

Polymer Composites with High Dielectric Constant

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A high dielectric constant polymer composite system is presented. The new composite uses a high dielectric constant cyanoresin polymer filled with ferroelectric ceramics, such as BaTiO₃ powder. While dielectric constant of the polymer is 21 at 1 kHz, the dielectric constant of the composite is over 130 at the BaTiO₃ volume fraction of 51%, which is the highest dielectric constant reported so far for the polymer composite materials based on BaTiO₃ filler. Frequency and temperature dependence of the dielectric constant of the composites are reported.

Keywords: Polymer composites; barium titanate; dielectric constant; ferroelectrics

INTRODUCTION

Polymers are low dielectric constant (low-K) materials. To increase the dielectric constant of a polymer a high dielectric constant (high-K) ceramic material needs to be added to form a polymer composite. High-K polymer composites are known to be very useful materials for variety of electronic applications, such as transducers, piezo-sensors, hydrophones, etc. [1–3] and several reviews concerning various ferroelectric ceramic/polymer composites and their electrical properties have been published [4–7]. Recently, the high-K composite materials have raised a lot of interest as potential candidates for integration into high-frequency electronic devices. New electronic applications, such as fast computers or high-frequency telecommunication devices, require de-coupling capacitors and low-impedance power planes to be integrated directly into the integrated circuits packaging, which in turn require development of high-K materials compatible with the circuits

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processing technologies [8]. The ferroelectric ceramic/polymer composites can offer not only higher dielectric constant than that of pure polymers but also advanced electronic properties such as controllable dielectric losses, which are important for low-impedance power planes to attenuate propagation of noise signals along the planes.

Recently, we have verified experimentally that from among variety of dielectric mixing rule equations proposed in literature, ferroelectric ceramic/polymer composites, with 0–3 type of connectivity [9], obey most closely logarithmic mixing rule [10]. Thus, for a simple two-phase material in which the ferroelectric filler is well dispersed in a polymer matrix, the effective dielectric constant can be calculated from Eq. (1):

$$\log \varepsilon'_{composite} = \log \varepsilon'_{matrix} + \varphi_{filler} \log \left(\frac{\varepsilon'_{filler}}{\varepsilon'_{matrix}} \right) \quad (1)$$

where φ_{filler} represents volume fraction of the filler in the composite, while ε'_{filler} and ε'_{matrix} are the dielectric constants of the filler and the polymer matrix respectively.

To increase dielectric constant of the composite, one can increase dielectric constant of the ceramic component or the polymer matrix. Although the dielectric constant of ferroelectric ceramic materials can be very high, its volume fraction in the composite cannot exceed the value for the percolation point, which for fillers with random distribution of grain size is typically below the volume fraction of 60%. Therefore, the dielectric constant of the composites is limited by the dielectric constant of the polymer matrix forming the continuous phase. The most studied high-K polymer matrix was poly(vinylidene fluoride) (PVDF) with the dielectric constant of about 12 at 1 kHz (i.e., the dielectric constant we are referring to in this paper is the room temperature value measured at 1 kHz, unless specified otherwise) [11–15]. For example, composites of PVDF with BaTiO₃ reached the dielectric constant of 82 at high BaTiO₃ loading [16].

Introducing polar groups such as C≡N, or C–O bonds into polymer structure increases the dielectric constant of the polymer. For example, cyanoethylated O-(2,3-dihydroxypropyl)-cellulose showed the dielectric constant of 30 [17]. However, very few reliable data has ever been reported for composite systems containing both a high-K polymer and a ferroelectric filler. Hence, we decided to investigate further the dielectric properties of composites based on a high-K polymer. In this paper we report the study of a barium titanate/polymer composite system based on cyanoethylated cellulose, where the barium titanate particles were distributed at random in the continuous polymer phase to form a 0–3 type of connectivity.

EXPERIMENTAL

Cyanoethylated cellulose polymer (CR-S) [18] and BaTiO₃ (99.9%) ceramic powder [19] were purchased from commercial sources [20]. Both components were used as received. The CR-S polymer is similar to the cyanoethylated O-(2,3-dihydroxypropyl)-cellulose polymer reported by Sato et al. [17]. The BaTiO₃ powder used as the ferroelectric filler had an average particle size of less than 2 μm [19]. We prepared the composites by thoroughly mixing BaTiO₃ powder into a CR-S solution in acetone. To ensure good dispersion of the powder, the mixture was sonicated in an ultrasound bath for 1 h. The solvent was evaporated from the well-mixed suspension, and, the composite was further dried at 80°C under vacuum. So prepared composites were molded into thin disks by pressing powdered solid composite at 120°C under vacuum. The temperature applied was above the plasticity temperature of CR-S polymer, which facilitated fusing the polymer phase, while the vacuum eliminated trapping of air bubbles within the composite structure. The resulting CR-S disks were typically 100 μm to 350 μm thick. For the dielectric measurements, both sides of the disks were coated with circular aluminum electrodes by vacuum evaporation. The diameter of the electrodes was 10 mm.

Complex dielectric permittivity measurements were carried out in the frequency range from 10² Hz to 10⁷ Hz at 25°C, using a Hewlett-Packard 4194A Network Analyzer. The temperature dependence of the dielectric properties was measured using a Hewlett-Packard 4274A Precision Multi-Frequency LCR Meter. The sample capacitor was placed inside a computer-controlled variable temperature oven, whose temperature could be programmed from -200°C to +200°C. The sample was first heated from room temperature to 150°C at 1 K/min and then cooled down at the same rate. The data were collected during the temperature ramp down.

The estimated combined standard uncertainty of the data obtained is below 10% of the measured values.

RESULTS AND DISCUSSION

We chose an engineered high-K polymer from a commercial source, and applied the polymer to form composites with barium titanate (BaTiO₃) as a ferroelectric filler. Barium titanate was not selected as the optimal filler for any specific application, but as a prototype ferroelectric material selected to demonstrate the dielectric behavior of the corresponding composites and the role of CR-S polymer in the composites. The high dielectric constant CR-S

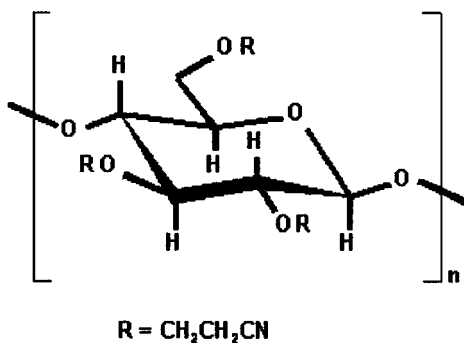


Figure 1. Structure of CR-S polymer.

polymer is based on chemically modified cellulose with polar groups both in the main and the side chains, as shown in Fig. 1. The presence of C—O and C≡N dipoles within the CR-S polymer structure is responsible for its high dielectric constant.

The frequency dependence of the dielectric constant of pure CR-S at room temperature is shown in Fig. 2. For comparison, the dashed line in

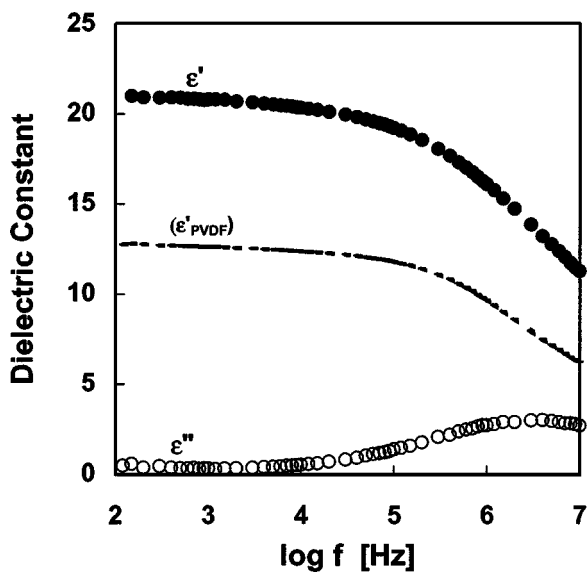


Figure 2. Frequency dependence of the real (ϵ') and the imaginary part (ϵ'') of complex dielectric constant of pure CR-S polymer at 25°C.

the figure shows the dielectric constant of PVDF. The dielectric constant of the CR-S is 21 at 1 kHz. This dielectric constant value is 1.75 times that of PVDF, which is a well-known high-K polymer. The observed high dielectric constant agrees with the data reported for similar materials [14]. The large dispersion of the dielectric constant of pure CR-S is also evident from the figure. The dielectric constant begins to decrease significantly at about 10^5 Hz. The decrease is consistent with the dielectric loss curve (i.e., the imaginary part of the complex dielectric permittivity), having a peak at about 4 MHz.

Adding BaTiO_3 powder to CR-S increases the dielectric constant of the composites. Figure 3 shows the dielectric constant of the CR-S/ BaTiO_3 composites as a function of volume fraction of BaTiO_3 . The maximum dielectric constant value we obtained was 133 at 1 kHz for the 51% BaTiO_3 composite. This dielectric constant value is higher than that of water and to our knowledge it is the highest dielectric constant ever obtained for the polymer composites based on BaTiO_3 filler. With such a high dielectric constant, the polymer composites can expand their usability for many potential electronic applications.

The solid line in Fig. 3 indicates an exponential fit to the experimental data points. For a pure two-phase composite, where the filler particles

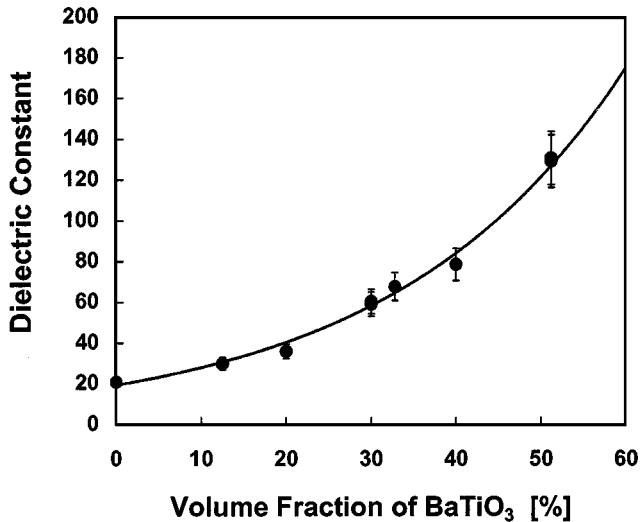


Figure 3. Dielectric constant (ϵ' at 1 kHz) of CR-S/ BaTiO_3 composites as a function of volume fraction of BaTiO_3 filler.

are randomly distributed within a continuous polymer matrix, the effective dielectric constant of the composite obeys Eq. (1). The data obtained for the CR-S/BaTiO₃ composites follow closely that equation (i.e., if the data were plotted in the corresponding semi-logarithmic coordinates a straight line would be obtained). Moreover, our data obtained for composites of BaTiO₃ with other polymers, such as polyacrylates, followed the same equation very closely [10]. Within this framework, we expect the dielectric constant of the CR-S polymer composites to exceed that of PVDF composites by at least 32% at comparable filler loadings also for any other suitable ferroelectric filler. Thus, replacement of BaTiO₃ filler with another ferroelectric material of higher dielectric constant than that of BaTiO₃ should afford polymer composites with the dielectric constant even higher than the one we achieved.

The frequency dependence of the dielectric constant of CR-S/BaTiO₃ composites with various volume fractions of the filler is shown in Fig. 4. In the frequency range from 100 Hz to 10 MHz, the dielectric constant of the composites decreases with increase of frequency in similar manner as that of pure CR-S polymer. Since the dielectric dispersion of BaTiO₃ ceramics is known to be small up to microwave frequencies, the dispersion observed in

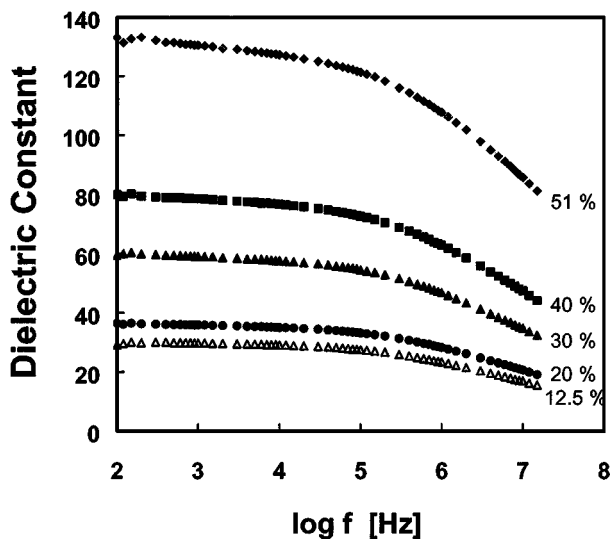


Figure 4. Dielectric constant (ϵ') of CR-S/BaTiO₃ composites as a function of frequency for various volume fractions of BaTiO₃.

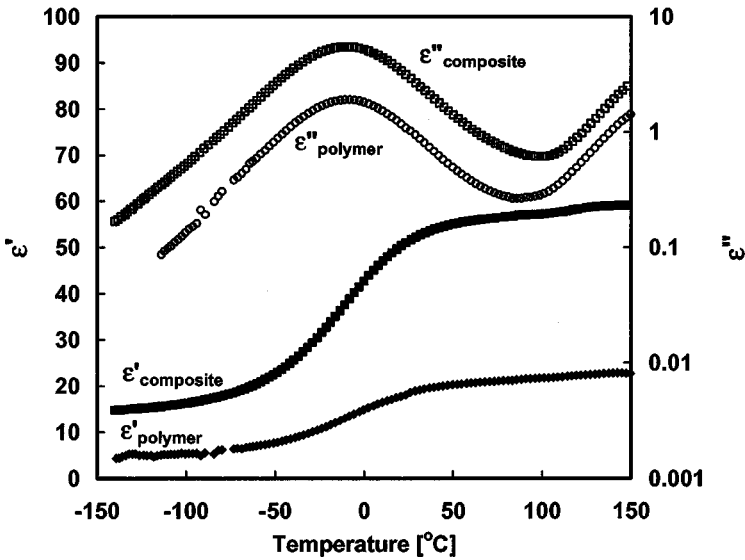


Figure 5. Temperature dependence of the dielectric constant (ϵ') and dielectric loss factor (ϵ'') of CR-S polymer and the corresponding 30% BaTiO₃/CR-S composite at 100 kHz.

the composites originates from the dielectric relaxation processes of CR-S polymer.

The temperature dependence of the dielectric properties of CR-S polymer and the corresponding 30% BaTiO₃ composite are shown in Fig. 5. From room temperature to about 150°C the dielectric constant (ϵ') of both the composite and the corresponding polymer is nearly independent of temperature. Below room temperature, the dielectric constant rapidly decreases with decreasing temperature. This behavior agrees with the decrease of dielectric constant at high frequency (Fig. 4), and reflects the relaxation process in the polymer matrix. Plots of the dielectric loss factor (ϵ'') versus temperature at 100 kHz show a peak at about -11°C for both the polymer and the composite (i.e., the maximum shifts to lower temperatures at lower frequencies). This is consistent with the highest decrease of the dielectric constant (ϵ') at this temperature. Hence, we conclude that both the frequency and the temperature dependence of dielectric constant of the polymer composite system studied resemble the behavior of the polymer component.

CONCLUSIONS

We have found a new polymer composite system that exhibits higher dielectric constant than most of the composites previously reported. The high dielectric constant of the polymer component contributes to the enhancement of dielectric constant of the composite. The dielectric constant of the composites studied follows the classic empirical mixing rule equation. Studies of frequency and temperature dependence of the dielectric properties indicate that the dielectric behavior of the composites is dominated by the dynamics behavior of the polymer matrix. Within the frequency range studied, the role of the barium titanate filler is only the enhancement of static dielectric constant of the polymer composite compared to that of pure polymer (i.e., BaTiO₃ does not affect dielectric losses of the composites within that frequency range). Most importantly, this study shows that while the high dielectric constant value is achievable through the use of a suitable high-K ceramic filler, molecular design of the polymer component is needed for tailoring the dynamics of the polymer composites to suit particular applications.

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