Stable dielectric response of low-loss aromatic polythiourea thin films on Pt/SiO₂ substrate

A. Eršte*, L. Fulanović*, L. Čoga†, M. Lin‡, Y. Thakur‡, Q. M. Zhang‡ and V. Bobnar*§

*Jožef Stefan Institute

Jamova cesta 39, SI-1000 Ljubljana, Slovenia

†Faculty of Mathematics and Physics

University of Ljubljana, Jadranska ulica 19, SI-1000 Ljubljana, Slovenia

‡Department of Electrical Engineering and Materials Research Institute

The Pennsylvania State University, University Park, Pennsylvania 16802, USA

§vid.bobnar@ijs.si

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We have investigated dielectric properties of aromatic polythiourea (ArPTU, a polar polymer containing high dipolar moments with very low defect levels) thin films that were developed on Pt/SiO₂ substrate. The detected response is compared to the response of commercially available polymers, such as high density polyethylene (HDPE) and polypropylene (PP), which are at present used in foil capacitors. Stable values of the dielectric constant $\epsilon' \approx 5$ (being twice higher than in HDPE and PP) over broad temperature and frequency ranges and dielectric losses as low as in commercial systems suggest ArPTU as a promising candidate for future use in a variety of applications.

Keywords: Aromatic polythiourea; dielectric polymer; film capacitor; dielectric spectroscopy; ellipsometry.

1. Introduction

Dielectric materials with high electric energy density and low loss are of great importance for a broad range of applications in modern electronics and electrical power systems such as hybrid electric vehicles, medical defibrillators, filters and various switched-mode power supplies.^{1–3} Compared with ceramic dielectrics, 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.

One of the major challenges in developing dielectric polymers is realizing high energy density while maintaining low dielectric loss, even at very high applied fields.⁴ In order to achieve such an advanced dielectric performance (generally, dielectric losses increase exponentially with the electric field and cause ohmic heating of the capacitors), strongly dipolar materials with the dipole moment larger than 1.5 Debye should be exploited.⁵ Recently, a new class of dielectric polymer based on aromatic polythiourea (ArPTU) showed a lot of promise for applicatory development: ArPTU is a polar polymer containing high dipolar moments (4.89 Debye)⁶ with very low defect levels, capable of maintaining its low dielectric loss up to very high operation fields ($> 1 \text{ GVm}^{-1}$) with a very high electric energy density ($> 20 \text{ Jcm}^{-3}$).⁷ In addition, most PTU-based polymers have good temperature stability ($> 150^\circ\text{C}$).

In this paper, we present (i) dielectric response of ArPTU thin films that were developed on Pt/SiO₂ substrate, detected over broad temperature and frequency ranges and (ii) its comparison to the response of commercially available polymers, such as high density polyethylene (HDPE) and polypropylene (PP), which are at present both used in foil (film) capacitors. We will show that our films exhibit stable values of the dielectric constant $\epsilon' \approx 5$ (being twice higher than in both commercial systems) over broad temperature and frequency ranges while maintaining relatively low dielectric loss of $1\text{--}2 \times 10^{-3}$, which suggests ArPTU as a candidate material for novel dielectric applications.

2. Materials and Methods

ArPTU (the chemical structure is presented in Fig. 1) was synthesized via microwave-assisted polycondensation of 4,4'-diphenylmethane diamine (MDA) with thiourea in N-methyl-2-pyrrolidone (NMP) with p-toluenesulfonic acid (p-TSOH) as a catalyst.⁸ After purification with ethanol, PTU was isolated as a powder, which was soluble in either NMP or N,N-dimethylformamide (DMF). For this study, spin-casting was used to deposit films on silicon substrates, which were coated with platinum electrodes. The thickness of the film can be varied from $1 \mu\text{m}$ to more than $5 \mu\text{m}$ by adjusting the concentration of the solutions and/or the spin-rate. The films

Fig. 1. Chemical structure of ArPTU.

were then dried in vacuum at 110°C overnight and annealed at 140°C for 12 h.

For dielectric measurements, ArPTU films on Pt/SiO₂ substrate as well as HDPE and PP films were covered by sputtered electrodes (100 nm of gold on 10 nm of chromium for better adhesion). The complex dielectric constant $\varepsilon^*(\nu, T) = \varepsilon' - i\varepsilon''$ was measured by novocontrol alpha high resolution dielectric analyzer in a frequency range of 1 Hz–1 MHz. The real part of the complex AC conductivity $\sigma^* = \sigma' + i\sigma''$ was calculated via $\sigma' = 2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of free space. The amplitude of the probing AC electric signal was 50 mV. The data was obtained in the temperature range of 100–375 K during cooling runs with temperature change rate of $\Delta T/\Delta t = 0.9$ K/min. The temperature of the samples was stabilized within 10 mK using a lock-in bridge technique with a Pt100 resistor as a thermometer.

3. Results and Discussion

The thickness of ArPTU thin films was determined by using an auto-nulling imaging ellipsometer Nanofilm EP3SE (Accurion, Germany). Figure 2 shows the image of the ArPTU films on Pt/SiO₂ substrate, captured under the ellipsometer. Several air bubbles can be seen embedded in the sample. Ellipsometry probes the change in the state of polarization of the light beam after its reflection from the sample surface. Ellipsometric angles Ψ and Δ , which represent amplitude ratio and phase difference between the parallel p and perpendicular s polarized light components, are obtained

Fig. 2. Image of the ArPTU film on Pt/SiO₂ substrate, captured under the ellipsometer. Several air bubbles can be seen embedded in the sample.

Fig. 3. Optical model for the ArPTU film spin-casted on a platinum surface. The refractive index for platinum substrate, $N_2 = 1.998 + i4.913$, was used for the thickness calculation.

from the change in the state of polarization. The sample was illuminated with a laser light at a wavelength of 658 nm. Ellipsometric angles Ψ and Δ were measured as a function of the angle of incidence (AOI) in the range from 50° to 73° with an increment of 0.5° (multiple angles of incidence (MAI) ellipsometry). Measurements were taken at three different regions in order to verify the film homogeneity. The thickness of the ArPTU film (d_1) was obtained by fitting the suitable optical model (shown in Fig. 3) to the measured angles Ψ and Δ . For this purpose, the optical modeling software EP4 model (Accurion surface analysis, Germany) was used. The refractive index for the platinum on the surface, $N_2 = 1.998 + i4.913$, was used for the thickness calculation. The best agreement between the calculated spectra and experimental spectra was obtained for the film thickness of $d_1 = 1617 \pm 17$ nm and refractive index of $N_1 = 1.49 \pm 0.01$.

Figure 4 depicts the temperature-dependent dielectric response (the real part of the complex dielectric constant, a_1 – c_1 , dielectric losses, a_2 – c_2 and the real part of the complex electrical conductivity, a_3 – c_3) in ArPTU and commercially obtainable PP and HDPE. PP, (C₃H₆)_n is a thermoplastic polymer used in a wide variety of applications including packaging and labeling, textiles (e.g., ropes, thermal underwear, and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components and polymer banknotes. In addition, polymer made from the monomer propylene is rugged and unusually resistant to many chemical solvents, bases and acids. HDPE, (C₂H₄)_n, unlike PP, cannot withstand normally required autoclaving conditions. The lack of branching is ensured by an appropriate choice of catalyst and reaction conditions. HDPE is known for its large strength-to-density ratio and is widely used in the production of plastic bottles, corrosion-resistant piping, geomembranes and plastic lumber. Additionally, both systems, PP and HDPE are at present widely used in the production of foil capacitors.⁹

In comparison, the ε' values of ArPTU are almost twice higher than in HDPE and PP over entire measured temperature range and at all measuring frequencies. The difference undoubtedly results from much higher values of the dipole

Fig. 4. (Color online) Comparison of temperature dependences of the real part of the complex dielectric constant, ϵ' (a_1)–(c_1), dielectric losses, $\tan \delta$ (a_2)–(c_2) and the real part of the complex electrical conductivity, σ' (a_3)–(c_3) in ArPTU on Pt/SiO₂ substrate and in commercially obtainable PP and HDPE.

moment in ArPTU (4.89 Debye in comparison to 0.366 Debye in PP, for example).⁶ This result suggests ArPTU as an extremely promising candidate for future use in a variety of applications, particularly film capacitors. Despite slightly higher values of the electrical conductivity in ArPTU, the dielectric losses namely also remain at low values, similar to those detected in HDPE and PP. Indeed, an increase in dielectric losses was detected at higher temperatures, however, at room temperature the values of $\tan \delta$ are between 0.0012 and 0.0025.

Finally, in order to have an application potential a dielectric film needs to exhibit a stable dielectric response. Figure 5 thus presents the 3D surface plot of the real part of the complex dielectric constant versus temperature and frequency, revealing such a stability — ϵ' values of ArPTU thin films on Pt/SiO₂ substrate range from 4.8 to 5.4 over broad temperature (150–375 K) and frequency (1 Hz–1 MHz) ranges. Indeed, the increase of dielectric losses at higher temperatures via Kramers–Kronig relation also slightly increases the dielectric constant, however, its values 50 K below and above room temperature change for less than 3%.

Here, it should be stressed out that contrary to the strongly coupled dipolar polymers such as polyvinylidene-fluoride (PVDF) which are semi-crystalline, ArPTU is an amorphous, glass-phase polymer, with weak coupling among the dipoles. Therefore, no transition into a long-range ordered phase (as in ferroelectric PVDF-based copolymers)¹⁰ or into a short-range ordered phase (as in relaxor PVDF-based terpolymers)¹¹

occurs at any temperature. Consequently, the dielectric constant indeed is lower than in the above mentioned PVDF-based systems,¹² however, due to the lack of any dipolar phase transitions the dielectric response is very stable over broad temperature and frequency ranges. Moreover, there is no electrical polarization hysteresis that would increase the dielectric losses, which thus remain at a very low level,

Fig. 5. (Color online) The real part of the complex dielectric constant versus temperature and frequency, revealing that ArPTU thin films on Pt/SiO₂ substrate exhibit ϵ' values ranging from 4.8 to 5.4 over broad temperature and frequency ranges.

despite the fact that the thiourea unit itself has a relatively high dipole moment.

4. Summary

ArPTU thin films on Pt/SiO₂ substrate exhibit stable dielectric constant values in the range of 4.8–5.4 over broad temperature (150 K–375 K) and frequency (1 Hz–1 MHz) ranges. These values are twice higher than values detected in commercially available polymers, HDPE and PP, which are at present both used in foil capacitors and undoubtedly result from much higher values of the dipole moment in ArPTU (4.89 Debye in comparison to 0.366 Debye in PP, for example).

On the other hand, despite slightly higher values of the electrical conductivity in ArPTU, the dielectric losses remain at low values of $1\text{--}2 \times 10^{-3}$, similar to those detected in HDPE and PP.

The obtained results suggest ArPTU as a promising candidate for future use in a variety of dielectric applications, where the next goal is the development of a free standing ArPTU-based film.

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References

- ¹M. Rabuffi and G. Picci, Status quo and future prospects for metallized polypropylene energy storage capacitors, *IEEE Trans. Plasma Sci.* **30**, 1939 (2002).
- ²B. Chu, X. Zhou, K. Ren, B. Neese, M. Lin, Q. Wang, F. Bauer and Q. M. Zhang, A dielectric polymer with high electric energy density and fast discharge speed, *Science* **313**, 334 (2006).
- ³P. Kim, N. M. Doss, J. P. Tillotson, P. J. Hotchkiss, M.-J. Pan, S. R. Marder, J. Li, J. P. Calame and J. W. Perry, High energy density nanocomposites based on surface-modified BaTiO₃ and a ferroelectric polymer, *ACS Nano* **3**, 2581 (2009).
- ⁴Q. Chen, Y. Wang, X. Zhou, Q. M. Zhang and S. Zhang, High field tunneling as a limiting factor of maximum energy density in dielectric energy storage capacitors, *Appl. Phys. Lett.* **92**, 142909 (2008).
- ⁵K.-C. Kao, *Dielectric Phenomena in Solids* (Elsevier Academic Press, London, 2004).
- ⁶S. Wu, Q. Burlingame, Z.-X. Cheng, M. Lin and Q. M. Zhang, Strongly dipolar polythiourea and polyurea dielectrics with high electrical breakdown, low loss, and high electrical energy density, *J. Electron. Mater.* **43**, 4548 (2014).
- ⁷S. Wu, W. Li, M. Lin, Q. Burlingame, Q. Chen, A. Payzant, K. Xiao and Q. M. Zhang, Aromatic polythiourea dielectrics with ultrahigh breakdown field strength, low dielectric loss, and high electric energy density, *Adv. Mater.* **25**, 1734 (2013).
- ⁸A. Banihashemi, H. Hazarkhani and A. Abdolmaleki, Efficient and rapid synthesis of polyureas and polythioureas from the reaction of urea and thiourea with diamines under microwave irradiation, *J. Polym. Sci. A, Polym. Chem.* **42**, 2106 (2004).
- ⁹Y. Vuillermet, O. Chadebec, J. M. Lupin, A. Saker, G. Meunier and J.-L. Coulomb, Optimization of low voltage metallized film capacitor geometry, *IEEE Trans. Magn.* **43**, 1569 (2007).
- ¹⁰T. Furukawa, Ferroelectric properties of vinylidene fluoride copolymers, *Phase Transit.* **18**, 143 (1989).
- ¹¹V. Bobnar, B. Vodopivec, A. Levstik, M. Kosec, B. Hilczer and Q. M. Zhang, Dielectric properties of relaxor-like vinylidene fluoride-trifluoroethylene-based electroactive polymers, *Macromolecules* **36**, 4436 (2003).
- ¹²G. Casar, X. Li, Q. M. Zhang and V. Bobnar, Influencing dielectric properties of relaxor polymer system by blending vinylidene fluoride-trifluoroethylene-based terpolymer with a ferroelectric copolymer, *J. Appl. Phys.* **115**, 104101 (2014).