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Energy Storage of Polyarylene Ether Nitriles at High Temperature

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Abstract

Polyarylene ether nitrile (PEN) was synthesized and used as film capacitors for energy storage at high temperature. Scanning electron microscopy observation indicated that the films of PEN have pinholes at nanoscales which restricted the energy storage properties of the material. The pinhole shadowing effect through which the energy storage properties of PEN were effectively improved to be 2.3 J/cm^3 was observed by using the overlapped film of PEN. The high glass transition temperature (T_g) of PEN was as high as 216 °C and PEN film showed stable dielectric constant, breakdown strength and energy storage density before the T_g. The PEN films will be a potential candidate as high performance electronic storage materials used at high temperature.

Keywords Energy storage · Pinhole shadowing effect · Polyarylene ether nitrile

1 Introduction

High energy storage film capacitors with high energy storage density, fast charge and discharge speed, chemical stability and high temperature resistance play an important role in the electric power system [1, 2]. Among the capacitor materials, polymers are excellent candidates because of their relatively high energy density low dielectric loss, fast charging speed and low cost [3, 4]. However, most of polymers used in capacitors show poor temperature resistance and low breakdown voltage. For example, the commercially available biaxially oriented polypropylene (BOPP) can operate only at temperature below 105 °C [4], and the breakdown voltage of poly(vinylidene fluoride) (PVDF) just reaches 170.0 kV/mm (40 μm in thickness) [5]. As a high performance material, PEN with excellent mechanical properties, chemical inertia and thermal stability has been used in vehicles and aerospace [6, 7]. Besides, PEN shows excellent solubility in polar organic solvents such as *N*-methyl pyrrolidone and *N*,*N*-dimethylformamide, and its wide range of processing window make it to be readily processed into different shaped products [8]. More importantly, The PEN has excellent electrical properties, including high dielectric constant and lower dielectric loss which are stable under varied temperature [9]. However, the application of PEN as film capacitor at high temperature has seldom reported.

In this work, PEN was synthesized and used as film capacitors for energy storage at high temperature. The PEN was characterized by SEM observation, differential scanning calorimetry (DSC), mechanical testing and dielectric measurement. Commercial available PVDF and BOPP films were also prepared for comparison. The energy storage properties especially these properties at high temperatures were studied in detail.

2 Experimental

2.1 Materials

NMP and DMF was purchased from Tianjin Bodi chemicals Co. Ltd (Tianjin, China). PEN were synthesized by nucleophilic aromatic substitution polymerization from 2,6-dichlorobenzonitrile and 4,4′-dihydroxybipheny [10]. PVDF (FR901) power was obtained from Shanghai 3F New Materials. BOPP was purchased from Qingdao Zhongzheng

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Materials. All chemicals and reagents were used as received without further purification.

2.2 Preparation of PEN films

The PEN films were prepared through a solution-casting method according to the literature [11]. 1.5 g PEN and 40 mL NMP were added into a 100 mL flask coupled with a mechanical stirrer. The mixture was stirred at 100 °C under ultrasonication to form a uniform solution. Then, the mixture was poured on a clean glass plate and dried in an oven to evaporate the solvent. The glass plate was heated as follows: 80 °C, 1 h; 100 °C 1 h; 120 °C, 1 h; 160 °C, 2 h and 200 °C, 2 h. Finally, the film was obtained by cooling naturally down to room temperature.

2.3 Preparation of PVDF films

1.5 g PVDF was dissolved in 40 mL DMF at 60 °C under stirring until the solution was transparent. Then, the solution was poured into a clean glass which was placed in an incubator at 100 °C for 24 h [12]. Afterward, the films were heated at 200 °C for 5 min [12]. Finally, the PVDF films with a thickness of 20–100 μm were obtained.

2.4 Characterizations

The micro-structures of PEN films were characterized by a SEM (JSM, 6490LV) operating at 20 kV after gold sputtering. The DSC measurements of PVDF, PEN and BOPP were performed with a TA Instruments (New Castle, DE, USA) DSC-Q100 modulated thermal analyzer at a heating rate of 10 °C/min from room temperature to 350 °C. Dielectric properties of the samples were tested with a TH 2819A precision LCR meter (Tong hui Electronic Co. Ltd.). Electric breakdown strength of the films was tested by Dielectric Withstand Voltage Tester (ZJC-50 kV). Mechanical properties of the samples were tested with a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen, China).

3 Results and Discussion

The morphological property of PEN was investigated using SEM observation. Figure 1a, b shows the typical SEM images of the surface and cross-section of PEN film. As shown in Fig. 1, it can be intuitively seen pinholes at nanoscales both on the surface and cross-section of PEN. The pinholes are formed during the solution-casting procedure. In addition, the pinhole cannot be completely eliminated due to the high molecular weight of the polymer. Pinholes are filled with air, and breakdown strength of the air is far below the polymer. When testing, the pinholes and defects reduce the breakdown strength significantly. Therefore, the pinhole decreases the breakdown strength of film and thus restricts the energy storage density of the film [13]. As a result, it is essential to eliminate the effect of the pinhole to improve the energy storage properties of the films.

The phase transition behaviors of the PEN, PVDF and BOPP films were investigated by DSC under a nitrogen atmosphere. As shown in Fig. 2a, PVDF and BOPP shows a melting point around 166 °C, just as Liu [14] and Valentini [15] reported, while the glass transition temperature (T_g) of PEN is as high as 216 °C. The high T_g of PEN indicates it can be used at higher temperature conditions. Figure 2b shows the tensile strength and tensile modulus of the polymer films. As a high performance polymer, the

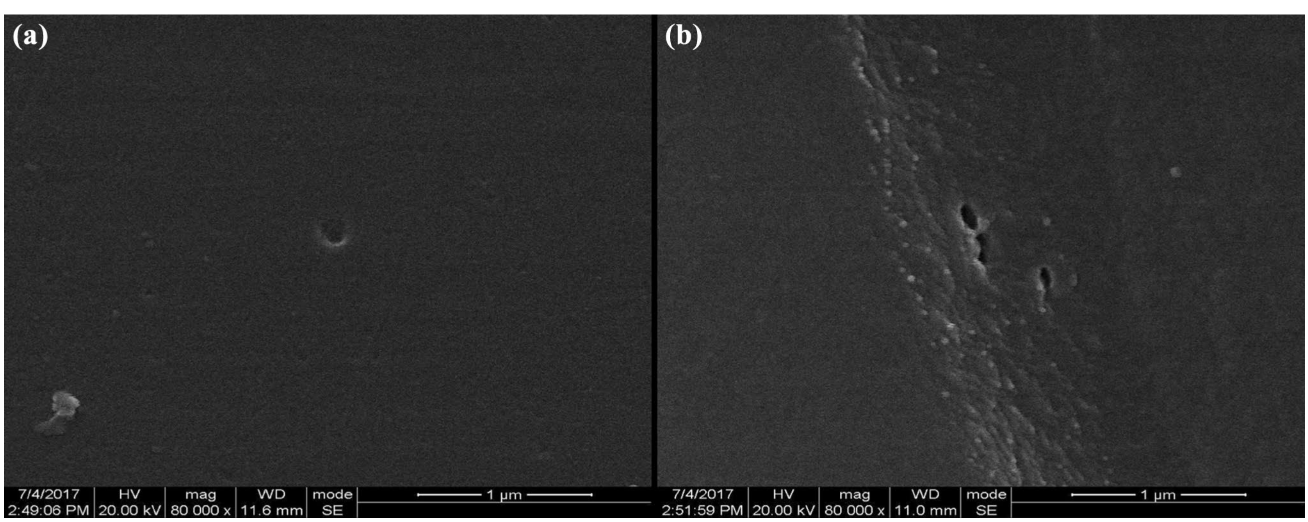

Fig. 1 SEM images of **a** the surface; **b** the cross-section of the PEN film

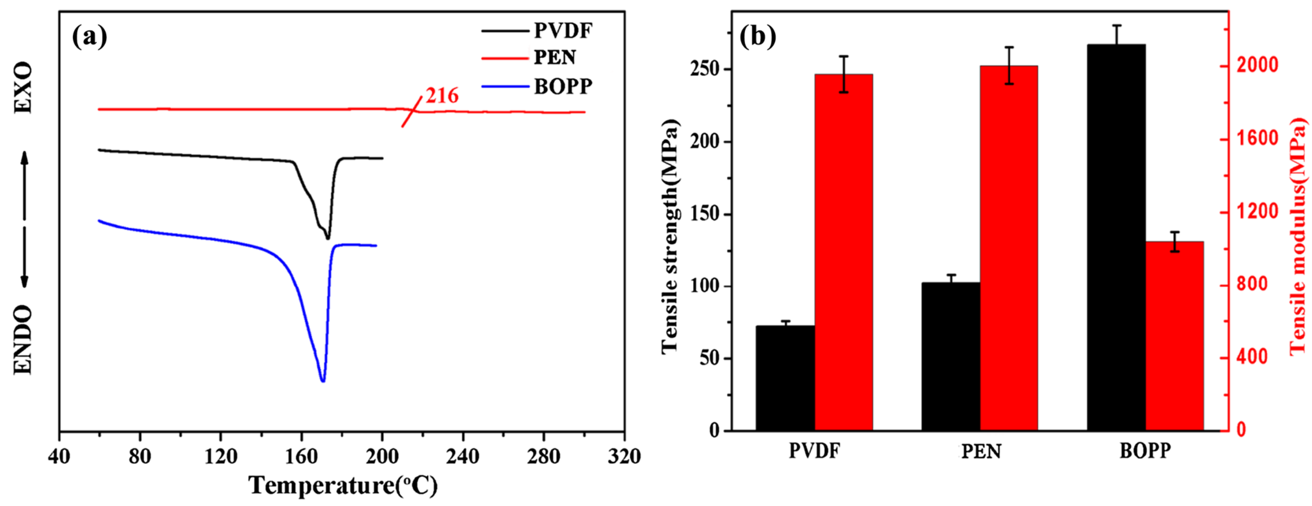

Fig. 2 DSC curves (**a**) and mechanical properties (**b**) of PVDF, PEN and BOPP

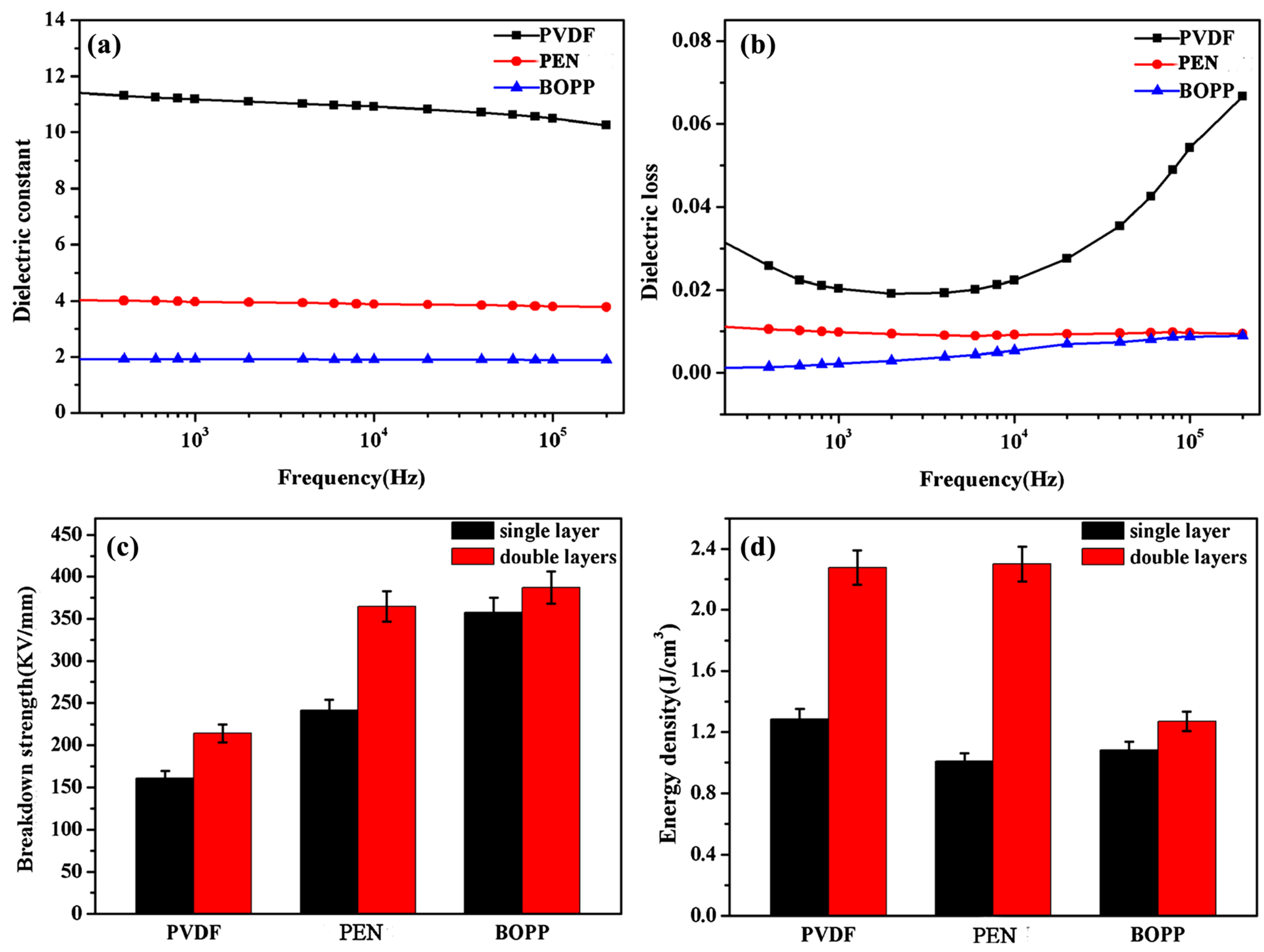

Fig. 3 The dielectric properties (**a**), dielectric loss (**b**), breakdown strength (**c**), and energy density (**d**) of the polymer films at 1 kHz

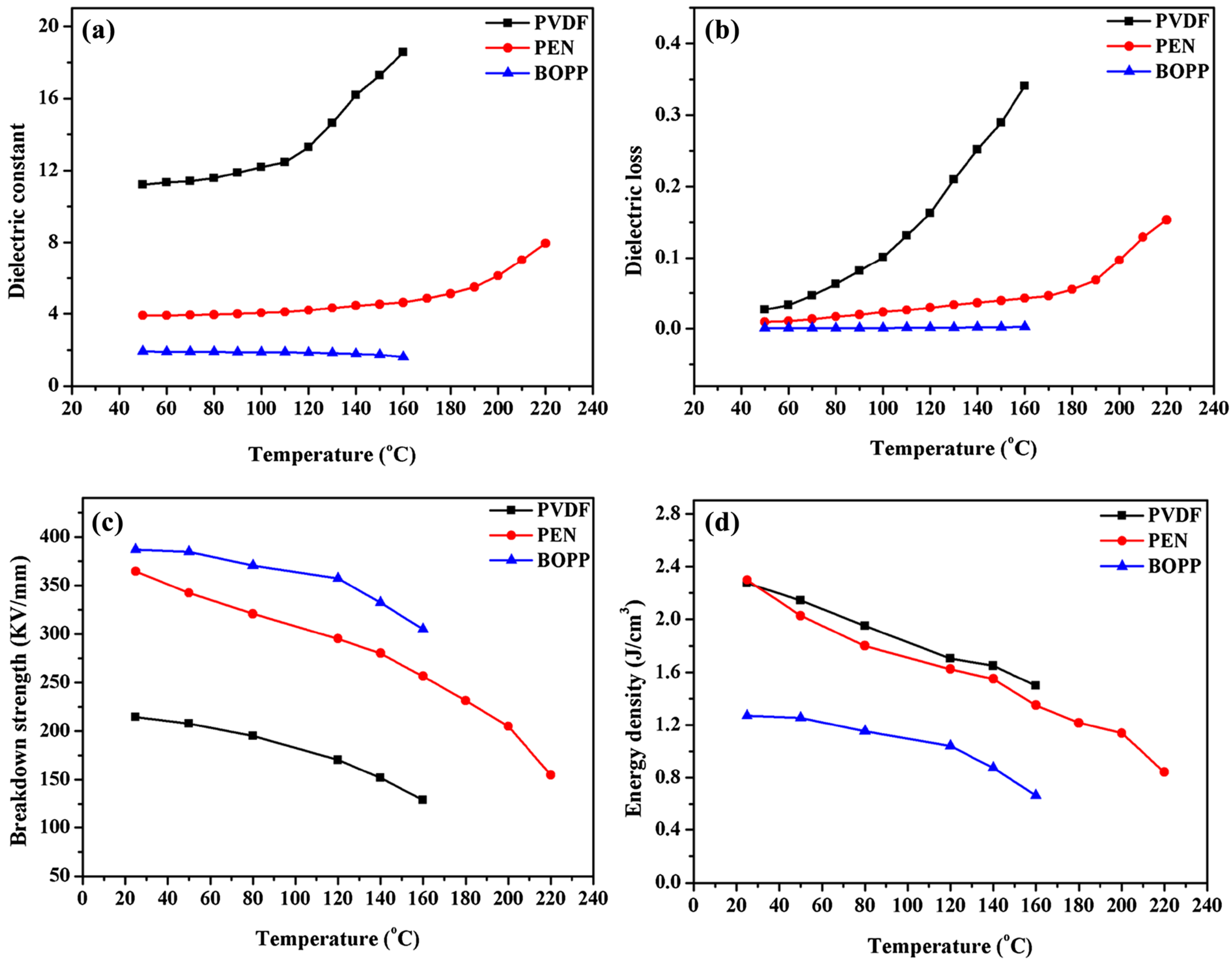

Fig. 4 The dielectric constant (**a**), dielectric loss (**b**), breakdown strength (**c**) and energy density (**d**) of the overlapped polymer films at 1 kHz

tensile strength and modulus of PEN is up to 108.7 MPa and 2002 MPa respectively, much better than the mechanical properties of PVDF reported by Liu [14], signifying this material is suitable for the application in flexible dielectric materials.

After the characterization of PEN, the energy storage properties of it were studied. The maximum energy storage density (U_{max}) of film capacitors can be calculated by Eq. (1):

$$U_{max} = 0.5e_0e_rE_b^2 \quad (1)$$

where ε_0 is the vacuum perpitivity (dielectric constant), ε_r is the permittivity of the polymer and E_b is the breakdown strength [16]. Firstly, the dielectric constant and dielectric loss of the samples were measured as a function of frequency from 100 Hz to 200 kHz at room temperature. As shown in Fig. 3a, PVDF is used as energy storage materials due to its high dielectric constant. However, the dielectric loss of PVDF is also higher than the others. In comparison, resulting from the polar –CN on the side-chain, PEN shows relatively high dielectric constant. In addition, the dielectric loss of PEN is much more stable than that of PVDF [17] and BOPP (Fig. 3b). These unique dielectric properties of PEN make it suitable as dielectric materials. Then, the breakdown strength of the polymer films (40 μm in thickness) were tested at room temperature with DC current, and the results were shown in Fig. 3c. BOPP is used as energy storage materials due to its high breakdown strength. The effect of sample thickness and electrode area [18], we got the results in Fig. 3c. The breakdown strength of the PEN is between that of PVDF [19] and BOPP. However, when two films of PEN (20 μm in thickness) superimposed over one another, the middle of the film with high temperature silicone oil bonding, the thickness of silicone oil is about 0.3 μm. The breakdown strength of the overlapped film increases obviously and is even comparable to that of the BOPP. As shown in Fig. 1, the PEN film has many pinholes. When the two films superimposed over one another, the pinholes in one film are largely shaded by the flat part of another film, resulting in the pinhole shadowing effect. Comparing with the single layer film, the pinhole shadowing effect improves the breakdown strength of the double layer film. According to the dielectric constant and breakdown strength, the energy storage density of the films was calculated by using Eq. (1) and the results were presented in Fig. 3d. The energy storage density of overlapped PEN film is 2.24 J/cm^3 which is higher than that of the PVDF (1.0 J/cm^3) [16] and BOPP (1.0–1.2 J/cm^3) [4]. This result indicates that the overlapped PEN can be used as flexible film capacitor material.

The energy storage properties of PEN at high temperature were further studied basing on its high temperature resistance and high energy storage at room temperature. Figure 4a, b show the dielectric constant and dielectric loss at 1 kHz of the samples from 25 to 220 °C. It can be seen that the dielectric constant and dielectric loss of PEN are comparatively steady under the temperature of its T_g. In comparing with PVDF and BOPP whose dielectric constant and dielectric loss cannot be measured at temperatures higher than 160 °C, the dielectric constant and dielectric loss of PEN are stable even at temperature as high as 220 °C due to its high T_g. These stable dielectric properties make PEN to be used as high temperature dielectric materials. Figure 4c shows the breakdown strength of the overlapped films of the samples at different temperature. The trend of breakdown strength with temperature increasing is the same as the reported [7] [20]. Although the breakdown strength of PEN decreases with the increasing of temperature, it is much higher than that of PVDF, especially at temperatures higher than 160 °C. In addition, the energy storage density of the samples at high temperature was calculated correspondingly. As shown in Fig. 4d, the energy storage density of PEN is as high as 0.84 J/cm^3 even at 220 °C. It can be concluded that the PEN film can be worked at high temperature as film capacitors.

4 Conclusions

PEN films prepared through solution casting method was used as film capacitors for energy storage at high temperature. The dielectric constant of PEN is 4.1 and the breakdown strength of it is as high as 364.7 kV/mm by using the overlapped film which results in the energy density of 2.3 J/cm^3. In addition, the dielectric properties are stable at high temperature due to the high T_g of PEN and the energy density is 0.84 J/cm^3 even at 220 °C. The results suggest that the PEN film can be used as high temperature film capacitors.

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References

1. Dang, Z., Yuan, J., Zha, J., et al.: Fundamentals, processes and applications of high-permittivity polymer-matrix composites. Prog. Mater Sci. **57**, 660 (2012)
2. Watson, J., Castro, G.: High-temperature electronics pose design and reliability challenges. Analog Dialog **46**, 1 (2002)
3. Chu, B.J., Zhou, X., Ren, K.L., et al.: A dielectric polymer with high electric energy density and fast discharge speed. Science **313**, 334 (2006)
4. Rabuffi, M., Picci, G., Trans, I.E.E.E.: Status quo and future prospects for metallized polypropylene energy storage capacitors. Plasma Sci. **30**, 1939 (2002)
5. Rahman, M.A., Chung, G.S.: Synthesis of PVDF-graphene nanocomposites and their properties. J. Alloys Compd. **581**, 724 (2013)
6. Wei, R., Wang, J., Zhang, H., et al.: Crosslinked polyarylene ether nitrile interpenetrating with zinc ion bridged graphene sheet and carbon nanotube network. Polymers **9**, 342 (2017)
7. You, Y., Han, W., Tu, L., et al.: Double-layer core/shell-structured nanoparticles in polyarylene ether nitrile-based nanocomposites as flexible dielectric materials. RSC Adv. **7**, 29306 (2017)
8. Yang, W., Yang, X., Pu, Z., et al.: The properties (rheological, dielectric, and mechanical) and microtopography of spherical fullerene-filled poly (arylene ether nitrile) nanocomposites. J. Appl. Polym. Sci. **131**, 40100 (2014)
9. Wei, R., Li, K., Ma, J., et al.: Improving dielectric properties of polyarylene ether nitrile with conducting polyaniline. J. Mater. Sci. Mater. Electron. **9**, 9565 (2016)
10. Feng, M., Yang, J., Zhong, J., et al.: Synthesis of high glass transition temperature fluorescent polyarylene ether nitrile copolymers. Mater. Lett. **65**, 1703 (2011)
11. Huang, X., Feng, M., Liu, X.: Design of bristle-like TiO2–MWCNT nanotubes to improve the dielectric and interfacial properties of polymer-based composite films. RSC Adv. **4**, 4985 (2014)
12. Li, W., Meng, Q., Zheng, Y.: Electric energy storage properties of poly (vinylidene fluoride). Appl. Phys. Lett. **96**, 192905 (2010)
13. Huan, T.D., Boggs, S., Ramprasad, R., et al.: Advanced polymeric dielectrics for high energy density applications. Prog. Mater Sci. **83**, 236 (2016)
14. Long, C., Wei, R., Liu, X.: Mechanical, dielectric, and rheological properties of poly (arylene ether nitrile)–reinforced poly (vinylidene fluoride). High Perform. Polym. **29**, 178 (2017)
15. Lopez Manchado, M.A., Valentini, L., et al.: Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing. Carbon **43**, 1499 (2005)
16. Luo, B., Li, L., et al.: Fabrication, characterization, properties and theoretical analysis of ceramic/PVDF composite flexible films with high dielectric constant and low dielectric loss. J. Mater. Chem. A. **2**, 510 (2014)
17. Zhao, Y., Yang, W., Zhou, Y., et al.: Influence of molecular weight on the dielectric and energy storage properties of poly (vinylidene fluoride). Electron. Mater. Lett. **12**, 779 (2016)
18. Diaham, S., Lebey, T., et al.: Dielectric breakdown of polyimide films: Area, thickness and temperature dependence. IEEE Trans. Dielectr. Electr. Insul. **17**, 18 (2010)

19. Bunnak, N., Laoratanakul, P., Manuspiya, H., et al.: Dielectric properties improvement of polymer composite prepared from poly(vinylidene difluoride) and barium-modified porous clay heterostructure. Electron. Mater. Lett. **9**, 351 (2013)

20. Schneuwly, A., Groning, P., Schlapbach, L.: Breakdown behavior of oil-impregnated polypropylene as dielectric in film capacitors. IEEE Trans. Dielectr. Electr. Insul. **5**, 862 (1998)