Discharge Energy Efficiency Improvement of P(VDF-HFP) Copolymers Thin Films by Stretching and Electron Beam Irradiation

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Abstract. Toward improving the applications for energy-based technology, dielectric polymers is getting attention due to its relatively high dielectric constant, dielectric breakdown and flexibility, with easily preparation, lightweight and low cost. Dielectric contribution and polarization responses lead to different shape and size of hysteresis loop. This work presents the techniques on reducing domain size for slimmer loop, indicating lower energy loss. As-casted P(VDF-HFP), stretched P(VDF-HFP) and electron irradiated-stretched P(VDF-HFP) thin films were prepared by solution casting method. The irradiation was prepared by emitting electron beam. The dielectric and AC conductivity properties were investigated by LCR meter, while polarization-electric field loops were observed by P-E loop instrument. The results show that stretching and electron beam irradiation significantly increase the dielectric constant of P(VDF-HFP). Their ability on modifying the domain size leads to reduce P-E loop of P(VDF-HFP), followed by reducing energy loss but improving storage energy density and discharge energy efficiency.

1. Introduction
The outstanding materials for current applications in renewable energy-based electronics [1], [2] and power electronics [3] cannot be separated from its high dielectric constant [4] as well as low dielectric loss. One of the applications of dielectric polymers related to energy-based electronics is capacitor [5]. Since invented in 1990, dielectric polymers film capacitor with higher capacitance stability, owning high-voltage characteristics and possessing extremely low losses [6], has been improved due to its advantages over electrolytic and ceramic capacitor. In power and energy-based applications, low dielectric loss and high dielectric constant could lead to a higher energy efficiency and better performance as well.

Beyond its advantages that can be fabricated into thin film and large size device, P(VDF)-based semi-crystalline polymers [7] are the best materials that containing all electroactive characteristics among other ferroelectric, piezoelectric and pyroelectric materials [8]. With addition of hexafluoropropylene (HFP) into the main chain of P(VDF), P(VDF-HFP) copolymers is rich on stability, chemically resistance, non-toxicity and ability on tailoring the size and shape as well as recycling capability [9], [10].

Based on ferroelectricity of P(VDF)-based polymers including P(VDF-HFP) copolymers, a normal ferroelectric dielectric materials polarization response on applied external electric field will exhibit a
broad hysteresis loop [11]. That phenomenon leads to a high energy loss and low storage energy density. As the consequence, the discharge energy efficiency is also drop. This work focuses on increasing storage energy density and energy efficiency with lowering energy loss at the same time.

2. Materials and methods

2.1. Materials and method

P(VDF-HFP) Solef 11010/1001 copolymers powder was supplied by Solvay Solexis, Belgium. DMF N,N-dimethylformamide with ≥ 99% purity was supplied by RCI Labscan, Thailand.

First condition, poly(vivylidene fluoride-hexafluoropropylene) thin films, named as-casted P(VDF-HFP) were kindly prepared by solution casting. The P(VDF-HFP) powder was stirred with DMF solvent in room temperature using magnetic stirrer for 16 hour. The solution then been filled out and casted on the glass plate using blade with the thickness of 30 ± 5 µm. The samples then been dried for 12 hour at 80 °C in the oven. The second condition, named stretched P(VDF-HFP) was prepared by stretching P(VDF-HFP) films from 120 ± 5 µm to 30 ± 5 µm by stretching machine at 70 °C. Lastly, the stretched film then been emitted by 15 kV electron beam using conventional scanning electron microscopy (SEM) HITACHI TM3030Plus from Germany for 5 minutes. This condition named electron beam irradiated-stretched P(VDF-HFP) or EI stretched P(VDF-HFP).

2.2. Characterizations and measurements

LCR meter IM 3533 HIOKI was carried out for measuring dielectric constant and dielectric loss as well as AC conductivity. It was conducted on 1 V of AC voltage with varying the range of frequency from 1 Hz to 100 kHz at room temperature. The Dielectric constant and AC conductivity can be generated by calculating the data of the capacitance (C) and conductance (G) that gained from the measurements. Meanwhile, the value of dielectric loss can be gained directly from the measurements.

The hysteresis loops of polarization and electric field were measured by P-E loop instrument Trek type 601E. Conducted in temperature range from 21 °C to 140 °C, a 40 MV m⁻¹ of external electric field with 10 Hz of frequency were applied to the thin films. Those P-E hysteresis loops were compared between each condition by calculating the area inside the loop (ferroelectric energy loss) and the area outside of the loop (ferroelectric energy density). Furthermore, the discharge energy efficiency can be obtained for each condition. Mathematically, it can be expressed as:

$$\eta = \frac{U_e}{U_e + U_l}$$  \hspace{1cm} (1)

where \(\eta\), \(U_e\), and \(U_l\) refers to energy efficiency, energy density and energy loss, respectively [12].

3. Results and discussion

3.1. LCR meter results

The dielectric constant of as-casted P(VDF-HFP), stretched P(VDF-FP) and EI stretched P(VDF-HFP) are presented by figure 1. Figure 1 clearly shows that as-casted P(VDF-HFP) possesses the lowest value of dielectric constant. As reported by other works, as-casted P(VDF-HFP) is dominated by α-phase that is the most stable crystalline phase due to its symmetric structures [13]. On the other hands, the dielectric constant is increase significantly after mechanical stretching in every frequency. There is no doubt that mechanical stretching is one of the most effective ways to increase dielectric constant of the materials. It is due to the ability of mechanical stretching on facilitating the transformation of non-polar α-phase to the most useful β-phase [11]–[14]. Furthermore, mechanical stretching is also responsible to rearrange the crystal grains orientation and increase its uniformity [15]. Those mechanism will leads to the more order β-phase dipole TTTT conformation of P(VDF-HFP).
The dielectric constant improvement of P(VDF-HFP) caused by electron beam irradiation on stretched P(VDF-HFP) is about two times compared than that of the only stretched thin films in all frequencies. This shows that both mechanical stretching and electron beam irradiation are effective to modify the structure of the thin film. As the results, the dielectric constant are increase significantly compare with as-casted condition. For example, dielectric constant of as-casted, stretched and EI stretched at 1 Hz frequency are 3.22, 3.66 and 4.48 respectively.

Dielectric loss is relatively referred to AC conductivity. Normally, the improvement of dielectric constant will be followed by the increasement of dielectric loss and AC conductivity also. That is a challenge that usually found in every dielectric material.

Nevertheless, figure 2 and 3 show that AC conductivity and dielectric loss of P(VDF-HFP) are not drastically change after stretching and electron beam irradiation. Somehow, at low frequency the numbers are even gradually drops. Some previous works reported that stretching [11], [15] is responsible to the improvement of dielectric constant due to its ability to convert non-polar α-phase to polar β-phase. At the same time, stretching also effects to destroy the big ferroelectric domain of P(VDF-HFP). Hence, the crystalline size/ferroelectric domain after stretching tends to be smaller as

![Figure 1. Dielectric constant of as-casted, stretched and EI stretched P(VDF-HFP) as a function of electric field frequency.](image1)

![Figure 2. AC conductivity of as-casted, stretched and EI stretched P(VDF-HFP) as a function of electric field frequency.](image2)

![Figure 3. Dielectric loss of as-casted, stretched and EI stretched P(VDF-HFP) as a function of electric field frequency.](image3)
reported by Li and Wang in 2016 [11]. As a final result, mechanical stretching could control the dielectric loss or even decrease its number, while increasing the dielectric constant at the same time.

Similar with the effect of stretching on AC conductivity and dielectric loss, electron beam irradiation is also responsible to stabilize those two parameters. It is well known that electron beam irradiation is becoming an alternative way to boost dielectric constant and keep control or even drop the AC conductivity and dielectric loss. Its ability is associated with its role when cutting the long chain to be shorter [16]. Furthermore, generating smaller crystalline size, electron beam irradiation would be very useful on generating smaller P-E loop that refers to smaller energy loss.

3.2. P-E loop measurements

Figure 4 shows P-E loop at room temperature (28 °C) with the external electric field of 40 MV/m. It shows clearly that stretched and electron beam irradiated stretched P(VDF-HFP) possess higher maximum polarization ($P_{max}$). $P_{max}$ is increase from 0.56 for as-casted film to 0.64 and 0.65 µ C/cm$^2$ for stretched and EI stretched films, respectively. At the same time, the remnant polarizations ($P_r$) of those two conditions are smaller than that of as-casted P(VDF-HFP). $P_r$ is decrease from 0.09 for as-casted film to 0.04 and 0.02 µ C/cm$^2$ for stretched and EI stretched films, respectively.

![P-E loop measurements](image_url)

Figure 4. P-E loop of as-casted, stretched and EI stretched P(VDF-HFP).

The bigger loop of as-casted films refers to large size of the ferroelectric domain that consist of big number of dipoles, causing higher remnant polarization [12], [17]. The dropping of $P_r$ that caused by stretching and electron irradiation effects to the polarization responses on external electric field, exhibiting the slimmer loops. In another word, stretching and electron beam irradiation are effectively reduce the area inside the loop of the P(VDF-HFP) thin films, confirming the previous work [15].

3.3. Energy efficiency

Based on P-E loop for each condition, the storage energy density, energy loss as well as energy efficiency value have been obtained. The results were shown by figure 5. It is clear that stretching and electron beam irradiation are effective to boost the storage energy density of P(VDF-HFP) thin films. At the same time, both treatments also drop the energy loss, drastically. The combination of these two parameters effects to the energy efficiency itself, as shown by figure 6. Hence, the discharge energy efficiency tends to exhibit much better value. The results of P-E loop measurements are also confirmed by dielectric constant result. In 2012, Zhu was reported that storage energy density can be improved by improving dielectric constant and electrical breakdown strength [12], [18].
4. Conclusion

Stretching and electron beam irradiation effectively improve the dielectric constant of P(VDF-HFP) copolymers thin films. The improvement was observed at all range of frequency. It corresponds to the ability of both mechanical stretching as well as electron beam irradiation on changing the crystalline phase from nonpolar α-phase to the polar β-phase. It also effect on changing the polarization-electric field loop (P-E loop) of the P(VDF-HFP). The improvement of maximum polarization and drops of remnant polarization cause the hysteresis loop getting slimmer. It represents that energy loss is decrease while storage energy density and discharge energy efficiency are increase at the same time. Hence, these properties are good to be applied on energy-based electronics.

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