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Complex conductivity of a conducting polymer composite at microwave frequencies

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A model is proposed for the complex conductivity σ^* of a conducting polymer composite as a function of frequency ω, based on an equivalent electrical network of series and parallel circuits containing resistors and capacitors. The results are similar to the power laws derived from percolation theory, i.e. $|\sigma^*| \propto \omega^x$. The effect of frequency and volume fraction of polypyrrole dispersant on the complex conductivity of a sample conducting polymer composite is analysed according to the model. The relationships between α, dispersant volume fraction and loss tangent of the composite permittivity can be predicted on a semi-quantitative basis.

(Keywords: complex conductivity; conducting polymer composite; microwave frequency)

INTRODUCTION

Polymers are electrical insulators that can only be made electrically conductive by filling with an electrically conducting phase such as carbon black, metal flakes or metal particles. These insulator/conductor composites have been exhaustively investigated because of their widespread applications. In particular, conducting carbon black composites have been examined in many respects, including their electrical conduction mechanisms and dielectric behaviour[1–9]. A large number of conducting polymers have been synthesized and, depending on synthesis conditions, the polymers can be in the form of a free-standing film or powder. Recently, the understanding of the transport mechanisms in these organic conductors and the potential use of the materials as electromagnetic interference (e.m.i.) shielding and absorbing materials have necessitated the measurement of dielectric behaviour at high frequencies in the megahertz to gigahertz range. Ngai and Rendell[10] have summarized the theoretical and experimental aspects of a.c. conductivity and dielectric relaxation of conducting polymers up to 10 MHz. Some studies on the dielectric behaviour of conducting polymers at microwave frequencies have been reported[11–16]. Because measuring accuracy on thin films is unsatisfactory[17], and different measuring techniques have been used, comparison of data obtained from different laboratories is difficult[12,14].

Although considerable effort has been made to understand the dielectric behaviour of carbon black- or metal-filled composites, data on conducting polymer composites are scarce. In a previous report[18], in an attempt to control the dielectric properties of conducting polymer composites at microwave frequencies, the permittivity of composites containing polypyrrole (PPy) or polyaniline (PAn) in silicone rubber or vinyl ester as a matrix was measured. In this study, we propose a model to describe the complex conductivity of a conducting polymer composite as a function of frequency in the range 2–18 GHz.

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MATERIALS AND METHODS

The conducting PPy powder was prepared by oxidizing pyrrole monomer with ferric chloride. Anhydrous ferric chloride, $FeCl_3$ (40 g, 2.5 mol), was added to chilled distilled water (100 ml). Freshly distilled pyrrole (6.7 g, 1 mol) was added slowly under constant stirring while the PPy precipitate formed. The precipitate was filtered from the mixture, washed with water and then dried under vacuum. The dried precipitate was ground into a powder. The conductivity of pressed powder sample was measured as $80\,S\,m^{-1}$ by the four-probe technique. Silicone rubber (Dow Corning 3110 RTV) was used as the matrix. The powder was mixed thoroughly into the matrix material and cured at room temperature with the supplied catalyst in a mould to give a 'doughnut' sample. The volume fraction v was calculated from the mass and density of silicone ($d = 1.2$) and of PPy powder ($d = 1.4$)[18].

A Hewlett-Packard network analyser (HP 8510) was used to determine the reflection coefficient S_{11} and transmission coefficient S_{21}, from which the real part ε' and the imaginary part ε'' of the permittivity ε^* were calculated[19]. The 'doughnut' sample was closely fitted into a coaxial measurement cell. All samples were measured twice to determine the reproducibility of the S coefficients. The samples were reversed in direction for the second

measurement. Teflon was used as a standard sample (5 mm thick). The values of ε' and ε'' of the standard sample agreed with the data shown in the Hewlett-Packard Product Note[19]. Measurements were carried out over the frequency range 2–18 GHz.

THEORY

The a.c. conductivity of insulator/conductor composites has been modelled by a resistance–capacitance (RC) network, where the conducting dispersants are represented as resistors and the dielectric of the insulating matrix is represented by capacitors[20,21]. The complex conductivity σ^* of n parallel components can be expressed by:

$$\sigma^* = \sum \alpha_n \sigma_n^* \qquad \left(\sum \alpha_n = 1\right) \tag{1}$$

and of n series components by:

$$(\sigma^*)^{-1} = \sum \alpha_n (\sigma_n^*)^{-1} \qquad \left(\sum \alpha_n = 1\right) \tag{2}$$

where σ_n^* and α_n are the complex conductivity and volume fraction of the nth component, respectively. The more general case can be described by[22,23]:

$$(\sigma^*)^v = \sum \alpha_n (\sigma_n^*)^v \qquad (-1 \leqslant v \leqslant 1) \tag{3}$$

If $v \to 0$ then $(\sigma_n^*)^v \to 1 + v \ln \sigma_n^*$ and equation (3) becomes:

$$\ln \sigma^* = \sum \alpha_n \ln \sigma_n^* \tag{4}$$

or

$$\sigma^* = \Pi (\sigma_n^*)^{\alpha_n} \tag{5}$$

Equation (4) reflects Brown's early suggestion[24] that $\ln \sigma_n^*$, rather than σ_n^* or $(\sigma_n^*)^{-1}$, should be averaged for a mixture of components.

In a conducting polymer composite having one conducting component, with $\sigma_1^* = \sigma$ for the conducting PPy (where σ is the d.c. conductivity) and $\sigma_n^* = i\omega\varepsilon_n (n > 1$, permittivity ε_n real, $\omega = 2\pi f$, where f is frequency) for the remaining lossless dielectric components of the mixture, equation (5) becomes:

$$\sigma^* = \sigma^{\alpha_1} \prod_{n>1} (i\omega\varepsilon_n)^{\alpha_n}$$

i.e.

$$\sigma^* = \sigma^{\alpha_1} \prod_{n>1} (\varepsilon_n)^{\alpha_n} (i\omega)^{1-\alpha_1} \tag{6}$$

Rewriting equation (6) gives:

$$\sigma^* = \beta(i\omega)^\alpha \tag{7}$$

where

$$\beta = \sigma^{\alpha_1} \prod_{n>1} (\varepsilon_n)^{\alpha_n} \qquad (\alpha = 1 - \alpha_1) \tag{8}$$

If σ^* is expressed in terms of its real and imaginary components:

$$\sigma^* = \sigma' + i\sigma'' \tag{9}$$

then

$$\sigma' = \beta\omega^\alpha \cos(\pi\alpha/2) \tag{10}$$

and

$$\sigma'' = \beta\omega^\alpha \sin(\pi\alpha/2) \tag{11}$$

The complex conductivity σ^* and the complex permittivity ε^* are related by:

$$\sigma^* = i\omega\varepsilon^* = i\omega(\varepsilon' - i\varepsilon'') \tag{12}$$

Hence, it follows from equations (10) and (11) that:

$$\varepsilon'' = \beta\omega^{\alpha-1} \cos(\pi\alpha/2) \tag{13}$$

$$\varepsilon' = \beta\omega^{\alpha-1} \sin(\pi\alpha/2) \tag{14}$$

If only one dielectric material is present, then $n = 2$ and equation (8) becomes:

$$\beta = \sigma(\varepsilon/\sigma)^\alpha \tag{15}$$

where ε_2 and α_2 are now denoted by ε and α for simplicity, and $\alpha + v = 1$ by definition.

The loss tangent of the composite material is defined by:

$$\tan\delta = \varepsilon''/\varepsilon' \tag{16}$$

Using equations (13) and (14) in conjunction with equation (16), it follows that:

$$\delta = (\pi/2)(1 - \alpha) = (\pi/2)v \tag{17}$$

RESULTS AND DISCUSSION

The percolation threshold of the PPy powder/silicone rubber composite was found to occur at a dispersant volume fraction v_c of approximately 0.033 (ref. 18). If conducting spherical particles are randomly placed in an insulating matrix and there is no interaction between particles, a particle volume fraction of 0.637 would be required to form a continuous electrical path[9]. In the PPy powder/silicone rubber composite, however, the low percolation threshold results from the aggregation of the PPy particles, which is driven by the difference in surface tension between the silicone rubber and PPy[25]. The formation of a conducting path was observed under a microscope[18].

Using the experimental data for $(\varepsilon', \varepsilon'')$ and equation (12), σ', σ'' and $|\sigma^*|$ can be calculated. *Figures 1–3* illustrate the log–log plots of σ', σ'' and $|\sigma^*|$, respectively, against frequency ω for the PPy powder/silicone rubber composites.

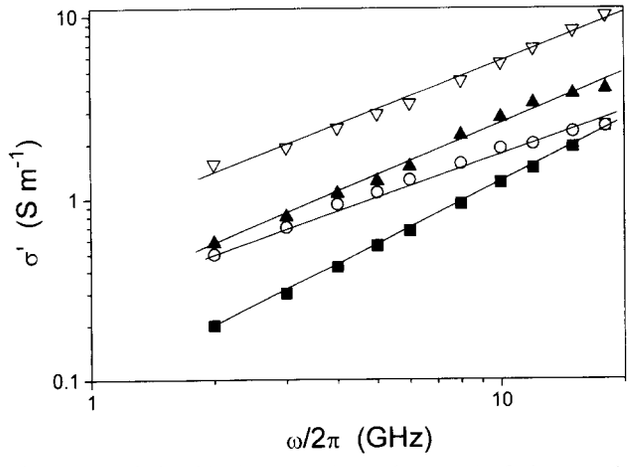

Figure 1 Relationship between the real part σ' of the complex conductivity of the PPy powder/silicone rubber composite and frequency at various volume fractions v: (■) 0.033; (○) 0.064; (▲) 0.093 and (▽) 0.114

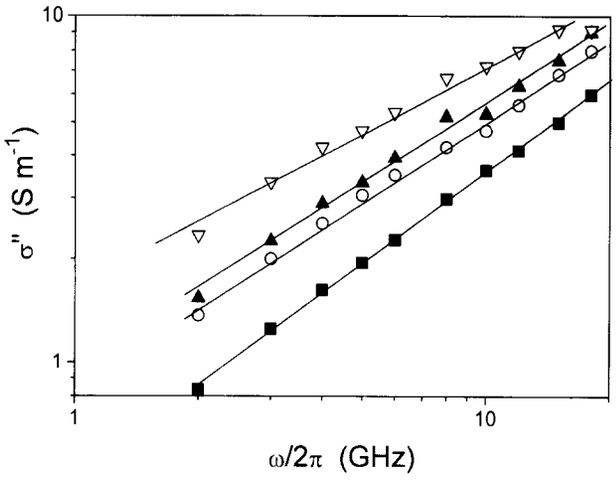

Figure 2 Relationship between the imaginary part σ'' of the complex conductivity of the PPy powder/silicone rubber composite and frequency at various volume fractions v. Symbols as in *Figure 1*

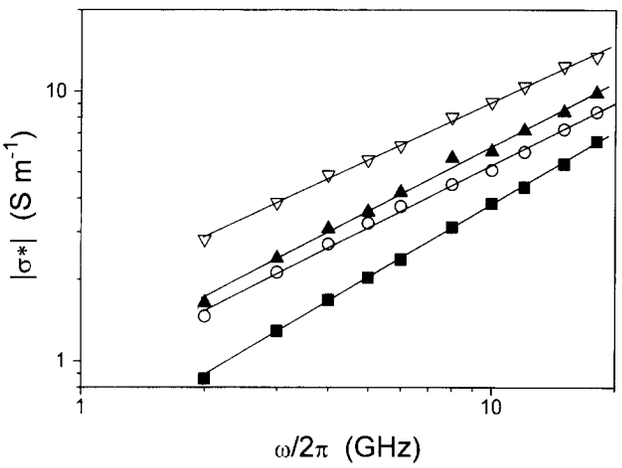

Figure 3 Relationship between the modulus $|\sigma^*|$ of the complex conductivity of the PPy powder/silicone rubber composite and frequency at various volume fractions v. Symbols as in *Figure 1*

Table 1

Composite number	v	α			β′	
		Fig. 1	Fig. 2	Fig. 3	Expt	Calc.
1	0.033	1.1	0.88	0.91	0.47	0.29
2	0.064	0.74	0.77	0.77	0.90	0.69
3	0.093	0.95	0.77	0.80	0.99	0.57
4	0.114	0.87	0.62	0.72	1.76	0.94

While a good linear relationship is observed with v in the range 0.033 to 0.114, the three sets of values of α obtained by linear regression from σ', σ'' and $|\sigma^*|$ data are not consistent (*Table 1*).

Although σ' is customarily considered as a.c. conductivity[21] and σ' is not well defined for disordered materials such as conducting polymers[10], σ' is often used to describe the frequency dependence of conductivity. In the present study, however, since the relation between conductivity and frequency was derived for σ^* (equation (7)), $|\sigma^*|$ is more useful for examining the constants α and β, and thus the adequacy of the model.

The slope α obtained by linear regression tends to decrease with increasing v (*Table 1*). This tendency was also observed in PPy/poly(ethylene oxide), PPy/poly(vinyl chloride) and PAn/poly(vinyl chloride) composites[21], poly(3-octylthiophene)/polyethylene gel[26] and carbon/Teflon composite[27]. At microwave frequencies, the polarized matrix between conducting elements modelled as a capacitor network becomes dominant. The displacement current flowing through the capacitor network contributes to a.c. conductivity and results in a high value of α, which can reach a maximum value of unity when the material is a perfect dielectric, i.e. no conducting elements. On the other hand, if the volume fraction of PPy powder increases and leads to a dense conducting network, then the capacitive effect on the a.c. conductivity will become less important. A decrease in the value of α (from the $|\sigma^*|$ data), from 0.91 for the PPy volume fraction of 0.033, to 0.72 for the volume fraction of 0.114, illustrates this effect. The value of α reduces to zero for a pure conductor[14] or for composites containing a high concentration of conducting dispersant[21,26,27].

The sum of α and v is smaller than the predicted value of unity (*Figure 4*). It is also noted that equation (7) gives a zero d.c. conductivity, whereas this conductivity is in fact finite. However, since the d.c. conductivity of the composite is at least two orders of magnitude smaller than the $|\sigma^*|$ values shown in *Figure 1*, equation (7) is an acceptable approximation.

Because the frequency is plotted as $\omega/2\pi$ in GHz, the intercepts β' of the straight lines on the axis $\omega/2\pi = 1$ GHz (*Figure 3*) are related to β (equation (15)) by:

$$\beta' = \beta(2\pi \times 10^9)^\alpha = \sigma[(\varepsilon \times 2\pi \times 10^9)/\sigma]^\alpha \quad (18)$$

Since for PPy the bulk conductivity σ is 80 S m^{-1} and ε is approximately $3\varepsilon_0$ (ref. 18), where ε_0 is the permittivity of vacuum, β' increases as α decreases according to equation (18). This prediction and the calculated values of β' are in moderate agreement with the experimental results (*Table 1*).

Furthermore, equation (17) indicates that $\varepsilon''/\varepsilon'$ is independent of ω for composites of a given v. The scaling law based on percolation theory also indicates a constant $\varepsilon''/\varepsilon'$ (refs. 20, 26). As shown in *Figure 5*, this is not the case for the PPy powder/silicone rubber composite. In the range of v from 0.033 to 0.114, δ tends to increase

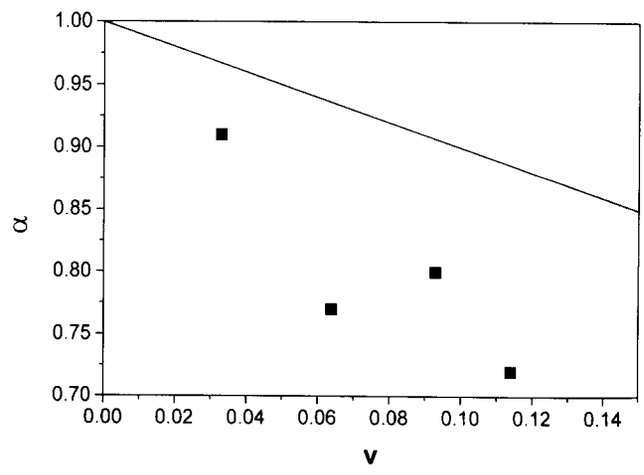

Figure 4 Relationship between α obtained from *Figure 3* and the volume fraction v. The straight line represents calculated values (1 − v)

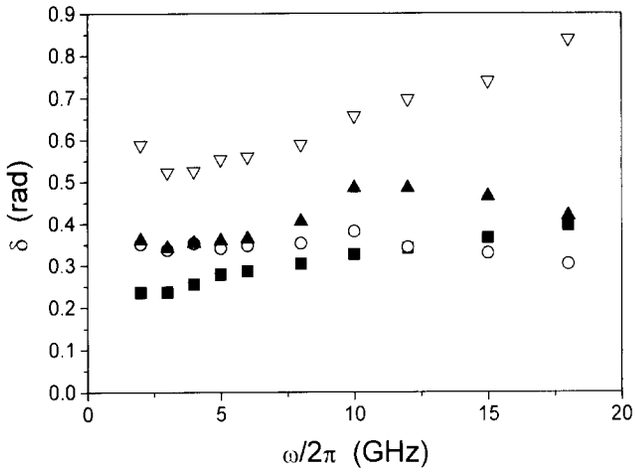

Figure 5 Relationship between the loss angle δ and frequency at various volume fractions v. Symbols as in *Figure 1*

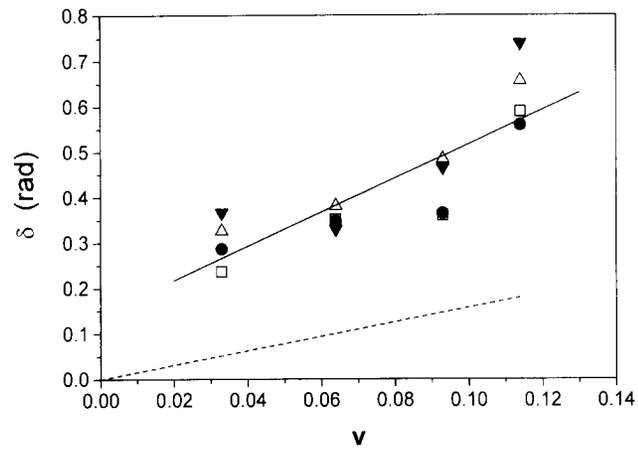

Figure 6 Relationship between the loss angle δ and the volume fraction v at various frequencies: (□) 2 GHz; (●) 6 GHz; (△) 10 GHz; (▼) 15 GHz. The full line represents the average values at the four frequencies. The broken line is the calculated value (equation (17))

with ω, but a clear dependence of δ on ω cannot be confirmed. A variation of δ was also observed in a polymer gel, where δ was derived from the ratio of the imaginary and real parts of the mechanical modulus[28].

Equation (17) suggests that δ increases linearly with v and $\delta = 0$ at $v = 0$. As illustrated in *Figure 6*, the experimental values of δ increase with v and the slope of the average straight line was found to be 3.7, which is higher than the predicted slope ($\pi/2$) by a factor of 2.4. Also, $\tan\delta$ of the matrix ($v = 0$) is approximately 0.03 (ref. 18), which reflects a small but finite conductance of silicone rubber.

Discrepancies between calculated and experimental data imply that the proposed model is not completely adequate for describing complicated polymer composite systems. Indeed, the intrinsic properties of dispersant and matrix materials, such as particle size and shape, spatial distributions, interfacial energy and interactions between dispersant and matrix or between dispersant particles, which affect the electrical properties of the resultant composites, are not taken into account in the model. A small but finite conductance of the matrix may also contribute to the deviation from the calculated values[4]. Nevertheless, the model has related the dielectric properties with frequencies and volume fraction of the dispersant of the composite. Since the model has only been applied with a moderate degree of success to composites with the dispersant concentrations at and beyond the percolation threshold, the question arises as to whether percolation is the prerequisite condition for the materials of interest. In particular, it should be noted that the equations derived in the present model are similar to formulae derived from the *RC* model as dispersant concentration v approaches the percolation threshold, v_c (ref. 20). As the derivation of equation (7) is based on the assumption $v \to 0$ (equation (4)) and percolation theory is not used, it is unclear whether the assumptions $v \to 0$ and $v \to v_c$ are equivalent.

It should also be noted that the assumption $v \to 0$ is arbitrary in the present context, and a more general model can be obtained by retaining v as a parameter in equation (3). This gives:

$$\sigma^* = \sigma[1 - \alpha + \alpha(i\omega\varepsilon/\sigma)^v]^{1/v} \qquad (-1 \leqslant v \leqslant 1) \quad (19)$$

for a mixture of a conductive component and a single insulating component. If $v < 0$, for instance, the phase of

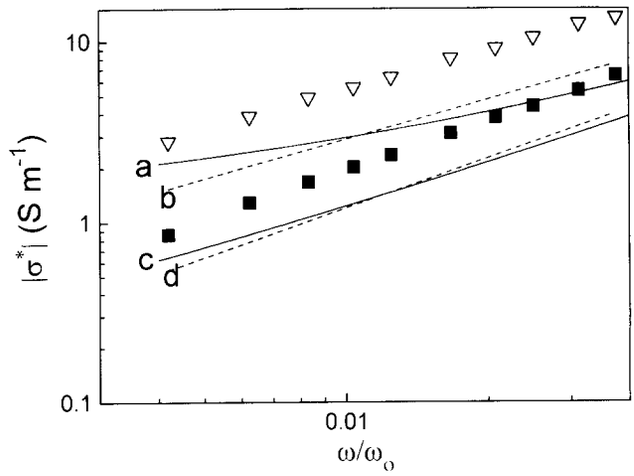

Figure 7 Calculated and experimental values of $|\sigma^*|$ as a function of normalized frequency ω/ω_0, where $\omega_0/2\pi = 480$ GHz ($\omega_0 = \sigma/\varepsilon$, $\sigma = 80\,\mathrm{S\,m^{-1}}$ and $\varepsilon = 3\varepsilon_0$ (see text)). Volume fraction v = 0.114: (▽) experimental data; (a) GEM equation (20); (b) equation (7). Volume fraction v = 0.033: (■) experimental data; (c) GEM equation (20); (d) equation (7)

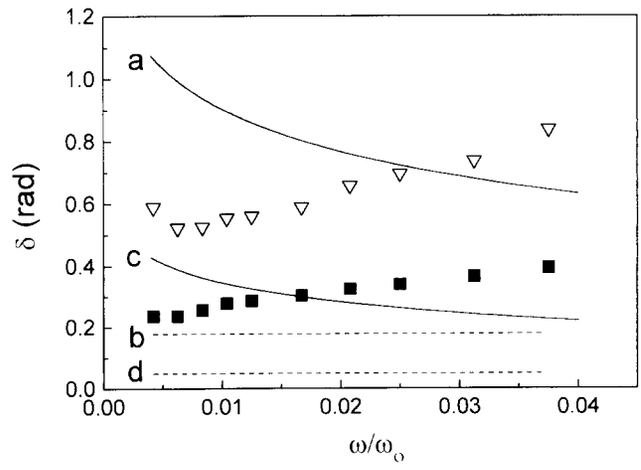

Figure 8 Calculated and experimental values of δ as a function of normalized frequency ω/ω_0. Volume fraction v = 0.114: (▽) experimental data; (a) GEM model; (b) equation (17). Volume fraction v = 0.033: (■) experimental data; (c) GEM model; (d) equation (17)

σ^* ($=\pi/2 - \delta$) decreases with increasing frequency, which agrees with the trend of δ shown in *Figure 5*.

McLachlan[29] has proposed a general effective medium (GEM) model for a two-component mixture. This model is expressed by:

$$\frac{(1-\mathbf{v})[(i\omega\varepsilon)^{1/t} - (\sigma^*)^{1/t}]}{(i\omega\varepsilon)^{1/t} + A(\sigma^*)^{1/t}} + \frac{\mathbf{v}[\sigma^{1/t} - (\sigma^*)^{1/t}]}{\sigma^{1/t} + A(\sigma^*)^{1/t}} = 0 \quad (20)$$

where $A = (1 - \mathbf{v}_c)/\mathbf{v}_c$. The value of t is taken as 1.7 (ref. 30), which is a typical value for conductivity in three dimensions. Equation (20) reduces to equation (5) for a two-component mixture as $t \to \infty$. *Figures 7* and *8* illustrate the experimental and calculated values of $|\sigma^*|$ and δ as a function of frequency, respectively. As shown in *Figure 7*, calculated values of conductivity for conducting composites are almost independent of the selected value of t. Although the GEM prediction of a decreasing δ with increasing frequency does not agree with experimental results, the calculated magnitude is comparable to experimental values (*Figure 8*). The broken lines represent the values of δ calculated by equation (17), which are lower than the experimental results due to a small slope value ($\pi/2$).

CONCLUSIONS

On the assumption that insulator/conductor composites behave as *RC* networks and obey a logarithmic mixing rule, the calculated results derived from this heuristic model are similar to the power laws of percolation theory, although percolation has not been incorporated in the model. The linear log–log relationships between complex conductivity (or permittivity) and frequency demonstrate that the power laws can be applied beyond the percolation threshold. In fact, in the literature the power laws derived on the basis of percolation theory have been used implicitly for composites with the dispersant content much higher than the percolation concentration[20,21,26,27]. The present model can be used on a semi-quantitative basis to understand the dependence of complex conductivity (or permittivity) on frequency, the effect of dispersant concentration on α and relation between loss tangent and α.

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