Electrical Energy Storage in Ferroelectric Polymer Nanocomposites Containing Surface-Functionalized $BaTiO_3$ Nanoparticles

Junjun Li,[†] Jason Claude,[†] Luis Enrique Norena-Franco,[‡] Sang Il Seok,[§] and Qing Wang*,[†]

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, 16802, Department of Basic Science, Metropolitan Autonomous University, Azcapotzalco, Mexico City, 02200, Mexico, and Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejon 305-600, South Korea

Received August 7, 2008
Revised Manuscript Received September 17, 2008

The continued success of dielectric polymers in capacitor applications imposes a challenge to improve energy density of these materials for advanced electronic devices and electric power systems with reduced weight, size, and cost.[1−3] Recently, nanocomposites composed of ceramic particles and polymer matrices have been prepared as a means of engineering dielectric property and energy storage capacity.[4] The idea underlying this composite approach is to integrate complementary elements, such as high dielectric permittivity from the inorganic dopants and high breakdown strength from the polymer matrix, for a substantially enhanced energy density.[5] In general, the energy density of a diphasic composite is the sum of the energy density of each constituent. In most of the ceramic−polymer composites, the volume fractions of the two constituents are on the same order of magnitude. Therefore, to achieve a high energy density of a composite, a sizable energy density from each constitute must be needed.

The polymers currently used as matrices in the dielectric nanocomposites, including polyethylenes, poly(methyl methacrylate)s, epoxy resins, and polyimides, usually possess dielectric permittivities of ∼2−5 that are significantly lower than their inorganic counterparts, thus severely limiting the energy density obtained in the polymer matrix and, consequently, in the resulting composites.[6−9] Ferroelectric poly(vinylidene fluoride) (PVDF) and its copolymers, such as poly(vinylidene fluoride-*co*-trifluoroethylene) [P(VDF-TrFE)] and poly(vinylidene fluoride-*co*-hexafluoropropylene) [P(VDF-HFP)], have also been utilized in the formation of the dielectric nanocomposites, owing to their relatively high dielectric permittivity at approximate 10.[10−13] The unique dielectric properties of PVDF based polymers originate from the presence of highly electronegative fluorine on the polymer chains and the spontaneous alignment of the C−F dipoles in the crystalline phases.[14] However, dispersion of inorganic fillers in these fluorinated polymers is always problematical because of the low surface energy of the polymers. The agglomeration of the ceramic dopants gives rise to electron conduction for a high dielectric loss and undesirable porosity for dielectric failure at much lower fields. In this contribution, we describe the preparation and dielectric properties of the nanocomposites comprised of the ferroelectric polymers and surface-functionalized $BaTiO_3$ nanoparticles. The effect of polymer matrix on the energy storage capability of the nanocomposites has been examined.

Ferroelectric poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) [P(VDF-CTFE) 91/9 mol %] and poly(vinylidene fluoride-*ter*-trifluoroethylene-*ter*-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE) 78.8/5.4/15.8 mol %] were employed as matrices in the nanocomposites investigated herein. P(VDF-TrFE-CTFE) was synthesized by a suspension polymerization of VDF and CTFE followed by a partial dechlorination of CTFE.[15,16] The dielectric permittivities measured at 1 kHz and room temperature are 12 and 42 for P(VDF-CTFE) and P(VDF-TrFE-CTFE), respectively. Crystalline $BaTiO_3$ nanoparticles were prepared via decomposition of ethylene diamine modified titanium(IV) isopropoxide and barium hydroxide in aqueous solution.[17] The nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).[17] A dielectric permittivity of 180 at 1 kHz was determined on the nanoparticle using impedance spectroscopy.[18] The chemical functionalization of the $BaTiO_3$ nanoparticles with ethylene diamine moieties on the surface renders the particles a greatly enhanced dispersibility in organic solvents and in turn a homogeneous distribution in the polymer matrix. The dynamic light scattering (DLS) measurements disclose an

---

* To whom correspondence should be addressed. E-mail: wang@matse.psu.edu.
[†] The Pennsylvania State University.
[‡] Metropolitan Autonomous University.
[§] Korea Research Institute of Chemical Technology.

(1) Jain, P.; Pymaszewski, E. J. *Thin Film Capacitors for Packaged Electronics*; Kluwer: Norwell, MA, 2003.
(2) Cao, Y.; Irwin, P. C.; Younsi, K. *IEEE Trans. Dielect. Elect. Insul.* **2004**, *11*, 797.
(3) Nalwa, H., Ed. *Handbook of Low and High Dielectric Constant Materials and Their Applications*; Academic Press: London, 1999.
(4) Tanaka, T.; Montanari, G. C.; Mülhaupt, R. *IEEE Trans. Dielect. Elect. Insul.* **2004**, *11*, 763.
(5) Li, J. Y.; Zhang, L.; Ducharme, S. *Appl. Phys. Lett.* **2007**, *90*, 132901.
(6) Ma, D.; Hugener, T. A.; Siegel, R. W.; Christerson, A.; Mårtensson, E.; Önneby, C.; Schadler, L. S. *Nanotechnology* **2005**, *6*, 724.
(7) Guo, N.; DiBenedetto, S. A.; Kwon, D.-K.; Wang, L.; Russell, M. T.; Lanagan, M. T.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 766.
(8) Gilbert, L. J.; Schuman, T. P.; Dogan, F. *Ceram. Trans.* **2006**, *179*, 17.
(9) Slenes, K. M.; Winsor, P.; Scholz, T.; Hudis, M. *IEEE Trans. Magn.* **2001**, *37*, 324.
(10) Dang, Z. M.; Lin, Y. H.; Nan, C. W. *Adv. Mater.* **2003**, *15*, 1625.
(11) Wei, T.; Jin, C. Q.; Zhong, W.; Liu, J. M. *Appl. Phys. Lett.* **2007**, *91*, 222907.
(12) Kim, P.; Jones, S. C.; Hotchkiss, P. J.; Haddock, J. N.; Kippelen, B.; Marder, S. R.; Perry, J. W. *Adv. Mater.* **2007**, *19*, 1001.
(13) Chu, B.; Lin, M.; Neese, B.; Zhou, X.; Chen, Q.; Zhang, Q. M. *Appl. Phys. Lett.* **2007**, *91*, 122909.
(14) Lovinger, A. J. *Science* **1983**, *220*, 1115.
(15) Lu, Y.; Claude, J.; Neese, B.; Zhang, Q. M.; Wang, Q. *J. Am. Chem. Soc.* **2006**, *128*, 8120.
(16) Claude, J.; Lu, Y.; Li, K.; Wang, Q. *Chem. Mater.* **2008**, *20*, 2078.
(17) Pramanik, N. C.; Seok, S. I.; Ahn, B. Y. *J. Alloys Compd.* **2008**, *449*, 77.
(18) Petrovsky, V.; Manohar, A.; Dogan, F. *J. Appl. Phys.* **2006**, *100*, 014102.

10.1021/cm8021648 CCC: $40.75

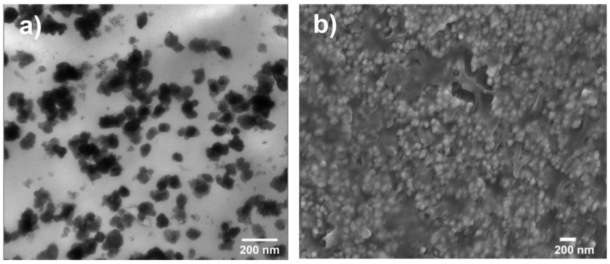

Figure 1. (a) TEM image of P(VDF-CTFE)−$BaTiO_3$ composites with 5 vol % $BaTiO_3$. (b) Cross-sectional FE-SEM image of the P(VDF-TrFE-CTFE)−$BaTiO_3$ nanocomposite thin film containing 23 vol % $BaTiO_3$.

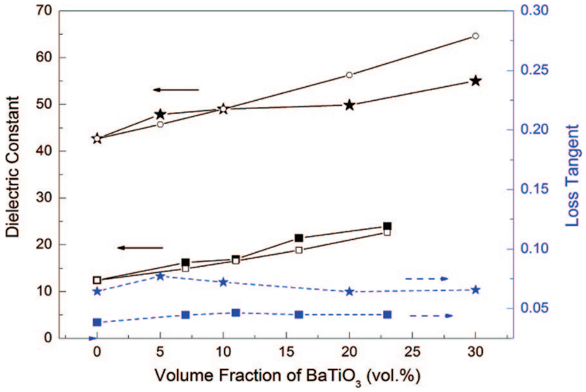

Figure 2. Dielectric constant and loss tangent of the P(VDF-TrFE-CTFE)-$BaTiO_3$ (star) and P(VDF-CTFE)-$BaTiO_3$ (square) nanocomposites measured at 1 kHz and room temperature. Open circles and squares are the calculated effective permittivity from the Lichtenecker law for the P(VDF-TrFE-CTFE) and P(VDF-CTFE) based composites, respectively.

average aggregation size of ~60 nm for the suspension of the ethylene diamine-stabilized $BaTiO_3$ nanoparticles in DMF. The nanocomposite films were prepared by mixing the polymer and nanoparticles in DMF and then drying the cast films at 120 °C under vacuum. The resulting films were further melt pressed at 200 °C for P(VDF-CTFE) based composites and 160 °C for P(VDF-TrFE-CTFE) based composites under 3000 psi. The uniformity of the nanocomposite films is evidenced in the cryo-microtomed TEM and cross-sectional field-emission SEM (FE-SEM) images as shown in Figure 1, where the $BaTiO_3$ nanoparticles are homogeneously dispersed in the polymer matrix with an average particle size of ~50−70 nm. The typical thickness of the nanocomposite film for the dielectric measurements is ~25 μm.

Dielectric permittivity and loss tangent were measured using an Agilent LCR meter from 100 Hz to 2 MHz.[19] The variation of the weak-field dielectric permittivity and loss tangent with the nanoparticle concentration in the nanocomposites is plotted in Figure 2. The dielectric permittivity steadily increases with the increase of the $BaTiO_3$ content, which is ascribed to a higher permittivity of the filler relative to the polymer matrix. At a 20 vol % content of the $BaTiO_3$ nanoparticle, P(VDF-TrFE-CTFE) based nanocomposite exhibits a dielectric permittivity of 50, whereas a permittivity of 24 was found in the P(VDF-CTFE) based nanocomposite. The effective dielectric permittivity of the nanocomposite was calculated based on the Lichtenecker logarithmic rule, which is commonly used in a two-phase composite system: $\log \varepsilon = y_1 \log \varepsilon_1 + y_2 \log \varepsilon_2$, where y_1 and y_2 denote the volume fractions of ceramic fillers and polymer matrix which have dielectric permittivities of ε_1 and ε_2, respectively.[20] As shown in Figure 2, the calculated results agree reasonably well with the experimental data except at high $BaTiO_3$ concentrations (>20 vol %) in the P(VDF-TrFE-CTFE)-based composites where the Lichtenecker logarithmic law overpredicts those measured. It is also noteworthy that the dielectric loss of the nanocomposites arises primarily from the polymer matrices and is almost independent of the volume content of the $BaTiO_3$ filler, further indicating a minimized agglomeration of the filler in the nanocomposites.

Temperature dependence of the dielectric permittivity and loss tangent of the polymers and nanocomposites at frequencies ranging from 10^2 to 10^6 Hz has been investigated using a LCR meter equipped with a temperature chamber at 1 V bias. The dielectric spectra of the nanocomposites are dominated by the dielectric responses of the polymer matrix (Figures 1S and 2S, Supporting Information). For the polymers, the dielectric relaxation peaks shift progressively toward high temperatures with an increase of frequency, corresponding to glass-transition related micro-Brownian motions of chain segments in the amorphous region. At temperatures above 60 °C, both the dielectric permittivity and loss increase markedly with temperature at low frequencies, which are usually interpreted as the Maxwell−Wagner−Sillars (MWS) interfacial polarization in heterogeneous systems and conduction from space charge. The introduction of the $BaTiO_3$ nanoparticles into the polymers drastically decreases the weak-field dielectric permittivity and loss at high temperatures (>60 °C) and low frequencies (e.g., 100 Hz), implying that an increased trapping density in the nanocomposites suppresses the space charge effect and reduces the conduction loss.[21] The surface groups of the $BaTiO_3$ and the nanoparticle/polymer interface are possible charge trapping centers.

The electrical energy density of the polymers and nanocomposites was measured by a modified Sawyer-Tower circuit.[22] As summarized in Figure 3a, the addition of the $BaTiO_3$ nanoparticles into the polymers greatly increases the energy density of the materials. At 150 MV/m, the stored energy density of the P(VDF-TrFE-CTFE) composite with 30 vol % $BaTiO_3$ is 7.0 J/cm^3, which corresponds to a ~120% improvement compared with pure P(VDF-TrFE-CTFE) with a energy density of 3.2 J/cm^3. For P(VDF-CTFE), the achieved stored energy density nearly doubles from 1.9 J/cm^3 to 3.7 J/cm^3 for the nanocomposite containing 23 vol % $BaTiO_3$ nanoparticles under the same field. These energy densities far exceed those reported in the composites based on the conventional polymers such as epoxy and polyethylene, which are less than 3 J/cm^3 in most cases.[8,9] Importantly, the P(VDF-TrFE-CTFE) based nanocomposites generally exhibit much higher energy densities than the

---

(19) Claude, J.; Lu, Y.; Wang, Q. *Appl. Phys. Lett.* **2007**, *91*, 212904.

(20) Rao, Y.; Qu, J. M.; Marinis, T.; Wong, C. P. *IEEE Trans. Compon., Packag. Technol.* **2000**, *23*, 680.

(21) Smith, R. C.; Liang, C.; Landry, M.; Nelson, J. K.; Schadler, L. S. *IEEE Trans. Dielect. Elect. Insul.* **2008**, *15*, 187.

(22) Sinha, J. K. *J. Sci. Instrum.* **1965**, *42*, 696.

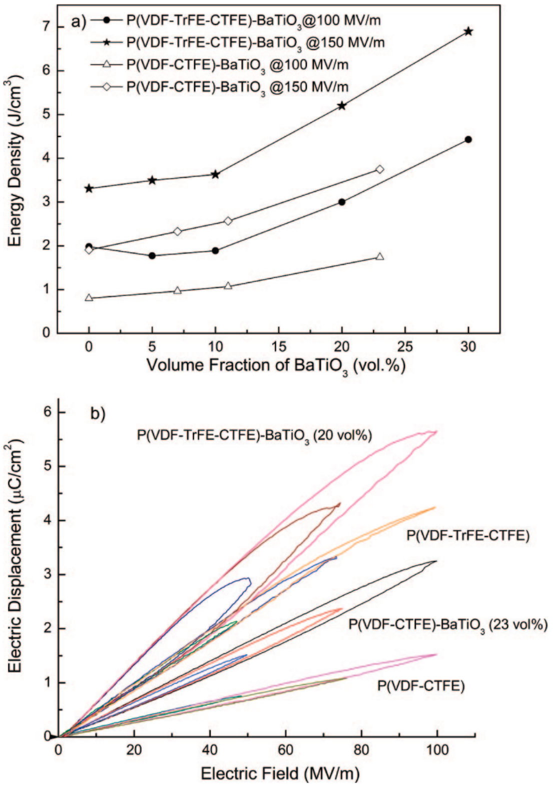

Figure 3. (a) The dependence of energy density on the BaTiO$_3$ content in the P(VDF-TrFE-CTFE) and P(VDF-CTFE) based nanocomposites measured under 100 and 150 MV/m. (b) Electric displacement-field (*D*−*E*) loop measured under different applied fields at room temperature and 10 Hz for the polymers and nanocomposites.

corresponding composites based on P(VDF-CTFE). This is in accordance with the weak-field trend presented in Figure 2 and can be attributed to larger electric displacement achieved in the P(VDF-TrFE-CTFE) matrix. As exampled in Figure 3b, under a field of 100 MV/m the electric displacement reaches more than 5.6 μC/cm^2 in the P(VDF-TrFE-CTFE) composite with 20 vol % BaTiO$_3$, while the electric displacement in the composite composed of P(VDF-CTFE) and the same volume content of BaTiO$_3$ is less than 3.3 μC/cm^2. Similarly, the incorporation of the nanoparticles notably raises the electric displacement, which accounts for the remarkably improved energy densities in the nanocomposites over the pristine polymer. As also shown in Figure 3b, compared to the polymer matrix, the nanocomposites exhibit increased polarization hysteresis and dielectric loss, which also increase progressively with the applied field. These results are consistent with earlier studies, indicating strong charge injection and trapping in the composites because the BaTiO$_3$ nanoparticles with a higher permittivity greatly enhance the local electric field dropped across the polymer phase.[23]

It is well-known that the polarization and dielectric properties of the PVDF based ferroelectric polymers originate from their crystalline domains.[14] To acquire the influence of the BaTiO$_3$ nanoparticles on the crystallization behavior of the polymer matrix, differential scanning calorimery (DSC) measurements were carried out. The DSC profiles of the polymers and nanocomposites recorded during heating and cooling scans are displayed in Figures 3S and 4S, Supporting Information. The introduction of the nanoparticles into the polymers raises the crystallization temperatures, from ~100 °C for P(VDF-TrFE-CTFE) to ~106 °C for the nanocomposite containing 5 vol % BaTiO$_3$. An even larger shift of about 20 °C has been observed in the P(VDF-CTFE) composite with 7 vol % BaTiO$_3$ nanoparticles (Figure 4S, Supporting Information), illustrating the role of the nanoparticles as a nucleating agent in the crystallization of the polymer matrix. Consistent with the change in the crystallization temperatures, the heat of fusion in the nanocomposites increases from 18.3 J/g from P(VDF-TrFE-CTFE) to 20.7 J/g for the composite with 5 vol % BaTiO$_3$ nanoparticles, which corresponds to a change of the degree of crystallinity from 21% for the neat polymer to 24% for the composites. On the contrary, the melting temperatures decrease in the composites compared to that in the polymer. This suggests that the presence of the nanoparticles in the matrix decreases the crystal size of the polymer, which is in agreement with the decrease of the crystallization temperatures and the heat of fusion with further increasing of the volume fraction of the BaTiO$_3$ nanoparticle.[24] Nevertheless, it is believed that the enhanced electric displacement yielded from the nanoparticles, rather than the changes in the crystallinity of the polymer matrix, is mainly responsible for the observed increase in the energy density in the nanocomposites.[13]

In summary, two series of the polymer nanocomposites based on the surface-functionalized BaTiO$_3$ nanoparticles and ferroelectric polymers were prepared. The presence of organic surface layers on the particle affords excellent compatibility between the fillers and the polymer matrix and ensures uniform composite films even at higher filler concentrations. The dominant role of dielectric permittivity of the polymer matrix in determining the energy density of the nanocomposite has been demonstrated. This study suggests that the polymer matrix must be properly selected for the nanocomposites to realize significantly enhanced energy density.

Acknowledgment. This work is supported by the National Science Foundation (CAREER DMR-0548146) and the Office of Naval Research (N000-14-05-1-0541). We thank Prof. Fatih Dogan at Missouri University of Science and Technology for his help on the impedance spectroscopy.

Supporting Information Available: Experimental details for the synthesis and characterization (PDF). This material is available free of charge via the Internet at http://pub.acs.org.

CM8021648

---

[23] Kilaru, M. K.; Heikenfeld, J.; Lin, G.; Mark, J. E. *Appl. Phys. Lett.* **2007**, *90*, 212906.

[24] Kim, K. M.; Park, N. G.; Ryu, K. S.; Chang, S. H. *Polymer* **2002**, *43*, 3951.