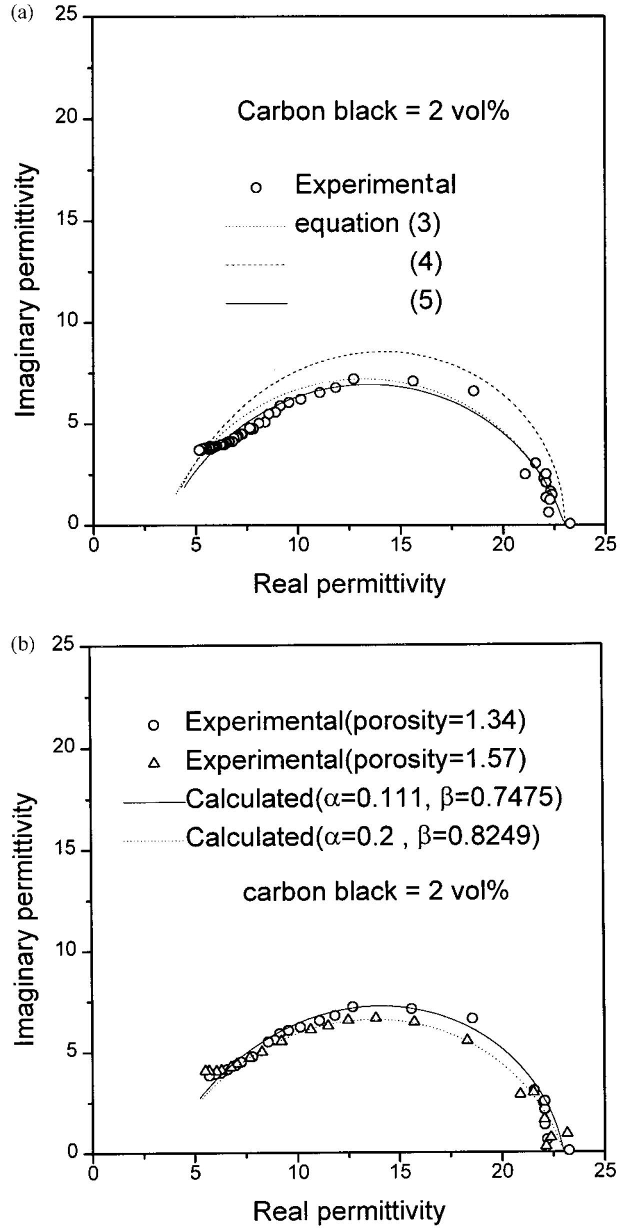

Figure 3 (a) Comparison of the experimental value with various models. (b) Comparison of the experimental values with the calculated values for the complex permittivity of composite.

Frequency Dispersion Behavior

As mentioned above, the frequency dispersion behavior of the permittivity of epoxy–carbon black composites converted the resonance into the relaxation spectrum as the amount of carbon black decreased. To investigate the model for the frequency dispersion of the complex permittivity of composite, therefore, it should be explained in terms of the relaxation and the resonance, respectively.

Relaxation Type

The Cole–Cole,[6] the Cole–Davidson,[7] and the Havriliak–Negami[8] models have been proposed for the relaxation behavior of the complex permittivity. Each model was expressed as follows

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\left(\dfrac{f}{f_r}\right)^{(1-\alpha)}} \tag{3}$$

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{\left[1 + j\left(\dfrac{f}{f_r}\right)\right]^{\beta}} \tag{4}$$

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{\left[1 + j\left(\dfrac{f}{f_r}\right)^{(1-\alpha)}\right]^{\beta}} \tag{5}$$

where f_r is the relaxation frequency at which the imaginary part of the complex permittivity reaches a maximum. The empirical constant $\alpha(0 \leq \alpha < 1)$ is the damping factor of the relaxation type and describes the degree of flatness of the relaxation region. The constant $\beta(0 < \beta \leq 1)$ is the asymmetric factor. ε_0 and ε_∞ are the permittivities of composite at zero and infinite frequencies.

The Cole–Cole model [eq. (3)] describes the relaxation properties of the material that are symmetrical about f_r and have a distribution of relaxation times. The Cole–Davidson model [eq. (4)] describes the relaxation properties that are asymmetrical about f_r. Equation (5), introduced by Havriliak–Negami, is asymmetrical about f_r and the imaginary part has a large damping. This model is a generalization of the two models above.

The complex permittivity values of the composite were compared to the values calculated by eqs. (3)–(5) in Figure 3(a). It is clear from the figure that the experimental data are almost identical to the values calculated by eq. (5), because the epoxy–carbon black composite has a large damping of the imaginary part and the relaxation curve shows a skewed arc, i.e., asymmetrical relaxation behavior about f_r. In this case, ε_0 of composite is about 23, and ε_∞ will be about 3.4, the permittivity of pure epoxy. The empirical constants α and β are 0.111 and 0.7475, respectively. Consequently, it is obvious that the frequency dispersion behavior of the complex permittivity of the epoxy composite filled with 2 vol % carbon black can be well described by the Havriliak–Negami model. Figure 3(b) shows a comparison of the Cole–Cole plot of the experimental permittivity of the 2 vol % carbon black composite as a function of the porosity with the result calculated by eq. (5). The calculated values were also well matched with the experimental values. α and β increased with increasing the porosity. This means that the relaxation spectrum of composites becomes broader and flatter as the porosity increases. Consequently, the empirical constants α and β depend on the pore within composite.

Resonance Type

The frequency dispersion spectra of the composites of more than 3 vol % carbon black was shown as the resonance type. Born and Wolf[9] proposed the model for the resonance spectra of the complex permittivity, and Miles, Wertphal, and Hippel[10] the model for the resonance spectra of the magnetic susceptibility. By modifying the above two models, the equation of the resonance spectra of the complex permittivity of the epoxy composites could be constructed as follows

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)(f_0)^2}{(f_0^2 - f^2 + jf\gamma)} \qquad (6)$$

where f_0 is the resonance frequency. The empirical constant γ is the damping factor of a resonance type and represents the half-width or line-breadth of a spectral line.

Figure 4(a,b) show a comparison of the experimental data of the complex permittivity for the composites with 7 and 10 vol % carbon black with the values calculated by eq. (6), respectively. The experimental data are relatively identical to the calculated values. The damping factors (γ) of composites are 4.35 and 3.62. Hence, γ increases and the complex permittivity of composite has a large damping with decreasing the carbon black content. According to Landau and Lifshitz,[11] the frequency dispersion spectra of magnetic susceptibility gradually converts the resonance type into the relaxation type with increasing damping magnitude. In the case of the epoxy–carbon black composites, the frequency dispersion spectra change the resonance type to relaxation type with decreasing carbon black content, because the damping factor increases. As shown in Figure 4, the maximum and minimum value of the real part

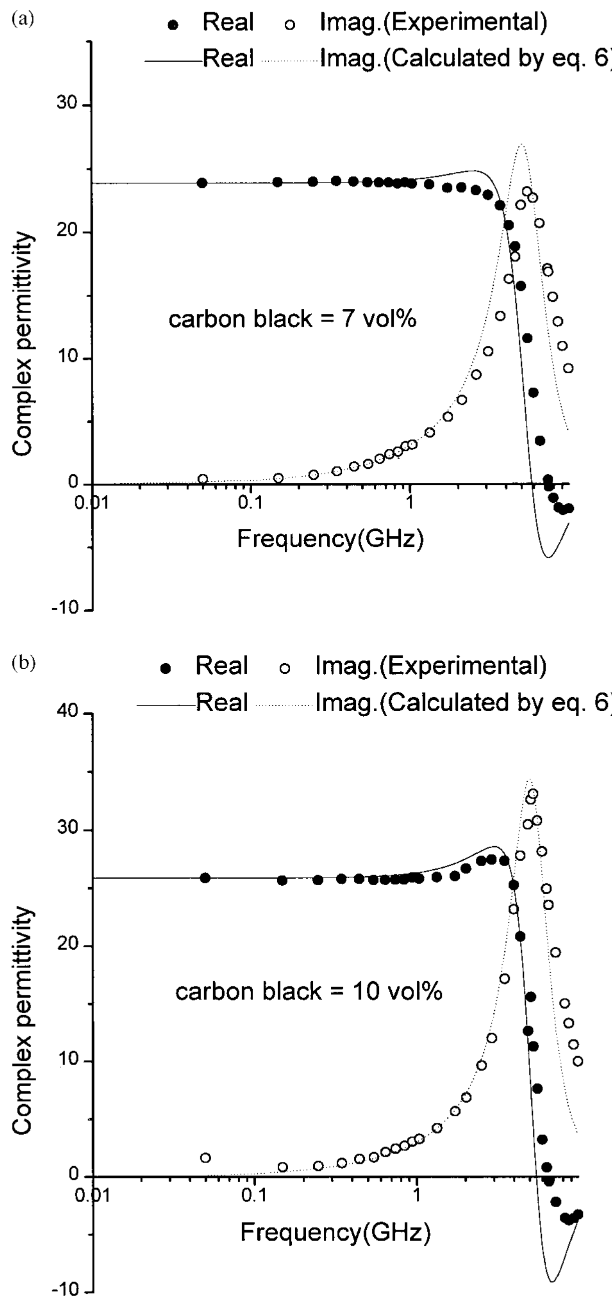

Figure 4 (a) Comparison of the experimental values with the calculated values for complex permittivity at carbon black 7 vol %. (b) Comparison of the experimental values with the calculated values for complex permittivity at carbon black 10 vol %.

of permittivity and the half-width of the imaginary part of permittivity obtained by eq. (6) slightly deviated from the experimental values, its deviation being larger with decreasing carbon black content. This may be considered as an effect of the interfacial state between the matrix and filler. A modified equation was proposed as follows

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1 - \left(\frac{f}{f_0}\right)^2 + j\,\frac{f\gamma}{(f_0)^2}\right]^\kappa} \tag{7}$$

where the empirical constant $\kappa (0 < \kappa \leq 1)$ is the asymmetrical factor of a resonance type and shows the degree of deviation from the circle in the Cole–Cole plot.

Figure 5(a) shows a comparison of the experimental data of the complex permittivity for the composites containing 7 vol % carbon black with the values calculated by eq. (7), and Figure 5(b) shows the Cole–Cole plot for the composites containing 10 vol % carbon black. As shown in the figures, the calculated values from eq. (7) gave better fitting to the measured values than eq. (6). The empirical constants γ and κ are 4.35 and 0.83 in the composite containing 7 vol % of carbon black, and 3.56 and 0.83 in 10 vol % of carbon black, respectively. The damping factor (γ) was decreased with the filler content, but the asymmetrical factor (κ) was increased reversely. Therefore, the damping and asymmetrical factor must be dependent on the content of carbon black in the epoxy–carbon black composites exhibiting the resonance type and must have a close relationship with the shape variation of the frequency dispersion curve.

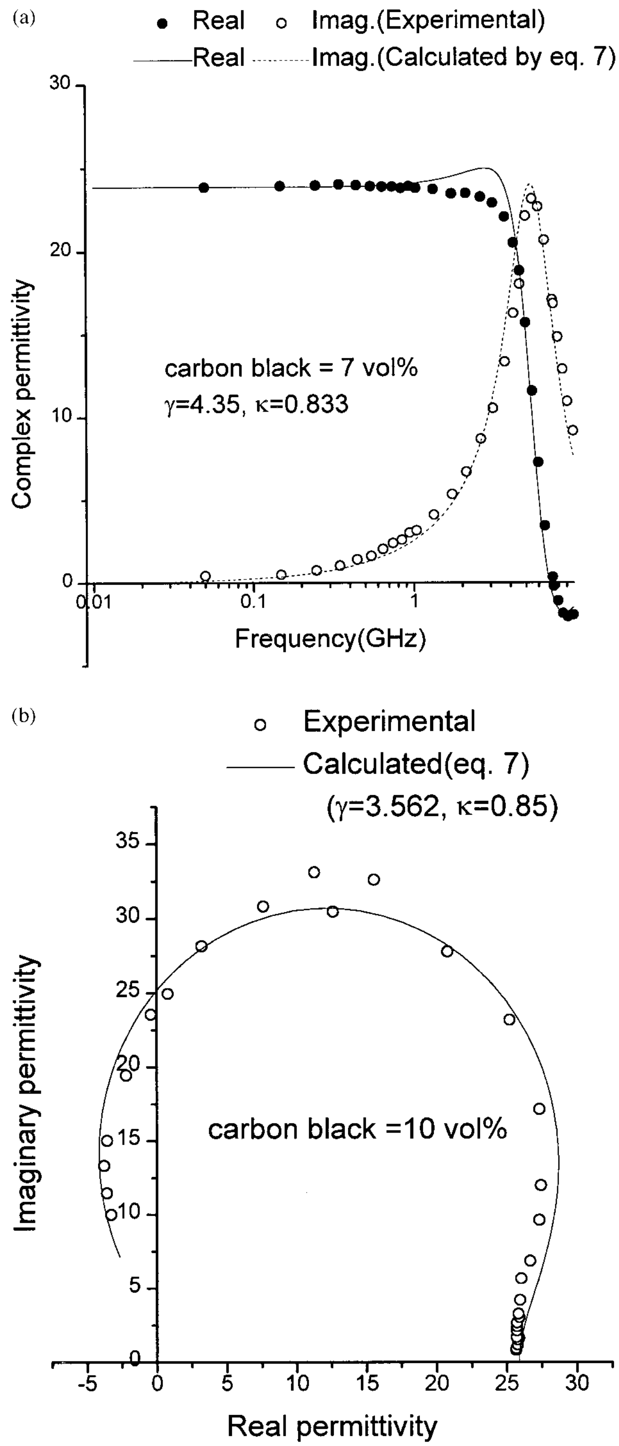

Figure 5 (a) The complex permittivity of composite by the calculated and the experimental values at carbon black 7 vol %. (b) The Cole–Cole plot for the complex permittivity of composite by the calculated and experimental values at carbon black 10 vol %.

CONCLUSION

The effects of carbon black content and porosity on the complex permittivity of the epoxy–carbon black composites have been investigated and various models are compared in terms of relaxation and resonance spectra. The complex permittivity increased and the frequency dispersion behaviors of the complex permittivity changed from the relaxation spectrum to the resonance one as the carbon black content increased. The complex permittivity of composite increased with decreasing porosity. The relaxation behavior of the permittivity in the composite filled with 2 vol % carbon black was found to coincide with the Havriliak–Negami model. The damping (α) and asymmetrical factor (β) values increased with increasing porosity in the composite. The empirical equation (7) proposed here was greatly useful to explain the complex permittivity of composites of more than 3 vol % carbon black, that is, composites showing the resonance behavior. It was also found that the damping factor (γ) decreased as the filler content increased, but the asymmetrical factor (κ) increased reversely.

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