

Dielectric Properties of Polymer/Ferroelectric Ceramic Composites from 100 Hz to 10 GHz

R. Popielarz,[†] C. K. Chiang,* R. Nozaki,[‡] and J. Obrzut

National Institute of Standards and Technology, Polymers Division, Bldg 224/B320,
100 Bureau Drive, Gaithersburg, Maryland 20899

Received September 11, 2000; Revised Manuscript Received June 4, 2001

ABSTRACT: Dielectric properties of model BaTiO₃/polymer composites were measured over a broad frequency and temperature range. A series of BaTiO₃/monomer suspensions were photocured into thin wafers. The wafers were equipped with aluminum electrodes, and the dielectric permittivity of the composites was investigated at frequencies from 100 Hz to 10 GHz and at temperatures from -140 to +150 °C. It has been found that for the same BaTiO₃ loading dielectric characteristics of the composites strongly depend of the type of polymer. Polar polymers increase dielectric constant of the composites at low frequencies but have little effect at gigahertz frequencies. Dielectric losses of the composites show a maximum at some intermediate frequency within megahertz to gigahertz range that reflects the relaxation behavior of the polymer matrix. The magnitude of the losses increases with increasing polarity of the polymer component. At constant frequency and temperature, the composites follow a linear relationship between logarithm of their dielectric constant and volume fraction of the ferroelectric filler. Practical implications of such composites behavior are discussed.

Introduction

Development of electronic devices working at high operating frequencies, such as fast computers, cellular phones, etc., require new high-dielectric constant (high-*K*) materials that combine good dielectric properties with both mechanical strength and ease of processing. In particular, the high-*K* materials are required for making embedded capacitors for integrated electronic devices.^{1,2} The unique combination of dielectric and mechanical properties is hard to achieve in a one-component material. Pure polymers are easy to process into mechanically robust components but generally suffer from a low dielectric constant.³ On the other hand, typical high-*K* materials, such as ferroelectric ceramics, are brittle and require high-temperature processing,⁴ which is often not compatible with current circuits integration technologies. The ideal solution would be a high-*K* material that is mechanically robust and processable at ambient temperatures. This has raised a great interest in hybrid materials, such as ferroelectric ceramic/polymer composites, that may combine desired properties of the components.^{5,6}

Development of the composite materials for high-frequency applications requires thorough understanding of the materials behavior at the frequencies of interest. However, only limited data are available in the literature for ferroelectric ceramic/polymer composites at the frequencies above 1 MHz, because of experimental difficulties related to high-frequency measurements.^{5,7–9} To-date, no systematic study on the dielectric properties of ferroelectric ceramic/polymer composites over a broad frequency range that would include microwave frequencies has been reported. Recently, a new measurement technique has been developed for solid films which

facilitated dielectric study of materials at high frequencies.¹⁰ That technique has expanded the practical frequency range for dielectric studies of materials up to 10 GHz.

In the present paper we have synthesized model ferroelectric ceramic/polymer composites and measured their dielectric properties over a broad frequency range of 100 Hz–10 GHz. The aim of this research was to better understand how materials parameters influence the dielectric behavior of polymer/ceramic composites for high-frequency electronics. Specifically we address the following issues: (i) dielectric response of model BaTiO₃/polymer composites over a broad frequency range of 100 Hz–10 GHz; (ii) effect of different polymer matrices on dielectric properties of the composites; (iii) the relationship between the dielectric constant and the composite composition; and (iv) thermal sensitivity of the dielectric response over the temperature range of -140 to +150 °C.

Experimental Details

Materials. Trimethylolpropane triacrylate (TMPTA) was purchased from Monomer Polymer & Dajac Labs.¹¹ Poly(ethylene glycol) diacrylate (PEGDA, *M_n* = 575), 1,14-tetradecanediol dimethacrylate (TDDMA), 2,2-dimethoxy-2-phenylacetophenone (photoinitiator), and barium titanate (ferroelectric filler) were obtained from Aldrich.

Sample Preparation. First, solutions of 1% mass fraction of the photoinitiator in the monomers were prepared. Next, barium titanate powder was mixed into the solutions to form liquid formulations of various filler concentrations. The formulations were cured by exposure of a few drops of each formulation squeezed between microscope slides to UV light. During the exposure, the slides were kept at a constant distance of about 100 μm using self-adhesive labels in the role of spacers. The cured composites did not adhere strongly to the glass and were carefully separated from the slides in the form of thin wafers. Circular aluminum electrodes, 12.7 or 3.0 mm in diameter, were vacuum-deposited on both sides of the composite samples.

Measurements. At low frequencies (i.e., from 100 Hz to 1 MHz), the samples capacitance and loss tangent were mea-

[†] On leave from: Department of Engineering and Chemical Technology, Cracow University of Technology, Krakow, Poland.

[‡] On leave from: Division of Physics, Graduate School of Science, Hokkaido University, Sapporo, Japan.

* To whom correspondence should be addressed.

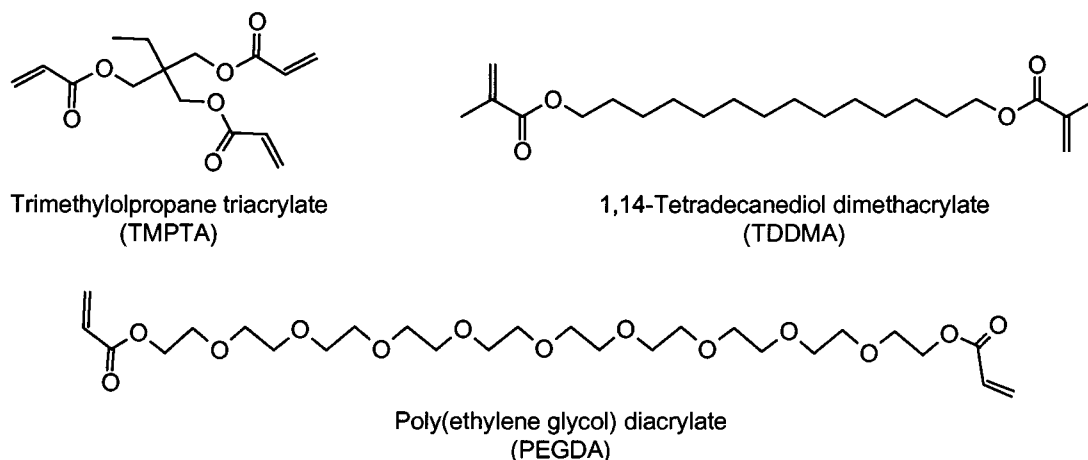


Figure 1. Structure of the monomers.

sured at 25 °C with a Hewlett-Packard 4194A impedance/gain-phase analyzer. The instrument had been calibrated with an air capacitor prior to performing the sample measurements. In this frequency range, the samples with 12.7 mm electrodes were used.

The measurements within the intermediate frequency range (i.e., from 1 to 400 MHz) were performed at 22 °C with a 4191A rf impedance analyzer in its high-precision mode, using a 7 mm coaxial test fixture configuration. The test specimen was a 3 mm diameter film capacitor treated as a lumped element.

The dielectric permittivity at microwave frequencies (i.e., from 100 MHz to 10 GHz) was measured with the newly developed technique for solid dielectric films.¹⁰ The test specimen for the high-frequency measurements consisted of a 3 mm diameter film capacitor terminating a 7 mm coaxial waveguide. The specimen geometry was measured using a Mitutoyo micrometer model 293-301 with 1 μ m resolution.¹¹ The complex permittivity of the materials in frequency domain was obtained from the complex reflectivity coefficients, for which a computational algorithm was developed to account for wave propagation in the specimen section. Dielectric measurements in this frequency range were carried out with a network analyzer (HP 8720D). One-port S_{11} (open, short, and broad-band load) calibration was performed using a HP 85050B APC-7 calibration kit.

The relative uncertainty in geometrical capacitance measurements was typically 2% with the primary contribution from the uncertainty in the film thickness measurements. The relative uncertainty of S_{11} was assumed to be within the manufacturer specification for the HP 8720D. The combined standard uncertainty in complex permittivity measurements was less than 8% while the experimental resolution of the dielectric loss tangent was about 0.01. All the high-frequency measurements were performed at room temperature (22 °C).

The capacitance and the dielectric loss tangent data obtained from different instruments were combined together into a single broad-band dielectric spectrum for each composite material. Offset adjustment between the data sets from different instruments was less than 8% of the measured values. Low-frequency data series, which had standard uncertainty below 2% of absolute values, were taken as a reference for the offset adjustments of the intermediate- and high-frequency series by using the data within overlapping frequency ranges for the offset correction.

The dielectric properties were also measured as a function of temperature using a Sun Electronic Systems EC12 environmental chamber. The temperature ramps were controlled by the chamber microprocessor using a combination of heating and cooling with liquid nitrogen duty cycles. The samples were initially heated to 165 °C at the rate 1.0 °C/min and then cooled to -140 °C at the same rate. The dielectric data were acquired in 2.5 °C intervals during the cooling scan. The four-terminal capacitance and loss tangent measurements were carried out using a Hewlett-Packard 4274A multifrequency LCR meter

in the frequency range 100 Hz–100 kHz. The LCR meter was calibrated to the short and open standards using its internal automatic calibration routine. The electrode diameter of the samples was 12.7 mm.

Results and Discussion

The photopolymerization technique was chosen for making the composites, because it allows for solvent-free mixing of a ceramic filler with liquid monomers to form suspensions that can be spread in liquid form onto any surface and then cured into thin films at ambient temperatures with UV radiation. Liquid monomers can easily penetrate between the filler particles and even inside pores (if any), which facilitates the mixing and allows to avoid air trapping into the composites. Consequently, void-free composites were obtained. In addition, the large selection of monomers that are photocurable ultimately leads to considerable control over the final mechanical properties of the composites, which is important for potential applications.

We selected three photocurable monomers of distinctly different properties for the polymer matrix and barium titanate as the ferroelectric filler. The chemical structures of the monomers are shown in Figure 1. The TMPTA monomer contained three polymerizable acrylic groups separated by short hydrocarbon chains. Hence, TMPTA formed highly cross-linked rigid networks upon cure. The PEGDA monomer had only two reactive groups separated by a long chain of about 10 ethylene oxide units. The resulting PEGDA polymer was very flexible. Moreover, PEGDA was much more polar than TMPTA, due to the presence of a large number of C–O bonds in its structure. In contrast, TDDMA monomer contained a long hydrocarbon chain between the acrylic groups. Consequently, TDDMA matrix was of very low polarity, lower than the polymer networks obtained from the other two monomers. Thus, by appropriate selection of the polymer matrices of distinctly different properties, the effect of polymer characteristics on the dielectric properties of the composites was probed.

We chose barium titanate (BaTiO_3) as a model ferroelectric filler, since it is a well-known and characterized ferroelectric material. For the purpose of this study, we used BaTiO_3 with an average particle size of about 1 μ m.

Dielectric Constant of BaTiO_3 /Polymer Composites as a Function of Frequency. The influence of barium titanate concentration on the dielectric constant of the composites was studied over a broad frequency

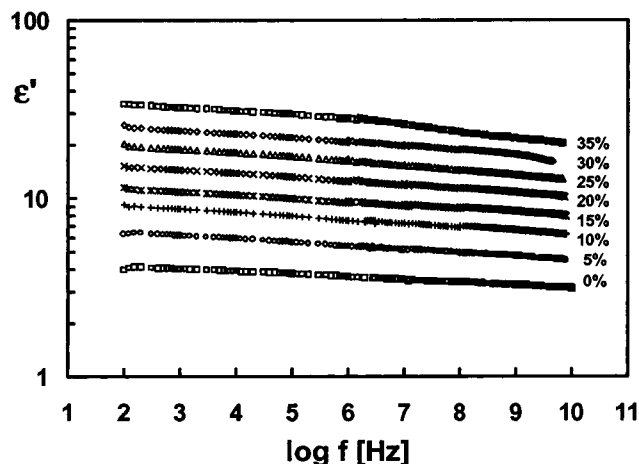


Figure 2. Dielectric constant of BaTiO₃/TMPTA composites as a function of frequency for various volume fractions of BaTiO₃.

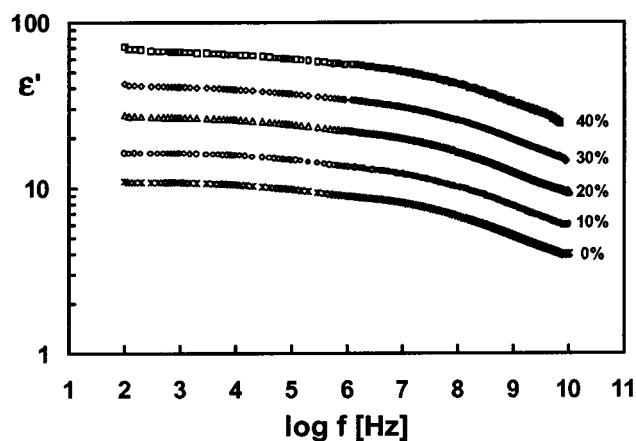


Figure 3. Dielectric constant of BaTiO₃/PEGDA composites as a function of frequency for various volume fractions of BaTiO₃.

range. Figures 2 and 3 show the dependence of the dielectric constant of BaTiO₃/TMPTA and BaTiO₃/PEGDA composites on frequency for different volume fractions of barium titanate at 25 °C. The dielectric constant plots for BaTiO₃/TDDMA composites (not shown) were similar to those of BaTiO₃/TMPTA, except for the slopes and positions of the lines, which were lower.

In the case of TMPTA polymer matrix, logarithm of the dielectric constant decreases linearly with the logarithm of frequency for all of the BaTiO₃ concentrations (Figure 2). Below 1 MHz, the logarithm of the dielectric constant decreases by 0.0211 per frequency decade with a standard deviation of 0.0008, regardless of the BaTiO₃ concentration (i.e., except for pure TMPTA matrix, which has slightly lower slope). Within the high-frequency range above 100 MHz, the slope changes from -0.023 for 5% of BaTiO₃ to -0.033 for 35%. This corresponds to about 5–7% decrease of the dielectric constant per frequency decade.

At low frequencies, BaTiO₃/PEGDA composites have much higher dielectric constants than the corresponding BaTiO₃/TMPTA composites (Figure 3 vs Figure 2). For example, the dielectric constant of 30% BaTiO₃/PEGDA composite is 41 at 1 kHz, while the corresponding dielectric constant of 30% BaTiO₃/TMPTA is 24. This is due to the higher polarity of the PEGDA matrix. However, the dielectric constant of BaTiO₃/PEGDA

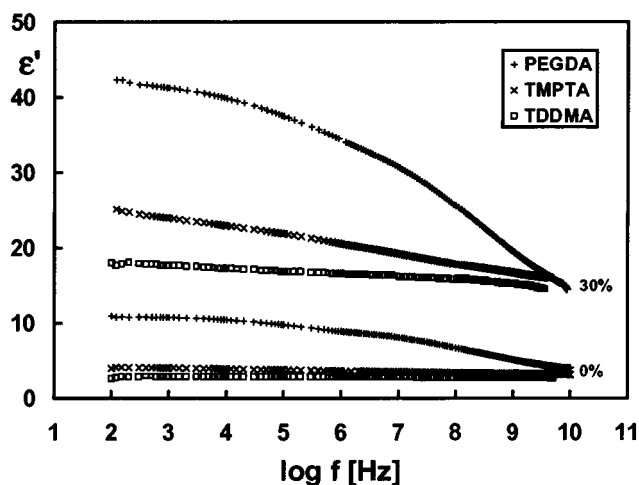


Figure 4. Comparison of the frequency characteristics of dielectric constant of 30% BaTiO₃/polymer composites and the corresponding pure polymer matrices.

composites decreases more significantly with increasing frequency, and by 10 GHz, the PEGDA- and TMPTA-based composites exhibit similar ϵ' values, as demonstrated in Figure 4. This indicates that at high frequency the mobility of polar groups in polymer chains is too slow to contribute to the dielectric constant. It appears that at frequencies of the order of 10 GHz the ceramic component dominates the dielectric constant of the composites. This conclusion is further supported by the BaTiO₃/TDDMA composites also shown in Figure 4. The dielectric constant of the BaTiO₃/TDDMA is less dependent on frequency than that of the previous two composites but still approaches the same high-frequency limit as the BaTiO₃/TMPTA and BaTiO₃/PEGDA composites. In summary, the data in Figures 2–4 indicate that at low frequencies the dielectric constant of BaTiO₃/polymer composites strongly depends of the dielectric properties of both the polymer and the ceramic components, while at gigahertz frequencies the dielectric constant becomes dependent primarily of the ceramic filler and its concentration.

As shown in Figure 2, at 35% volume fraction, barium titanate filler can provide the dielectric constant of about 20 at 10 GHz. We have found that the highest volume fraction of 45% can be achieved for BaTiO₃ with 1 μm average particle size in some monomers (e.g., PEGDA) without losing the material processability. At that concentration the dielectric constant of the corresponding composite reached about 30 at 10 GHz. Hence, the dielectric constant of 30 at microwave frequencies is the maximum achievable value for the photocurable composites based on BaTiO₃ filler.

Dielectric Losses of BaTiO₃/Polymer Composites. The magnitude of dielectric loss is an important material parameter for making capacitors. Ideally, in a capacitor the dielectric losses should be as low as possible. Figure 5 compares loss tangent ($\tan \delta$) of the three polymer matrices loaded with 30% volume fraction of BaTiO₃ particles. It is well-known that BaTiO₃ ceramic does not show significant dielectric losses up to megahertz frequencies, while the BaTiO₃ loss tangent reaches a maximum within the gigahertz to terahertz frequency range. Hence, the dielectric losses of the BaTiO₃/polymer composites observed within low frequency range (Figure 5) originate primarily from the polymer component. Slight increase of the loss tangent

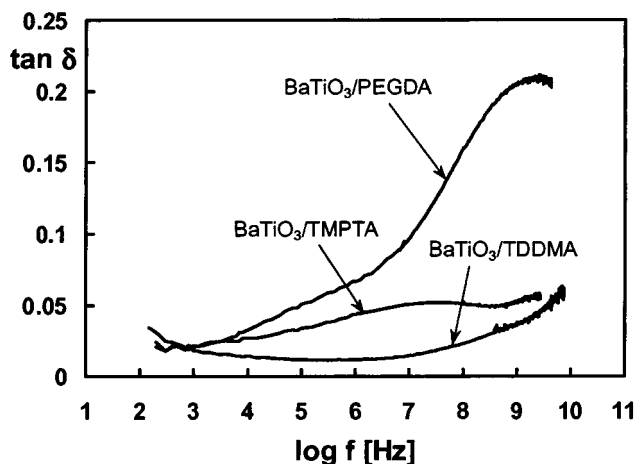


Figure 5. Comparison of the dielectric losses ($\tan \delta$) of 30% BaTiO_3 /polymer composites and the corresponding pure polymer matrices.

of BaTiO_3 /TDDMA and BaTiO_3 /TMPTA composites when approaching 10 GHz is an indication of the onset of BaTiO_3 loss contribution, because pure TDDMA polymer showed only a small (i.e., below 0.02) loss tangent within this frequency range. In the case of BaTiO_3 /TMPTA composite, the loss contribution from BaTiO_3 is overlapped with the loss maximum of TMPTA showing up at megahertz frequencies, while in the case of BaTiO_3 /PEGDA, BaTiO_3 loss is completely obscured by much larger loss of PEGDA polymer.

The dielectric losses of the composites follow the same general trend as the polymer polarity with $\tan \delta$ increasing in the order TDDMA < TMPTA < PEGDA. Hence, while a highly polar polymer matrix increases the low-frequency dielectric constant of the ceramic/polymer composites, the dielectric losses are also increased, particularly within the intermediate- and high-frequency ranges (Figure 5). This suggests that, for high-frequency applications where the dielectric losses need to be minimized, composites with nonpolar polymer matrices will perform better.

Effect of BaTiO_3 Content on Dielectric Constant of BaTiO_3 /Polymer Composites. It is perceptible that higher concentrations of ferroelectric filler lead to higher dielectric constant composites. What is not obvious is the quantitative relationship between the filler content and the dielectric properties of the composite, particularly at high frequencies. Several quantitative rules of mixture models have been proposed for predictions of the dielectric constant of heterogeneous two-component systems on the basis of dielectric properties of the components.^{12–18} However, while different models had been developed, usually little or no experimental evidence was provided to support the derived equations, and it turns out that most of these theoretical models fail when it comes to prediction of the dielectric constant of ferroelectric ceramic/polymer composites, where there is a large contrast between the dielectric constant of the components, especially at high filler contents.^{12,15} In the case of the ferroelectric ceramic/polymer composites, the rules of mixture proposed by Yamada–Ueda–Kitayama¹⁸ and Jayasundere–Smith¹⁹ have been used most often. However, even these equations do not fit experimental data precisely.^{15,18,20}

Figures 2 and 3 show that the plots of the dielectric constant vs frequency are practically equidistant in logarithmic scale for equally spaced BaTiO_3 volume

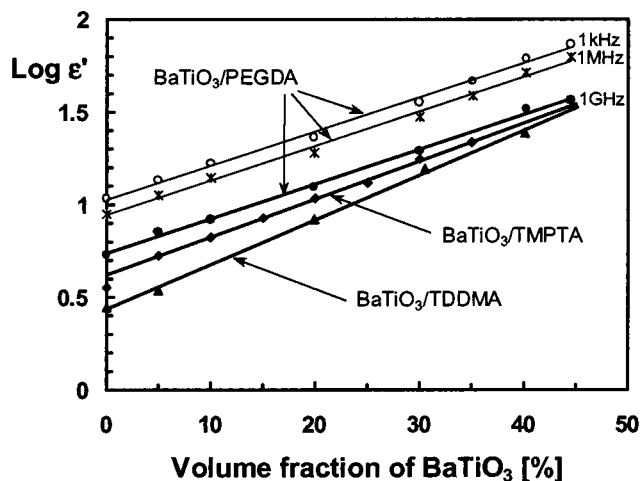


Figure 6. Relationship between the dielectric constant of BaTiO_3 /polymer composites and BaTiO_3 content at selected frequencies.

fractions (i.e., with the exception of pure TMPTA matrix, which is lower; Figure 2). This indicates the logarithm of the dielectric constant is linearly proportional to the volume fraction of BaTiO_3 , even at high frequencies. Hence, the BaTiO_3 /TMPTA composites follow the “log-law” relationship, originally proposed by Lichtenecker,^{16,21} in which the dielectric constant (ϵ') of a clean two-component system can be represented by

$$\log \epsilon'_{\text{composite}} = \log \epsilon'_{\text{polymer}} + \varphi_f \log \left(\frac{\epsilon'_{\text{filler}}}{\epsilon'_{\text{polymer}}} \right)$$

where φ_f represents volume fraction of the filler in the composite.

Figure 6 shows the dielectric constant of the three composites as a function of volume fraction of BaTiO_3 at representative frequencies of 1 kHz, 1 MHz, and 1 GHz. These data are consistent with the log-law relationship and provide the first experimental evidence that the ferroelectric ceramic/polymer composites follow the log-law relationship over a broad frequency range.

The relationship between the logarithm of the dielectric constant of the composites and the volume fraction of the ferroelectric filler is linear at each frequency within the range studied. However, this does not imply that the log-law parameters determined at one frequency can be used to predict the dielectric constant of a composite at other frequencies. The slope and intercept of the relationship depend of the dielectric characteristics of the system components, which are generally frequency dependent.

According to the dielectrics theory, at very high frequencies the dielectric constant of most of polymer matrices is going to drop down to the square of the polymer refractive index as the limiting value. The data shown in Figure 4 provide the first experimental evidence that the decay of influence of polymer matrix on the dielectric constant of ferroelectric ceramic/polymer composites can occur at frequencies as low as 10 GHz. As most of polymers have refractive index within the range 1.35–1.70,²² the dielectric constant of the polymer matrices at microwave frequencies will be of the order of 1.8–2.9. By substituting these numbers into the log-law equation, it can be predicted that when a ferroelectric filler with the dielectric constant of 10 000 at microwave frequencies is applied, the composites with

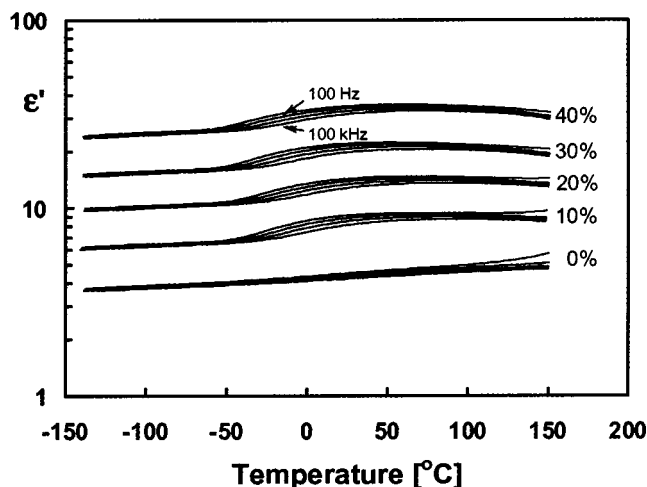


Figure 7. Effect of temperature on dielectric constant of BaTiO₃/TMPTA composites at 100 Hz, 1 kHz, 10 kHz, and 100 kHz.

dielectric constant of 87–113 at these frequencies will be attainable at 45% filler content.

Effect of Temperature on Dielectric Properties of BaTiO₃/Polymer Composites. For most of practical applications, the dielectric constant of the materials used for capacitors should be stable within the operational temperature range of electronic devices. Figure 7 shows the temperature dependence of the dielectric constant for various volume fractions of BaTiO₃ in TMPTA polymer matrix. It is noteworthy that the curves for various BaTiO₃ volume fractions are parallel to each other and practically equidistant in the logarithmic scale with the exception of the curve for pure TMPTA matrix. This indicates that the composites follow the log-law also within the entire range of temperatures studied. It is peculiar, however, that the curve for pure TMPTA polymer is parallel to that of the composites below $-50\text{ }^{\circ}\text{C}$, but at higher temperatures the composites behave differently than the pure polymer. This suggests that the pure polymer matrix does not necessarily have to follow the same trend as the corresponding composites. Consequently, the dielectric constant of pure TMPTA polymer, measured at $25\text{ }^{\circ}\text{C}$, is slightly lower than the intercept point of the log-law equation fitted to the BaTiO₃/TMPTA composites (Figure 6). However, this exception does not seem to be a general phenomenon, because the dielectric constants of the other pure polymer matrices fit well to the log-law.

Figure 8 compares the temperature dependence of dielectric constant of the composites containing 30% of BaTiO₃ in different polymer matrices with that of the pure polymers at four selected frequencies. It is evident that the thermal characteristics of the dielectric constant strongly depends of the type of polymer matrix. The composites based on the polar PEGDA polymer show very large dielectric constant variation with temperature, particularly at low frequencies. For example, the dielectric constant of 30% BaTiO₃/PEGDA composite at 1 kHz is about 40 at $25\text{ }^{\circ}\text{C}$ but drops to 20 upon cooling the composite to $-50\text{ }^{\circ}\text{C}$. On the other hand, the dielectric constant of the least polar BaTiO₃/TDDMA composite varies less than 15% over the temperature range from -150 to $+150\text{ }^{\circ}\text{C}$. This further emphasizes that for practical applications of the composites, where the dielectric constant needs to be stable against both

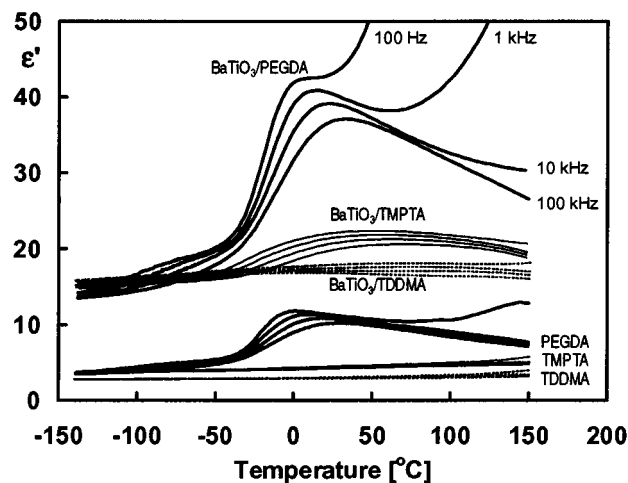


Figure 8. Comparison of the temperature dependence of dielectric constant of 30% BaTiO₃/polymer composites with that of the corresponding polymers.

frequency and temperature variations, nonpolar polymer matrices are superior.

Figures 7 and 8 indicate that the temperature dependence of dielectric constant of BaTiO₃/polymer composites is a complex function of the dielectric characteristics of both of the components. The characteristic enhancement of the dielectric constant of BaTiO₃/TMPTA composites at the temperatures above $-50\text{ }^{\circ}\text{C}$ compared to that at lower temperatures (Figure 7) can be attributed to behavior of BaTiO₃ filler, because no such behavior is observed in pure TMPTA polymer. It is well-known that barium titanate undergoes phase transitions upon heating or cooling.²³ Upon cooling, BaTiO₃ transforms from cubic state to tetragonal, then to orthorhombic, and finally to rhombohedral one. In the case of pure BaTiO₃ ceramic with grain size of about $1.1\text{ }\mu\text{m}$, these three transitions take place at about 120 , 20 , and $-70\text{ }^{\circ}\text{C}$, respectively, and are accompanied by sharp maxima in the dielectric constant magnitude around the phase transition temperatures.²⁴ Each crystalline phase has different dielectric properties with the tetragonal one having highest dielectric constant. Hence, the largest enhancement of the dielectric constant within the temperature range where the tetragonal form dominates (i.e., between 20 and $120\text{ }^{\circ}\text{C}$, Figure 7) is consistent with the intrinsic behavior of the BaTiO₃ filler. However, no sharp maxima around the BaTiO₃ phase transition temperatures are observed in the case of the composites (Figure 7). This may suggest that the phase transitions within BaTiO₃ particles are slow compared to the time scale of the experiments (i.e., the heating/cooling rates applied). However, further studies will be necessary to explain this phenomenon in detail.

Polymer flexibility has an influence on low-frequency dielectric constant of the composites. In particular, the presence of dipoles in the polymer matrix and their mobility strongly affects the dielectric constant magnitude. In the case of PEGDA polymer, the concentration of the dipoles was highest, because the poly(ethylene oxide) segments contained dipolar C–O bonds at every third atom. Moreover, at ambient temperatures PEGDA polymer was the most flexible of the three polymers studied. Consequently, the variation of dielectric constant of BaTiO₃/PEGDA composites with temperature is highest (Figure 8). The large decrease of dielectric constant of BaTiO₃/PEGDA composites upon cooling to

low temperatures can be explained primarily as the effect of decreasing mobility of polymer dipoles with some contribution from the changes in the filler. We found by DSC that PEGDA polymer had a glass transition temperature (T_g) originating mostly from its poly-(ethylene glycol) segments at about -20 °C. This temperature corresponds to the inflection point on the PEGDA and BaTiO₃/PEGDA curves obtained at 100 Hz (Figure 8). Hence, transition of a polar polymer from its glassy to its elastic state has a huge effect on the dielectric constant of both the polymer and the corresponding composites. In the case of BaTiO₃/PEGDA composites the transition more than doubled their low-frequency dielectric constant. TMPTA and TDDMA form highly cross-linked polymer networks, which restrict movements of most of polymer segments. Both of these polymers were in their glassy state within the temperature range studied. Consequently, the polymer dipole mobility in TMPTA was restricted, while in the case of TDDMA few dipoles were present. These are the likely reasons of much lower sensitivity of the dielectric constant of BaTiO₃/TMPTA and BaTiO₃/TDDMA composites to changes of temperature. At very low temperatures, where the mobility of any dipoles is restricted ("frozen"), the dielectric constant of all the composites becomes similar and independent of the type of polymer matrix. In that sense, the behavior of composites at low temperatures resembles their behavior at high frequencies.

Conclusions

By mixing liquid photocurable monomers with a ferroelectric filler, liquid suspensions are easily obtained that can be spread into thin layers (i.e., easily processed) and then photopolymerized into solid composite films. The photopolymerization processes can be carried out at ambient temperatures, which are compatible with current electronic circuits integration technologies. Moreover, the liquid suspensions can be easily patterned onto printed wiring boards or integrated circuit packaging by lithography, microcontact printing, or other patterning techniques.

The dielectric constants of the BaTiO₃/polymer composites follow a logarithmic mixing rule at the filler volume fractions above 5%. The log-law is obeyed within the frequency range of 100 Hz–10 GHz and within the temperature range of -140 to $+150$ °C. Pure polymer matrices do not always obey the log-law of the corresponding composites. The slope and intercept of the relationships depend on the dielectric characteristics of the composite constituents. For a particular composite system, these parameters also depend of the measurement frequency. Hence, the relationship parameters obtained for a single frequency should not be used to predict the dielectric response at other frequencies. The log-law parameters need to be determined for the frequency and composite of interest.

Polar polymers increase dielectric constant of the composites at low frequencies. However, the presence of polar groups in the polymer matrix also increases dielectric losses, particularly within the intermediate- and high-frequency ranges. The mobility of the polar groups ceases at the frequency of the order of 10 GHz. Consequently, at that high frequency the dielectric

constant of BaTiO₃/polymer composites becomes independent of the polymer type.

At low frequencies, thermal characteristics of dielectric constant of the composites strongly depend on both the polymer polarity and flexibility. The composites based on a nonpolar polymer matrix show little variation of their dielectric constant with temperature. On the other hand, the dielectric constant of the composites based on a polar polymer matrix strongly depends of the polymer state. At the temperatures where the polymer matrix is in its glassy state, the dielectric constant is much lower than that in the elastic state with a steep increase around the glass transition temperature.

Acknowledgment. R. Popielarz gratefully acknowledges the U.S. Department of Commerce and the Management of the National Institute of Standards and Technology for the Guest Researcher compensation received during accomplishment of this research project.

References and Notes

- (1) Bhattacharya, S. K.; Tummala, R. R. *J. Mater. Sci.: Mater. Electron.* **2000**, *11*, 253.
- (2) Chahal, P.; Tummala, R. R.; Allen, M. G.; Swaminathan, M. *IEEE Trans. Comput. Pack. Manuf. Technol., Part B: Adv. Packaging* **1998**, *21*, 184.
- (3) *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York, 1974; p VIII-7.
- (4) Dimos, D.; Lockwood, S. J.; Schwarz, R. W.; Rodgers, M. S. *IEEE Trans. Comput. Hybrids, Manufact. Technol.* **1994**, *18*, 174.
- (5) Walpita, L. M.; Pleban, W. M.; Eckhardt, H. U.S. Patent 5,962,122, Oct 5, 1999.
- (6) Ogitani, S.; Bidstrup-Allen, S. A.; Kohl, P. *1998 IEEE/CPMT International Manufacturing Technology Symposium*, p 199.
- (7) Jones, F. G.; Shrout, T. R.; Jang, S. J.; Lanagan, M. T. *Applications of Ferroelectrics, 1990, 7th International Symposium on Applications of Ferroelectrics*, p 455.
- (8) Walpita, L. M.; Ahern, M. R.; Chen, P.; Goldberg, H.; Hanley, S.; Pleban, W. M.; Weinberg, S.; Zipp, C.; Adams, G.; Wong, Y. H. *IEEE Trans. Microwave Theory Tech.* **1999**, *47*, 1577.
- (9) Truong, V. T.; Codd, A. R.; Forsyth, M. *J. Mater. Sci.* **1994**, *29*, 4331.
- (10) Obrzut, J.; Nozaki, R. *Proceedings of the IPC EXPO Technical Conference*, April 2–8, 2000, San Diego, CA.
- (11) 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.
- (12) van Beek, L. K. H. *Prog. Dielectr.* **1967**, *7*, 69.
- (13) Paletto, J.; Goutte, R.; Eyraud, L. *J. Solid State Chem.* **1973**, *6*, 58.
- (14) Sihvola, A. H.; Pekonen, O. P. M. *J. Phys., Part D: Appl. Phys.* **1996**, *29*, 514.
- (15) Bhimasankaram, T.; Suryanarayana, S. V.; Prasad, G. *Curr. Sci.* **1998**, *74*, 967.
- (16) Frost, N. E.; McGrath, P. B.; Burns, C. W. *Conference Record of the 1996 IEEE International Symposium on Electrical Insulation*, Montreal, Canada, June 16–19, 1996; pp 300–303.
- (17) Wakino, K. *J. Am. Chem. Soc.* **1995**, *76*, 2588.
- (18) Yamada, T.; Ueda, T.; Kitayama, T. *J. Appl. Phys.* **1982**, *53*, 4328.
- (19) Jayasundere, N.; Smith, E. V. *J. Appl. Phys.* **1993**, *73*, 2462.
- (20) Nagata, K.; Kodama, S.; Kawasaki, H.; Deki, S.; Mizuhata, M. *J. Appl. Polym. Sci.* **1995**, *56*, 1313.
- (21) Lichtenecker, K. *Phys. Z.* **1924**, *25*, 225.
- (22) *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York, 1975; pp III-241–III-244.
- (23) Frenkel, A. I.; Frey, M. H.; Payne, D. A. *J. Synchrotron Radiat.* **1999**, *6*, 515.
- (24) Kinoshita, K.; Yamaji, A. *J. Appl. Phys.* **1976**, *47*, 371.