JOURNAL OF MATERIALS SCIENCE 30 (1995) 3567–3570

Dispersion characteristics of the complex permeability–permittivity of Ni–Zn ferrite–epoxy composites

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The effects of volume fraction and particle size of ferrite on the electric and magnetic properties of epoxy composites containing Ni–Zn ferrite were investigated. The composites were prepared by the cement mixed method and shaped as coaxial, toroidal and disc types. The complex permeability and permittivity were measured using an impedance–gain phase analyser (HP4194A) and a network analyser (HP8753C) in the frequency range 1 MHz–5 GHz.

The complex permeability of the composites was found to increase as the ferrite content increased, and was characteristic of the frequency dispersion. A model to describe the frequency dispersion characteristics of the composite, which was a function of the ferrite content, is proposed here. The complex permittivity of the composite was found to be dependent mainly on the volume fraction of the ferrite and was relatively independent of frequency and particle size of the ferrite.

1. Introduction

Electric and magnetic properties of polymers, well-known for their insulating properties, may be improved by adding various functional fillers. Most of the functional fillers in such composite materials require at least 50% in volume of the polymer matrix in order to produce such desired properties. The use of ferrites is common in applications such as tapes for magnetic recorders and electromagnetic wave absorbers [1, 2]. Polymer–ferrite composites have been a subject of recent extensive research [3–5]. Electric and magnetic properties of such composites depend on the size, shape and amount of added filler in general [6]. When polymer–ferrite composites particularly are used as electromagnetic wave absorbers and EMI shielding materials, it is very important to explain the variation of permittivity and permeability in the measured frequency ranges, i.e. the frequency dispersion characteristics.

In this paper, epoxy–Ni–Zn ferrite composites were used. The effects of the volume fraction and particle size of ferrite on the frequency dispersion characteristics of the complex permittivity and permeability are studied.

Johnson and Visser [7] studied the dependency of complex permeability on grain size and grain boundary thickness, providing a model of polycrystalline ferrite grains with an intrinsic complex permeability, μ_i, surrounded by non-magnetic grain boundaries. A modified Johnson's model is proposed in this paper, i.e. ferrite surrounded by polymers of non-magnetic material. The frequency dispersion characteristics of the composite are measured and compared with those of the results obtained from the modified Johnson's model.

2. Experimental procedure

The samples used in this experiment were epoxy–ferrite composite materials and the polymer matrix was Cresol novolac epoxy resin (ESCN 195-6, Sumitomo Chemical Co., Japan). As shown in Table I, Fe_2O_3, NiO and ZnO (Aldrich, 99%) were weighed, then ballmilled with ethyl alcohol for 24 h, and dried in an oven for 10 h. The dried sample was sintered in a box furnace at 900 °C for 2 h and the ferrite powder was obtained by remilling.

The obtained ferrite powder was sieved, and particle sizes of 88–105, 74–88, 62–74, 53–62, 44–53 and less than 45 μm were obtained, respectively. To increase the adhesion between the filler and the polymer matrix, the ferrite surface was treated by adding 1 wt% aqueous solution of silane coupling agent, A-187 (r-glycinoxypropyltrimethoxysilane, Union Carbide Inc.). Some 35, 40, 50 and 60 vol% of thus treated ferrite powder were added to the composite. The epoxy resin was previously hardened with Tamanol 758 (phenol novolac resin, Arakawa Co.). Finally, the composite was mixed using the cement mixed method [8]. After compression moulding into disc, toroidal

TABLE I Experimental composition of ferrite

Raw material	Fe_2O_3	ZnO	NiO
Wt %	68.2	13.03	18.77

and coaxial types, samples were cured at 180 °C for 5 h.

The apparent density, ρ_a and porosity, $\%P$, of the specimen were measured by Archimedes' method.

Enamel wire (diameter = 0.35 mm) was uniformly wrapped around the toroidal type specimen 20 times, and the complex permeability was calculated measuring inductance L_s, and $Q(=\mu_r'/\mu_r'')$ in the frequency range 1–40 MHz using an impedence–gain phase analyser (HP4194A). The complex permittivity and permeability of the coaxial type specimen were calculated by measuring S_{11} and S_{21} using a coaxial air line (HP85051-60007) and a network analyser (HP8753C) in the frequency range 10 MHz–5 GHz [9].

3. Results and discussion

Prior to studying the electric and magnetic properties of the epoxy–ferrite composite material, the reliability of the measuring method of Kim *et al.* [10] was established.

Fig. 1 shows the change of the complex permittivity of the composite material when 60, 50, 40 and 35 vol % of ferrite, with a particle size of 44–53 μm was added. As the volume fraction of ferrite increased, the real part of the permittivity increased, and complex permittivity obtained regardless of the frequency up to 3 GHz. However, as the frequency increased above 3 GHz, the real and imaginary parts of the permittivity increased. This may be due to a possible polarization transition in the composite material.

The general rule of mixture can be applied to the permittivity of the epoxy–ferrite composite as follows

$$\varepsilon_c = V_f\varepsilon_f + V_m\varepsilon_m(V_f + V_m = 1) \quad (1)$$

where ε_c, ε_f and ε_m represent the permittivity of composite, ferrite, and polymer and V_f, V_m represent the volume fraction of ferrite and polymer, respectively. If some pores are formed during sample preparation, the permittivity of the composite will change and Equation 1 must be modified as follows

$$\varepsilon_{cg} = P + (1 - P) \times (V_f\varepsilon_f + V_m\varepsilon_m) \quad (2)$$

where ε_{cg} is the permittivity of the composite material with pores and P is the porosity.

Fig. 2 shows the permittivity of the composite with 44–53 μm ferrite, as well as the result calculated by Equation 2. It is clear from the figure that the experimental values are almost identical to the calculated values.

Fig. 3 represents the relationship between the complex permeability and frequency as a function of ferrite particle size of the composite containing 60 vol %

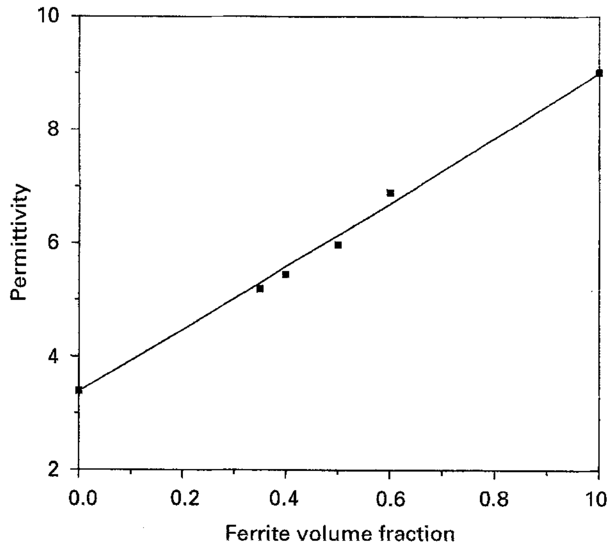

Figure 2 Comparison of experimental (■) with the calculated (—) values for permittivity as a function of ferrite volume fraction at a fixed particle size distribution of 44–53 μm.

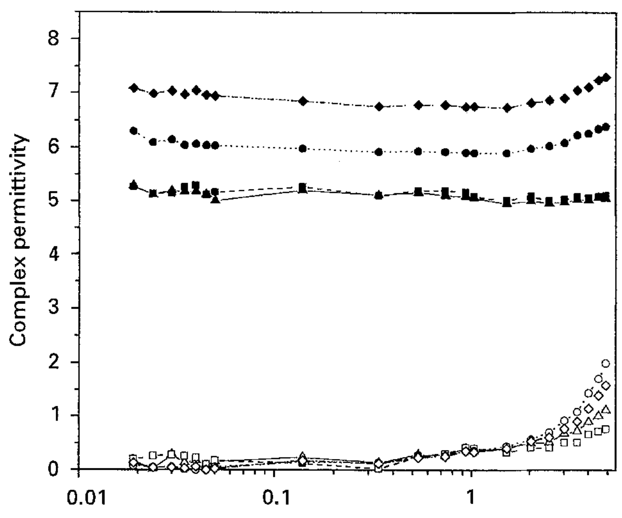

Figure 1 Complex permittivity of the composite for various ferrite volume fractions at a fixed particle size distribution of 44–53 μm. For real ferrite volume fractions equal to: (▲) 0.35, (■) 0.4, (●) 0.5, (◆) 0.6. For imaginary ferrite volume fractions of: (△) 0.35, (□) 0.4, (○) 0.5, and (◇) 0.6.

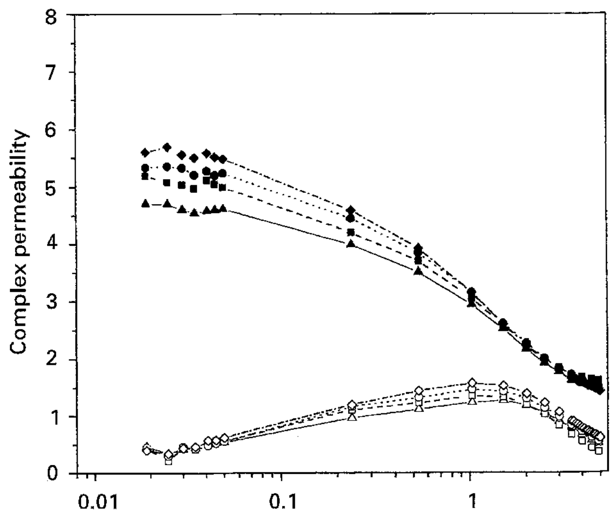

Figure 3 Effect of particle size on the complex permeability of the composite at a (ferrite volume fraction of 0.6). Particle size distribution: (▲) real, (△) imaginary, 88–105 μm; (■) real, (□) imaginary, 62–74 μm; (●) real, (○) imaginary, 53–62 μm; and (◆) real, (△) imaginary, 44–53 μm.

ferrite. In the case of sintered ferrite, it is reported that the permeability value increased as the grain size increased [11]. The present experiment, however, shows that the complex permeability becomes smaller as the particle size becomes larger in the measured frequency range.

Fig. 4 shows porosity (%) of the specimen containing 60 vol % ferrite as a function of the particle size. As the particle size increases, the porosity becomes larger. Therefore, in an epoxy–ferrite composite material, the major effect on the magnetic property can be deduced as being caused by the porosity rather than the particle size.

Fig. 5 shows the frequency dispersion characteristics of the complex permeability of the composite with a particle size of 44–53 μm as a function of ferrite volume fraction. The real part of the permeability increases within the measured frequency range as the ferrite volume fraction increases, and the maximum value of the imaginary part tends to increase also.

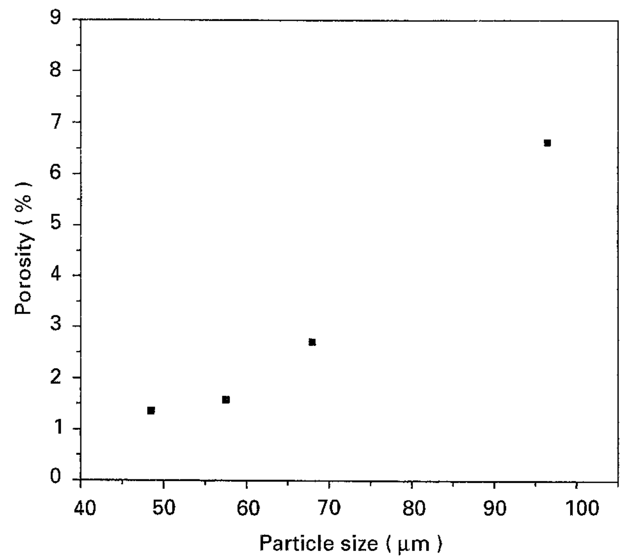

Figure 4 Relationship between porosity (%) and particle size for the composite (ferrite volume fraction = 0.6).

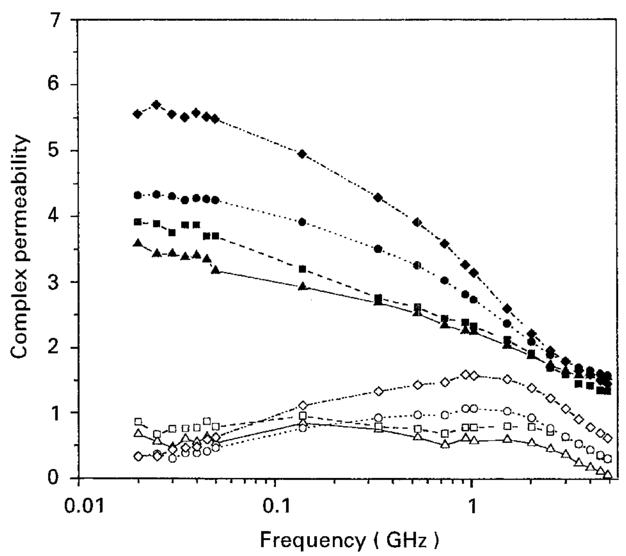

Figure 5 Complex permeability spectra of the composite for various ferrite volume fractions (f/e) at a fixed particle size distribution of 44–53 μm. For: (▲) real, (△) imaginary, f/e = 0.35–0.65 (■) real, (□) imaginary f/e = 0.4–0.6; (●) real, (○) imaginary f/e = 0.5–0.5; (◆) real, (◇) imaginary f/e = 0.6–0.4.

In the case of the complex permeability, the general rule of mixture cannot be applied due to its frequency dispersion. It is assumed that the non-magnetic material polymer circumscribes to the magnetic ferrite material; based on this assumption, Johnson's model can be applied to the composite, as follows

$$\mu_e = \frac{\mu_i(D + \delta)}{\mu_i\delta + D} = \frac{\mu_i(1 + X)}{\mu_i X + 1} \quad (3)$$

where μ_i represents intrinsic permeability, D is the grain size, δ is the grain boundary thickness, μ_e is the measured permeability and $X = \delta/D$. The relationship between the volume fraction of ferrite, V_f, and X can be expressed as follows

$$V_f = \frac{D^3}{(D + \delta)^3} = \frac{1}{(1 + X)^3} \quad (4)$$

Since the pore is non-magnetic material in nature, a modification has to be made on the basis, by adding the porosity to the volume fraction of epoxy. The permeability of composite material, μ_e, obtained by Equation 3 in 50 MHz is shown in Fig. 6, comparing the experimental values. It is found that the solid line which represents the calculated or theoretical values is well matched with the experimental values.

When the frequency dispersion characteristics of complex permeability are represented by simple relaxation phenomena [12], it can be expressed as follows

$$\mu_e' = \frac{\mu_e}{1 + f^2(\mu_e/\mu_i \times f_r)^2} \quad (5)$$

$$\mu_e'' = \frac{\mu_e \times f(\mu_e/\mu_i \times f_r)}{1 + f^2(\mu_e/\mu_i \times f_r)^2}$$

where f_r is the resonance frequency of the sintered ferrite and $\mu_i \times f_r/\mu_e$ is the resonance frequency of the polymer composite f_0.

The resonance frequency values obtained by experiment and by calculation using Equation 5 are shown in Fig. 7. As the volume fraction of ferrite increased, μ_e

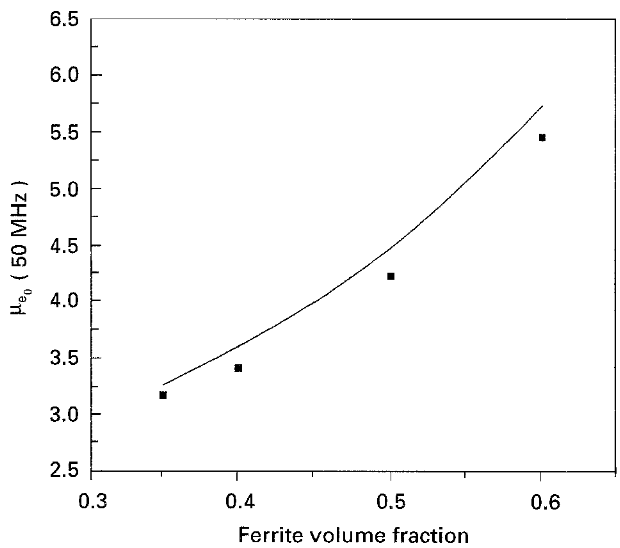

Figure 6 Comparison of experimental (■) with the calculated (—) values for μ_{e0}(50 MHz) as a function of ferrite volume fraction for a fixed particle size distribution of (44–53 μm).

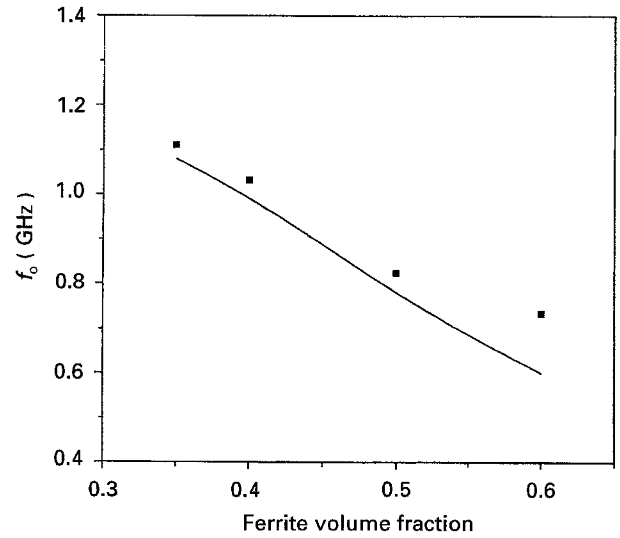

Figure 7 Comparison of experimental (■) with calculated (—) values for resonance frequency at a fixed particle size distribution of 44–53 μm.

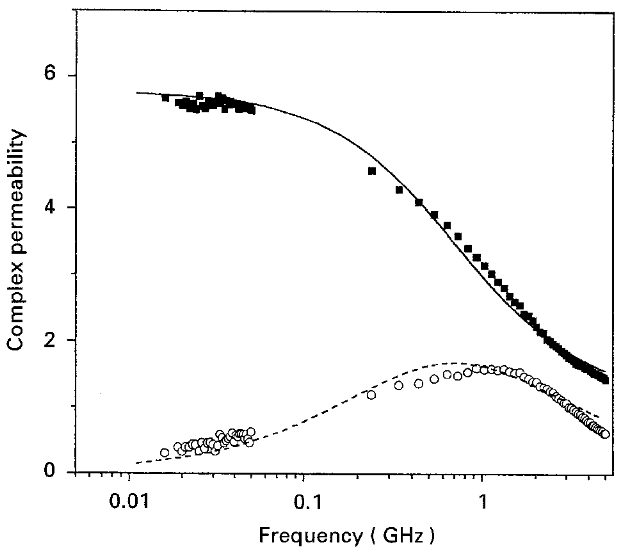

Figure 8 Comparision of experimental [(■) real, (O) imaginary] values with the calculated [(—) real, (– – –) imaginary] values for frequency spectra of the complex permeability of the composite at a ferrite volume fraction of 0.6 and a fixed particle size distribution of 44–53 μm.

increased and f_0 decreased. The results enable one to use the Snoek limit [13] to composite material

$$\mu_e \times f_0 \;=\; \mu_i \times f_r \cong 3.5$$

Fig. 8 shows the experimental values of the frequency dispersion characteristics of the complex permeability for the composite materials with 60 vol % ferrite in comparison with that of the calculated values obtained using Equation 5. Again, the coincidence of measured and calculated values is clear from the figure.

Therefore, the frequency dispersion characteristics of the complex permeability of the composite materials with different amounts of ferrite can be estimated by Equations 3, 4, and 5, if the intrinsic permeability of magnetic material and the resonance frequency are known.

4. Conclusions

1. The complex permittivity of epoxy–ferrite composite is found to be increased as the volume fraction of ferrite increased, and decreased as the porosity increased. The permittivity of the composite can be determined by the general mixing rule which is dependent upon permittivities and volume fraction, because permittivity is nearly constant regardless of the frequency change.

2. The complex permeability of the epoxy–ferrite composite increased as the volume fraction of ferrite increased and depended on the porosity rather than the particle size of the ferrite. Especially, the frequency dispersion characteristics of complex permeability of composite can be predicted when the initial permeability, the resonance frequency and the volume fraction of ferrite are known.

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Received 3 November
and accepted 25 November 1994