TABLE OF CONTENT GRAPHIC

Effects of internal and external electronic conduction in sodium titanate nanotubes on dielectric loss mechanisms in relaxor ferroelectric polymer nanocomposites

Zhe Liu, Guoqiang Zhang, Saide Tang, Zhongbo Zhang, Hong Zhu, and Lei Zhu

**Effects of Internal and External Electronic Conduction in Sodium Titanate Nanotubes on
Dielectric Loss Mechanisms in Relaxor Ferroelectric Polymer Nanocomposites**

Zhe Liu,^{a,b} Guoqiang Zhang,^b Saide Tang,^b Zhongbo Zhang,^b Hong Zhu,^{*,a} and Lei Zhu^{*,b}

^a State Key Laboratory of Chemical Resource Engineering, Institute of Modern Catalysis,
Department of Organic Chemistry, School of Science, Beijing University of Chemical
Technology, Beijing 100029, P. R. China

^b Department of Macromolecular Science and Engineering, Case Western Reserve University,
Cleveland, Ohio 44106-7202, United States

* Corresponding authors, E-mails: lxz121@case.edu (L.Z.); zhuho128@126.com (H.Z.).

Abstract

In this report, we studied dielectric loss mechanisms in a 1-3 type of polymer nanocomposites, i.e., nanofibers or nanotubes in a polymer matrix. Sodium titanate nanotubes (TiNTs, 8-10 nm outer diameter and 300-500 nm long), which were synthesized by the hydrothermal method, were used as the fillers. The polymer matrix was a high permittivity relaxor ferroelectric polymer, poly(vinylidene fluoride-*co*-trifluoroethylene-*co*-chlorotrifluoroethylene). The nanocomposites were fabricated using solution-blending followed by hot-pressing above the melting temperature. Because of the high aspect ratio of TiNT fillers, the percolation threshold was found to be around 10-12.5 vol.%. Below the percolation threshold, significant dielectric losses (both linear and nonlinear) were identified using bipolar and unipolar electric displacement - electric field (D-E) loop tests. For aggregated/percolated TiNTs, external electronic conduction was the major linear dielectric loss. For isolated TiNTs, internal electronic conduction contributed significantly to the nonlinear dielectric loss. From this study, we conclude that it is better to develop highly insulating nanofibers or nanotubes for the 1-3 type polymer nanodielectrics and the nanofillers content should be kept far below the percolation threshold in order to avoid significant dielectric losses.

Keywords: P(VDF-TrFE-CTFE) terpolymer, sodium titanate nanotubes, nanodielectrics

1. Introduction

High energy density dielectric polymers are promising for a variety of emerging electrical and power applications, such as DC-link capacitors for power electronics in electric vehicles, implantable defibrillators, artificial muscles, and electrocaloric cooling.[1-3] Current research is focused on enhancing the dielectric constant for neat polymers and polymer/inorganic nanocomposites, because conventional linear dielectric polymers only exhibit a relatively low dielectric constant between 2 and 5. For pure polymers, various strategies have been used to enhance dielectric constants via electronic/atomic polarization, orientational polarization, and ionic polarization.[2] Utilizing electronic and atomic polarizations, the maximum dielectric constant calculated for existing hydrocarbon-based polymers is ca. 5 when the lower limit of band gap for highly insulating polymers is 4 eV.[4] Recently, the dielectric constant for amorphous aromatic polythiourea is reported to be 5-6.[5, 6] The mechanism is attributed to the large atomic polarization of the aromatic thiourea bonds. Using ionic polarization (i.e., electric double layer), the capacitance can be over 1000 times higher than that of linear dielectric polymers. However, ions have a low mobility and will not respond above 10^4 Hz,[7] even though their movement within the double layer is only about 2-5 nm. Therefore, electric double layer capacitors (EDLCs) are not suitable for high frequency power applications. Meanwhile, the voltage limit for EDLCs is about 2 V for aqueous electrolytes and 2.7 V for organic electrolytes.[8] Orientational (or dipolar) polarization is promising in enhancing dielectric constant and shifting the relaxation of molecular dipoles into MHz frequency or above.[2] For example, a dipolar glass polymer, poly(methylsulfonyl ethyl methacrylate) (PMSEMA), is reported to exhibit a high dielectric constant of 11-12 below the glass transition temperature (T_g).[9] Paraelectric poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] has an apparent dielectric constant of ca. 40 in the

high temperature paraelectric phase.[10] Relaxor ferroelectric P(VDF-TrFE-X) terpolymers [X is 1,1-chlorofluoroethylene (CFE) or chlorotrifluoroethylene (CTFE)] have shown high dielectric constants between 55 and 70.[2] However, the higher the dielectric constant, the higher dielectric loss is observed.

The other branch of research focuses on polymer/inorganic nanocomposites or nanodielectrics.[11-13] The idea is to combine the high dielectric constant from inorganic nanofillers and the high breakdown and low loss property from the polymer matrix. Numerous theoretical/simulations and experimental results have been reported, covering a broad range of material design parameters: i) linear dielectric polymer matrices[14-16] versus ferroelectric/relaxor ferroelectric polymer matrices,[17-20] ii) different inorganic nanoparticles (NPs) with various permittivities (e.g., ZrO_2 : $\epsilon_r \sim 25$, anatase TiO_2 : $\epsilon_r \sim 40$,[20] BaTiO_3 or $\text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3$: $\epsilon_r \sim 200$),[14, 17, 18, 22-24] and metals/carbons (nanotubes and graphenes; $\epsilon_r \sim \infty$),[15, 16, 25] iii) NPs with different aspect ratios (i.e., spheres, nanowires, and nanoplatelets),[22, 25-28] iv) surface modification of nanofillers with small molecule ligands or polymer brushes for better dispersion,[14-18, 27, 29] v) matrix-free hairy particle composites,[30-32] and vi) multicomponent systems with complex architectures.[24, 33, 34] Although enhanced apparent dielectric constants and increased discharge energy density are reported, the fundamental understanding of dielectric loss mechanisms in polymer nanodielectrics is just emerging. On the basis of a recent report,[35] dielectric losses of polymer nanodielectrics are closely related to the large contrast in permittivity and conductivity between the nanofillers and the polymer matrix. First, the high permittivity (ϵ_r) nanofillers tend to increase the local electric field in the polymer matrix,[36-39] especially between chained or clustered particles,[40] resulting in decreased electrical breakdown strength.[18, 37, 41] Second, high conductivity contrast between the

nanofillers and the polymer matrix results in a higher concentration of space charges (most likely thermally activated free electrons) in the nanofillers than in the polymer matrix. Under an applied electric field, these space charges form Maxwell-Wagner-Sillars (MWS) interfacial polarization. Upon an AC electric poling, the internal electronic conduction loss leads to a significantly decreased discharge efficiency (η); the higher the poling field, the lower the η .

To mitigate the effect of nonuniform electric field distribution on decreased breakdown strengths, several strategies are proposed: (i) reducing the ϵ_r contrast by utilizing a high permittivity polymer matrix and moderate permittivity nanofillers;[20, 21] (ii) addition of exfoliated hexagonal boron nitride (h-BN) in polymer nanodielectrics to prevent dielectric breakdown;[24, 28] and (iii) achieving high dielectric constants at a low filling ratio (< 10 vol.%) by using a high ϵ_r interfacial material between the nanofiller and the polymer matrix.[42-44] To reduce the internal electronic conduction loss, unipolar, instead of bipolar, electric poling should be used.[35] Alternatively, highly insulating (conductivity $\sigma < 10^{-13}$ S/m) nanoparticles with a high ϵ_r (> 100) should be used for polymer nanodielectrics; however, such nanoparticles are yet to be discovered.[35]

In this study, we continue to investigate the effect of high aspect ratio nanofiber or nanotube fillers on the dielectric loss mechanisms in polymer nanodielectrics. Sodium titanate nanotubes (TiNTs), about 8-10 nm outer diameter and 300-500 nm long, are used as nanofillers. A relaxor ferroelectric P(VDF-TrFE-CTFE) terpolymer with a high ϵ_r value of 50-70 is used as the polymer matrix. Due to the high aspect ratio of the TiNTs, percolation is easier to be achieved at about 12.5 vol.% TiNTs, instead of ca. 35 vol.% for spherical nanofillers. As a result, both external and internal electronic conduction contribute significantly to the dielectric loss in the terpolymer/TiNT nanodielectrics.

2. Experimental

2.1. Sodium titanate nanotube synthesis and nanodielectric film preparation

TiNTs [$\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$] were synthesized following a hydrothermal method reported previously.[45] Briefly, 0.4 g of TiO_2 (P25, Aldrich) was added to 40 mL of 10 M NaOH aqueous solution under stirring. After 10 min, the suspension was transferred to a 100-mL Teflon-lined autoclave and maintained at 140 °C for 48 h. After the reaction, the resulting white precipitate was centrifuged, washed with ethanol and water several times, and then dried under vacuum at 60 °C. To eliminate the influence of impurity ions, the product was further dialyzed using a dialysis tube with a molecular weight cut-off of 3000 Da (Spectrum Laboratories, Inc.) in deionized water for 3 d. Finally, purified **TiNTs** were dried in a vacuum oven at 60 °C for 3 d.

The P(VDF-TrFE-CTFE) 62.2/30.2/7.6 (molar ratio) terpolymer was kindly supplied by Piezotech, Inc./Arkema (Lyon, France). The P(VDF-TrFE-CTFE)/**TiNT** nanocomposites with different **TiNT** volume fractions (2.5, 7.5, 10.0, and 12.5 vol.%) were prepared via a solution-blending method. First, the required amounts of **TiNTs** and P(VDF-TrFE-CTFE) were dissolved in N,N-dimethylformamide (DMF) under ultrasonication. The mixture was stirred at room temperature for 24 h. The resulting mixture suspension was quickly precipitated in deionized water and centrifugation was used to obtain the nanocomposites. The obtained P(VDF-TrFE-CTFE)/**TiNT** nanocomposites were dried under vacuum at 70 °C for 3 d. Finally, the dried nanocomposites were hot-pressed at 190 °C with a 10-ton pressure to obtain ~50 μm thick films.

2.2. Instrumentation and characterization

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 DSC at a scanning rate of 10 °C/min. Two-dimensional (2D) X-ray diffraction (XRD) experiments were performed on a Rigaku XRD instrument (MacroMax 002⁺) equipped with a Confocal Max-Flux optic and a microfocus X-ray tube source operating at 45 kV and 0.88 mA. The X-ray wavelength was Cu K α at 0.1542 nm. The 2D XRD patterns were collected using a Fujifilm image plate scanned by a Fujifilm FLA-7000 scanner at a resolution of 50 μ m/pixel. One-dimensional (1D) XRD curves were obtained by integrating the corresponding 2D WAXD patterns radially using the Polar software developed by Stonybrook Technology and Applied Research, Inc.

Transmission electron microscopy (TEM) was carried out on an FEI Tecnai T12 electron microscope at an accelerating voltage of 100 kV, and bright-field images were recorded using a bottom-mounted Gatan CCD camera. The nanocomposites were embedded in standard epoxy and were cured at 60 °C overnight. Thin sections were obtained by microtoming (Leica Ultracut UCT microtome) the film cross-sections using a freshly cleaved glass knife. Thin sections were floated onto the surface of a water boat and collected using 400-mesh copper TEM grids.

Broadband dielectric spectroscopy (BDS) measurements were performed on a Novocontrol Concept 80 broadband dielectric spectrometer (Montabaur, Germany) with temperature control. The applied voltage was 1 V_{rms} (root-mean square voltage) with the frequency ranging from 0.01 Hz to 10 MHz and the temperature from -50 to 100 °C. Silver electrodes (50 nm thick) were evaporated by using an EvoVac Deposition System (Angstrom Engineering Inc., Kitchener, Ontario, Canada) on both sides of the film. The electrode area was 0.786 cm². The electric displacement-electric field (D-E) hysteresis loop measurements were carried out on a Premiere II ferroelectric tester (Radiant Technologies, Inc.) in combination with a Trek 10/10B-HS high voltage amplifier (0-10 kV AC, Lockport, NY, U.S.A.). The applied voltage had a bipolar or

unipolar sinusoidal waveform in the frequency range of 10 to 1000 Hz. The sample was immersed in a silicon oil bath during tests at room temperature. Again, silver was evaporated on both sides of the film as electrodes (50 nm thick), and the electrode area was 0.0515 cm².

Fig. 1. (A) First cooling and (B) second heating DSC curves for P(VDF-TrFE-CTFE)/TiNT nanocomposites having different filler contents (0, 2.5, 7.5, and 10.0 vol.%).

3. Results and discussion

3.1. Crystalline structures in P(VDF-TrFE-CTFE)/TiNT nanocomposites

It is known that the relaxor ferroelectric property of the P(VDF-TrFE-CTFE) terpolymer originates from its isomorphous (or defect-modified) crystalline structure.[2, 10] To investigate the influence of the TiNT content on the crystallinity, DSC was carried out, as shown in Fig. 1. During the first cooling, the crystallization temperature (T_c) for the neat P(VDF-TrFE-CTFE) terpolymer located at 97.4 °C. The T_c increased to 99.7 °C for the 2.5 vol.% TiNT nanocomposite, and this could be attributed to the nucleating effect of TiNTs for the P(VDF-TrFE-CTFE) terpolymer.[20] As the TiNT volume fraction further increased to 10.0 vol.%, the T_c decreased to 98.2 °C, possibly due to the dipolar interaction between TiNTs and the P(VDF-TrFE-CTFE) matrix. During the second heating process, the melting temperature (T_m) decreased from 127.2 °C for the neat

terpolymer to 123.2 °C for the nanocomposite with 10.0 vol.% **TiNTs**. The degree of crystallinity (χ_c) was calculated by $\chi_c = \Delta H_f / (w \Delta H_f^\circ) \times 100\%$, where ΔH_f is the heat of fusion during the second heating, ΔH_f° the heat of fusion for the 100% crystalline terpolymer (42.0 J/g), [46] and w the weight fraction of the terpolymer. The density of **TiNTs** was taken as 3.90 g/cm³. [45] The χ_c values were 38 wt.% for the terpolymer, and 40, 25, and 22 wt.% for the nanocomposites with 2.5, 7.5, and 10 vol.% **TiNTs**, respectively. The decreased T_m and χ_c values for the 7.5 and 10.0 vol.% **TiNT** nanocomposites suggested again strong dipolar interactions between the **TiNTs** and the P(VDF-TrFE-CTFE) matrix. Finally, broad Curie transition peaks were observed at 17-19 °C upon cooling and 23-25 °C upon heating for the terpolymer and different nanocomposites. The relatively stable Curie temperatures (T_c) could be attributed to the solid phase transition inside the crystals.

Fig. 2. XRD profiles of P(VDF-TrFE-CTFE) and its nanocomposites having 2.5, 7.5, and 10.0 vol.% **TiNTs**.

Fig. 2 shows the XRD patterns of P(VDF-TrFE-CTFE) and its nanocomposites with different **TiNT** contents. For P(VDF-TrFE-CTFE), the (110) and (200) reflections were observed

at $2\theta = 18.08^\circ$ and 18.44° , respectively.[47] For the **TiNT** nanocomposites, weak and broad peaks at $2\theta = 9.8^\circ$, 24° , and 28° corresponded to the (200), (110), and (600) reflections of the **TiNTs**. [45] Upon increasing the **TiNT** content, the (110) reflection peak at $2\theta = 18.08^\circ$ gradually merged with the (200) reflection.

Fig. 3. Bright-field TEM micrographs of (A) **TiNTs** and microtomed thin sections (ca. 70 nm thick) of P(VDF-TrFE-CTFE)/**TiNT** nanocomposites with (B) 2.5 vol.%, (C) 7.5 vol.%, and (D) 10 vol.% **TiNTs**, respectively.

3.2. TEM morphology study of **TiNTs** and various P(VDF-TrFE-CTFE)/**TiNT** nanocomposites

Fig. 3A shows the TEM image of TiNTs. The diameter of the TiNTs was ca. 8-10 nm and the length was about 300-500 nm. Figs. 3B-D show the TEM micrographs of microtomed thin sections of the P(VDF-TrFE-CTFE)/TiNT nanocomposites containing different filler contents (2.5, 7.5, and 10.0 vol.%). When the TiNT content was 2.5 vol.% (Fig. 3B), TiNTs dispersed in the terpolymer matrix without significant aggregation (only some flocculation). When the TiNT content increased to 7.5 vol.% (Fig. 3C), certain aggregation was observed. Finally, when the TiNT content reached 10.0 vol.% (Fig. 3D), significant nanotube aggregation was seen. We speculate that at 10.0 vol.%, the TiNTs might have already percolated (at least locally) in the terpolymer matrix.

Fig. 4. (A,C) Real (ϵ') and (B,D) imaginary (ϵ'') parts of relative permittivity as a function of temperature for (A,B) P(VDF-TrFE-CTFE) and (C,D) the nanocomposite with 7.5 vol.% TiNTs under various frequencies.

3.3. Linear dielectric property study

The low-field linear dielectric properties for the terpolymer and the nanocomposites having various **TiNT** contents were studied by BDS. Fig. 4 shows the temperature-scan results for the P(VDF-TrFE-CTFE) terpolymer and the P(VDF-TrFE-CTFE)/**TiNT** nanocomposites having 7.5 vol.% **TiNTs**. For the terpolymer, there were two relaxation peaks at -18 and 25 °C at 1 Hz (Fig. 4B), which were assigned to the **dynamic** glass transition temperature (T_g) and the T_C , respectively. The **dynamic** T_g increased with increasing temperature, eventually merged with T_C above 10^5 Hz. The upturns in both ϵ_r' and ϵ_r'' at low frequencies and high temperatures were ascribed to the migration of impurity ions in the polymer matrix (mainly inherited from surfactants used in the suspension terpolymerization).[48] After adding 7.5 vol.% **TiNTs**, the ϵ_r' increased slightly (Fig. 4C). This could possibly be attributed to the higher dielectric constant of the **TiNTs**. However, ϵ_r'' increased substantially for the nanocomposite under all frequencies when the temperature was below 40 °C (Fig. 4D). Judging from the similar ϵ_r'' values for both the terpolymer and the 7.5 vol.% **TiNT** nanocomposite at 100 °C and 1 Hz (see Figs. 4B,D), the amount of impurity ions introduced by **TiNTs** was insignificant (note that the **TiNTs** had been stringently dialyzed using deionized water). Therefore, the enhanced loss mechanism needs to be attributed to other mechanisms (which will be discussed later).

Fig. 5. Frequency-scan BDS results for the P(VDF-TrFE-CTFE) terpolymer and its nanocomposites with **TiNT** at different compositions: (A,B) 0 °C, (C,D) 25 °C, (E,F) 50 °C, and (G,H) 75 °C. ϵ'_r results are in (A,C,E,G) and ϵ''_r results are in (B,D,F,H).

To understand the loss mechanism for the 7.5 vol.% **TiNT** nanocomposite, the **TiNT** content was varied and the corresponding frequency-scan BDS results at various temperatures are shown in Fig. 5. At 0 °C, the ϵ'' peaks around 4×10^4 Hz in Fig. 5B were attributed to the relaxation of amorphous dipoles of the terpolymer. These relaxation peaks were nearly the same for the terpolymer and its nanocomposites with various amount of **TiNTs**. When the frequency was below 1000 Hz, the higher the **TiNT** content, the higher the upturn of the ϵ'' (i.e., the higher the loss). Usually, ion mobility at 0 °C could be negligibly small for PVDF and its copolymers.[49] The enhanced ϵ'' at low frequencies for the nanocomposites again could not be explained by the migrational loss of impurity ions from blending **TiNTs** in the terpolymer. At 25 °C, the relaxation peaks for the amorphous dipoles shifted to a higher frequency (i.e., 5×10^5 Hz). An obvious upturn was observed for the terpolymer below 0.2 Hz, which could be attributed to the migrational loss from impurity ions in the terpolymer. Again, the higher the **TiNT** content, the higher the ϵ'' for the nanocomposites. When the temperature increased to 50 and 75 °C, the relaxation peaks for the amorphous dipoles further shifted to higher frequencies. Meanwhile, a similar trend was observed:

the higher the **TiNT** content, the higher the dielectric loss at low frequencies. Only from the linear dielectric results in Figs. 4 and 5, it is difficult to unravel the underlying reason for the higher loss of the terpolymer/**TiNT** nanocomposites. Below, we will study their nonlinear dielectric properties using high-field D-E loops study.

Fig. 6. Continuous four bipolar D-E hysteresis loops for (A,B,C) P(VDF-TrFE-CTFE), (D,E,F) 2.5 vol.% **TiNT** nanocomposite, and (G,H,I) 7.5 vol.% **TiNT** nanocomposite films at room temperature under different poling frequencies: (A,D,G) 10 Hz, (B,E,H) 100 Hz, and (C,F,I) 1000 Hz. For (D and G), the blue horizontal loops represent the external electronic conduction. After subtracting the external electronic conduction, the remaining loops are shown in red.

3.4. Nonlinear dielectric property study

High-field bipolar D-E hysteresis loop was used to study the nonlinear dielectric properties (i.e., dielectric loss mechanism) for the P(VDF-TrFE-CTFE)/TiNT nanocomposites. Fig. 6 shows continuous four bipolar D-E loops for the P(VDF-TrFE-CTFE), the 2.5 vol.% TiNT, and the 7.5 vol.% TiNT nanocomposite films at room temperature under different frequencies (i.e., 10, 100, and 1000 Hz). Here, the poling field was limited to 60 MV/m, because the nanocomposites easily broke down at higher fields. As we can see, the unoriented terpolymer exhibited relatively narrow bipolar D-E loops under all frequencies because of its relaxor ferroelectric behavior.[47] Adding 2.5 vol.% TiNTs into the terpolymer matrix significantly increased the dielectric loss, which was represented by the hysteresis loop area (Figs. 6D-F). Upon increasing the TiNT content to 7.5 vol.%, the dielectric nonlinearity (or loss) further increased (Figs. 6G-I). Meanwhile, the lower the poling frequency, the higher the dielectric loss. For example, for the 7.5 vol.% TiNT nanocomposite at 10 Hz, the bipolar D-E loop became a rounded shape, representing significant dielectric loss. This observation was consistent with the linear dielectric results for the terpolymer/TiNT nanocomposites having different TiNT contents in Fig. 5D.

One of the dielectric loss mechanisms is the external electronic conduction, which is linear in nature (i.e., it only causes a phase shift for the measured electric displacement or current as a function of time, and no shape change is involved [50]). It can be judged from the upshift of the upper part of the bipolar D-E hysteresis loop, when there is no remanent polarization.[48] In Figs. 5A-C, no upshift for the upper parts of the bipolar D-E loops was observed for P(VDF-TrFE-CTFE), suggesting negligible external electronic conduction for the terpolymer at room temperature. For the P(VDF-TrFE-CTFE)/TiNT nanocomposites, no loop-upshift (or no external electronic conduction) was observed when the poling frequency was 100 Hz and above. However, when the poling frequency was 10 Hz, significant upshift in the upper parts of the bipolar loops

was observed. Therefore, at low frequencies and high poling electric fields, one major dielectric loss mechanism should be the external electronic conduction for the terpolymer/TiNT nanocomposites.

According to our previous report,[48] external electronic conduction loss (represented by the horizontal blue loops in Figs. 5D and G) could be subtracted from the bipolar D-E hysteresis loop. After subtraction, the remaining red D-E loops in Figs. 5D and G still appeared fairly broad, indicating other important loss mechanisms. In a most recent report,[35] we report internal electronic conduction for BaTiO₃ nanoparticles in a polypropylene matrix. Because it was the internal electronic current within BaTiO₃ nanoparticles (i.e., no electronic current flowing from the cathode to the anode through the sample), no upshift in the upper bipolar loop was seen. However, a broad bipolar hysteresis loop having a symmetric shape with respect to the origin was still observed. Therefore, the broad bipolar hysteresis loops in Figs. 6D and G (and in Fig. 6H) could also be attributed to the internal electronic conduction in the TiNTs. Here, internal electronic conduction is a nonlinear dielectric loss, because it changes the shape of the measured electric displacement or current as a function of time from the sinusoidal wave function.[50]

To mitigate the internal electronic conduction loss from bipolar poling, continuous unipolar D-E loop poling was used. Only the first unipolar loop showed a high hysteresis loop loss, and the rest unipolar loops had much less loop loss. This is exactly seen in the unipolar D-E loops for the terpolymer/TiNT nanocomposites in Fig. 7. For the neat terpolymer under different frequencies (Figs. 7A-C), the first unipolar loop had a higher loop area (or loss) than the rest loops. This could be explained by the electric poling of certain irreversible ferroelectric domains in the sample.[47] After poling of the irreversible ferroelectric domains in the first unipolar loop, the rest unipolar poling became reversible, although there was still certain hysteresis. As a result, the

rest unipolar loops largely overlapped. With increasing the poling frequency to 1000 Hz, the first loop became increasingly closer to the rest loops, indicating that the irreversible ferroelectric domains could not follow the high frequency poling.

Fig. 7. Continuous four unipolar D-E hysteresis loops for (A,B,C) P(VDF-TrFE-CTFE), (D,E,F) 2.5 vol.% TiNT nanocomposite, and (G,H,I) 7.5 vol.% TiNT nanocomposite films at room temperature under different poling frequencies: (A,D,G) 10 Hz, (B,E,H) 100 Hz, and (C,F,I) 1000 Hz. The starting point of each unipolar loop is shifted down to the origin for all plots.

For the terpolymer/TiNT nanocomposites, the first unipolar loops were significantly broader than the rest unipolar loops. When the poling frequency was 100 Hz and above (Figs. 7E,F,H,I), the large difference between the first and the rest unipolar loops could be attributed to the internal electronic conduction, because there was negligible external electronic conduction as

demonstrated in Figs. 6E,F,H,I (i.e., no upshift for the upper parts of the bipolar loops). When the poling frequency was 10 Hz (Figs. 7D,G), both internal and external electronic conductions resulted in broad unipolar D-E loops.

Fig. 8. Discharged energy densities at 60 MV/m for (A) P(VDF-TrFE-CTFE), (B) 2.5 vol.% **TiNT** nanocomposite, and (C) 7.5 vol.% **TiNT** nanocomposite under different poling frequencies. Discharge efficiencies at 60 MV/m for (D) P(VDF-TrFE-CTFE), (E) 2.5 vol.% **TiNT** nanocomposite, and (F) 7.5 vol.% **TiNT** nanocomposite under different poling frequencies.

The discharged energy densities (U_e s) at 60 MV/m for the terpolymer and the **TiNT** nanocomposites in both bipolar and unipolar poling processes are shown in Figs. 8A-C. Comparing Fig. 8A with Fig. 8B, the U_e s for the 2.5 vol.% **TiNT** nanocomposite appeared to be similar to those of the unoriented terpolymer under various frequencies, no matter bipolar or unipolar poling. For the 7.5 vol.% **TiNT** nanocomposite, the U_e values were higher at high frequencies, but lower at low frequencies. The mediocre performance in discharged energy density

for the **TiNT** nanocomposites could be explained by their poor discharge efficiencies (η) in Figs. 8E and F, compared to those for the terpolymer. For the terpolymer (Fig. 8D), the discharge efficiencies for the bipolar and the first unipolar loops were nearly the same, but slightly smaller than those for the fourth unipolar loops. The frequency dependency of the η for the terpolymer was fairly weak. For the **TiNT** nanocomposites, strong frequency dependency was observed (Figs. 8B and C). The lower the frequency, the lower the η as the **TiNT** content increased. The η values for the bipolar and the first unipolar loops were similar. However, they were much lower than those for the fourth unipolar loops.

Fig. 9. Proposed dielectric loss mechanisms for P(VDF-TrFE-CTFE)/**TiNT** nanocomposites: (I) internal electronic conduction inside the nanotube (a cross-section view) and (II) external electronic conduction along the (percolated) nanotube.

The above experimental results suggest significant dielectric loss mechanisms for the P(VDF-TrFE-CTFE)/**TiNT** nanocomposites. They are (I) internal electronic conduction inside the **TiNTs** and (II) external electronic conduction via aggregation or percolation of **TiNTs** in the polymer matrix (see Fig. 9). Compared to spherical nanoparticle/polymer nanocomposites,[35] there are certain similarity and difference. The similarity is the internal electronic conduction inside the inorganic nanoparticle or nanotubes, because they are more conductive (usually $10^{-8} \sim 10^{-10}$ S/m) than the polymer matrix (about $10^{-14} \sim 10^{-17}$ S/m). The difference lies in the external electronic conduction through the nanocomposite sample. For spherical nanoparticle composites,

the percolation threshold is about 30-35 vol.%. However, for nanotubes, the percolation threshold can be much lower because of their high aspect ratios. Depending upon the aspect ratio, the percolation threshold varies: the higher the aspect ratio, the lower the percolation threshold. For example, when the aspect ratio was 3, the percolation threshold was reported to be 18 vol.% on the basis of finite element analysis.[38]

Fig. 10. Continuous four bipolar D-E loops at (A) 100 Hz and (B) 1000 Hz and continuous unipolar D-E loops at (C) 100 Hz and (D) 1000 Hz for the 10 vol.% **TiNT** nanocomposite film at room temperature. For the continuous unipolar loops in (C and D), the starting points are shifted down to origin.

Similar continuous bipolar and unipolar D-E loop results were also obtained for the 10 vol.% **TiNT** nanocomposites (see Fig. 10). Significant dielectric losses were observed even under 100 and 1000 Hz, which could again be attributed to both internal and external electronic conduction

caused by TiNTs in the terpolymer matrix. No results could be obtained for the 10 Hz poling frequency because the hot-pressed films were easy to electrically breakdown. Electrical breakdown was even worse for the 12.5 vol.% TiNT nanocomposite, and nearly no bipolar and unipolar D-E loops could be obtained. This result indicated that the percolation threshold could be somewhere around 12.5 vol.%. Note that these TiNTs were not surface-functionalized. Nanotube aggregation (e.g., see Fig. 3D) could also contributed to the lower breakdown strength at >10 vol.% TiNT content.

4. Conclusions

By varying the nanotube content, a series of P(VDF-TrFE-CTFE)/TiNT nanocomposites was prepared by solution-blending followed by hot-pressing. Due to the high aspect ratio of TiNTs and certain aggregation, the percolation threshold was estimated to be around 10-12.5 vol.%. Below the percolation threshold, both continuous bipolar and unipolar D-E loops were used to study the dielectric loss mechanisms in the terpolymer/TiNT nanocomposites. When the poling frequency was 10 Hz, significant upshift in the top part of the bipolar loops was observed for the nanocomposites, indicating the existence of the external electronic conduction loss mechanism. Above 100 Hz, no external electronic conduction could be observed; however, significant dielectric nonlinearity was still seen. This could be attributed to the internal electronic conduction in the TiNTs. It was the internal electronic conduction that made the first unipolar loop significantly different from the rest unipolar loops during continuous unipolar poling. From this study, we can propose future designing rules for polymer/nanotube composites for electric energy storage applications. First, nanotubes need to be functionalized by polymer brushes[51] to achieve uniform dispersion and thus a higher percolation threshold and a higher breakdown strength.

Second, much more insulating inorganic nanotubes are desired to reduce the dielectric loss from internal electronic conduction.[35] In the future, we will carry out both studies to achieve better dielectric performance for polymer/nanotube nanocomposites.

Acknowledgment

This work is supported by National Science Foundation (NSF) Science and Technology Center, Center for Layered Polymeric Systems (DMR-0423914). ZL acknowledges financial support from Chinese Scholarship Council and the National Natural Science Foundation of China (No. 21176022, 21376022).

References

- [1] W.J. Sarjeant, I.W. Clelland, R.A. Price, Capacitive components for power electronics, *Proc. IEEE*. 89 (2001) 846-855.
- [2] L. Zhu, Exploring strategies for high dielectric constant and low loss polymer dielectrics, *J. Phys. Chem. Lett.* 5 (2014) 3677-3687.
- [3] Q. Chen, Y. Shen, S. Zhang, Q.M. Zhang, Polymer-based dielectrics with high energy storage density, *Annu. Rev. Mater. Res.* 45 (2015) 433-458.
- [4] C.C. Wang, G. Pilania, S.A. Boggs, S. Kumar, C. Breneman, R. Ramprasad, Computational strategies for polymer dielectrics design, *Polymer* 55 (2014) 979-988.
- [5] S. Wu, W. Li, M. Lin, Q. Burlingame, Q. Chen, A. Payzant, K. Xiao, Q.M. Zhang, Aromatic polythiourea dielectrics with ultrahigh breakdown field strength, low dielectric loss, and high electric energy density, *Adv. Mater.* 25 (2013) 1734-1738.

- [6] Y. Thakur, R. Dong, M. Lin, S. Wu, Z. Cheng, Y. Hou, J. Bernholc, Q.M. Zhang, Optimizing nanostructure to achieve high dielectric response with low loss in strongly dipolar polymers, *Nano Energy* 16 (2011) 227-234.
- [7] S.H. Kim, K. Hong, W. Xie, K.H. Lee, S.P. Zhang, T.P. Lodge, C.D. Frisbie, Electrolyte-gated transistors for organic and printed electronics, *Adv. Mater.* 25 (2013) 1822-1846.
- [8] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.* 7, (2008) 845-854.
- [9] J. Wei, Z. Zhang, J.-K. Tseng, I. Treufeld, X. Liu, M.H. Litt, L. Zhu, Achieving high dielectric constant and low loss property in a dipolar glass polymer containing strongly dipolar and small-sized sulfone groups, *ACS Appl. Mater. Interfaces* 7 (2015) 5248-5257.
- [10] L. Yang, X. Li, E. Allahyarov, P.L. Taylor, Q.M. Zhang, L. Zhu, Novel polymer ferroelectric behavior via crystal isomorphism and the nanoconfinement effect, *Polymer* 54 (2013) 1709-1728.
- [11] Q. Wang, L. Zhu, Polymer nanocomposites for electrical energy storage, *J. Polym. Sci., Part B: Polym. Chem.* 49 (2011) 1421-1429.
- [12] J.K. Nelson, *Dielectric Polymer Nanocomposites*, Springer, New York (2010).
- [13] Z.M. Dang, J.K. Yuan, S.H. Yao, R.J. Liao, Flexible nanodielectric materials with high permittivity for power energy storage, *Adv. Mater.* 25 (2013) 6334-6365.
- [14] N. Guo, S.A. DiBenedetto, P. Tewari, M.T. Lanagan, M.A. Ratner, T.J. Marks, Nanoparticle, size, shape, and interfacial effects on leakage current density, permittivity, and breakdown strength of metal oxide-polyolefin nanocomposites: experiment and theory, *Chem. Mater.* 22 (2010) 1567-1578.

- [15] L.A. Fredin, Z. Li, M.T. Lanagan, M.A. Ratner, T.J. Marks, Substantial recoverable energy storage in percolative metallic aluminum-polypropylene nanocomposites, *Adv. Funct. Mater.* 23 (2013) 3560-3569.
- [16] L.A. Fredin, Z. Li, M.T. Lanagan, M.A. Ratner, T.J. Marks, Sustainable high capacitance at high frequencies: metallic aluminum-polypropylene nanocomposites, *ACS Nano* 7 (2013) 396-407.
- [17] P. Kim, S.C. Jones, P.J. Hotchkiss, J.N. Haddock, B. Kippelen, S.R. Marder, J.W. Perry, Phosphonic acid-modified barium titanate polymer nanocomposites with high permittivity and dielectric strength, *Adv. Mater.* 19 (2007) 1001-1005.
- [18] P. Kim, N.M. Doss, J.P. Tillotson, P.J. Hotchkiss, M.J. Pan, S.R. Marder, J. Li, J.P. Calame, J.W. Perry, High energy density nanocomposites based on surface-modified BaTiO₃ and a ferroelectric polymer, *ACS Nano* 3 (2009) 2581-2592.
- [19] J. Li, J. Claude, L.E. Norena-Franco, S.I. Seok, Q. Wang, Electrical energy storage in ferroelectric polymer nanocomposites containing surface-functionalized BaTiO₃ nanoparticles, *Chem. Mater.* 20 (2008) 6304-6306.
- [20] J. Li, S.I. Seok, B. Chu, F. Dogan, Q. Zhang, Q. Wang, Nanocomposites of ferroelectric polymers with TiO₂ nanoparticles exhibiting significantly enhanced electrical energy density, *Adv. Mater.* 21 (2009) 217-221.
- [21] B. Chu, M. Lin, B. Neese, Q.M. Zhang, Interfaces in poly (vinylidene fluoride) terpolymer/ZrO₂ nanocomposites and their effect on dielectric properties, *J. Appl. Phys.* 105 (2009) 014103.
- [22] H. Tang, H.A. Sodano, Ultra high energy density nanocomposite capacitors with fast discharge using Ba_{0.2}Sr_{0.8}TiO₃ nanowires, *Nano Lett.* 13 (2013) 1373-1379.

- [23] C.W. Beier, J.M. Sanders, R.L. Brutchey, Improved breakdown strength and energy density in thin-film polyimide nanocomposites with small barium strontium titanate nanocrystal fillers, *J. Phys. Chem. C* 117 (2013) 6958-6965.
- [24] Q. Li, K. Han, M.R. Gadinski, G.Z. Zhang, Q. Wang, High energy and power density capacitors from solution-processed ternary ferroelectric polymer nanocomposites, *Adv. Mater.* 26 (2014) 6244-6249.
- [25] F. He, S. Lau, H.L. Chan, J.T. Fan, High dielectric permittivity and low percolation threshold in nanocomposites based on poly (vinylidene fluoride) and exfoliated graphite nanoplates, *Adv. Mater.* 21 (2009) 710-715.
- [26] G. Wang, X. Huang, P. Jiang, Tailoring dielectric properties and energy density of ferroelectric polymer nanocomposites by high-k nanowires, *ACS Appl. Mater. Interfaces* 7 (2015) 18017-18027.
- [27] S. Wang, X. Huang, G. Wang, Y. Wang, J. He, P. Jiang, Increasing the energy efficiency and breakdown strength of high-energy-density polymer nanocomposites by engineering the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ nanowire surface via reversible addition-fragmentation chain transfer polymerization, *J. Phys. Chem. C* 119 (2015) 25307-25318.
- [28] Q. Li, L. Chen, M.R. Gadinski, S.H. Zhang, G.Z. Zhang, H.Y. Li, A. Haque, L.Q. Chen, T. Jackson, Q. Wang, Flexible high-temperature dielectric materials from polymer nanocomposites, *Nature* 523 (2015) 576-579.
- [29] J. Li, P. Khanchaitit, K. Han, Q. Wang, New route toward high-energy-density nanocomposites based on chain-end functionalized ferroelectric polymers, *Chem. Mater.* 22 (2010) 5350-5357.

- [30] A. Maliakal, H. Katz, P.M. Cotts, S. Subramoney, P. Mirau, Inorganic oxide core, polymer shell nanocomposite as a high K gate dielectric for flexible electronics applications, *J. Am. Chem. Soc.* 127 (2005) 14655-14662.
- [31] C.A. Grabowski, H. Koerner, J.S. Meth, A. Dang, C.M. Hui, K. Matyjaszewski, M.R. Bockstaller, M.F. Durstock, R.A. Vaia, *ACS Appl. Mater. Interfaces* 6 (2014) 21500-21509.
- [32] S.A. Paniagua, Y. Kim, K. Henry, R. Kumar, J.W. Perry, S.R. Marder, Surface-initiated polymerization from barium titanate nanoparticles for hybrid dielectric capacitors, *ACS Appl. Mater. Interfaces* 6 (2014) 3477-3482.
- [33] P. Hu, Y. Shen, Y. Guan, X. Zhang, Y. Lin, Q. Zhang, C.W. Nan, Topological-structure modulated polymer nanocomposites exhibiting highly enhanced dielectric strength and energy density, *Adv. Funct. Mater.* 24 (2014) 3172-3178.
- [34] X. Zhang, Y. Shen, Q. Zhang, L. Gu, Y. Hu, J. Du, Y. Lin, C.W. Nan, Ultrahigh energy density of polymer nanocomposites containing BaTiO₃@TiO₂ nanofibers by atomic-scale interface engineering, *Adv. Mater.* 27 (2015) 819-824.
- [35] G. Zhang, D. Brannum, D. Dong, L. Tang, E. Allahyarov, S. Tang, K. Kodweis, J.-K. Lee, L. Zhu, Interfacial polarization-induced loss mechanisms in polypropylene/BaTiO₃ nanocomposite dielectrics. *Chem. Mater.* 28 (2016) 4646-4660.
- [36] K.C. Kao, *Dielectric phenomena in solids: with emphasis on physical concepts of electronic processes*, Elsevier Academic Press, Boston, (2004).
- [37] J.Y. Li, L. Zhang, S. Ducharme, Electric energy density of dielectric nanocomposites, *Appl. Phys. Lett.* 90 (2007) 132901.

- [38] L. An, S.A. Boggs, J.P. Callame, Energy storage in polymer films with high dielectric constant fillers, *IEEE Electr. Insul. Mag.* 24 (2008) 5-10.
- [39] E. Allahyarov, H. Loewen, L. Zhu, A simulation study of the electrostriction effects in dielectric elastomer composites containing polarizable inclusions with different spatial distributions, *Phys. Chem. Chem. Phys.* 17 (2015) 32479-32497.
- [40] E. Allahyarov, H. Löwen, L. Zhu, Dipole correlation effects on the local field and the effective dielectric constant in composite dielectrics containing high-k inclusions, *Phys. Chem. Chem. Phys.* 18 (2016) 19103-19117.
- [41] C.A. Grabowski, S.P. Fillery, N.M. Westing, C. Chi, J.S. Meth, M.F. Durstock, R.A. Vaia, Dielectric breakdown in silica-amorphous polymer nanocomposite films: the role of the polymer matrix, *ACS Appl. Mater. Interfaces* 5 (2013) 5486-5492.
- [42] H.T. Vo, F.G. Shi, Towards model-based engineering of optoelectronic packaging materials: dielectric constant modeling, *Microelectronics Journal* 33 (2002) 409-415.
- [43] J.M. Park, H.Y. Lee, J.J. Kim, E.T. Park, Y.K. Chung, Dielectric properties of Ni-coated BaTiO₃-PMMA composite, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 55 (2008) 1038-1042.
- [44] J. Wang, F. Guan, L. Cui, J. Pan, Q. Wang, L. Zhu, Achieving high electric energy storage in a polymer nanocomposite at low filling ratios using a highly polarizable phthalocyanine interphase, *J. Polym. Sci., Part B: Polym. Chem.* 52 (2014) 1669-1680.
- [45] J. Yang, Z. Jin, X. Wang, W. Li, J. Zhang, S. Zhang, X. Guo, Z. Zhang, Study on composition, structure and formation process of nanotube Na₂Ti₂O₄(OH)₂, *Dalton Trans.* (2003) 3898-3901.

- [46] R.J. Klein, J. Runt, Q.M. Zhang, Influence of crystallization conditions on the microstructure and electromechanical properties of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) terpolymers, *Macromolecules* 36 (2003) 7220-7226.
- [47] L. Yang, B.A. Tyburski, F. Domingues Dos Santos, M.K. Endoh, T. Koga, D. Huang, Y. Wang, L. Zhu, Relaxor ferroelectric behavior from strong physical pinning in a poly(vinylidene fluoride-*co*-trifluoroethylene-*co*-chlorotrifluoroethylene) random terpolymer, *Macromolecules* 47 (2014) 8119-8125.
- [48] L. Yang, E. Allahyarov, F. Guan, L. Zhu, Crystal orientation and temperature effects on double hysteresis loop behavior in a poly(vinylidene fluoride-*co*-trifluoroethylene-*co*-chlorotrifluoroethylene)-*graft*-polystyrene graft copolymer, *Macromolecules* 46 (2013) 9698-9711.
- [49] L. Yang, J. Ho, E. Allahyarov, R. Mu, L. Zhu, Semicrystalline structure-dielectric property relationship and electrical conduction in a biaxially oriented poly(vinylidene fluoride) film under high electric fields and high temperatures, *ACS Appl. Mater. Interfaces* 7 (2015) 19894-19905.
- [50] Y. Li, J. Ho, J. Wang, Z.-M. Li, G.-J. Zhong, L. Zhu, Understanding nonlinear dielectric properties in a biaxially oriented poly(vinylidene fluoride) film at both low and high electric fields, *ACS Appl. Mater. Interfaces* 8 (2016) 455-465.
- [51] S.K. Kumar, N. Jouault, B. Benicewicz, T. Neely, Nanocomposites with polymer grafted nanoparticles, *Macromolecules* 46 (2013) 3199-3214.