

# Ferroelectric properties and breakdown strength of layer-by-layer poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and polyurethane (PU) for energy storage application

C Chooseng, S Chaipo and C Putson\*

Department of Physics, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

\*Corresponding author's e-mail: chatchai.p@psu.ac.th

**Abstract.** Ferroelectric polymers are one of the next-generation pulsed capacitor materials for the potential application in capacitive energy storage. This polymer with higher saturated polarization, smaller remnant polarization, and higher electrical breakdown are the most promising candidates. In this work, the dielectric properties and energy storage capacity of the bilayer polymer films of Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and polyurethane (PU) were studied. These bilayer polymers were prepared by layer-by-layer method at the condition of variable layer thickness. The results show that the dielectric constants and the saturated polarization of the bilayer films increased, and bilayer films with P70/PU30 exhibit electrical high breakdown strength up to 379 V/ $\mu\text{m}$ . Moreover, enhanced energy storage density and the energy efficiency of the bilayer constrictors will be discussed for the capacitive energy storage polymers.

## 1. Introduction

Dielectric polymer materials are principal for capacitors due to their attributed lightweight, flexibility, scalability, and high dielectric strength. Dielectric constant ( $\epsilon_r$ ) and electrical breakdown strength ( $E_b$ ) were the two main keywords to enhance energy storage density of dielectric materials, which depend on the volume of interfacial polarization and structure [1]. Polyurethane (PU) is one of the electroactive polymers that have a high  $\epsilon_r$  and easily respond to an external electric field [2]. However, the increasing  $\epsilon_r$  of material reduced their  $E_b$  and energy efficiency causes an increment of energy loss within material [3]. For instance, the PU/BT50 polymer composites presented the  $\epsilon_r$  and  $E_b$  were 13.6 and 59.8 MV/m, compared to pure PU  $\epsilon_r$  and  $E_b$  were 7.4 and 88.6 MV/m [4]. Therefore, it is important to enhance both the energy storage density and the energy efficiency of dielectric materials. The consequence of layered films can enhance dielectric properties and energy capacity. The layer-structured 15 vol% BT/P(VDF-HFP) composite exhibits simultaneously increasing dielectric constant and breakdown strength ( $\epsilon_r \sim 20$  @10 kHz,  $E_b$  241 MV/m), and comparison with their single-layer ( $\epsilon_r \sim 11$  @10 kHz,  $E_b$  97 MV/m) [5]. Ferroelectric copolymer, Poly(vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) is a semi-crystalline polymer that provided high energy density and

high  $E_b$  (317 MV/m) [6]. In this research, we are interested in the bilayer film of P(VDF-HFP) and PU using the layer-by-layer solution casting method, and studied on the electrical properties and energy storage capacity.

## 2. Experimental

### 2.1. Fabrication of polymer films

The solution of single-layer film, 5 g of P(VDF-HFP) was dissolved in 20 mL of N, N-dimethylformamide (DMF) by stirring with 500 rpm at 50°C for 3 h and 5 g of PU was dissolved in 25 mL of DMF by stirring with 600 rpm at 80°C for 3 h. Then, single-layer film was cast onto the glass substrate by the casting method. After that, the films were dried in an oven at 80 °C for 12 h of P(VDF-HFP) and 14 h of PU. The thickness of the films was controlled around  $30 \pm 5 \mu\text{m}$  and measured via the thickness gauge (PEACOCK, G-7C). Fabrication of bilayer film, with the volume fractions of P(VDF-HFP) to PU was 100: 0, 70: 30, 50: 50, 30: 70, and 0: 100. The solution was prepared with the same ratio of single-layer film. First, the P(VDF-HFP) was cast onto glass substrate as the first layer and dried for 1 h in the oven at 80°C and then the PU was cast onto P(VDF-HFP) layer. Finally, bilayer films were dried at 80°C for 12 h in the oven.

### 2.2. Characterization

The dielectric properties were measured by LCR meter (IM 3533 HIOKI) in the frequency range of  $1-10^5$  Hz at room temperature. The dielectric constant ( $\epsilon_r$ ) and conductivity ( $\sigma$ ) were calculated by equations (1) and (2), respectively.

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (1)$$

$$\sigma = \frac{Gd}{A} \quad (2)$$

where  $C$  is the capacitance,  $d$  is the sample thickness,  $\epsilon_0$  is the permittivity of air ( $8.853 \times 10^{-12}$  Fm<sup>-1</sup>),  $A$  is the electrode area, and  $G$  is the conductance. The Energy storage density ( $U_e$ ) and the energy efficiency ( $\eta$ ) can be estimated in equations (3) and (4), respectively.

$$U_e = \int_{P_r}^{P_s} EdP \quad (3)$$

$$\eta = \frac{U_e}{U_e + U_l} \times 100 \% \quad (4)$$

where  $P$  is the polarization,  $P_s$  is the saturation polarization,  $P_r$  is the remnant polarization,  $E$  is the electric field, and  $U_l$  is energy loss was calculated in the close area of the hysteresis loop.

The breakdown strength ( $E_b$ ) was measured by Dielectric Breakdown Test System (PolyK Technologies State College) at the applied external electric field ( $E$ ) 0-10 kV, and the Weibull model as equation (5) was used to analyze the breakdown probability of all samples.

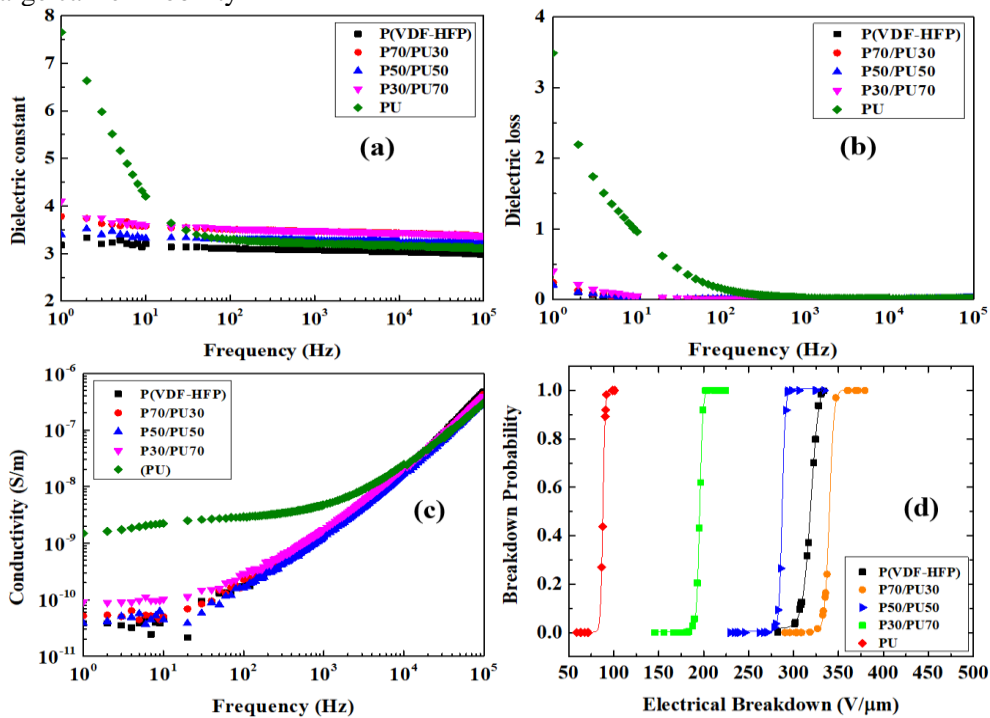
$$P(E) = 1 - \exp\left[-(E/\lambda)^k\right] \quad (5)$$

where  $P(E)$  is the breakdown probability of the material when the electric field was applied,  $k$  is the parameter related to the reliability of the sample and the shape parameter  $k$  shows the distribution of  $E_b$ ,  $\lambda$  is the breakdown probability of dielectric breakdown [7].

### 3. Results and discussion

#### 3.1. Electrical properties

Figure 1(a) shows the dielectric constant of bilayer films is higher than the single-layer film of P(VDF-HFP). The values of dielectric constant and dielectric loss of PU increase when the frequency was decreased (figure 1(a) and 1(b)). Also, the conductivity increased with frequency (figure 1(c)). The dielectric constant and dielectric loss depend on the frequency with polarization in the dielectric material. At low frequencies, the motion and rotation of dipoles in polymer films easily respond to the electric field. In case of neat PU, the dielectric constant and dielectric loss have the highest when compared with other conditions due to the interfacial polarization between soft and hard segments. The increment of the dielectric constant of bilayer films is also with two matrix and interfacial polarization at the boundary region. The conductivity of all conditions increased with frequency because of the charge carrier mobility.



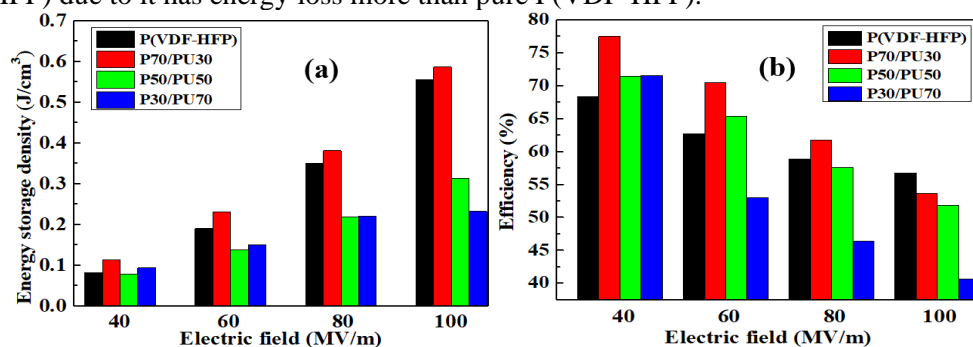
**Figure 1.** Frequency dependence of (a) dielectric constant, (b) dielectric loss, (c) conductivity and (d) breakdown probability of all polymer films with different volume fractions.

Figure 1(d) shows the probability of electrical breakdown ( $P(E)$ ) of PU, P30/PU70, P50/PU50, P(VDF-HFP) and P70/PU30, respectively. The breakdown strength of polymers depends on the external electric field. The influences such as structure, grain size, the porosity of materials, and environmental contamination affected to  $E_b$ . The bilayer P70/PU30 exhibited the highest  $E_b$  at 379  $V/\mu m$  compared with pure P(VDF-HFP) at 333  $V/\mu m$  that had more conductive pathway interface in the neat film. The intrinsic electric breakdown is a material characteristic and is electronic in nature [8]. The charge with interfacial polarization of heterogeneous polymer causes PU has lowest breakdown strength.

#### 3.2. Energy storage capacity

The polarization of film increased with electric field due to the motion and alignment in domain film. For instance, the saturation polarization ( $P_s$ ) of P70/PU30 was 0.60  $\mu C/cm^2$  at the electric field of 40

MV/m and increased to  $1.75 \mu\text{C}/\text{cm}^2$  at the electric field of 100 MV/m. The remnant polarization ( $P_r$ ) of pure P(VDF-HFP) was  $0.32 \mu\text{C}/\text{cm}^2$  under the electric field of 100 MV/m, while the remnant polarization of P70/PU30 is  $0.43 \mu\text{C}/\text{cm}^2$  under the same electric field. The single-layer of P(VDF-HFP) and bilayer of P70/PU30 show that the energy storage density is higher than bilayer P50/PU50 and P30/PU70 (figure 2(a)) due to the result of saturation polarization from ferroelectric properties. The energy efficiencies of all films are drop when electric field was increased (figure 2(b)) due to an increase of the energy loss and the remnant polarization. The highest energy efficiency of bilayer film P70/PU30 at 40, 60, and 80 MV/m, is 77%, 70%, and 61%, respectively. The energy loss of polymer films importantly consists of the dielectric loss and the conduction loss from leakage current at the high electric field. The resulting of efficiency at 100 MV/m, the bilayer film P70/PU30 has lower than pure P(VDF-HFP) due to it has energy loss more than pure P(VDF-HFP).



**Figure 2.** Energy storage density (a) and energy efficiency (b) of polymer films with different volume fractions as a function of the electric field.

#### 4. Conclusions

In summary, the bilayer films provided high dielectric constant, energy efficiency, and the breakdown strength of pristine P(VDF-HFP) film. The result showed that the energy storage density of P70/PU30 is higher than other films. The energy efficiency of P70/PU30 increases with increasing interfacial polarization of PU, and decreasing dielectric loss of P(VDF-HFP) segment. Moreover, the electrical breakdown strength of bilayer P70/PU30 provided the highest  $E_b$ .

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