Dielectric Mixing Laws in Ceramic/polymer Composites

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ABSTRACT

Dielectric mixing laws were examined for the composites consisting of ferroelectric ceramics particles dispersed in the polymer matrix. The rate of increase in the dielectric permittivity with increasing ceramics content was shown to be consistent with classical Bruggeman predictions. The use of semiconductive polymer matrix generates dielectric as well as conductive relaxations associated with interfacial polarization. Analysis of the observed electrical spectra led to estimates of the dielectric permittivity of the ferroelectric ceramics particles. Discussion will be given with respect to the size effect on the dielectric response of the ferroelectric fine particles.

INTRODUCTION

When polymeric materials serve for practical uses, they are commonly mixed with other materials to achieve desired performance. Dielectric and conductive properties can be controlled over a broad range by inorganic inclusions. An introduction of ferroelectric ceramics power into a polymer matrix imparts piezoelectric and pyroelectric activities [1-3]. In this paper, we examine the composite consisting of barium titanate ($BaTiO_3$) particles and lithium perchlorate ($LiClO_4$)-doped polyethylene oxide (PEO) matrix. PEO and related polyethers have attracted great attention during the last two decades as solid-state electrolytes [4,5]. When a variety of metal-salts are added, they exhibit relatively high dc conductivity because dissociated ions gain mobility in accord with the segmental motion of polyether chains. $BaTiO_3$ is a typical ferroelectric having a high dielectric permittivity as well as large spontaneous polarization. Their composites show both dielectric and conductive characteristics and are expected to provide useful data for testing the mixing laws proposed earlier [6].

EXPERIMENTAL

The composite samples used in this investigation were prepared by mixing $BaTiO_3$ powders 3µm, 1.4µm, 0.7µm in diameter (Aldrich, milled) and 0.5µm, 0.3µm, 0.1µm in diameter (Sakai Chemical Ind. Co.Ltd., hydrothermally produced) into low molecular weight liquid PEO (M=400, Aldrich) in that 0.1mol% $LiClO_4$ had been added. The maximum concentration of $BaTiO_3$ was 40% in volume. The samples thus prepared were sandwiched between 10mmϕ circular stainless steel electrodes using fused silica fiber spacer 125µm in diameter and were placed in a vacuum dielectric cell. Dielectric measurements were made over a broad frequency range (10mHz – 13.5GHz) to obtaine the results in terms of either the complex permittivity or the complex conductivity. We also performed wide-angle X-rays measurements in order to investigate the fine structures of $BaTiO_3$ powder.

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Results and Discussion

Figure 1 shows the double logarithmic plots of the real components of the complex permittivity against frequency f for Li-PEO composites with 3μm diameter $BaTiO_3$ at 20°C. It is seen that e' shows a three-step increase with decreasing f. The first increase near 1GHz is attributed to the segmental-mode relaxation of PEO molecules, the second near 10kHz to the interfacial polarization due to ions accumulated at the $BaTiO_3$-PEO interface and the third to the electrode polarization. The value of e' increases with increasing $BaTiO_3$ content above 1kHz and vice versa below 1kHz.

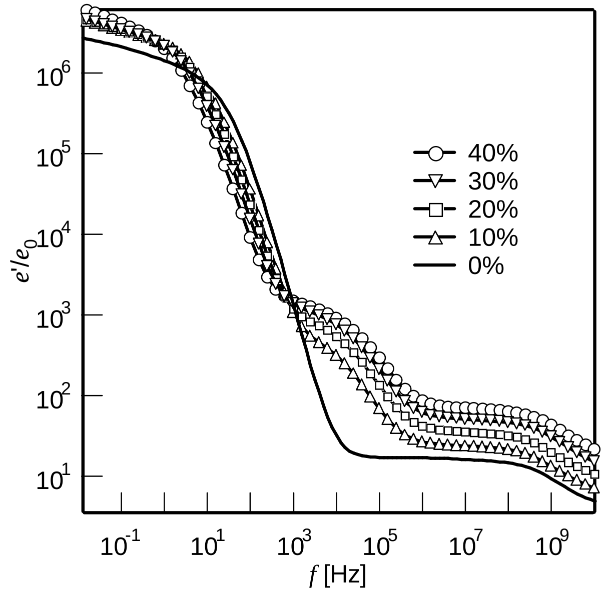

Fig.1 Dielectric spectra of $BaTiO_3$/Li-PEO composites with f=0, 0.1, 0.2, 0.3 and 0.4 at 20°C.

For quantitative analysis, we fitted the observed spectra to the empirical fanction

$$e = e_{\infty} + \frac{De}{\left(1+(iwt)^{b}\right)^{a}} + De_{\mathrm{if}}\left(1-\frac{1}{1+(iwt_{\mathrm{if}})^{g_{\mathrm{if}}}}\right) + \frac{s_{\mathrm{el}}}{iw}\left(1-\frac{1}{1+(iwt_{\mathrm{el}})^{g_{\mathrm{el}}}}\right) \qquad (1)$$

where e_8 is the instantaneous permittivity, De is the strength of segmental-mode relaxation, and De_{if} is the strength of interfacial polarization. An excellent agreement between observed and fitted spectra was confirmed by Fig.2.

The composite sample used here can be regarded as a two phase system where the spherical inclusions ($BaTiO_3$) are dispersed in a continuous matrix (Li-PEO). We then tried to reproduce the observed spectra using several mixing laws. The best reproduction was obtained by the use of a Bruggeman equation,

$$1-f = \frac{e_2 - e}{e_2 - e_1}\left(\frac{e_1}{e}\right)^{\frac{1}{3}} \quad , \qquad (2)$$

where e_1 is the permittivity of the matrix and e_2 is that of inclusions. In our composite sample, e_1 is the permittivity of pure Li-PEO, which is essentially a complex quantity containing dc conductivity

$$e_1 = e_{\infty} + \frac{De}{\left(1+(iwt)^{b}\right)^{a}} + \frac{s_1}{iw} \quad . \qquad (3)$$

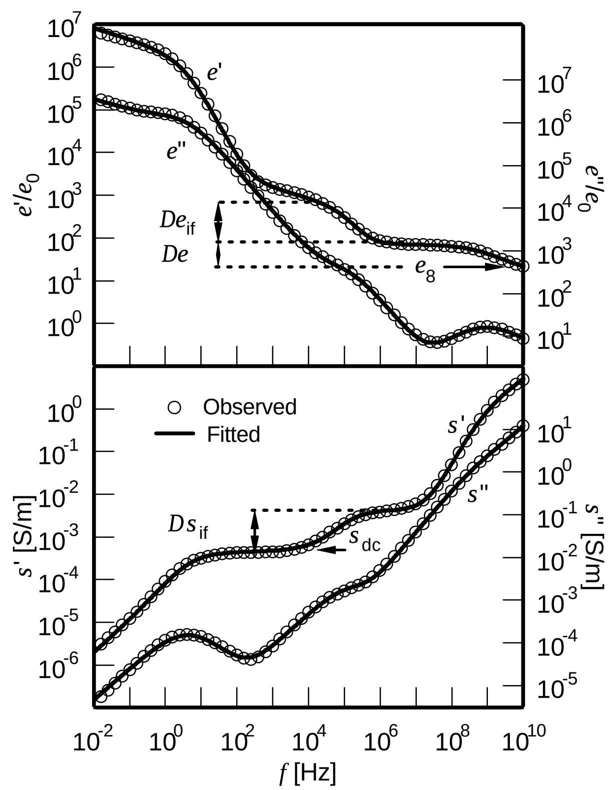

Fig.2 Observed and fitted dielectric and conductive spectra of $BaTiO_3$/Li-PEO composites with f=0.4 at 20°C.

We determined the parameters comprising the above equation by the use of experimental date shown in Fig.1 (f =0). The permittivity of $BaTiO_3$ powder, e_2, is expected to be weakly dependent on frequency, but its value is unknown. We determined the value of e_2 so that eq. (2) best-fits the observed spectra.

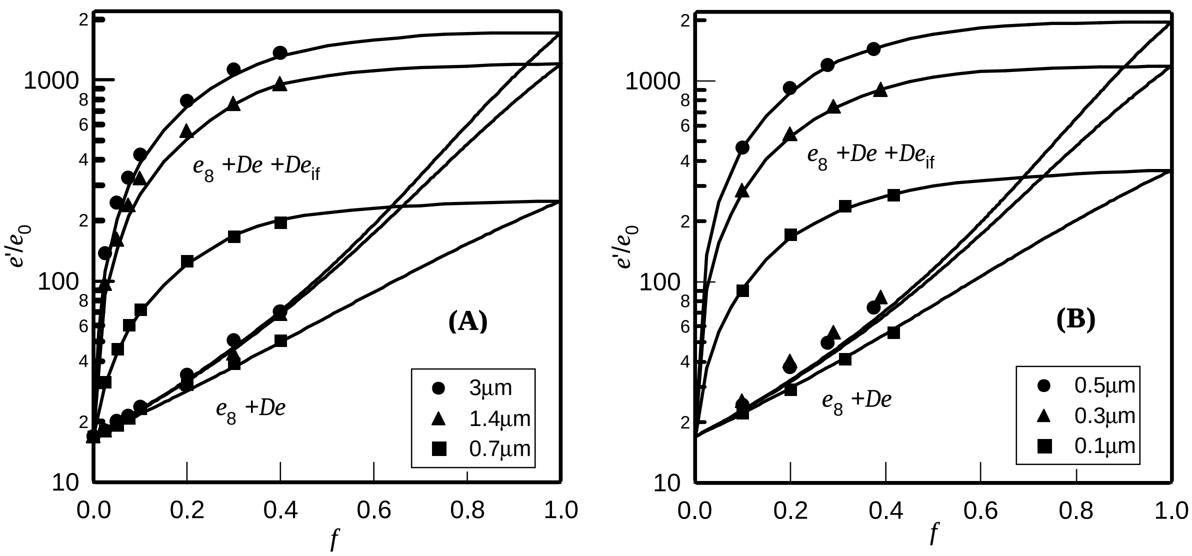

Fig.3 Dependence of observed and predicted permittivities of the composites on the volume fraction of $BaTiO_3$ powder produced by mill method (A) and hydrothermal synthesis (B.)

Figure 3 shows the dependence of observed and predicted permittivities on the volume fraction of $BaTiO_3$ f . We chose two permittivities, $e_8 + De$ containing contribution f segmental-mode relaxation and $e_8 + De + De_{if}$ with an additional contribution from the interfacial polarization. There permittivities reach a unique value at f =1 which equals e_2. It is found that e_2 strongly depends upon the particle size. It also depends upon the method of powder formation. The hydrothermally produced $BaTiO_3$ powder has much larger e_2 than the milled one even though the particle size is equal.

We made X-ray measurements for these $BaTiO_3$ samples and fond that the milled sample exhibits much broader diffraction pattern compared to the hydrothermally produced one. More importantly, the ratio of a and c axis of the tetragonal $BaTiO_3$ depends upon the particle size as well as the production method. We then plotted e_2 against c/a and found a liner relationship as shown in Fig.4. These results indicate that the milled $BaTiO_3$ powder consists of small domains.

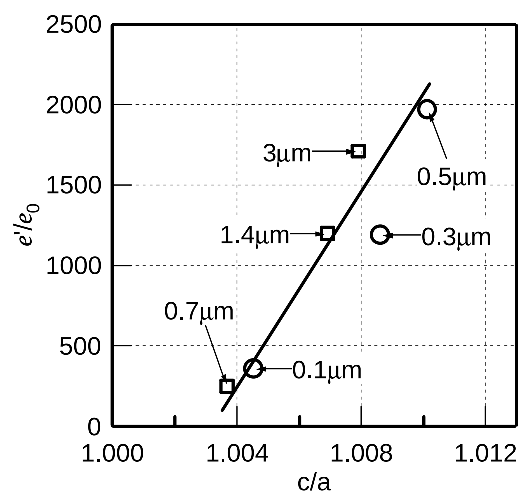

Fig.4 Linear relationship between the dielectric constant of $BaTiO_3$ powder and axis ratio c/a. (? ; milled, ? ; hydrothermal)

In the composite system consisting of ferroelectric ceramics powder dispersed in a polymer matrix, the former has much larger permittivity than the latter. Thus the effective permittivity of composite is primarily governed by that of the polymer phase and weakly depends upon that of the ceramic phase unless f is extremely high. In this investigation, we used an ionically conductive polymer and found that the effective permittivity associated with the interfacial polarization accurately predicts the permittivity of ferroelectric ceramics powder. This finding would lead to a proposed for a useful technique that allows an accurate determination of the permittivity of ferroelectric nano-particles.

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