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Tailoring the dipole properties in dielectric polymers to realize high energy density with high breakdown strength and low dielectric loss

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High energy density polymer materials are desirable for a broad range of modern power electronic systems. Here, we report the development of a new class of polymer dielectrics based on polyurea and polythiourea, which possess high thermal stability. By increasing the dipole density, the dielectric constant of meta-phenylene polyurea and methylene polythiourea can be increased to 5.7, compared with aromatic polyurea and aromatic polythiourea, which have a dielectric constant in the range of 4.1–4.3. The random dipoles with high dipolar moment and amorphous structure of these polyurea and polythiourea based polymers provide strong scattering to the charge carriers, resulting in low losses even at high electric fields. Consequently, this new class of polymers exhibit a linear dielectric response to the highest field measured (>700 MV/m) with a high breakdown strength, achieving high energy density (>13 J/cm³) with high efficiency (>90%). © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Polymer materials with high electrical energy density are desirable for a broad range of modern power electronic systems such as medical devices, hybrid electrical vehicles (HEVs), filters, switched-mode power supplies, and power weapon systems.1–5 Compared with ceramic capacitors, polymer-film capacitors are more attractive for these applications because they are inexpensive, possess high dielectric strength, high energy density, and low dielectric loss, and fail gracefully. However, in modern electric power systems, these capacitors contribute significant (>30%) volume and weight.1,2,6 Therefore, to keep up with the continuous miniaturization and increase in functionality, it is important to develop novel dielectric materials possessing high energy density. One major challenge in developing these dielectric polymers is realizing high energy density while maintaining low dielectric loss, even at very high applied fields.6 Currently, one of the most commonly used polymer capacitor films is biaxially oriented polypropylene (BOPP). It is attractive for energy storage and regulation applications, such as capacitors in HEVs and power grids due to its high dielectric breakdown strength and low dielectric loss (<0.018% when measured at low electric field). However, the low dielectric constant (K ≈ 2.2) of BOPP limits its energy density (U_e).3 For a linear dielectric, U_e is proportional to the square of the electric field E, given by

\[
U_e = \frac{1}{2} K \varepsilon_0 E^2, \quad (1)
\]

where \( \varepsilon_0 \) (≈ 8.85 \( \times \) 10\(^{-12}\) F/m) is the vacuum dielectric permittivity, \( K \) is dielectric constant, and \( E \) is the maximum operating electric field. Hence, raising the dielectric constant \( K \) can lead to an increase in the energy density of the capacitors.

Equation (1) indicates that \( U_e \) increases significantly at high electric field since \( U_e \sim E^2 \). However, for many widely used linear dielectrics, including BOPP, it was found that the conduction loss becomes more significant at higher applied fields.6,7 Normally, these losses increase exponentially with the electric field, and cause Ohmic heating of the capacitors.2,6–8 This results in the need to have a cooling system to avoid overheating the BOPP film capacitors. For example, in hybrid electric vehicles, an extra cooling loop has to be introduced in the BOPP capacitor banks in order to prevent a runaway temperature increase caused by the conduction loss heating.

In this paper, we present results from our recent studies in developing polymer dielectrics with higher dielectric constant, and higher operation temperature than that of BOPP, while achieving a low dielectric loss at high electric fields. A few years ago, we showed that ferroelectric polymers based on poly(vinylidene fluoride) (PVDF) with proper defect modifications can possess a high dielectric constant (\( K > 12 \)). The defects introduced in these polymer systems can breakdown large coherent polar domains and reduce the remnant polarization to nearly zero.4,9,10 It was demonstrated that these modified PVDF polymers, such as P(VDF-CTFE) and P(VDF-HFP) (CTFE: chlorotrifluoroethylene; HFP: hexafluoropropylene), possess very high energy densities (\( U_e > 25 \) J/cm³) at high electric fields (>600 MV/m).4,9,10 However, these polar polymers with strongly coupled dipoles exhibit pronounced polarization hysteresis at high
electric fields which leads to high loss. For high energy density capacitor applications, besides energy density, loss is also an important criterion. A considerable loss can cause severe heating during operation, and eventually lead to failure of the capacitors.\textsuperscript{11,12}

To reduce or even eliminate the polarization hysteresis loss, we selected a class of amorphous polymers, containing high density dipoles of high dipole moment, i.e., urea and thiourea (see Fig. 1). In strongly dipolar polymer materials, such as the polyurea and polythiourea, the orientation polarization is the dominant polarization mechanism compared with the electronic, atomic, or ionic polarization. Orientation polarization occurs by the reorientation of the permanent dipole moment toward the direction of the electric field. Compared with other models, the Frohlich model takes both the short-range interaction between molecules, and the deformation polarizations into consideration. This model has been used widely to describe the dielectric response in polymers.\textsuperscript{7}

In this model, the dielectric constant, or the relative permittivity, is proportional to the dipole moment and dipole density, and correlation factor between the dipoles. It is given as

\[ \frac{(\varepsilon_r - \varepsilon_{\infty})(2\varepsilon_r + \varepsilon_{\infty})}{\varepsilon_r(\varepsilon_{\infty} + 2)^2} = \frac{Ngp^2}{9\varepsilon_0kT}, \]

(2)

where \( \varepsilon_r \) and \( \varepsilon_{\infty} \) are the dielectric constants at low frequency and optical frequency, respectively; \( N \) is the volumetric dipole density; \( g \) is the correlation factor; \( p \) is the dipole moment; \( k \) is the Boltzmann constant; and \( T \) is the temperature.

We show that by increasing the dipole moment and the dipole density, the dielectric constant in this series of polymers increases from 4.1 to 5.7. The high dipole moments in these amorphous polymers provide strong polar-scattering centers and traps, which significantly reduces the conduction loss at high electric fields. As a result, these polymers exhibit an improved electrical energy density than BOPP. The high glass transition temperature also leads to a higher operation temperature.

Four dielectric polymers based on polyurea and polythiourea have been developed, which include aromatic polyurea (ArPU),\textsuperscript{13} aromatic polythiourea (ArPTU),\textsuperscript{14,15} meta-phenylene polyurea (m-PhPU),\textsuperscript{16} and methylene polythiourea (MePTU) (Fig. 2), to study the influence of dipole moment and dipole density on the dielectric properties.

II. EXPERIMENTAL

A. Synthesis and film fabrication

All chemicals were purchased from Sigma-Aldrich. The polymers were purified by washing with acetone because all residues of monomer, ions, and by-products such as phenol are well soluble in acetone. The ArPU thin films were fabricated using a chemical vapor deposition (CVD) process through the reactions between two monomers: 4,4'-diaminodiphenylmethane (MDA) and 4,4'-diphenylmethane diisocyanate (MDI).\textsuperscript{13} The deposited films were then annealed at 200°C for 30 min to achieve full polymerization among oligomers produced during the vapor deposition process. The typical film thickness in this investigation was 2.5 \( \mu \)m and thermoevaporated aluminum (Al) electrodes were used for the electrical characterization. ArPTU was synthesized via microwave-assisted polycondensation of MDA with thiourea in N-methyl-2-pyrrolidone (NMP) with p-toluenesulfonic acid (p-TSOH) as a catalyst.\textsuperscript{14} After purification, ArPTU was isolated as yellow colored powder, which was used for film processing.

\( m-\text{PhPU} \) was synthesized by polycondensation of meta-phenylenediamine and diphenyl carbonate as shown in Fig. 3.\textsuperscript{16} This is a green process which is solvent free, catalyst free, and isocyanate free. After purification, \( m-\text{PhPU} \) was isolated as pinkish powder.

MePTU was synthesized by polycondensation of thiourea with formaldehyde in aqueous solution as shown in Fig. 3,\textsuperscript{17} where water is eliminated during condensation. After purification, polythiourea was isolated as tan colored powder.

ArPTU, \( m-\text{PhPU} \), and MePTU powders were dissolved in dimethylformamide (DMF) to make 1.0–2.0 wt. % solution. The thickness of films can be well controlled from 1 \( \mu \)m.
to 5 μm by changing the concentration of the solution. Then, the thin films were prepared by casting the solution onto 1 cm × 1 cm silicon substrates pre-coated with 40 nm of Platinum at 80°C overnight, and then annealed at 140°C under vacuum for 12 h. Gold electrodes of 2 mm to 6 mm in diameter were sputtered on the two surfaces of the films for electrical characterization.

B. Characterization

The thickness of the film was measured by alpha-step profilometry. The low-field dielectric constant and loss at variable temperature was measured using an HP 4284 impedance analyzer, which was connected to an environment test chamber (Delta 9023). The Polarization-Electric field (P-E) response was measured with a modified Sawyer-Tower circuit. The charge (stored) energy density, discharged (released) energy density, and efficiency were calculated from the P-E loop. The X-ray diffraction data were collected using a Panalytical Xpert Pro MPD diffractometer.

III. RESULTS AND DISCUSSION

Presented in Fig. 4(a) is the dielectric constant and loss measured at room temperature of ArPU, ArPTU, m-PhPU, and MePTU as a function of frequency. With a high dipole moment of 4.56 D in the urea unit, and 4.89 D in the thiourea unit, the dielectric constants of ArPU and ArPTU are 4.1 and 4.4 at 1 kHz, respectively, with a low dielectric loss (<1%). The dielectric constants of ArPU and ArPTU are higher than most of the linear polymer dielectrics, which are non-polar or weakly dipolar materials with dielectric constant around 2–3.5. As shown in Figs. 2(a) and 2(b), ArPU and ArPTU have nearly the same volumetric dipole density as they contain the same methylene diphenyl group between the two dipolar units. The dielectric constant of ArPTU is slightly higher than ArPU because of higher dipole moment of thiourea than urea. However, the increase in dielectric constant is not proportional to the square of dipole moment [Eq. (2)].

In ArPU and ArPTU (Figs. 2(a) and 2(b)), methylene diphenyl (two aromatic rings), as one blocking unit, separates neighboring dipoles along the polymer chain, leading to relatively low volumetric dipole density. Based on Frohlich model, dielectric constant can be enhanced by increasing the volumetric dipole density. Therefore, a new type of structure, m-PhPU and MePTU (Figs. 2(c) and 2(d)), with higher volumetric dipole density was synthesized by modifying the block structures between dipoles in the polymer chain. The two dipolar units are separated by an aromatic ring in m-PhPU, while methylene is the separating unit in MePTU. The dielectric constant of both m-PhPU and MePTU is 5.7 as shown in Fig. 4(a). As predicted, these two polymers have a higher dielectric constant than ArPU and ArPTU.

The distance between two dipolar unit can be estimated by bond length and bond angle. The bond length for ArPU and ArPTU is 1251 pm, while it is 754 pm and 512 pm for m-PhPU and MePTU, respectively. Comparing m-PhPU with ArPTU, the dipole density along the chain increases by 66% (distance reduced from 1251 pm to 754 pm), which leads to an increase of dielectric constant by more than 40%. This deviates from the results predicted by the Frohlich model. We presume that there might be changes in the inter-chain spaces due to the disordered amorphous structure of these polyurea and polythiourea based films. The amorphous structure of these polyurea and polythiourea based films will be discussed in the later part of this section.
Fig. 4(b) shows the dielectric measurement at 1 kHz as a function of temperature. For ArPU, ArPTU, and m-PhPU, relatively high temperature stability, up to 150°C, is achieved, and dielectric constant and losses are constant from −30°C to 150°C. The dielectric measurement of m-PhPU at different frequencies as a function of temperature is shown in Fig. 4(c). Besides higher dielectric constants, these polyureas or polythioureas also show higher thermal stability, compared with BOPP, where the maximum operation temperature is below 100°C.7

It should be pointed out that for most “linear” dielectric materials, even though their dielectric constant is independent of the applied field, the losses due to the conduction at high field may increase at high electric fields.19,20 The high field efficiency \( \eta \) is defined as the ratio of the released energy density and stored energy density in the charge-discharge cycle.21

\[
\eta = \frac{U_r}{U_s} = 1 - \frac{U_l}{U_s},
\]

where \( U_s \), \( U_r \), and \( U_l \) are the stored, discharged, and electric loss energy densities in the charge-discharge cycle, respectively.

Figs. 5(a)–5(c) present the charge-discharge curves (P vs. E) measured under different applied electric fields at 10 Hz for ArPU, ArPTU, and m-PhPU. Due to the high dielectric constant of m-PhPU, a high polarization of 3.75 μC/cm² was achieved at 670 MV/m. The data reveal that the dielectric loss, which is measured by the enclosed area between the charge and discharge curves, does not increase significantly at high fields, leading to high charge-discharge efficiency. The high field measurements were not performed on MePTU due to the quality of films with low breakdown field.

The energy densities are calculated from the charge-discharge curves in Figs. 5(a)–5(c) and presented in Fig. 6(a). Overall, high energy densities >13 J/cm³ can be achieved in these polyureas and polythioureas based polymers with charge discharge efficiency >90% (Fig. 6(b)). The high efficiency under high electric field is due to extremely low conductivity of these polymers, leading to very low current leakage at high electric fields. As it has been shown by Wu et al.22 the very smooth surface and high field quality leads to a high breakdown field of 1.1 GV/m for the ArPTU films. The high dielectric constant of m-PhPU due to the higher dipole density leads to an energy density of 13 J/cm³ at 670 MV/m, while ArPTU and ArPU with lower volume dipole density lead to lower energy density at the same electric field of 670 MV/m (Fig. 6(a)).
In order to understand the possible causes of the observed high energy storage efficiency and low high field conduction in these polyurea and polythiourea based polymers, X-ray diffraction measurements on these films were carried out and the results reveal the amorphous structures of the films. Presented in Fig. 7 is an example of the ArPTU films which does not show any sharp X-ray peaks, just a broad X-ray peak around $2\theta = 19^\circ$, indicating that the ArPTU films do not possess long range crystalline ordering and are amorphous. Structure analysis suggests that the X-ray peak around $2\theta = 19^\circ$ is likely due to the inter-chain diffraction. It was also found that the amorphous structure of ArPTU does not change much from 25°C to 205°C (Fig. 7(b)). This is quite different from BOPP, which is a semi-crystalline polymer and has a glass transition temperature below −30°C.2,23 Above $T_g$, the segmental motions of polymer chains will facilitate charge hopping and leads to the observed increase in conduction loss at high electric fields.7,8,24 While, the random dipoles with high dipolar moment and amorphous glass-phase structure in polyurea and polythiourea based polymers provide much stronger scattering to the charge carriers, resulting in a much lower conduction loss under high electric fields.7

IV. CONCLUSION

We have presented a method to improve dielectric properties of polymers by tailoring their dipole properties. As shown in Table I, which summarizes the dielectric and energy storage properties of these four polyurea and polythiourea based polymers, an enhanced dielectric constant around 4.1–5.7, which is higher compared with commercial dielectric polymers, can be achieved in these polymers by increasing the dipole moment and dipole density. This paper presents a general approach to design dielectrics with high dielectric constant and high energy density with low conduction loss at high electric fields.

ACKNOWLEDGMENTS

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FIG. 7. (a) XRD pattern of ArPTU at room temperature and the inset is the background normalized pattern, and (b) XRD patterns of ArPTU at varied temperatures from 25°C to 205°C.

TABLE I. Summary of dielectric properties of ArPU, ArPTU, m-PhPU, and MePTU.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Dielectric constant (1 kHz)</th>
<th>Loss tangent (1 kHz) (%)</th>
<th>Breakdown strength $E_b$ (MV/m)</th>
<th>Energy density at $E_b$ (J/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArPU</td>
<td>4.1</td>
<td>0.87</td>
<td>800</td>
<td>13.5</td>
</tr>
<tr>
<td>ArPTU</td>
<td>4.4</td>
<td>0.64</td>
<td>&gt;1000</td>
<td>20.1</td>
</tr>
<tr>
<td>m-PhPU</td>
<td>5.7</td>
<td>1.71</td>
<td>670</td>
<td>13</td>
</tr>
<tr>
<td>MePTU</td>
<td>5.7</td>
<td>1.55</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>


