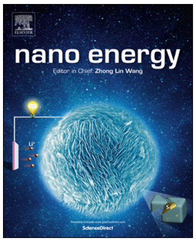
Available online at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

Q2 Optimizing nanostructure to achieve high dielectric response with low loss in strongly dipolar polymers

Yash Thakur[a,1], **Rui Dong**[b,1], **Minren Lin**[a], **Shan Wu**[a],
Q1 **Zhaoxi Cheng**[a,c], **Ying Hou**[a,d], **J. Bernholc**[b,*], **Q.M. Zhang**[a,*]

[a]*Department of Electrical Engineering and Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA*
[b]*Center for High Performance Simulation and Department of Physics, North Carolina State University, Raleigh, NC 27695-7518, USA*
[c]*Department of Polymer Science & Engineering, School of Chemistry & Chemical Engineering, Nanjing University, Nanjing 210093, China*
[d]*Department of Physics, East China University of Science and Technology, Shanghai 200237, China*

Received 19 May 2015; received in revised form 16 June 2015; accepted 19 June 2015

KEYWORDS
Nano-dielectrics;
Energy storage;
Free-volume effect;
High thermal stability

Abstract

Advances in modern electronics require the development of polymer-based dielectric materials with high dielectric constant, low dielectric loss, and high thermal stability. Fundamental dielectric theory suggests that strongly dipolar polymers have the potential to realize a high Q3 dielectric constant. In order to achieve high thermal stability, these polymers should also possess a high glass transition temperature T_g. However, it has been observed that in many dielectric polymers the dielectric constant decreases markedly at temperatures below T_g due to dipole freezing. This study shows, through combined theoretical and experimental investigations, that nano-structure engineering of a weakly-coupled strongly-dipolar polymer can result in a high energy density polymer with low loss and high operating temperature. Our studies reveal that disorder creates a significantly larger free volume at temperatures far below T_g, enabling easier reorientation of dipoles in response to an electric field in aromatic urea and thiourea polymers. The net result is a substantial enhancement in the dielectric constant while preserving low dielectric loss and very high breakdown field. These results here pave the way

---

[*] Corresponding authors.
E-mail addresses: bernholc@ncsu.edu (J. Bernholc), qxz1@psu.edu (Q.M. Zhang).
[1] Contributed equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2015.06.021

for engineering the nanostructure to create high energy density polymers with low loss and high operating temperature.

Introduction

Polymer dielectric materials are ubiquitous in modern power electronic systems [1-3]. They are highly desirable for applications in the area of capacitive energy storage [3-8], transistors [9-11], photovoltaic devices [12-14] and electrical insulation [15,16]. The demand for capacitive energy storage has increased due to continuing electrification of land [1,17] and sea [18] transportation, as well as military and civilian systems [18,19]. These applications require capacitors with high energy density, low loss, high efficiency and high operating temperature. Compared to ceramics and electrolytic capacitors, polymer-based capacitors are attractive because they feature low manufacturing cost and low dielectric loss, can be used under high voltage due to high breakdown strength, and fail gracefully with an open circuit [3]. In many of these devices and systems, capacitors constitute a substantial fraction of volume and weight (>30% volume and weight) [1,4,20-22]. To meet the demand of continued miniaturization of modern electrical and electronic devices and systems, the energy density of dielectric polymers must be improved. In general, the energy stored in a capacitor is proportional to the dielectric constant and the square of the electric field. Therefore, the materials of interest should display high dielectric constant and high breakdown strength. The present state-of-the-art high energy density film capacitors use biaxially oriented polypropylene (BOPP), with a low dielectric constant K of 2.2 and operating temperature below 100 °C, due to its low melting temperature ($T_m<140$ °C) [21]. Extensive materials development efforts have led to several alternative dielectric polymers, including polycarbonate (PC), poly(ethylene terephthalate) (PET), and poly(phenylene sulfide) (PPS) with high operating temperatures (>125 °C). However, the dielectric constant of these polymers is still below 3.3 [21,23].

The strong coupling among dipoles have led to high dielectric constants of polyvinylidene fluoride(PVDF)-based ferroelectric polymers ($K>10$) [4,24-26]. By proper defect modifications of PVDF-based polymers, we showed that these polymers can achieve either a high dielectric constant at room temperature ($K>50$) or a very high energy density (>25 J/cm^3) [27-29]. However, the strong dipolar coupling in these ferroelectric polymers causes high polarization hysteresis loss. Moreover, the operating temperature is still limited to below 125 °C due to low T_m (<140 °C) [21,23]. Nevertheless, the results demonstrate the potential of tailoring nano- and meso-structures of dielectric polymers to achieve high dielectric performance.

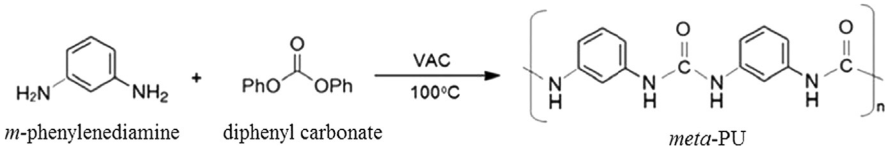
We note that in earlier studies of strongly dipolar polymers with very weak coupling among dipoles, such as polyurethane, the polymers show a low loss but also low dielectric constant at temperatures below the glass transition temperature. On the other hand, these polymers exhibit a large increase in dielectric constant after undergoing a glass transition at T_g, e.g., $K>6$ [30,31]. The penalty is that the dielectric loss is also increased markedly (loss>5%). The large increase in the dielectric constant observed above T_g in these strongly dipolar polymers is attributed to an increase of the empty spaces surrounding the dipoles termed “free-volume effect” which makes it easier for dipoles to follow the applied field, and hence reach a higher dielectric constant. However, large-chain-segment motions above T_g, which have long relaxation times, also causes high dielectric loss [31]. Now the question is whether one can design a strongly dipolar polymer that can generate the “free volume effect” at temperatures below T_g, thus leading to high K while avoiding large-chain-segment motion causing dielectric loss. If T_g is at a high temperature (for example, $T_g>200$ °C), the polymer may also have a high operating temperature (>150 °C).

In this work, through a combined theoretical and experimental investigation, we show that such a polymer with high T_g can be realized in several recently developed strongly dipolar polymers based on aromatic urea and thiourea units, with dipole moments of 4.5 Debye and 4.89 Debye, respectively, [8,32-34] which are much higher than for VDF in PVDF based polymers, with the dipole moment of 2 Debye [24-26]. It is the free volume effect (FVE) at temperatures below T_g (>200 °C) that leads to a high dielectric constant ($K>5.6$) in *meta*-phenylene polyurea (*meta*-PU) (see Scheme 1 for the chemical structure). It also possesses very low loss (high charge/discharge efficiency) even at very high electric fields (>600 MV/m).

Theoretical and experimental methods

Theoretical methods

To obtain the atomic structures of *meta*-PU, we first apply simulated annealing to the four starting geometries. Classical molecular dynamics package LAMMPS [36] is used, with



Scheme 1 Schematic of synthesis of *meta*-PU.

Please cite this article as: Y. Thakur, et al., Optimizing nanostructure to achieve high dielectric response with low loss in strongly dipolar polymers, Nano Energy (2015), http://dx.doi.org/10.1016/j.nanoen.2015.06.021