

Broadband Dielectric Relaxation of Polymer Composite Films

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ABSTRACT

The broadband dielectric relaxation of a BaTiO₃-polymer composite film was studied. The complex dielectric constant data from 10⁻⁴ Hz to 10¹⁰ Hz reveals the existence of relaxation process at frequency of 10 MHz in the polymer composite. On the basis of Cole-Cole analysis, the relaxation time of the system is of order of 10⁻⁸ s. The understanding of the broad dispersion in dielectric behavior of polymer composite materials is needed to support next generation electronic devices used in wireless communication and related applications.

INTRODUCTION

High dielectric constant materials are needed for electronic devices used in wireless communication and related applications. This stimulates revisit of the dielectric properties of the polymer and inorganic materials with high dielectric constant. Usually studies on the dielectric properties of materials were done at a single frequency or a limit of frequency range.¹ Considering heterogeneity of the composite materials, a broadband dielectric measurement should be able to probe the influence of various factors on effective dielectric constant of the polymer composites.

To simplify the complicated materials problem for general composite system, we have selected a model two-component polymer composite system. The system used a rigid crosslinked polymer as the host matrix and barium titanate (BaTiO₃) powder as ferroelectric filler. We found that this model polymer composite is not only a well-defined two-phase system but also has the dielectric constant at the level suitable for practical applications. In this paper we report the results of the broadband dielectric relaxation measurement of this model polymer composite.

EXPERIMENTAL

Materials

The polymer composite film composed of barium titanate (BaTiO₃) dispersed in trimethylolpropane triacrylate (TMPTA) polymer was prepared from the corresponding TMPTA monomer and the ceramic powder. The barium titanate was purchased from Aldrich Chemical

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Company, while TMPTA monomer was obtained from Monomer Polymer & Dajac Labs.² Both components were used as received.

According to the manufacturer certificate of analysis, BaTiO₃ was more than 99.9 % pure with average particle size of 1 μm (maximum size less than 2 μm). The dielectric constant of this material, estimated in separate studies, was 1070 at 1 kHz. TMPTA monomer structure is shown in Figure 1. This monomer formed a

highly crosslinked polymer network upon polymerization. The BaTiO₃-monomer mixture was prepared and cured photochemically into thin films under UV radiation from a mercury lamp. 2,2-Dimethoxy-2-phenylacetophenone (from Aldrich) was used as a photoinitiator. The resulting films were typically 100 μm to 120 μm thick with a thickness uniformity better than 1 %. From density measurement we determined that the composite was a two-phase system containing no porosity.

The polymer composite films used in this experiment contained 30 % of BaTiO₃ particles by volume dispersed at random in the TMPTA polymer matrix. At this concentration, the composite was in 0-3 type of connectivity, which means each particle of the BaTiO₃ powder was isolated in the polymer network. Circular aluminum electrodes of 1.27 cm in diameter were evaporated onto both sides of the film to form a parallel plate capacitor for dielectric measurements within low and intermediate frequency range. For high frequency measurements, above 10 MHz, specimens with 3 mm circular electrodes were used.

Dielectric Measurements

Dielectric measurements were carried out in the frequency range from 10⁻⁴ Hz to 10¹⁰ Hz using several instruments: HP8720A, HP4191A, HP4194A, HP4274A, and Gamry Impedance Meter². Each instrument covered a limited range of frequency, but the ranges were overlapping. The data were collected at ambient temperature and converted to the complex dielectric constants. The data set from all the instruments were linked together into a broadband frequency spectrum. The combined standard uncertainties of these data were estimated to be at the level of 10 % of the measured values. The magnitude of offset adjustment of the dielectric data obtained from different instruments was less than 15%.

RESULTS AND DISCUSSION

Figure 2 shows the real part of the complex dielectric constant of the BaTiO₃-TMPTA composite studied. The dielectric constant of the composite is much higher than that of TMPTA polymer ($\epsilon' = 3.85$ at 1 kHz). The dielectric constant of the composite decreases as the frequency increases. At the frequencies below 1 Hz, slope of the plot of dielectric constant as a function of frequency becomes steeper than that at higher frequencies. This can be attributed to charging at the electrodes. At high frequency, the dielectric constant shows signs of a broad dispersion with the inflection point at about 10 MHz.

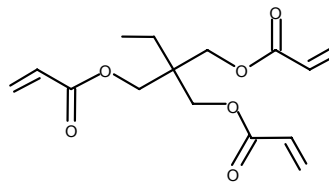


Figure 1 Structure of trimethylolpropane triacrylate monomer

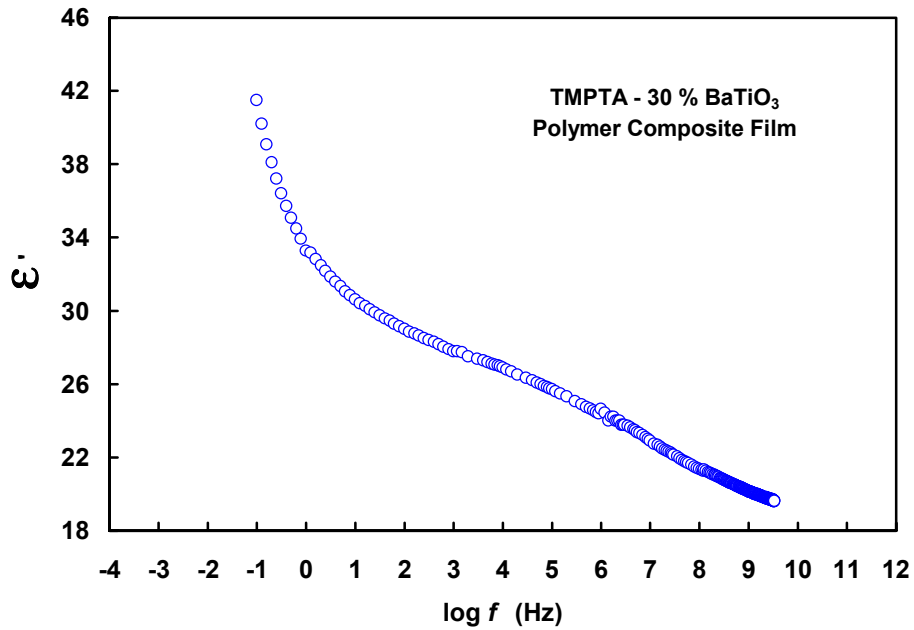


Figure 2. The dielectric constant of the polymer composite film of TMPTA-30 % BaTiO₃ as a function of frequency.

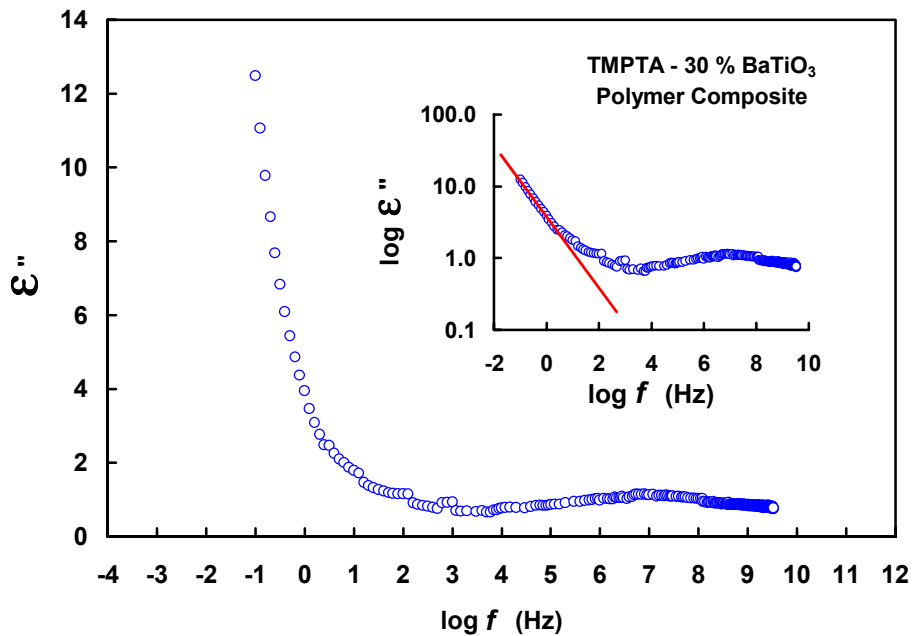


Figure 3 The imaginary part of the dielectric constant of the polymer composite film of TMPTA-30 % BaTiO₃ as a function of frequency.

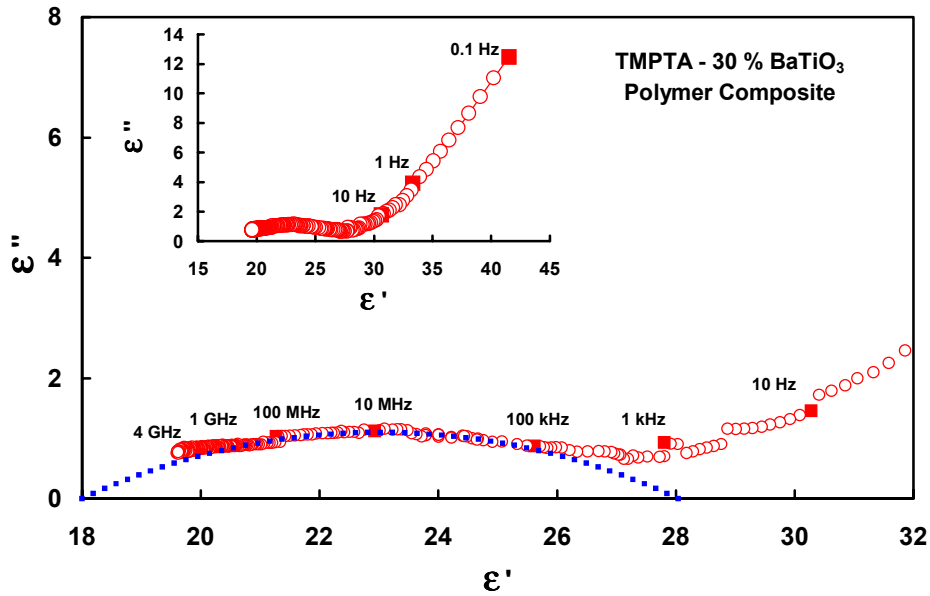


Figure 4. Cole-Cole plot of the polymer composite thin-film of TMPTA-30 % BaTiO₃.

Figure 3 shows the imaginary part (i.e. loss factor) of the dielectric constant of the composite film. The ϵ'' of the composite has a peak at 10 MHz. This is consistent with the behavior of the ϵ' shown in Figure 2. At low frequencies, the ϵ'' increases with lowering the frequency similarly as the ϵ' does. The frequency dependence of the ϵ'' within this range follows a slope of about $-1/2$ in a log-log plot (insert of Figure 3), which is due to the charging at electrodes.

It is convenient to analyze the dielectric relaxation processes on a complex plane. Figure 4 shows the Cole-Cole plot for the composite film. In this plot the measurement frequency becomes an implicit parameter. As the frequency increases, the data points move from right side to the left (Figure 4). The imaginary part of the complex dielectric constant reached a minimum at $\epsilon' = 27.5$ within the frequency region between 1 kHz and 10 kHz. With further increase of the frequency, the dielectric data form a highly depressed arc with the weak maximum ($\epsilon'' = 1.1$) at $\epsilon' = 23$. On the other hand, the onset of a large arc on the right hand side of the Cole-Cole plot (i.e., below 10 Hz) can be attributed to the response of electrodes. As seen in this plot the value of the dielectric constant strongly depends of the measurement frequency. This is the result of highly dispersive nature of the dielectric constant of the composite film. The dielectric constant value corresponding to the minimum point ($\epsilon' = 27.5 \pm 0.5$) can be taken as an estimate of the static dielectric constant of the polymer composite.

The arc shown in Figure 3 cannot be a simple Debye relaxation process. These results are in general agreement with earlier reports.^{3, 4} To analyze the data, we applied an empirical Cole-Cole equation (1) for the frequency dependence of the complex dielectric constant (ϵ^*).

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (i\omega\tau)^\beta} \quad (1)$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, ε_s is the static dielectric constant, ε_∞ is the electronic limit of the dielectric constant corresponding to infinite frequency, $\omega = 2\pi f$ where f is the frequency, τ is the relaxation time, and, β is a dispersion factor which is usually within the range $0 < \beta < 1$. The dashed line shown in Figure 3 represents a fit of the experimental data to the Cole-Cole equation for the data span $\hat{\varepsilon} = 10$ and $\varepsilon_\infty = 18$. The data follow an arc with a very large depression angle $\theta \approx 65^\circ$ below the ε' -axis. The corresponding relaxation time is of the order of 10^{-8} s. Considering the heterogeneous nature of the composite, it is possible to analyze the data with more than one arc.

Highly dispersive Cole-Cole curves are characteristic for polymeric materials. It is easy to visualize that in the composite the polymer is located between the BaTiO₃ particles and acts as a new "grain-boundary" for the ferroelectric "grains". Therefore, the arc in the Cole-Cole plot of the BaTiO₃-polymer composite contains information about the electrical behavior of the polymeric component. The dispersive nature of the polymer component dominates the behavior of the composite from low frequency to microwave frequencies.

CONCLUSION

The broadband dielectric relaxation of a well-defined two-phase BaTiO₃-polymer composite film has a very dispersive dielectric behavior. A dielectric relaxation process at the frequency of 10 MHz was observed in the dielectric data covering the range from 10^{-4} Hz to 10^{10} Hz. Using Cole-Cole analysis, the relaxation time of 10^{-8} s was found in the system studied. The broad dispersion in dielectric behavior of the polymer-ferroelectric ceramic composite indicates that polymers play an important role in the composites for high frequency microelectronics.

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