Electromagnetic and Electromagnetic Wave-Absorbing Properties of the $SrTiO_3$–Epoxy Composite

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ABSTRACT: The effects of $SrTiO_3$ content on the electromagnetic properties and electromagnetic wave-absorbering charateristics of $SrTiO_3$–epoxy composites were investigated. Also, the frequency dispersion behavior of the complex permittivity of composites was demonstrated. The complex permittivity and permeability were measured using a network analyzer in the frequency range of 130 MHz to 10 GHz. As the $SrTiO_3$ content increased, it was found that the complex permittivity and permeability of the composites increased and the resonance frequency moved toward low frequency range. The logarithmic model coincided with the effective permittivity of composite as a function of $SrTiO_3$ content comparatively well. The resonance frequency of composites was found to show good agreement with the theoretical values calculated by the equation proposed in this article. The electromagnetic wave-absorbing behavior showed that the center frequency of attenuation curve was shifted to a lower frequency band with increasing the amount of $SrTiO_3$ and the thickness of composite. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 75–83, 1999

Keywords: $SrTiO_3$; composite; permittivity; electromagnetic wave absorbing

INTRODUCTION

During recent years, the concerns have grown increasingly about EMI, EMS, and the effect on human body of electromagnetic wave radiation from electronics and telecommunication devices.[1] Human tissues may be accidentally or intentionally exposed to electromagnetic sources, such as radars, microwave oven, and industrial microwave equipments. There are still unclear things about the effects of electromagnetic exposure on human body. The research on these effects is an important subject that mankind has to solve.

Electric and magnetic properties of polymers, well known for their insulating properties, may be improved by adding various functional fillers. Electromagnetic properties of such composites depend on the size, microstructure,[2] and amount of added filler in general.[3] Particularly, The polymer composites that contained the dielectric materials will be used as the electromagnetic wave absorber[4] by the dielectric loss, the human phantom[5] for measuring SAR (specific absorption rate), etc. In the case of polymer–dielectric composite, the attenuation characteristics of electromagnetic wave absorber are influenced by the composition, thickness, complex permeability and permittivity of

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composite, and the frequency.[6] It is very important to analyze the electromagnetic properties in fabricating an electromagnetic wave absorber and a human tissue phantom because the change of electromagnetic properties is closely related to electromagnetic wave absorbing characteristics and the SAR distribution of human tissue phantom. The complex permeability and permittivity of composite is dependent on the frequency and have frequency dispersion behavior.[7] The attenuation characteristic of absorbing materials is defined as follows.

The structure of common electromagnetic wave absorbers consists of a layer of absorbing materials with relative permittivity ε_r and permeability μ_r attached to a metal plate. For anormally incident plane wave the input impedance (normalized by an impedance in free space) defines[8]

$$Z = \frac{Z_{\text{input}}}{Z_0} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tan h\left(i \, \frac{2\pi}{c} \, \sqrt{\mu_r \cdot \varepsilon_r} f \cdot d \right) \quad (1)$$

where c, f, and d represent the speed of light, the frequency of electromagnetic wave, and the thickness of an absorbing material, respectively.

Attenuation values are expressed as follows:

$$\text{Attenuation (dB)} = 20 \cdot \log \frac{|Z - 1|}{|Z + 1|} \quad (2)$$

When the perfect matching condition that satisfies $Z_{\text{input}}/Z_0 = 1$ is met, the reflection coefficient becomes zero and the attenuation value becomes infinite.

In this article, the $SrTiO_3$–epoxy composites are used to study the effects of $SrTiO_3$ content on the electromagnetic properties and electromagnetic wave absorbing characteristics of composites. The effects of $SrTiO_3$ content on the resonance frequency of composites and the mixing rule of permittivity of dielectric composites is investigated. The experimental results of the effective permittivity of binary mixture are compared with the values calculated by the several well-known dielectric mixture equations. Also, the frequency dispersion behavior model of complex permittivity of $SrTiO_3$–epoxy composites is determined.

EXPERIMENTAL

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.). $SrTiO_3$ powder, dielectric material used as a filler was calcined in a box furnace at 1380°C for 2 h and ground for further treatment. After removing the moisture at 80°C for 48 h, $SrTiO_3$ 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 to improve the dispersion of the $SrTiO_3$ and accelerate the polymerization, respectively.

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 vol % were kneaded by the double-shaft roll mill heated at 80–90°C for about 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 inner and 7-mm outer diameters, respectively, and the samples were finally obtained by postcuring at 180°C for 5 h.

The complex permittivity and permeability of composites were measured as a function of frequency from 130 MHz to 10 GHz by using the coaxial-line S-parameter method.[9] The inside and outside wall of test specimens were silver pasted to ensure electric contact to coaxial air line (HP85051-60007): an APC-7 Beadless Air Line from Hewlett-Packard. All measurements were performed on measured a network analyzer (HP8719A).

RESULTS AND DISCUSSION

Figure 1(a) shows the frequency dispersion behaviors of the complex permittivity of composites as a function of volume fraction of $SrTiO_3$. The real part of the permittivity increased with increasing the $SrTiO_3$ content. The imaginary values of the permittivity seemed to be independent of $SrTiO_3$ content up to 2 GHz. But the maximum peak of the imaginary part increased above 2 GHz and moved toward the low frequency band with increasing the volume fraction of $SrTiO_3$. That is, the resonance frequency of composite corresponding to 0.3, 0.4, 0.5, and 0.6 of the volume fraction

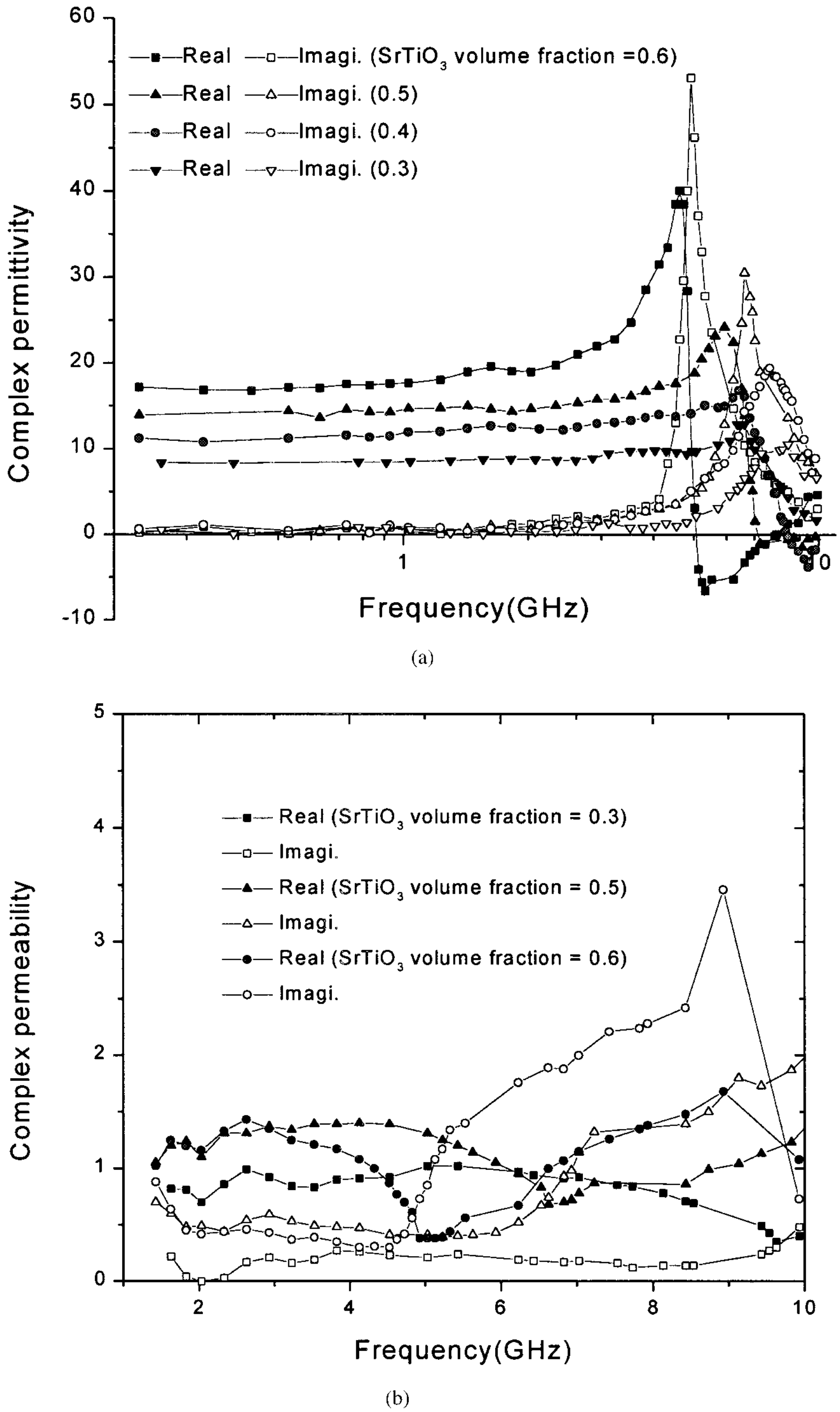


Figure 1 (a) The complex permittivity of the $SrTiO_3$–epoxy composite for various $SrTiO_3$ content. (b) The complex permeability of $SrTiO_3$–epoxy composite for various SrTiO3 content.

of $SrTiO_3$ are 9.73, 7.63, 6.63, and 4.93 GHz, respectively. Figure 1(b) shows the complex permeability of composites as a function of volume fraction of $SrTiO_3$. It is found that real values of permeability are about 0.5–1.5 and imaginary values change more than real values with the content of $SrTiO_3$. As the volume fraction of $SrTiO_3$ are 0.3, 0.5, and 0.6, the frequencies for $\tan \delta > 1$ are 9.73, 6.63 and 4.93, respectively. These frequencies are equal to the resonance frequencies of complex permittivity for composite.

Several well-known dielectric mixture equations were selected for this study. The notation used here applies to two component mixtures, where ε_{eff} represents the effective complex permittivity of composite, ε_m is the permittivity of matrix in which fillers of permittivity ε_f are dispersed, and V_f is the volume fraction of filler.

The best-known formula for ε_{eff} for a binary mixture is associated with Maxwell and Wagner. Maxwell, in his treatise, discussed the problem of the effective conductivity of a binary system consisting of spheres of one conductivity distributed uniformly in a continuum of a different conductivity. Wagner[10] adapted Maxwell's expression to the dielectric case. It can be expressed as follows:

$$\varepsilon_{\text{eff}} = \varepsilon_m \frac{\left[1 - 2V_f \dfrac{(\varepsilon_m - \varepsilon_f)}{(2\varepsilon_m + \varepsilon_f)}\right]}{\left[1 + V_f \dfrac{(\varepsilon_m - \varepsilon_f)}{(2\varepsilon_m + \varepsilon_f)}\right]} \tag{3}$$

the Nelson and You equation[11]

$$\varepsilon_{\text{eff}} = ((1 - V_f) \cdot \varepsilon_m^{1/2} + V_f \cdot \varepsilon_f^{1/2})^2 \tag{4}$$

the Lichtenecker[12] equation is

$$\log \varepsilon_{\text{eff}} = (1 - V_f)\log \varepsilon_m + V_f \log \varepsilon_f \tag{5}$$

The experimental data of effective permittivity to the volume fraction of composite were compared to the values calculated by eqs. (2)–(5) in Figure 2. It is clear from the figure that the experimental datas approximate the values calculated by eq. (5). According to Birks,[13] the permeability of ferrite–polymer composite has been generally calculated using Lichteneker's logarithmic model. It is also found that the effective permittivities of $SrTiO_3$–epoxy composites as a function of volume fraction show relatively good agreement with the values calculated by the logarithmic law.

The square root of permittivity multiplied the resonance frequency vary inversely with the volume of dielectric material. When V is the volume of dielectric and the resonance frequency is f_r,

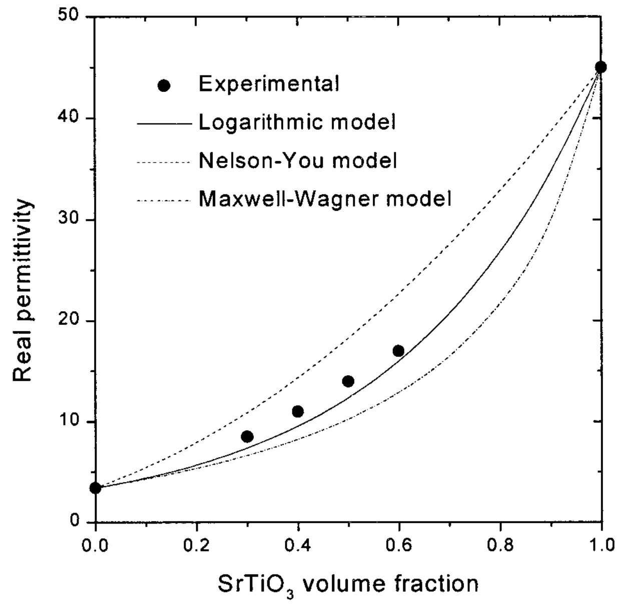


Figure 2 Comparison of effective permittivity of experimental values with several models in the $SrTiO_3$–epoxy composite.

$$\sqrt{\varepsilon_f} \cdot f_r \propto \frac{1}{V}.$$

Therefore, the change of permittivity to the resonance frequency can be predicted at a given volume of dielectric material.

However, in the case of the composite adding dielectric to polymer,

$$\sqrt{\varepsilon_f} \cdot f_r$$

is not constant at a given volume of composite, but it is increased with decreasing the volume fraction of dielectric material in composite as shown in Figure 3(a). This is similar to the result of the resonance frequency of ferrite–polymer composite by Han.[14] For the permeability characteristic of magnetic materials, the intrinsic permeability of sintered ferrite follows the Snoek's relation[15] that the intrinsic permeability multiplied the resonance frequency is constant. Han had reported that the effective permeability multiplied the resonance frequency of the ferrite–polymer composite was expressed as a function of volume fraction of ferrite in ferrite–polymer composite. We predicted that the effective permittivity times the resonance frequency of dielectric–polymer composite could be considered as a func-

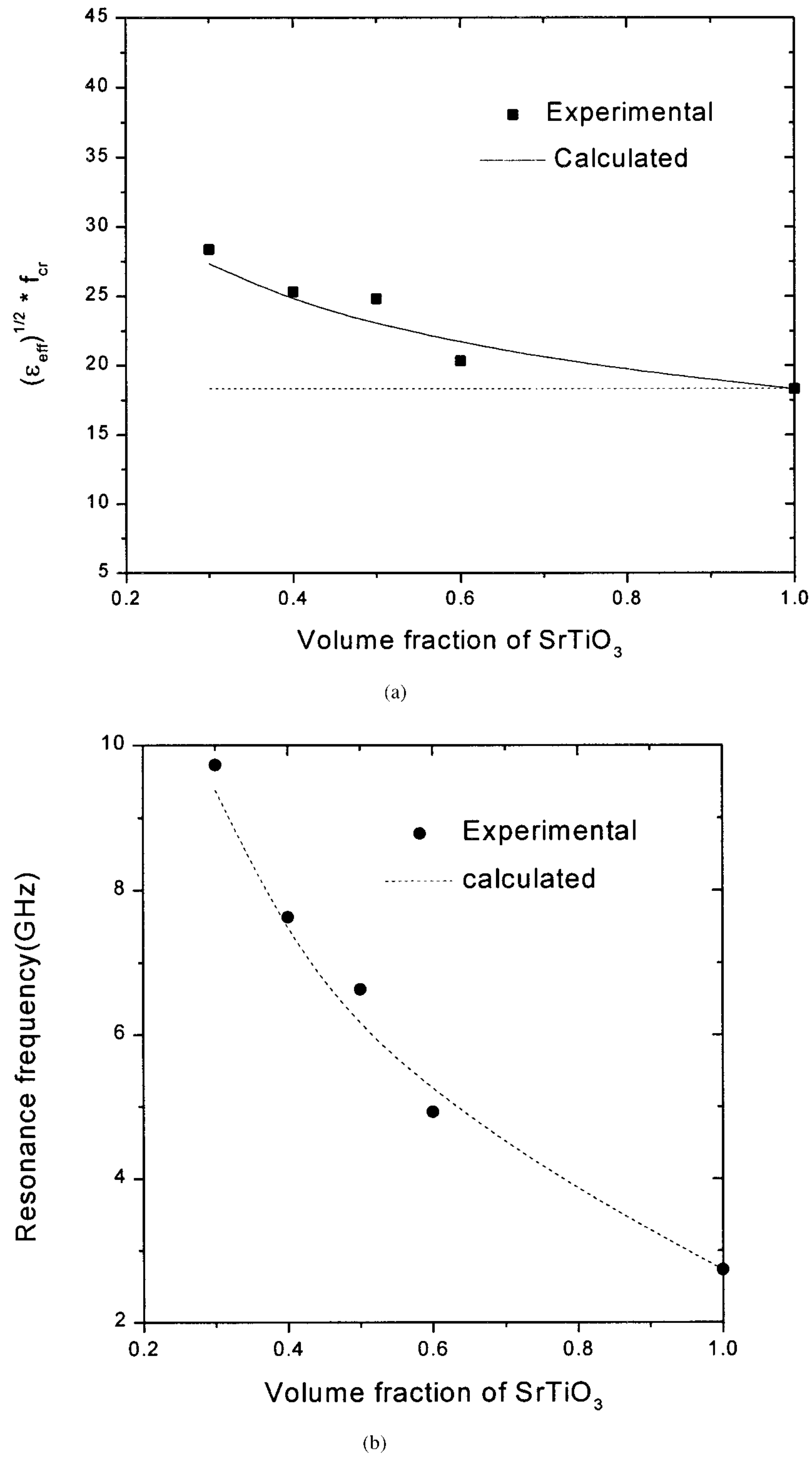


Figure 3 (a) $(\varepsilon_{\mathrm{eff}})^{1/2} \cdot f_{\mathrm{cr}}$ as a function of $SrTiO_3$ volume fraction. (b) Comparison of experimental values with calculated values. (b) Comparison of experimental values with calculated values for resonance frequency.

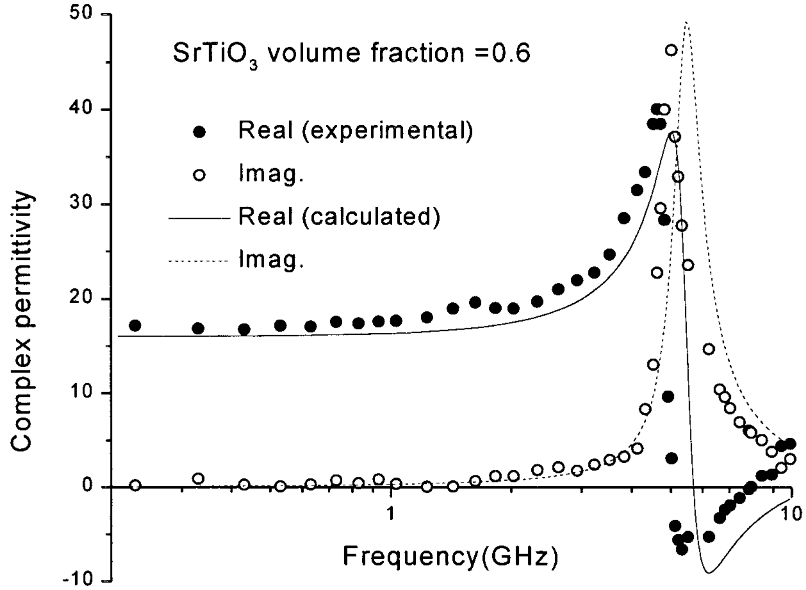


Figure 4 Comparison of experimental values with calculated values for the frequency spectra of the complex permittivity at 0.6 volume fraction of $SrTiO_3$.

tion of volume fraction of dielectric material. This could be indirectly found by exploiting the duality principle in Maxwell's equation.[16] Therefore, to predict he resonance frequency of the polymer–dielectric composite, we calculated the resonance frequency of composite by relationship expressed as follows:

$$f_{cr} = \frac{\sqrt{\varepsilon_r} \cdot f_r}{\sqrt{\varepsilon_{\mathrm{eff}}}} \left(\frac{1}{V}\right)^{1/3} \tag{6}$$

where f_{cr} is the resonance frequency of polymer composite.

The resonance frequency values obtained by experiment and by calculation using eq. (6) are shown in Figure 3(b). It is found that the dottted line, which represents the calculated values, is well matched with the experimental values (errors in calculating the resonace frequency values: <6%). As the volume fraction of $SrTiO_3$ increased, the effective permittivity increased and the resonance frequency decreased.

Choi et al.[17] has expressed the frequency dispersion characteristics of complex permittivity on the $SrTiO_3$–epoxy composite as follows:

$$\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_{\mathrm{eff}} - \varepsilon_\infty)}{\left(1 - \left(\frac{f}{f_{cr}}\right)^2 + j\,\frac{f\gamma}{(f_{cr})^2}\right)^\alpha} \tag{7}$$

where ε_∞ is the permittivity of polymer and f_{cr} is the resonance frequency of composite. The empirical constant γ is the damping factor and represents the half-width or line-breadth of a spectral line. The empirical constant $\alpha (0 < \alpha \leq 1)$ is the asymmetrical factor and shows the degree of deviation from the circle in Cole-Cole plot.

We predict the frequency dispersion behavior of $SrTiO_3$–epoxy composite using eq. (7).

Figure 4 shows a comparison of the experimental data of complex permittivity for the composites containing 0.6 volume fraction of $SrTiO_3$ with the values calculated by eq. (7), after substituting eqs. (5) and (6) into eq. (7). The empirical constants γ and α are 0.8 and 0.785, respectively. The real and imaginary part of permittivity obtained by eq. (7) slighly deviated from the experimental values. This may be considered due to a difference between the experimental values and the calculated values of the resonance frequency of composite, as shown in Figure 3(b). However, the calculated values were well matched with the experimental values. From the above results, the frequency dispersion charateristics of the complex permittivity of the composite materials with different amounts of $SrTiO_3$ can be estimated by eqs. (5), (6), and (7), if the effective permittivity and the resonance frequency of pure $SrTiO_3$ are known.

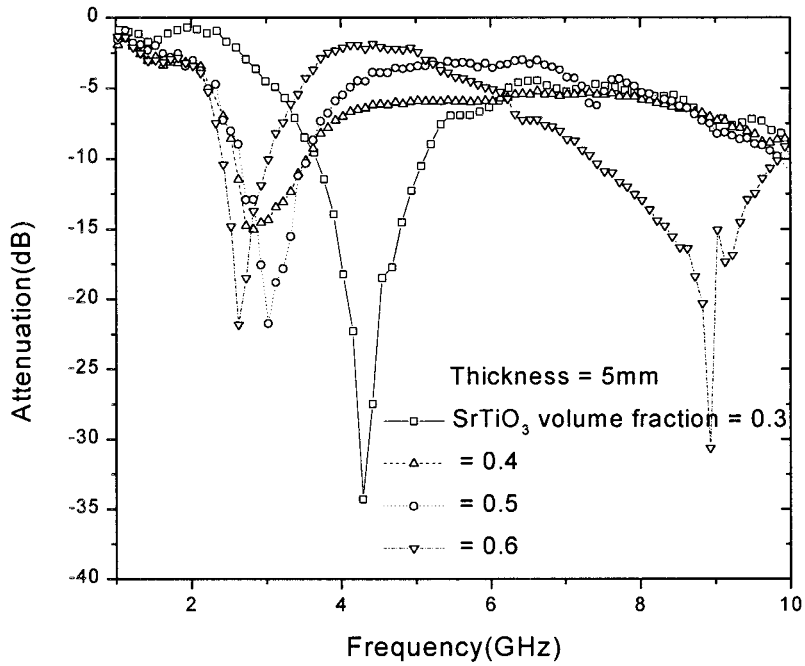


Figure 5 The attenuation behaviors of composites for various $SrTiO_3$ volume fraction.

It is clear from eqs. (1) and (2) that the attenuation characteristics of composite are influenced by the composition, thickness, complex permeability and permittivity of composite, and the frequency.

Figure 5 shows the attenuation behavior of composite for the various $SrTiO_3$ volume fractions at a given thickness. The maximum attenuation frequency was shifted to a lower frequency band with increasing the amount of $SrTiO_3$. The composite containing 0.6 volume fraction of $SrTiO_3$ with 5-mm thickness provides respectively 22 and 30 dB of attenuation at the 2.6 GHz and 9 GHz maximum attenuation point. Also, the composite containing 0.3 volume fraction of $SrTiO_3$ with a identical thickness provides a very impressive 34 dB of attenuation at 4.3 GHz.

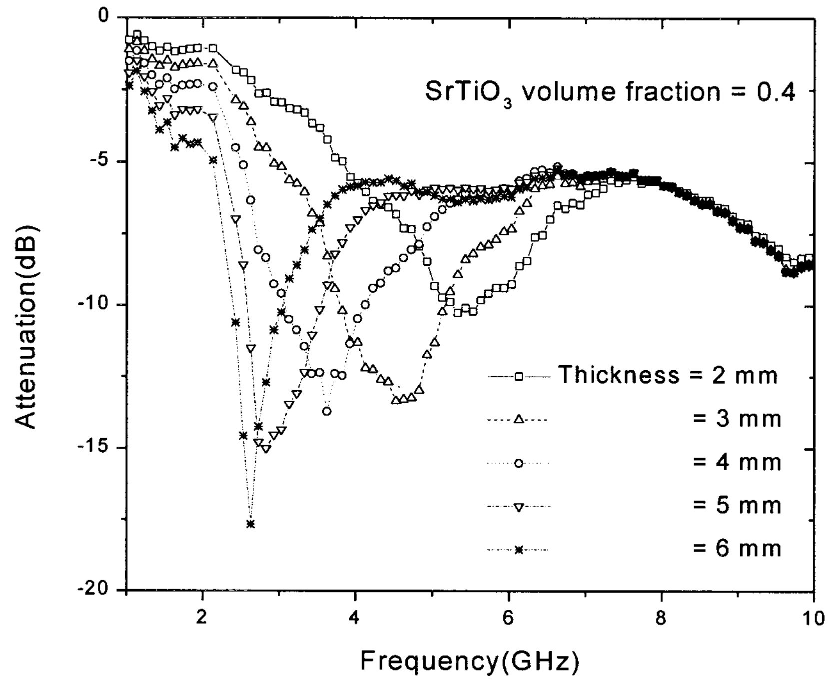
Figure 6(a) shows the attenuation behavior for the composites containing 0.4 volume fraction of $SrTiO_3$ having various thickness. The center frequency having maximum attenuation moved toward the low-frequency range, and the peak width was decreased with increasing the thickness of the composite. Considering the attenuation characteristics above the resonance frequency of composite, it is found that the attenuation behaviors of composite maintain the constant values according to the change of the thickness. But, as shown in Figure 6(b), which represents the attenuation behavior for the composite containing 0.6 volume fraction of $SrTiO_3$, this is no longer true, and it depends on the thickness of composite.

Conclusively, the electromagnetic wave absorbing characteristics of composites are controlled by changing the thickness and the composition of composites.

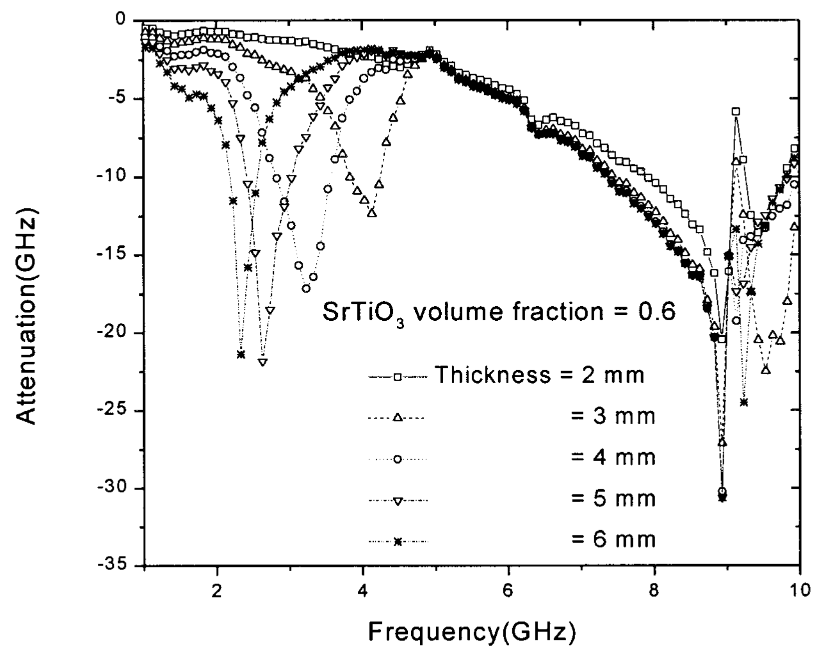
CONCLUSIONS

1. The complex permittivity and permeability of $SrTiO_3$–epoxy composite are found to be increased as the volume fraction of $SrTiO_3$. The effective permittvity of the composite can be determined by general mixing rule, which is dependent upon permittivity and volume fraction.

   The resonance frequency of composite moved toward the low-frequency range with increasing the volume fraction of $SrTiO_3$. The resonance frequency of composites was found to show good agreement with the theoretical values calculated by the eq. (7) proposed in this article. Especially, the frequency dispersion behavior of complex permittivity of composite can be predicted when the effective permittivity,



(a)



(b)

Figure 6 (a) The attenuation behaviors of composites for various thickness at 0.4 volume fraction of $SrTiO_3$.

the resonance frequency, and the volume fraction of $SrTiO_3$ are known.

2. The electromagnetic wave-absorbing characteristics are determined by the frequency dispersion behavior of complex permittivity and permeability and affected by the composition of the composite. The electromagnetic wave absorbing behavior showed

that the center frequency of attenuation curve was shifted to a lower frequency band with increasing the amount of $SrTiO_3$ and the thickness of composite.

REFERENCES

1. Hombach, V.; Meier, K.; Burkhardt, M.; Kühn, E.; Kuster, N. IEEE Trans Microwave Theory Technol 1996, 44, 1865.
2. Kim, T. H.; Park, J. R.; Lee, S. J.; Sung, H. K.; Lee, S. S.; Choy, T. G. ETRI J 1996, 18, 15.
3. Choi, H. D.; Kim, W. S.; Joon, I. S.; Yoon, H. G.; Moon, T. H. Polymer (Korea) 1997, 21, 112.
4. Naito, Y.; Yin, J.; Mizumoto, T. Inst Elec Commun Eng Jpn 1987, J70-C, 1141.
5. Kobayashi, T.; Nojima, T.; Yamada, K ; Uebayashi, S. IEEE Trans Microwave Theory Techniques 1993, 41, 136.
6. Han, K. C.; Kim, W. S.; Kim, K. Y. IEEE Trans Magn 1995, 31, 2285.
7. Choi, H. D.; Moon, K. S.; Joon, I. S.; Kim, W. S.; Moon, T. J. J Appl Polym Sci 1997, 66, 477.
8. Naito, Y.; Suetake, K. IEEE Trans Microwave Theory Technol 1971, MTT-19, 65.
9. Nicolson, A. M.; Ross, G. F. IEEE Trans Instrum Meas 1970, IM-19, 377.
10. Wagner, K. W. Arch Electrochem 1914, 2, 371.
11. Nelson, S.; Kraszewski, A.; You, T. J Micropower Electro Energy 1991, 26, 45.
12. Lichtenecker, K.Phys Z 1908, 10, 1005.
13. Birks, J. B. Proc Phys Soc 1951, 25, 81.
14. Han, K. C. Korea University Ph.D. Thesis, 1994.
15. Snoek, J. L. Physica, 1948, 14, 207.
16. Siwiak, K. Radiowave Propagation and Antennas for Personal Communication, London, 1995, p. 11.
17. Choi, H. D.; Cho, K. Y.; Han, S.; Yoon, H. G.; Moon, T. J. J Appl Polym Sci 1998, 67, 363.