Dielectric Properties of Epoxy-Dielectrics-Carbon Black Composite for Phantom Materials at Radio Frequencies

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ABSTRACT: In order to develop new dry phantom materials that can simulate the effect of electromagnetic wave on human tissues, the dielectric properties of the phantom materials composed of dielectrics, carbon black, and epoxy resin were investigated. For dielectrics/epoxy composite, the dielectric constants increased with the content of dielectric powder and were independent of frequency at the measured frequency range. The dielectric constants and conductivity of carbon black/epoxy composite also increased with the carbon black, but it showed the frequency dependence that the complex dielectric constants decreased with increasing frequency. The dielectric constants and conductivity corresponding to human tissues could be obtained by combining the frequency dependence of carbon black/epoxy composite with the dielectric properties of dielectrics/epoxy composite and by adjusting the composition ratios of carbon black, dielectrics, and epoxy. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1294–1302, 2000

Key words: phantom materials; carbon black; dielectrics; epoxy composite; dielectric constant

INTRODUCTION

One of the important problems in studying the biological effects of electromagnetic (EM) fields on the human body is to quantify the specific absorption rate (SAR) of the exposed system.[1] To study these effects, phantom models have been used to simulate EM wave distributions inside the human body. The phantom model should have the same dielectric properties such as dielectric constant and conductivity, shape, and size as human tissues. Because the dielectric constant and conductivity are material constants depending on a given frequency, it is very important to understand the dielectric characteristics of the materials in constructing the phantom model.

The human tissues can be classified into two categories: low water content tissues such as fat and skull, and high water content tissues such as brain and muscle.[2,3] Traditionally, phantom models have been widely used to simulate the latter. The dielectric constant of high water content tissues, however, is about 10 times as large as that of low water content tissues, thereby there are difficulties in manufacturing the phantom models. These compounds were generally constructed with the jelly materials consisting of saline water, polyethylene powder, and a gelling agent.[2] Even though those phantom models have been used so far, some intrinsic problems exist. A rigid shell is necessary to contain the jelly materials, and hence it is difficult to estimate directly the SAR

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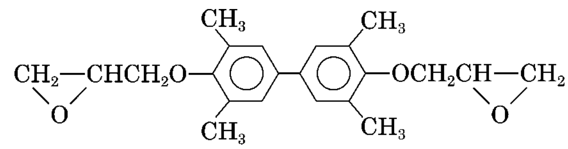
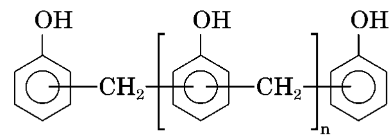
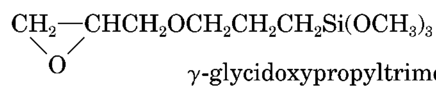
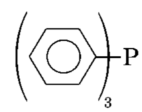
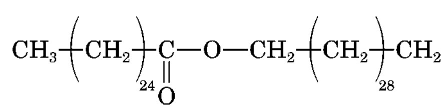
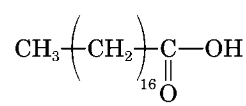
Table I Chemical Structures of Raw Materials

Component	Structure
Epoxy	 Biphenyl type
Curing Agent	 Phenol novalac
Coupling Agent	 γ-glycidoxypropyltrimethoxysilane
Accelerator	 Triphenylphosphine
	 Carnauba wax
Wax	 Stearic acid

distribution on the surface of the phantom model, and the jelly materials cannot be repeatedly used because they are dried out and decomposed over time. Thus, new materials should be needed to overcome such problems.[4, 5]

In this study, for developing new phantom materials to overcome the shortcomings of the traditional phantom model, the dehydrated solid composites composed of epoxy resin, dielectric powder, and carbon black were manufactured. To obtain the equivalent phantom materials corresponding to the various human tissues, the dielectric properties of composites were investigated in terms of the filler content and the composition ratio. The design method for the phantom model with the materials used in this study was also proposed.

EXPERIMENTAL

Materials

Table I shows the chemical structures of materials used in this study. Epoxy resin was the commercially available biphenyl-type epoxy resin obtained from Yuka Shell Epoxy Co. (Tokyo, Japan). Curing agent was phenol novolac (PN) received from Meiwa Kasei Co. (Tokyo, Japan). Small amounts of accelerator (triphenylphosphine, TPP) and coupling agent (γ-glycidoxypropyltrimethoxysilane) were used. Carnauba wax and stearic acid were used as the process agent. $SrTiO_3$ and (Ba, Ca)(Ti,Sn)O_3 were selected as the dielectric powders. $SrTiO_3$ (99.9%, High Purity Chemical Co., Tokyo, Japan) was heat treated at 1380°C for 3 h. The (Ba, Ca)(Ti, Sn)O_3 solid solution made of 0.88 mol $BaTiO_3$ and 0.12 mol $CaSnO_3$ was mixed and milled in methyl alcohol for 24 h, dried at 120°C for 24 h, and then heat treated at 1400°C for 2 h. They were pulverized to obtain the powders with the diameter below 45 μm (under 325 mesh). Carbon black (Ketchen EC, AKZO Co., Tokyo, Japan) was pretreated with the coupling agent in order to minimize the effect of air gap at the interface between particles and matrix in bulk composite. The treatment of coupling agent was carried out by immersing carbon black into a solution of ethanol:water (95:5 by volume) mixed with the coupling agent corresponding to 1 wt % of carbon black for 30 min and drying at room temperature for 1 h, at 40°C for 4 h, and finally at 120°C for 1 h.

Sample Preparation

All epoxy resin compositions contain the same equivalent weight ratio of epoxy and phenolic group. The organic materials except the accelerator were well mixed at 120°C until a homogeneous solution was obtained. The mixture was cooled down to 80°C, the accelerator was added, and then the mixture was fully stirred for 10 s. The organic mixture and dielectric powder and/or carbon black were premixed for 2 min at 80°C and subsequently mixed on a two-roll mill for 10 min at 80°C. The compounds were cooled down and crushed into powder with a pin crusher. Each compound was immediately quenched and stored in a refrigerator at 4°C. The specimens for dielectric measurement were molded using the coaxial shape mold with the inner and outer diameter of 3.02 and 7.05 mm, respectively, for 180 s and then postcured for 5 h at 180°C.

Measurements

Dielectric constant (ϵ') and dielectric loss factor (tanδ) were measured by using a network analyzer (HP 8510C, Hewlett-Packard, Palo Alto, CA) in the frequency range from 50 MHz to 9 GHz. The coaxial-line S-parameter method was adopted for the measurement. The inside and outside walls of the specimens were silver-pasted to ensure the perfect electric contact to the coaxial air line (APC7 Beadless Air Line, Hewlett-Packard).[6, 7]

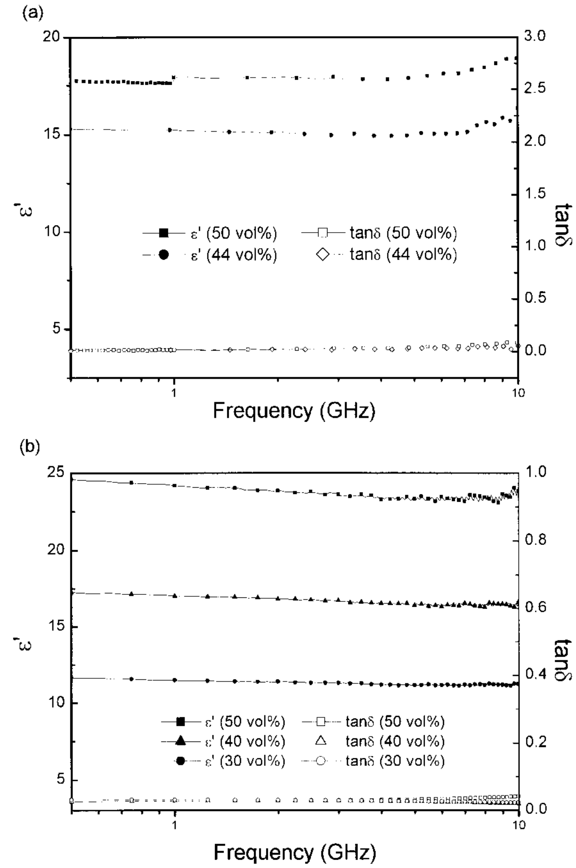


Figure 1 Dielectric constant (ϵ') and dissipation factor (tanδ) of dielectrics/epoxy composite as a function of frequency with the content of dielectric powder; (a) $SrTiO_3$ and (b) (Ba, Ca)(Ti, Sn)O_3.

RESULTS AND DISCUSSION

Electrical Properties of Dielectrics/Epoxy Composite

Figure 1 shows the dielectric constant (ϵ') and dissipation factor (tanδ) for $SrTiO_3$/epoxy and (Ba, Ca)(Ti, Sn)O_3/epoxy with the different contents of dielectric powders as a function of frequency. The ϵ' was constant regardless of the applied frequency until about 7 GHz and increased after that. The tanδ was close to zero in the measured frequency range without regard to the content of dielectrics. Because epoxy, $SrTiO_3$, and (Ba, Ca)(Ti, Sn)O_3 have the extremely low values of tanδ as 0.074~0.0855, below 10^{-4} and

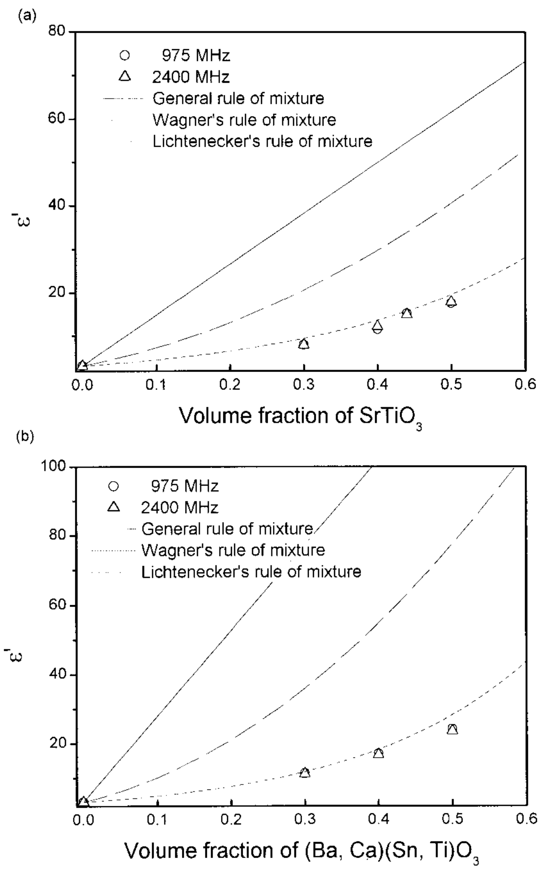


Figure 2 The dielectric constants at 975 and 2400 MHz as a function of volume fraction of dielectric powder; (a) $SrTiO_3$ and (b) (Ba, Ca)(Ti, Sn)O_3. The solid, dashed, and dotted lines represent the general rule, Wagner's rule, and Lichtenecker's rule of mixture, respectively.

0.05, respectively,[5,8] dielectrics/epoxy composites also exhibit low values of tanδ. The conductivity of the materials is proportional to tanδ, namely ϵ'', as the following equation, and thus $SrTiO_3$/epoxy composite seems to be an insulating material.

$$\sigma = \varepsilon'' \cdot \varepsilon_0 \cdot \omega (S/m) \quad (1)$$

where ϵ_0 is the dielectric constant of free space and ω is the radian frequency of applied fields.[9]

Figure 2 indicates the ϵ' of $SrTiO_3$/epoxy and (Ba, Ca)(Ti, Sn)O_3/epoxy with the volume fraction of dielectric powder at some fixed frequencies. The general rule, Wagner's rule,[10] and Lichtenecker's rule[11] of mixture are also plotted in Figure 2. The measured data agreed with the Lichtenecker's curve as reported by Choi et al.[12] It could be found that from Figures 1 and 2 the composite materials with the dielectric properties required up to 7 GHz can be easily obtained by applying the Lichtenecker's rule of mixture.

Electrical Properties of Carbon Black/Epoxy Composite

It is difficult to obtain the conductivity corresponding to the human tissue only using the di-

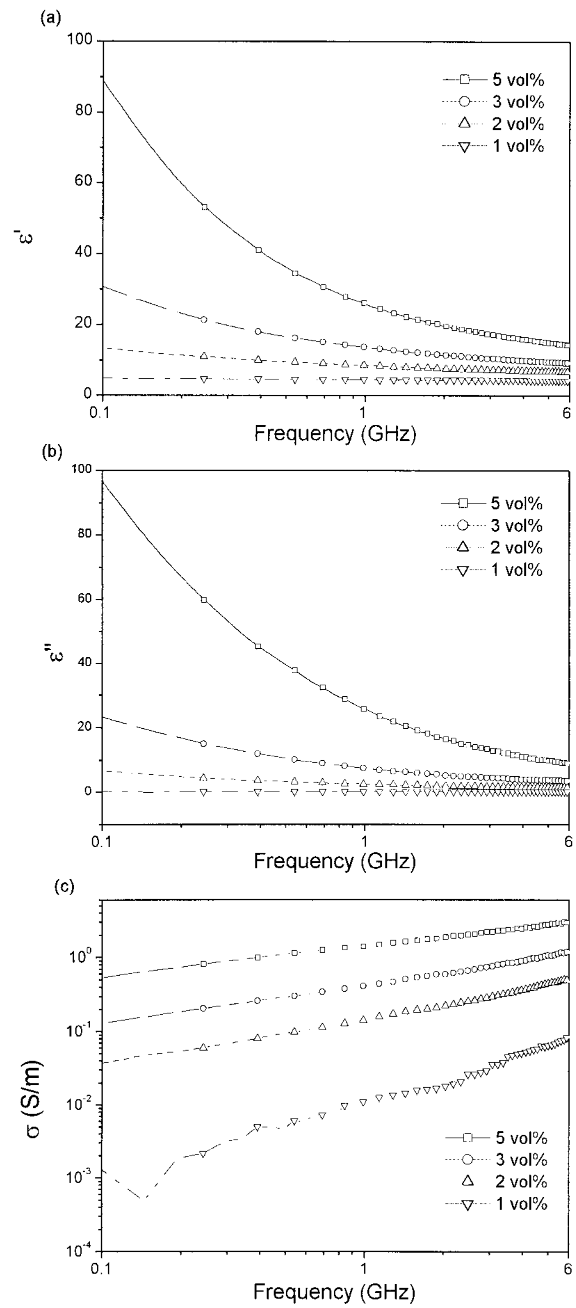


Figure 3 (a) ϵ', (b) ϵ'', and (c) σ of carbon black/epoxy composites as a function of frequency with the content of carbon black.

electrics, thus the conductive materials should be introduced. The ϵ', ϵ'', and σ for the carbon black/epoxy composite are shown in Figure 3. Both the ϵ' and ϵ'' increased with increasing the carbon black content at the same frequency. The larger difference of the constant values in the low frequency range was shown by the increase of carbon black and at the high frequency range the difference was lowered. This means that the frequency dependence of dielectric constants was generated by the addition of carbon black. The carbon black is a semiconductive material and does not work as dielectrics by itself. If it is covered with insulation materials, however, it shows a dielectric property by generating the space charge polarization at the interfaces. This can also be explained by Maxwell-Wagner-Sillars theory, which is to account for the dielectric loss due to the interfacial polarization of heterogeneous materials having the volume fraction of conductive filler lower than the percolation threshold.[13] The interfacial polarization can be more easily occurred at the lower frequency and/or with the number of interfaces between the carbon black and matrix and, consequently, contribute to the improvement of dielectric properties of the composite filled with carbon black. As the frequency is increased, the time required for the interfacial charges to be polarized or for the dipoles to be arranged is delayed,[14] and thus the frequency dependence of dielectric constant can be shown.

The polymer incorporated with conductive filler shows the conductivity due to the electrical loss (ϵ''). When the loading level of carbon black is below the content of percolation threshold, the conduction mechanism between the grains of carbon black can primarily be explained via hopping and tunneling.[8] The ϵ'' is a measure of both the friction associated with changing polarization and the drift of conduction charges. The effective conductivity of carbon black/epoxy composite in Figure 3c is calculated from eq. (1). The conductivity increases with the content of carbon black and exhibits the frequency dependence.

Gabriel et al.[15–17] have reported that the dielectric constants of the human tissues decreased and the conductivity increased with the increase of frequency. It should be noticed that Gabriel's data are not so large in the reduction rate of the dielectric constant with the frequency unlike the behavior of carbon black composite and show higher values than the results in Figure 3a. Therefore, the conductivity corresponding to the human tissues such as brain and muscle cannot

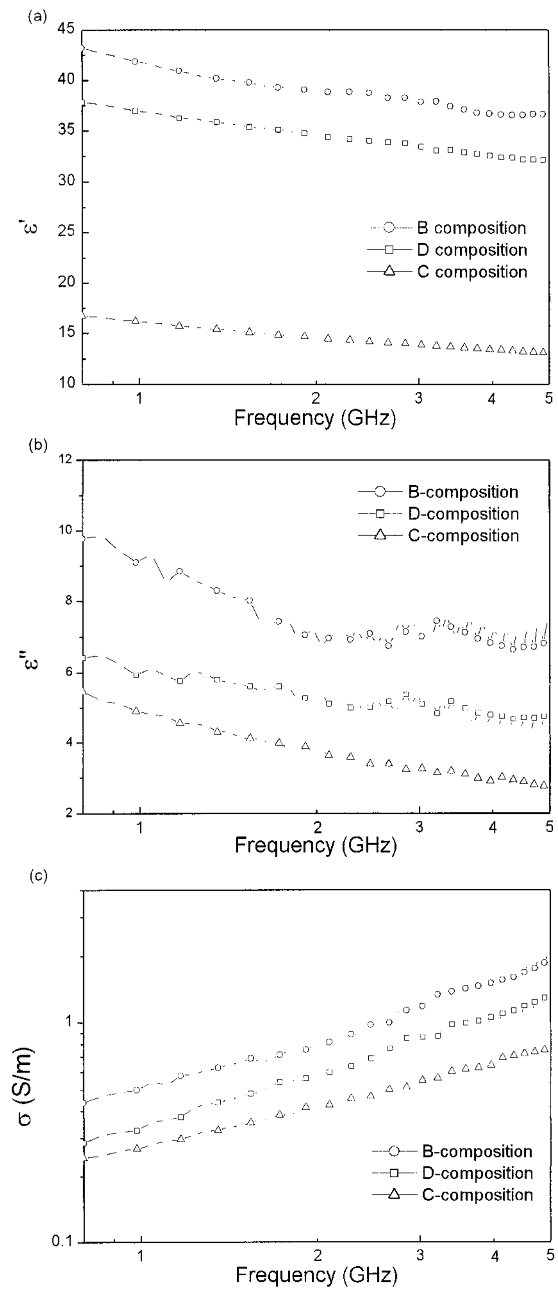


Figure 4 (a) ϵ', (b) ϵ'', and (c) σ for composites with B, C, and D compositions as a function of frequency.

easily be obtained and it is difficult to control the frequency dependence of the ϵ' only by the addition of carbon black. In other words, the dielectrics/epoxy or conductive particle/epoxy composite by itself has some problems to achieve the same properties with human tissues. In order to establish the appropriate frequency dependence of the ϵ' as well as the proper electrical properties of the composite it may be needed to incorporate the

Table II The Compositions of Ceramic Powder, Carbon Black, and Epoxy Resin by Volume

Composition	Epoxy Resin	Ceramic Powder	Carbon Black
A	0.50	0.48[a]	0.02
B	0.50	0.47[a]	0.03
C	0.82	0.15[a]	0.03
D	0.57	0.40[a]	0.03
F	0.60	0.35[a]	0.05
G	0.70	0.25[a]	0.05
J	0.60	0.33[a]	0.07
K	0.54	0.44[b]	0.02
L	0.24	0.74[b]	0.02

[a] (Ba, Ti) (Ca, Sn) O_3.
[b] $SrTiO_3$.

appropriate amounts of carbon black and dielectric powder, simultaneously, into the epoxy matrix.

Electrical Properties of Dielectrics-Carbon Black-Epoxy Composite

Table II shows the compositions of the epoxy resin, dielectric powder, and carbon black used in three-phase composite materials. For simplicity, the nine compositions are referred to A ~ L. Figure 4 shows the electrical properties for the composites with B, C, and D compositions. Because the concentration of carbon black is constant as 3 vol %, the significant difference in the frequency dependence between the three compositions is not shown, but all the values of ϵ', ϵ'', and σ increased with the increase of dielectric powder in the whole range of frequency. The ϵ' of three-phase composite seems to be leaded by the simple addition of the ϵ' occurred by the dielectric powder to the value shown in the carbon black composite. As the tanδ of the dielectric composite was not changed with the frequency as shown in Figure 1, it might be thought that the increase of ϵ'' in the three-phase composite with an increase in the dielectrics was influenced only by the amount of carbon black. However, the results of B, C, and D compositions as shown in Figure 4b, though under the same content of carbon black, showed the increasing values of ϵ'' with the increase of dielectric powder at a given frequency. The reason of this is not exactly understood, but it could be attributed to the additional interfacial polarization between the carbon black and dielectric powder as well as between the carbon black and epoxy resin.

Figure 5 shows the ϵ', ϵ'', and σ as a function of frequency for A, F, and J compositions. The ϵ', ϵ'', and σ showed increasing values with the content of carbon black and the decrease rate with the frequency was steeper. It is thought that all the ϵ', ϵ'', and σ of three-phase composite are more sensitive to the concentration of carbon black rather than dielectric powder.

The comparison of the dielectric constants for A and G compositions is shown in Figure 6. The

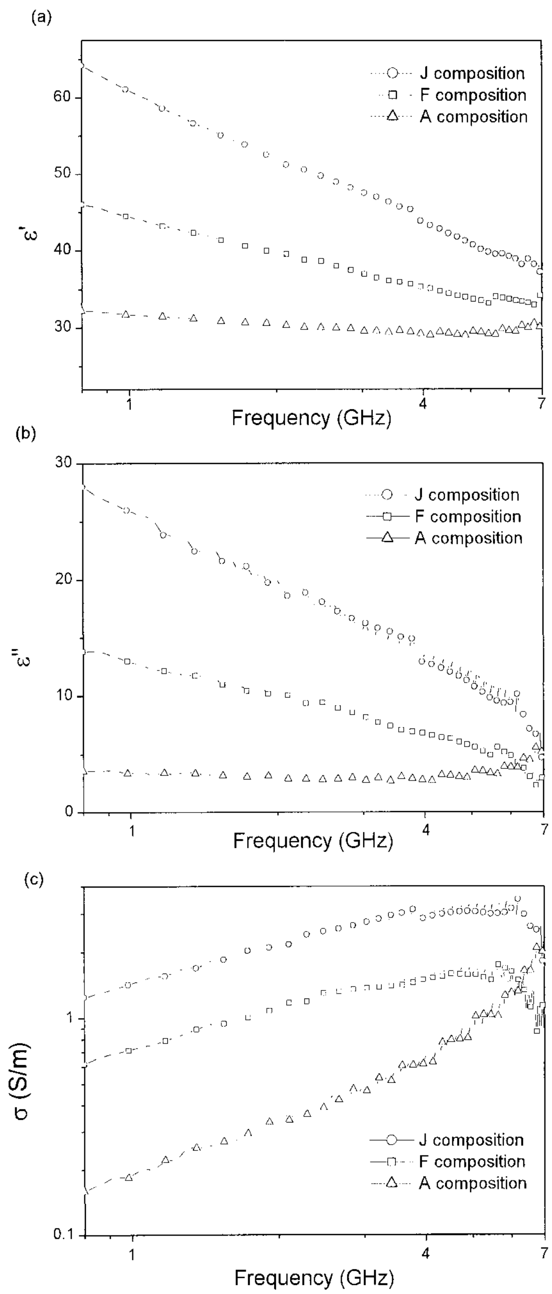


Figure 5 (a) ϵ', (b) ϵ'', and (c) σ for composites with A, F, and J compositions as a function of frequency.

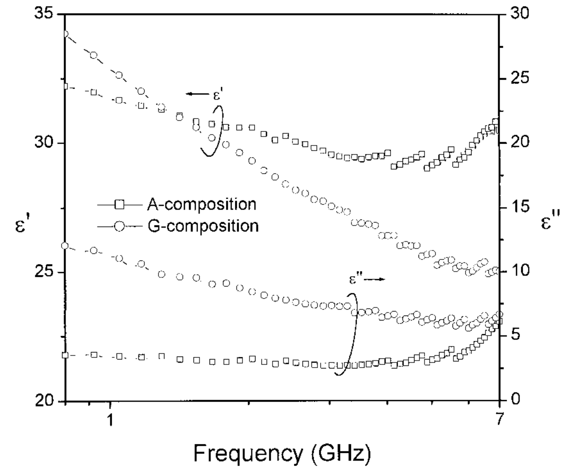


Figure 6 Comparison of dielectric constants for A and G compositions as a function of frequency.

decrease rate of ε′ in G composition was higher than A composition because of the large amount of carbon black. At about 1.4 GHz, a cross-over point between the two curves of ε′ was observed. The ε′ of the carbon black/dielectrics/epoxy composite would be occurred due to the dipole polarization in dielectric powder as well as the interfacial polarization at the interface between the carbon black and epoxy and between the carbon black and dielectric powder. The effect of the interfacial polarization by the carbon black decreases with increasing the frequency while the dipole polarization by dielectric powder is not changed. As a result, in high-frequency range above 1.4 GHz, the ε′ of A composition becomes higher because of the large amount of dielectric powder.

The ε′ of two-phase or three-phase composites in the given frequency range is sensitively influenced by the composition ratio. To predict the dielectric properties of three-phase composite it is needed to understand the relationships between the ε′ of two-phase composite and three-phase composite with their compositions. The representative plots of the ε′ for the two-phase composite of carbon black/epoxy or dielectrics/epoxy and for the three-phase composite of dielectrics/carbon black/epoxy composite are presented in Figure 7. Figure 7a shows the ε′ of carbon black/epoxy composite with different contents of carbon black. The carbon black content of curve 1 is higher than that of curve 2. Because the number of the interfaces is proportional to the concentration of carbon black and the interfacial polarization can be more easily occurred at lower frequency, both cases show the frequency dependence of the ε′ in the whole frequency range and the curve 1 shows much stronger frequency dependence. Figure 7b shows the ε′ of dielectrics/carbon black/epoxy composite with the same content of carbon black but different contents of dielectric powder. The composite of curve 3 has higher dielectrics than curve 4. The frequency dependence is analogous to each other as they have the same content of carbon black. Therefore, their ε′ values depend on the content of dielectric powder and the larger dielectric content, the higher ε′ can be obtained. Figure 7c shows the ε′ of dielectrics/carbon black/epoxy composite with different contents of dielectric powder and carbon black. The curve 5 has the large amount of carbon black and lower dielectric content than the curve 6. Two curves have different decrease rate. At low frequency the ε′ is more sensitive to the content of carbon black but at high frequency the ε′ is more influenced by the dielectric powder. Thus the cross-point between two curves could be occurred. Figure 7d shows the relationship between the ε′ of two-phase composite and that of three-phase composite. The ε′ of three-phase composite is approximately the addition of the ε′ of carbon black/epoxy composite to that of dielectrics/epoxy composite, and it can be expressed as follows:

$$\varepsilon_{CB+dielec} \approx \varepsilon_{CB} + \varepsilon_{dielec} \tag{2}$$

where $\epsilon_{\mathrm{CB+dielec}}$ is the ε′ of three-phase composite, ϵ_{CB} is the ε′ of carbon black/epoxy composite and $\epsilon_{\mathrm{dielec}}$ is the ε′ of dielectrics/epoxy composite. Therefore the ε′ and its frequency dependence of three-phase composite can be approximately predicted, provided the ε′ values of two-phase composites are known with the corresponding composition. The three-phase composites having the ε′ of human tissues could be designed from these methods. Because there must be the additional interfacial polarization of carbon black and dielectric powder in three-phase composite, however, it cannot be concluded that the ε′ of three-phase composite is precisely equal to the summation of each value of two-phase composite.

Figure 8 is the plot of dielectric constants and conductivity for the carbon black/dielectrics/epoxy composite applicable to human phantom materials as a function of frequency. The composition labels are the same as shown in Table II. The reported dielectric constants and conductivity of human tissue are also plotted in Figure 8.[18,19]

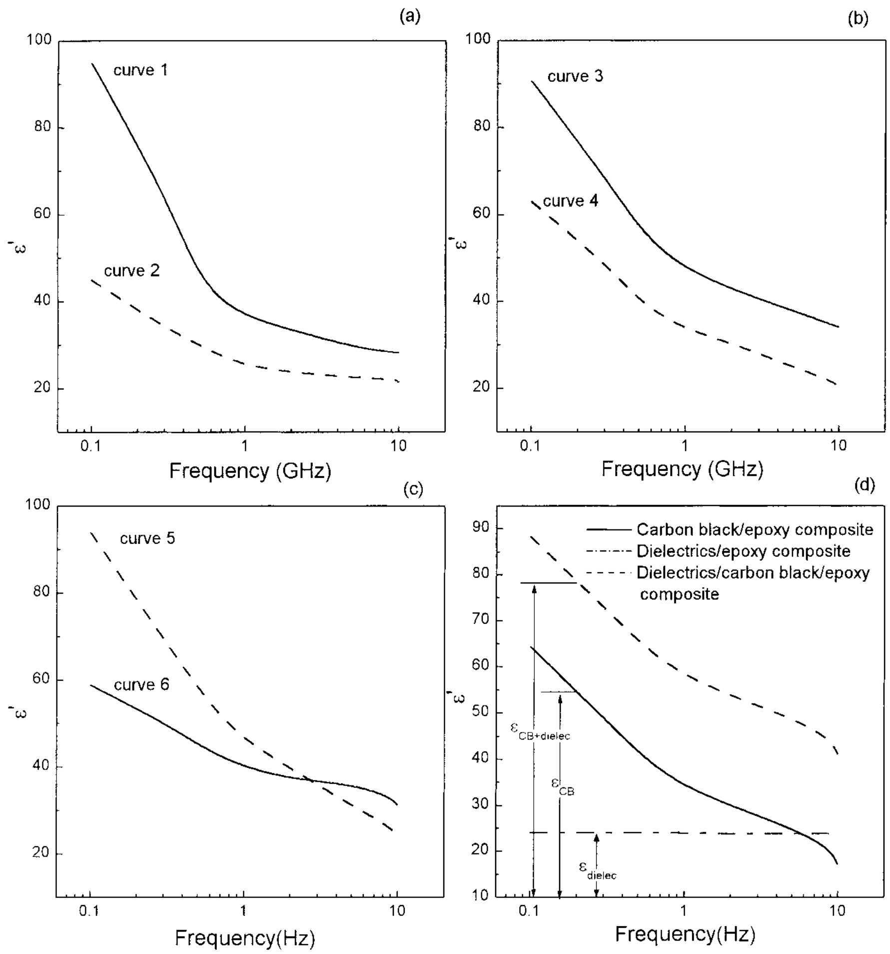


Figure 7 The representative plot of the ϵ' of carbon black/epoxy composite and dielectrics/carbon black/epoxy composite. (a) carbon black/epoxy composites with different contents of carbon black; (b) dielectrics/carbon black/epoxy composites with the same content of carbon black but different content of dielectrics; (c) dielectrics/carbon black/epoxy composite with different contents of carbon black and dielectrics; and (d) the relation between the ϵ' of two-phase composite and that of three-phase composite.

The experimental values for C, K, and L compositions agreed well with the reported data of skull, brain, and muscle in the frequency range of 835~915 MHz, respectively, but the deviations are shown in the range above 1 GHz. $SrTiO_3$ for K and L composition and (Ba, Ca)(Sn, Ti)O_3 for C composition, respectively, were used as the dielectric powder. It is found that the three-phase polymeric composites with the carbon black and dielectric powder can be applied to the fabrication of human phantom materials for skull, brain, and muscle.

CONCLUSIONS

Dielectric constants of dielectrics/epoxy composites increased with the content of dielectric powder, whereas the frequency dependence of changing with the frequency did not appear. The change of dielectric constants with the volume fraction of dielectrics could be well expected by applying the Lichtenecker's rule of mixture. In the case of epoxy filled with the carbon black added to give the conductivity, the dielectric constants also increased with the content of carbon black but showed the frequency dependence that the constants decreased with the frequency. The higher the content of carbon black, the larger the decrease rate in dielectric constants. The electrical properties of the carbon black/dielectrics/epoxy composite would be more sensitively influenced by the concentration of carbon black than that of dielectric powder. The dielectric constants and the frequency dependence of the composites

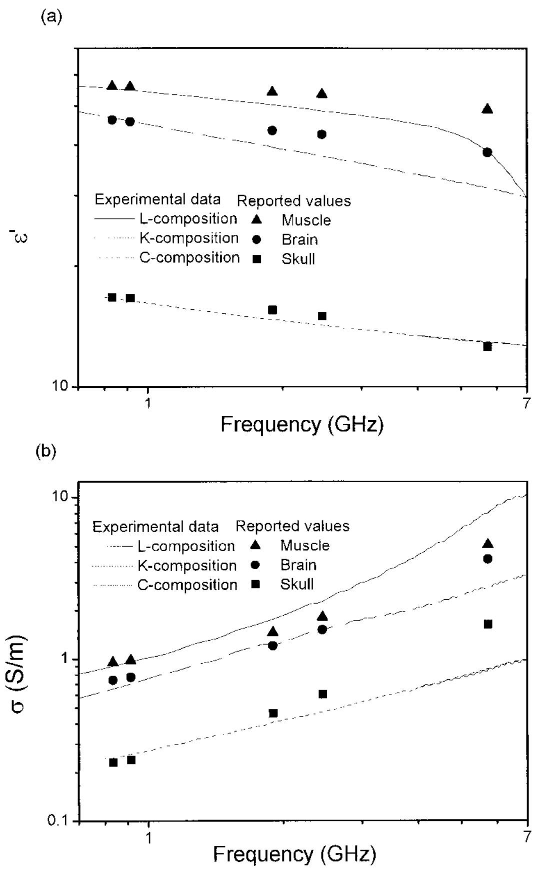


Figure 8 Comparison of (a) $\epsilon'$and (b) σ of the dielectrics/carbon black/epoxy and the reported values for human tissues.

required for the human tissues could be obtained by adjusting the composition ratios of the carbon black, dielectrics, and epoxy, and the approximate design method could be proposed for establishing the phantom materials. Finally, the phantom models to simulate the electrical properties of skull, brain and muscle at 815~915 MHz could be fabricated using the epoxy composite loaded with the dielectric powder and carbon black, simultaneously.

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