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Preparation and Characterization of Photopatternable $BaTiO_3$ /Polymer Composites

Roman Popielarz,[a] C.K. Chiang, Ryusuke Nozaki,[b] and Jan Obrzut
National Institute of Standards and Technology, Polymers Division,
100 Bureau Drive, Gaithersburg, MD 20899, U.S.A.

ABSTRACT

The dielectric properties of acrylic resin composites filled with $BaTiO_3$, have been evaluated over a broad frequency range. These materials were used as models to study the dielectric response in polymer composite films for de-coupling capacitance applications. A series of photocurable resin formulations were prepared and photocured into films of approximately 100 μm to 120 μm thick. Dielectric permittivity of the materials was investigated at frequencies from 100 Hz to 10 GHz and temperatures from –140 ^{o}C to +150 ^{o}C. The dielectric constant of the composites reached 35 at 1 GHz. A high frequency dielectric relaxation process was identified and related to the molecular structure of the polymer matrix.

INTRODUCTION

Electronic applications, such as fast computers or wireless communication devices, use a large number of rapidly switching circuits, which require de-coupling capacitance and low impedance power planes for proper operation at microwave frequencies. Polymer-based high dielectric constant films may be used to construct embedded de-coupling capacitors and low impedance power planes that can satisfy the functional requirements. The demand for low impedance power planes grows faster than for the clock speed. Low impedance circuits can be obtained by increasing capacitance and reducing parasitic inductance that is inherent to wire interconnections of discrete components [1]. To eliminate selectively switching noise at operational frequencies, the embedded dielectric materials should exhibit certain dielectric loss, which desirably could be controlled at the molecular level. According to the Semiconductor Industry Association Roadmap, the dielectric materials capable for providing the embedded capacitance density of the order of 20 nF/cm^2 and 72 nF/cm^2 will be required by the year 2006 for wireless communications and computer technologies respectively [2]. This is the area where ferroelectric ceramic/polymer composites could provide the desired performance. However, fundamental factors that control the dielectric response of polymer composites are poorly understood, especially at high, microwave frequencies.

We studied model photocurable polymer composites of relatively high dielectric constant to elucidate their behavior over a broad frequency range. The dielectric properties of these materials were evaluated in a film configuration at frequencies from 100 Hz to 10 GHz, the range relevant for practical applications.

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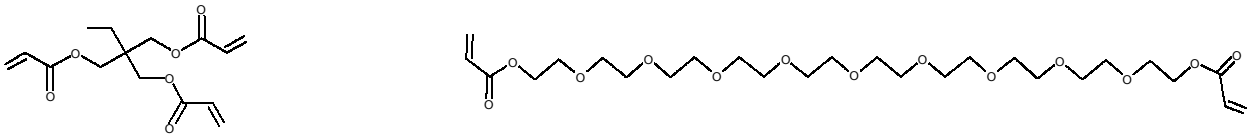
[a] on leave from: Department of Engineering and Chemical Technology, Cracow University of Technology, Krakow, Poland.
[b] on leave from: Division of Physics, Graduate School of Science, Hokkaido University, Sapporo, Japan.

EXPERIMENTAL DETAILS

Materials

We selected two photocrosslinkable monomers, trimethylolpropane triacrylate (TMPTA), and poly(ethylene glycol) diacrylate (PEGDA). The monomer structures are shown in Figure 1. Barium titanate powder ($BaTiO_3$) with an average particle size of about 1 μm was used as the ferroelectric filler. The TMPTA monomer was obtained from Monomer Polymer & Dajac Labs, while PEGDA monomer and $BaTiO_3$ were obtained from Aldrich, and used as received, [8].



Trimethylolpropane triacrylate (TMPTA) Poly(ethylene glycol) diacrylate (PEGDA)

Figure 1. Structure of the monomers.

About 10 g samples of $BaTiO_3$/monomer liquid mixtures were prepared by mixing appropriate proportions of $BaTiO_3$ powder with the monomers, thorough stirring of the mixture with a glass rod, sonication for 30 min in an ultrasound bath to deagglomerate the particles, and finally, stirring again before application. A few drops of each formulation were squeezed between microscope slides separated with two spacers, and cured photochemically into thin films under UV radiation from a mercury lamp. 2,2-Dimethoxy-2-phenylacetophenone was used as a photointiator. The resulting composite films did not adhere strongly to glass and were carefully separated from the slides by inserting a razor blade between the film and the glass surface. The films were typically 100 μm to 120 μm thick with the thickness spatial distribution of less than 1 % of the thickness values. For the dielectric measurements circular aluminum electrodes were coated on both sides of the film by vacuum evaporation through a mask.

Dielectric Measurements

Measurements of the dielectric permittivity in the low frequency range from 100 Hz to 10 MHz were carried out in accordance with the ASTM D150 standard test method [3]. To measure the dielectric permittivity at the frequencies 100 MHz to 10 GHz, we used a newly developed technique for high dielectric constant films [4]. The test specimen for high frequency measurements consisted of a planar thin film capacitor terminating coaxial waveguide. The complex permittivity of the dielectric in the frequency domain was obtained from appropriate analysis of the complex reflectivity coefficients. In order to improve accuracy at higher frequencies, a computational algorithm was developed to account for wave propagation in the specimen section. The combined standard uncertainties of these data were estimated to be at the level of 10 % of the measured values.

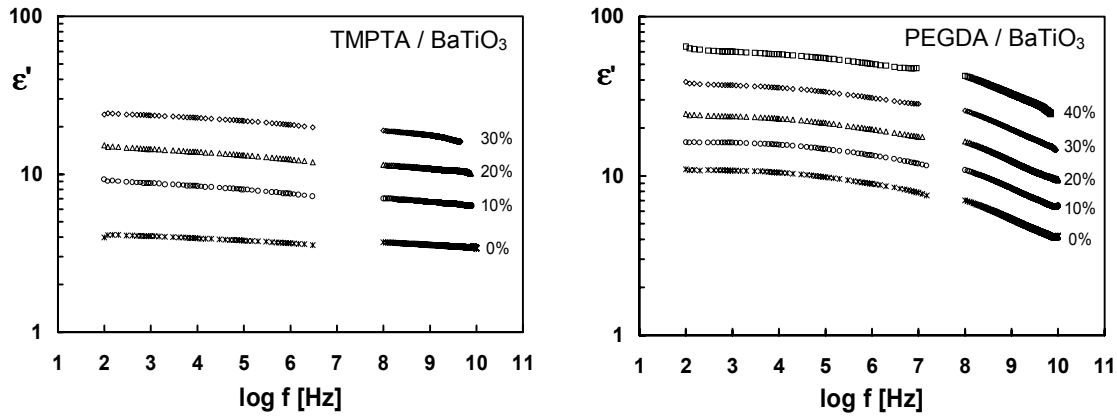


Figure 2. Dielectric constant ε' of TMPTA/$BaTiO_3$ and PEGDA/$BaTiO_3$ composites at various volume fractions of $BaTiO_3$ in the frequency range from 100 Hz to 10 GHz

RESULTS AND DISCUSSION

Figure 2 shows the dependence of the dielectric constant of TMPTA/$BaTiO_3$ and PEGDA/$BaTiO_3$ composites on frequency at room temperature for several concentrations of barium titanate filler. Both monomers were chosen to obtain model polymer matrices with distinguishable dielectric properties that could diversify electromagnetic responsiveness of the corresponding composites. Moreover, low viscosity of the monomers before photo-polymerization permitted high ceramic loading without introduction of solvents or interfacial modifiers. Such ingredients typically cause non-negligible alterations to the composite structure that complicate the dielectric analysis.

The dielectric constant of TMPTA polymer in the low frequency range is lower than the dielectric constant of PEGDA due to lower polarizability and lower concentration of molecular dipoles in TMPTA. For example, at 1 MHz the ε' of neat TMPTA polymer is 3.7 while the corresponding value of ε' for PEGDA polymer is about 10. Consequently, the dielectric constant of the TMPTA composites is lower than the dielectric constant of the corresponding PEGDA composites. In the case of the TMPTA matrix, the dependence of the dielectric constant on frequency is linear in the logarithmic scale for all concentrations of the ceramic component. Up to about 10 MHz, the logarithm of the dielectric constant decreases with a similar slope of -0.0211 per frequency decade for all volume fractions of $BaTiO_3$ studied. At higher frequencies, the slope changes from -0.023 for 5 % $BaTiO_3$ concentration to -0.033 for 35 % $BaTiO_3$. Such decrease in the dielectric constant with frequency indicates a relaxation process that is dependent on the content of the ceramic component. As it is seen in

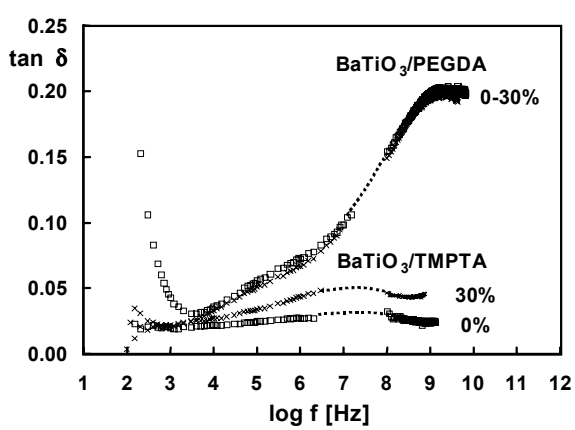


Figure 3. Loss tangent of PEGDA/$BaTiO_3$ and $BaTiO_3$/PEGDA composites

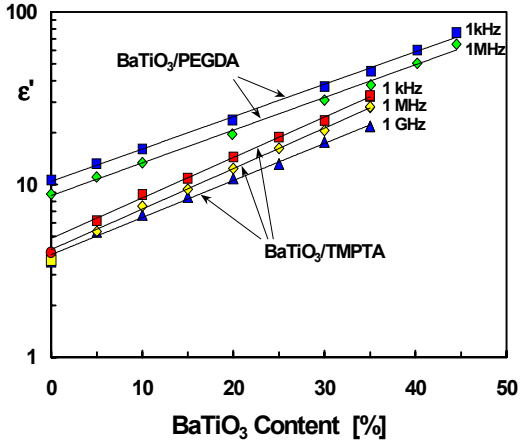


Figure 4. Dependence of the dielectric constant on the volume fraction of the $BaTiO_3$ at selected frequencies for TMPTA and PEGDA composites at 25 ^oC.

Figure 3, the relaxation process in the TMPTA/$BaTiO_3$ composites gives rise to a dielectric loss with a maximum at about 10 MHz. In comparison, the dielectric dispersion of the PEGDA/$BaTiO_3$ composites is considerably larger. The dielectric constant decreases with frequency faster and approaches similar value to that of the TMPTA/$BaTiO_3$ composites at about 10 GHz., (Figure 2). Such behavior indicates that the molecular polarizability process enhancing the dielectric constant in the PEGDA polymer rapidly decays at microwave frequencies. This change in the polarizability contributes to an increased dielectric loss with a maximum at about 1 GHz (Figure 3). The relaxation frequency of the PEGDA formulations is higher than the relaxation frequency of the TMPTA composites due to larger flexibility of the polymer backbone in PEGDA. A comparison of the loss tangent data of TMPTA/$BaTiO_3$ and PEGDA/$BaTiO_3$ composites indicates that the magnitude of the dielectric loss tangent and the relaxation frequency in the composites are influenced primarily by the molecular structure of the polymer matrix. To our knowledge the results shown in Figures 2 and 3 represent the first experimental evidence of dielectric relaxation in polymer composite films measured directly at high frequencies.

$$\log \varepsilon'_{composite} = \log \varepsilon'_{polymer} + \varphi_f \log(\varepsilon'_{filler} / \varepsilon'_{polymer}) \qquad (1)$$

φ_f - represents volume fraction of the ceramic filler in the composite

The data shown in Figure 2 indicate that the dielectric constant of the composite increases with increasing concentration of the ferroelectric filler. Several models have been proposed to predict the dielectric constants of polymer/ceramic composites [5,6]. These relationships are known as mixing rules. Many of the mixing rules describe well dielectric behavior of two-component composites at small filler concentrations, usually less than 10 %. However, most of the rules fail in prediction of the dielectric constant of ceramic/polymer composites, if the difference in dielectric constant of the components is large, like in the case of ferroelectric ceramic/polymer composites, or, when the filler concentration is high. We found that for pure two component polymer/$BaTiO_3$ mixtures the relationship between the dielectric constant of the composite and the volume fraction of the filler is clearly logarithmic, as shown in Figure 4. The relationship can be described by equation (1).

The experimental results fit the equation (1) well (i.e., correlation coefficient $R > 0.997$ at 8 data points), except when the volume fraction of the filler is lower than 0.05. Hence, the logarithmic relationship can be used for description of the composite properties at high filler concentrations, while other mixing rules can be used for low filler contents. The slope and intercept of the logarithmic relationship depend of frequency (Figure 4). This means that the relationship obtained from low frequency measurements cannot be used for predictions of the dielectric constant at high frequency range; the relationship parameters have to be obtained

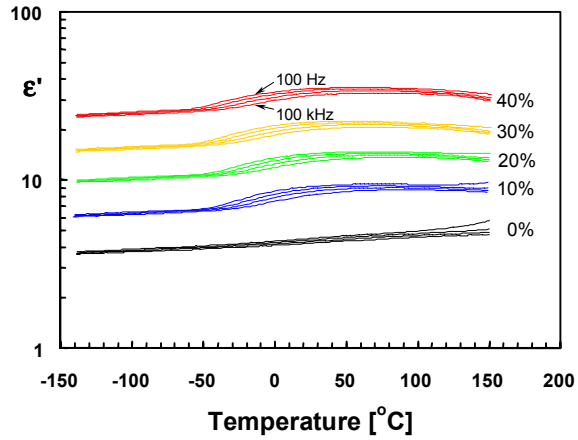


Figure 5. Effect of temperature on dielectric constant of TMPTA/$BaTiO_3$ composites at 100 Hz, 1 kHz, 10 kHz and 100 kHz.

individually by measurements at the frequency of interest. For example, the plot shown in Figure 4 for the TMPTA composite at 1 GHz has a smaller slope than the analogous plot of data obtained at 1 kHz. However, the relationship between the logarithm of the dielectric constant and the volume fraction of the filler is linear for every frequency. Similar relationship has been observed for the PEGDA composites.

We have determined that for composites containing different polymer matrices but the same filler, plots of the dielectric constant at a constant frequency intersect in a single point corresponding to the filler volume fraction of 1. Thus equation (1) can be used to determine the dielectric constant of pure materials in the form of powders, which otherwise cannot be measured directly.

Figure 5 shows the dependence of the dielectric constant on temperature for TMPTA/$BaTiO_3$ composites during cooling from 150 °C to -145 °C at a rate of 1.0 °C/min. The contributions of the $BaTiO_3$ ceramic to the dielectric constant of the composites is enhanced in the temperature range between –60 °C and 110 °C. In this temperature range, $BaTiO_3$ transforms from the paraelectric cubic phase to the ferroelectric tetragonal phase, then to orthorombic phase and finally to the rhombohedral one. For the grain size of 1.1 μm to about 3.0 μm these three transformations take place at about 110 °C, 10 °C and –70 °C respectively and are accompanied by an increase in the dielectric constant around the phase transition temperatures [7]. However, the data obtained for the composites (Figure 5) do not exhibit any corresponding singularities characteristic to pure $BaTiO_3$ ceramic. Only a broad dielectric constant enhancement is seen in Figure 5. This difference cannot stem from different properties of $BaTiO_3$ filler we used compared to that reported in literature, because we reproduced the behavior of pure $BaTiO_3$ powder. Hence it is possible, that the lack of sharp maxima at the phase transition temperatures of $BaTiO_3$ in the characteristics of polymer/$BaTiO_3$ composite is the effect of particle confinement in the polymer network. However, further studies will be necessary to elucidate this phenomenon.

CONCLUSIONS

We studied photocurable acrylic resins filled with $BaTiO_3$ as model polymer composites of relatively high dielectric constant. The dielectric properties of these materials were studied on films 100 μm to 120 μm thick at frequencies from 100 Hz to 10 GHz and temperatures from -140 °C to +150 °C, the range relevant for practical applications. The two polymer matrices, TMPTA with the dielectric constant of 3.6 and PEGDA with the dielectric constant of 10 allowed for the formulation of composites with diversified dielectric relaxation properties and a dielectric constant exceeding value of 35 at 1 GHz. The low viscosity of the monomers before

photo-polymerization permitted high ceramic loading of volume fraction up to 0.45 (mass fraction 0.82) of $BaTiO_3$ without the introduction of solvents or interfacial modifiers.

The experimental dependence of the dielectric constant of composites on volume concentration of the $BaTiO_3$ filler correlates well with the logarithmic mixing rule equation. We have determined that for the two-phase polymer/$BaTiO_3$ composites with 0-3 type connectivity, plots of the dielectric constant corresponding to the same frequency intersect in a single point at the filler volume fraction of 1. Thus the technique can be used to determine the dielectric constant of pure ceramic powders, which otherwise cannot be measured directly.

A high frequency dielectric relaxation process was identified. It was found that the relaxation is influenced primarily by the type of polymer matrix. Modifying the polymer matrix can control the position and magnitude of the loss peak. Such selective dielectric behavior is beneficial for de-coupling capacitance applications. These results represent the first experimental evidence of dielectric relaxation in polymer composite films measured directly at high frequencies.

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8. Certain materials and equipment identified in this manuscript are solely for specifying the experimental procedures and do not imply endorsement by NIST or that they are necessarily the best for these purposes.