Dielectric Mixing Laws in Ceramic/polymer Composites

K. Yasuda*, Y. Sato, Y. Takahashi and T. Furukawa,
Faculty of Science, Tokyo University of Science, Shinjuku, 162-8601, Tokyo, Japan

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 obtain 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.
**Report Documentation Page**

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE
   00 JUN 2003

2. REPORT TYPE
   N/A

3. DATES COVERED
   -

4. TITLE AND SUBTITLE
   Dielectric Mixing Laws in Ceramic/polymer Composites

5a. CONTRACT NUMBER
   -

5b. GRANT NUMBER
   -

5c. PROGRAM ELEMENT NUMBER
   -

5d. PROJECT NUMBER
   -

5e. TASK NUMBER
   -

5f. WORK UNIT NUMBER
   -

6. AUTHOR(S)
   -

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
   Tokyo University of Science, Shinjuku, 162-8601, Tokyo, Japan

8. PERFORMING ORGANIZATION REPORT NUMBER
   -

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
   -

10. SPONSOR/MONITOR’S ACRONYM(S)
    -

11. SPONSOR/MONITOR’S REPORT NUMBER(S)
    -

12. DISTRIBUTION/AVAILABILITY STATEMENT
    Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
    See also ADM001697, ARO-44924.1-EG-CF, International Conference on Intelligent Materials (5th)
    (Smart Systems & Nanotechnology), The original document contains color images.

14. ABSTRACT
    -

15. SUBJECT TERMS
    -

16. SECURITY CLASSIFICATION OF:
    a. REPORT
       unclassified
    b. ABSTRACT
       unclassified
    c. THIS PAGE
       unclassified

17. LIMITATION OF ABSTRACT
    UU

18. NUMBER OF PAGES
    4

19a. NAME OF RESPONSIBLE PERSON
    -

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18
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 $\varepsilon'$ 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 $\varepsilon'$ increases with increasing BaTiO$_3$ content above 1kHz and vice versa below 1kHz.

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

$$\varepsilon = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega \tau_s)^\beta} + \Delta \varepsilon_d \left( 1 - \frac{1}{1 + (i\omega \tau_{\varepsilon_d})^{\beta_d}} \right) + \frac{\sigma_{dc}}{i\omega} \left( 1 - \frac{1}{1 + (i\omega \tau_{\varepsilon_{\sigma_{dc}}})^{\beta_{\sigma_{dc}}}} \right),$$

(1)

where $\varepsilon_\infty$ is the instantaneous permittivity, $\Delta \varepsilon$ is the strength of segmental-mode relaxation, and $\Delta \varepsilon_d$ 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,

$$1 - \phi = \frac{\varepsilon_1 - \varepsilon}{\varepsilon_2 - \varepsilon} \left( \frac{\varepsilon}{\varepsilon_0} \right)^\gamma,$$

(2)

where $\varepsilon_1$ is the permittivity of the matrix and $\varepsilon_2$ is that of inclusions. In our composite sample, $\varepsilon_1$ is the permittivity of pure Li-PEO, which is essentially a complex quantity containing dc conductivity

$$\varepsilon_1 = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega \tau_s)^\beta} + \frac{\sigma_{dc}}{i\omega}.$$ 

(3)

Fig.1 Dielectric spectra of BaTiO$_3$/Li-PEO composites with $\phi=0, 0.1, 0.2, 0.3$ and 0.4 at 20°C.

Fig.2 Observed and fitted dielectric and conductive spectra of BaTiO$_3$/Li-PEO composites with $\phi=0.4$ at 20°C.
We determined the parameters comprising the above equation by the use of experimental data shown in Fig.1 (\(\phi = 0\)). The permittivity of BaTiO\(_3\) powder, \(\varepsilon_2\), is expected to be weakly dependent on frequency, but its value is unknown. We determined the value of \(\varepsilon_2\) so that eq. (2) best-fits the observed spectra.

Figure 3 shows the dependence of observed and predicted permittivities on the volume fraction of BaTiO\(_3\) powder produced by mill method (A) and hydrothermal synthesis (B.)

We made X-ray measurements for these BaTiO\(_3\) samples and found 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 \(\varepsilon_2\) 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.

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 \(\phi\) is extremely high. In this investigation, we used...
an ioniically 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.

REFERENCES


