論文

고주파에서의 카본 블랙/에폭시 복합재료 복소유전율 모사에 대한 연구

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A Study on the Simulation of Complex Permittivities of Carbon Black/Epoxy Composites at a High Frequency Band

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ABSTRACT

This paper presents a study on the permittivities of the carbon black/epoxy composite at microwave frequency. The measurements were performed at the frequency band of 1 GHz~18 GHz. The experimental data show that the complex permittivities of composites depend strongly on the natures and concentrations of the carbon black dispersion. The frequency characteristics of dielectric constants and ac conductivities of composites show the good conformity with descriptions of the percolation theory, satisfying the general scaling relation. The measuring frequency band is over the critical frequency, below that the ac conductivities of composites are constant to the frequency. The values of dielectric constants and ac conductivities have consistent relationships with the carbon black concentration. The A new scheme, that is a branch of Lichtenecker-Rother formula, is proposed to obtain a mixing law to describe the complex permittivities of the composites as function frequency and concentration of carbon black.

초 록

본 논문에서는 카본 블랙/에폭시 복합재료 적층판의 유전율에 대한 연구를 수행하였다. 유전율 측정은 1 GHz~18 GHz의 주파수 영역에서 수행하였으며, 복합재료의 유전율은 카본 블랙 함유율의 주파수의 함수로 얻을 수 있었다. 유전율 및 전기 전도도의 주파수 특성은 Percolation 이론에서 제시된 경향을 만족하였다. 측정에 사용된 주파수 영역은 전기 전도도가 주파수의 함수관계를 가지는 최소 주파수인 임계주파수보다 크며, 복합재료의 유전율과 전기 전도도는 카본 블랙의 함유량과 일정한 관계를 가졌다. 본 연구에서는, 카본 블랙의 함유율에 따른 복합재료의 유전율을 모사하는 혼합법칙을 얻기 위하여 Lichteneker-Rother 방정식에 기초한 새로운 방법이 제시되었으며, 혼합법칙으로 계산된 복합재료 유전율 모사 결과는 실험적으로 얻은 유전율을 비교적 잘 모사하는 결과를 얻을 수 있었다.

Key Words: Dielectric, Conductivity, Carbon Black, Epoxy, Composite, Simulation, Microwave, Complex permittivity

1. Introduction

As a means to increase complex permittivity of polymeric material, composites containing conductive fillers such as carbon black, carbon fiber, metallic powders are widely used [1]. Carbon black is one of most popular fillers. Conduction of polymeric materials mixed with carbon black is induced by strong electric field effect between the conductive particles or by movements of

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electrons through physically direct contacts of particles. In the former case, the processes such as tunneling, field emission and space charge limited transport should be considered; whereas, in the latter case, resistive (ohmic) relation between current and voltage generated through consistent conductive network formed by the direct contacts between carbon black particles. Thus, due to these variable phenomena mentioned above, it is apparent that the mathematical models describing the properties of electro-conductive composite materials tend to be very complicated [2]. Dielectric constants and ac conductivity of composite materials are related with anomalous diffusion within each cluster and depolarization effects between clusters composed of conductive fillers inside composites. These phenomena also cause the dielectric constants and electric conductivity of composite materials to become a function of all frequencies [3,4]

The following presents 3 different factors to determine the dielectric constants and conductivities of composites:

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

Percolation theory, a representative approach of the macroscopic point of view, is typical for simulating dielectric constants and conductivities of composites at relatively low frequency band including DC [5,6]. In this study, we show the experimental value of complex permittivities of carbon black/epoxy composites at a microwave frequency band of 1 GHz~18 GHz. The characteristics of complex permittivities of composites were investigated by using percolation theory, moreover, using a newly proposed simulation method based on rule of mixture.

2. Experimental

2.1 Manufacture of specimens

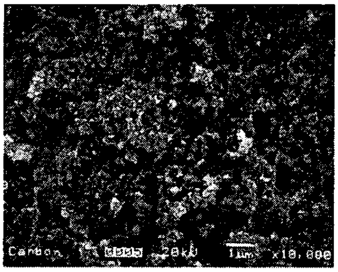

Fig. 1 Scanning electron microscope photo of the carbon black.

Table 1 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

* Refer to ASTM D 2414, ASTM D6854 to see the meaning

Table 2 Volume fraction of components in composites

Material Name	Weight fraction of carbon black	Concentration of carbon black (p)	Concentration of epoxy resin
CB00	0.0 wt%	0.000%	100.00%
CB01	0.1 wt%	0.064%	99.936%
CB02	0.2 wt%	0.128%	99.872%
CB05	0.5 wt%	0.321%	99.679%
CB07	0.7 wt%	0.450%	99.550%
CB10	1.0 wt%	0.644%	99.356%

Composite materials used in this study were manufactured using compounds which are composed of 4wt% of carbon black of XE2 grade from DEGUSSA and 96wt% of YD115 epoxy resin from KUKDO Chemicals mixed by 3-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 is 10:9. Figure 1 shows the SEM photograph of carbon black used, and it specification is presented in Table 1.

Dilution was performed using stirrer at 1500 RPM for 30 minutes. After extracting vapors from the material at a vacuum condition, the diluted mixtures were poured into the mold at an atmospheric pressure to make composite plates of 2mm thick. The composite plates were cured at a temperature of 120℃ for over 2 hours. Table 2 presents carbon black concentration (p) of the fabricated composites, the concentration were calculated using the density of epoxy resin(1.2 g/cm^3), carbon black(1.87 g/cm^3) and the weight contents of carbon black within the composites.

2.2 Measurement of complex permittivity

Complex permittivity is expressed with a simple form of $\epsilon^* = \epsilon' - j\epsilon''$, where ϵ' is dielectric constant and ϵ'' is lossy term

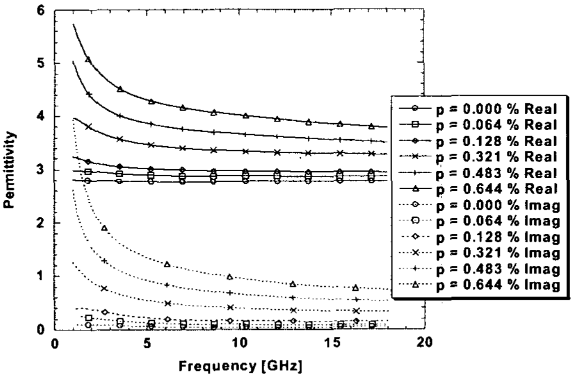

Fig. 2 The complex permittivity of carbon black/epoxy composites.

that is related with electric conductivity (σ) of the material. The relationship between ϵ'' and σ takes a form of $\sigma = \omega\epsilon_0\epsilon''$

Figure 2 shows real parts and imaginary parts of complex permittivities obtained from experiments. All experimental data are averaged value of 3 different specimens. Both real parts and imaginary parts increase as the carbon black concentration increases. It was observed that, as compared to real parts, imaginary parts much more rapidly increases as the carbon black concentration increases.

In order for the measurement of complex permittivities at microwave frequency band, HP8722D (VNA; Vector Network Analyzer) and 7 mm coaxial airline were used. The specimens used for the complex permittivity measurements were mechanically manufactured from the composite plates so that the specimen could be inserted into the coaxial airline. The complex permittivities were obtained using Nicolson-Ross-Weir method from scattering parameters for reflected and transmitted TEM microwaves which were continuously measured from 1 GHz to 18 GHz [7].

3. Theories and results

3.1 Percolation theory

As to the electric conductivities at a low frequency or DC of composites, percolation theory was first introduced by Kirkpatrick's resistance network model. Percolation theory says, Percolation threshold (p_c), that is the concentration of a conductive filler at which the composites transform from insulating materials into conductive materials at DC or low frequency AC current, exists; and, if the concentration of filler is greater than 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

$$\sigma_{DC} \sim (p_c - p)^{s},\ \text{if } p<p_c$$

and

$$\sigma_{DC} \sim (p - p_c)^{t},\ \text{if } p>p_c.$$

where s and t are universal exponents indicating the characteristics of composites [6]. Static dielectric constant of the composite, $\epsilon_s = \epsilon'(\omega \rightarrow 0)$, is expressed with a form

$$\epsilon_s \sim |\, p - p_c \,|^{-s}$$

in both cases $p<p_c$ and $p>p_c$ [6]. In order to analyze the dielectric constants and conductivities of composites at lower frequency band by applying the Percolation theory, a number of researches were performed to determine the universal exponents [8-10].

The frequency dependencies of dielectric constants and conductivity around the Percolation threshold can be expressed as $\sigma(\omega) \sim w^{x}$ and $\epsilon'(\omega) \sim w^{-y}$, 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, and is called general scaling relation. The description of the dielectric constant and conductivity of a composite as function of overall range of frequency and filler concentration needs some semi-empirical curve fitting and mathematical assumptions; they are not so simple to use intuitively [4-6,8-10].

It is well known that, when the filler concentration is over than the percolation threshold, conductivity is frequency independent below to critical frequency. Over the critical frequency, there are simple models that imply the relation of $\sigma(\omega) \sim w^{x}$ between the frequency and conductivity for any filler concentration [5,8].

Figures 3, 4 show the dielectric constants and conductivities as a function of frequency for various concentrations of composites. They show an obvious trend that, in the vicinity of percolation threshold, the dielectric constant and the ac conductivity can be expressed as $\sigma(\omega) \sim w^{x}$ and $\epsilon'(\omega) \sim w^{-y}$. The exponents x are all about 0.75 and the exponents y are all about 0.25. The summations of exponents x and y are all about unity in all composites. This is well satisfying the general scaling relation in percolation theory [3-6, 8-10].

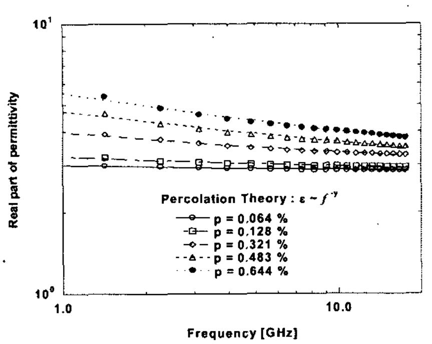

Fig. 3 The frequency characteristics of the dielectric constants of carbon black/epoxy composites.

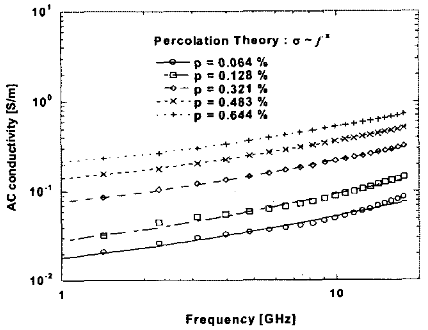

Fig. 4 The frequency characteristics of the ac electrical conductivities of carbon black/epoxy composites.

This fact means that all the composites are in the vicinity of percolation threshold [3]. Percolation threshold can vary due to the manufacturing method of the composites, even if polymeric matrix material and power are the same. According to the study results conducted through Schueler *et al.* in 1996, in case of carbon black and epoxy resin, percolation threshold may exists between 0.06% ~ 0.9% of concentration of carbon black [11].

All the measured conductivities have continuous increment in the frequency range of this study, so that we can be sure that all data are above the critical frequency [8].

Figures 5, 6 show the characteristics of dielectric constants and conductivities as a function of concentration of carbon black. All the lines are drawn by the assumption that the values of dielectric constant (ϵ') and ac conductivity (σ) are proportional to p^{δ}, where the values δ are simple constants. All the plots have consistent tendency in all filler concentration (p).

3.2 Lichtenecker-Rother Theory

A representative equation to simulate dielectric constants of composites containing the fillers, with very high dielectric constant

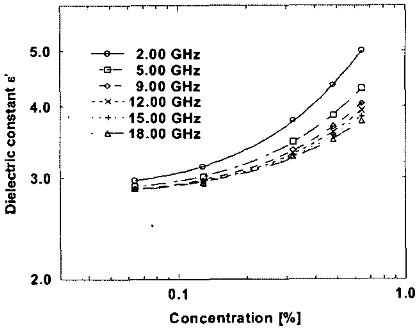

Fig. 5 The carbon black concentration dependencies of the dielectric constants of carbon black/epoxy composites.

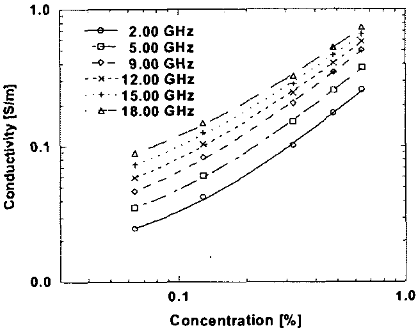

Fig. 6 The carbon black concentration dependencies of the ac electrical conductivities of carbon black/epoxy composites.

value and without any loss, has been proposed by Lichtenecker and Rother, as shown below [12].

$$(\epsilon'_c)^k = p(\epsilon'_f)^k + (1-p)(\epsilon'_m)^k \qquad (1)$$

In equation (1), ϵ'_c, ϵ'_f and ϵ'_m are dielectric constants of composite, pure dielectric filler and polymer matrix material, respectively. k is a constant determined by the mechanism of wave propagating through fillers contained in insulating medium. It is known that k = 1 when the filler distribution is serial with direction of wave propagation, whereas k = -1 when the filler distribution is parallel with the direction of wave propagation [13]. It is also known that k = 1/3 when the fillers are randomly distributed at low concentration [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 k of Lichtenecker-Rother equation as the 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 consisting of function of $k(p)$ are material constants determined by the types of fillers and medium.

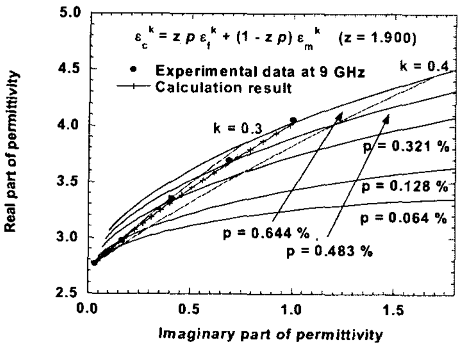

Fig. 7 The role of exponent k ; simulated complex permittivities and experimental data of carbon black/epoxy composites at 9 GHz.

Applying Lichtenecker-Rother theory to composites containing conductive fillers, the physical meaning of k becomes different from the cases of applying to 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 real part and imaginary part of complex permittivity for composites. Carbon black, shaped as agglomeration with irregularity of porosity, is not perfect sphere. It may affect the characteristics of composites as well [3-4,13]. In this study, this effect was induced by applying a correction factor (z) into equation (1). So, a new equation was expressed as following form

$$(\epsilon_c^*)^k = zp(\epsilon_f^*)^k + (1 - zp)(\epsilon_m^*)^k \tag{2}$$

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

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

Figure 7 shows the role of exponent k by drawing the experimental values and simulation values of complex permittivity of the composites at the frequency of 9 GHz. The constant concentration lines show how the real and the imaginary parts of permittivity can vary according to the exponent k. The two constant k lines show the boundaries in that the real and the imaginary parts of permittivity can be. In the figure 7, we can see how the equation of $k=Ap+B$ works.

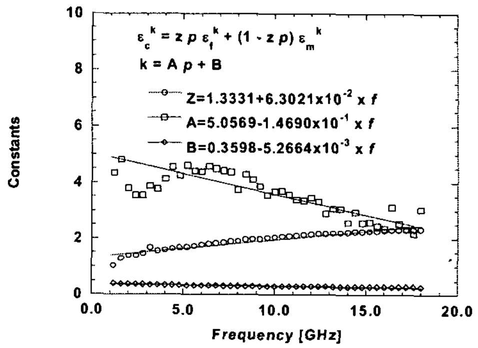

Fig. 8 The frequency characteristics of constants: A, B and z.

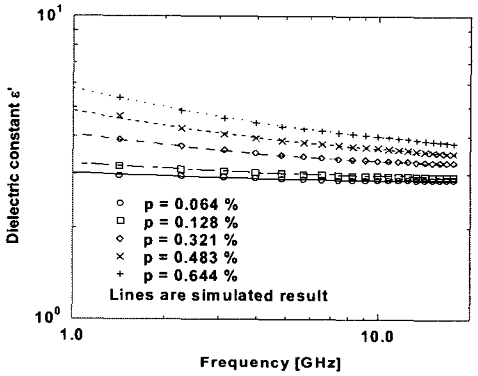

Fig. 9 The frequency characteristics of the dielectric constants of carbon black/epoxy composites.

Figure 8 shows frequency characteristics of A, B and z obtained using the experimental complex permittivities of the composites. The frequency characteristics of A, B and z are linear in overall frequency range of this study. The obtained functions are as follows:

$$z = 1.3331 + 6.3021 \times 10^{-2} \times f \tag{3}$$

$$A = 5.0569 - 1.4690 \times 10^{-1} \times f \tag{4}$$

$$B = 0.3598 - 5.2664 \times 10^{-3} \times f \tag{5}$$

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

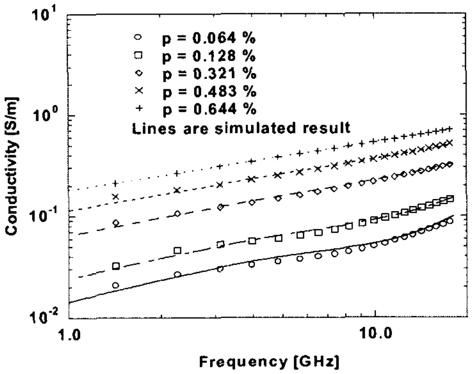

Fig. 10 The frequency characteristics of the ac electrical conductivities of carbon black/epoxy composites.

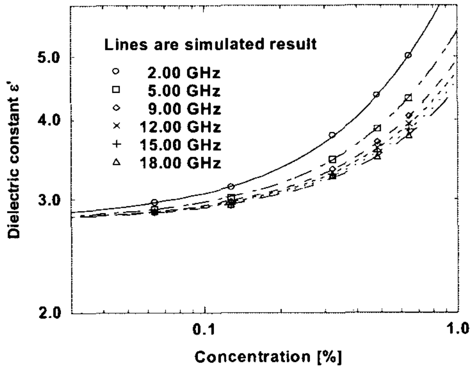

Fig. 11 The carbon black concentration dependencies of the dielectric constants of carbon black/epoxy composites.

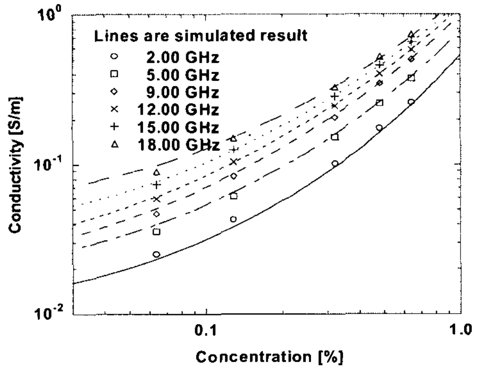

Fig. 12 The carbon black concentration dependencies of the ac electrical conductivities of carbon black/epoxy composites.

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

Conclusions

(1) Composite materials containing carbon black were manufactured, and the complex permittivities were measured at the microwave frequency band from 1 GHz to 18 GHz.

(2) The exponents x are all about 0.75 and the exponents y are all about 0.25. The summations of exponents x and y are all about unity in all composites. This is well satisfying the general scaling relation in percolation theory. All the measured conductivities have continuous increment in the frequency range of this study, so that we can be sure that all data are above the critical frequency.

(3) The values of dielectric constant (ϵ') and ac conductivity (σ) are proportional to p^{δ}, where the δ values are simple constants.

(4) A new simulation method, which satisfies both frequency spectrum at microwave frequency band and carbon black concentration dependency of dielectric constants and conductivity of the composites, was presented, and compared with the experimental values, providing excellent results.

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