



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



Zhe Liu <sup>a, b</sup>, Guoqiang Zhang <sup>b</sup>, Saide Tang <sup>b</sup>, Zhongbo Zhang <sup>b</sup>, Hong Zhu <sup>a, \*\*</sup>, Lei Zhu <sup>b, \*</sup>

<sup>a</sup> 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, PR China

<sup>b</sup> Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, United States

## ARTICLE INFO

### Article history:

Received 20 July 2016

Received in revised form

4 September 2016

Accepted 12 September 2016

Available online 13 September 2016

### Keywords:

P(VDF-TrFE-CTFE) terpolymer

Sodium titanate nanotubes

Nanodielectrics

## 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.

© 2016 Elsevier Ltd. All rights reserved.

## 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

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zhuho128@126.com](mailto:zhuho128@126.com) (H. Zhu), [lxz121@case.edu](mailto:lxz121@case.edu) (L. Zhu).

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.,  $\text{ZrO}_2$ :  $\epsilon_r \sim 25$  [21], anatase  $\text{TiO}_2$ :  $\epsilon_r \sim 40$  [20],  $\text{BaTiO}_3$  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 ( $\epsilon_r$ ) 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 AC electric poling, the internal electronic conduction loss leads to a significantly decreased discharge efficiency ( $\eta$ ); the higher the poling field, the lower the  $\eta$ .

To mitigate the effect of nonuniform electric field distribution on decreased breakdown strengths, several strategies are proposed: (i) reducing the  $\epsilon_r$  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  $\epsilon_r$  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  $\epsilon_r$  (>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  $\epsilon_r$  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  $\text{TiO}_2$  (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  $\mu\text{m}$  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<sup>+</sup>) 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  $\text{Cu K}\alpha$  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  $\mu\text{m}$ /pixel. One-dimensional (1D) XRD curves were obtained by integrating the corresponding 2D WAXD patterns radially using the Polar software developed by Stony Brook 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  $V_{\text{rms}}$  (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

Download English Version:

<https://daneshyari.com/en/article/5178684>

Download Persian Version:

<https://daneshyari.com/article/5178684>

[Daneshyari.com](https://daneshyari.com)