Preparation and enhanced electrical breakdown strength of PVDF-TrFE-CTFE/PVDF-HFP film composites

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Abstract. Poly(vinylidene fluoride-trifluoroethylenechlorotrifluoroethylene), PVDF-TrFE-CTFE composite films with addition poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP at different copolymer loading was prepared by using the tape casting solution method. Electrical breakdown strength (E_b) was measured by the dielectric breakdown test system and fitting the E_b by the Weibull model. The experimental results illustrated that the breakdown probability, P(E) of the neat terpolymer and copolymer film was 316 V/μm and 495 V/μm, respectively. In addition, the breakdown probability of composite films between terpolymer and copolymer is higher than the neat PVDF-TrFE-CTFE film, in which the value of E_b is almost double when compared with terpolymer film. We will discuss on their crystallinity, material homogeneity and crystalline size to provide the method to improve the electrical breakdown strength with addition copolymer for energy storage applications.

1. Introduction

Ferroelectric properties are at the origin of various applications, especially in the field of dielectric capacitor, batteries and storage devices [1-2]. The energy storage capabilities can be improved by increasing the voltage and capacitance. However, there is a limit for applied voltage of the dielectric or ferroelectric materials in which the maximum voltage is related to the electrical breakdown strength (E_b). Obviously, one of the key to maximize the efficiency of those devices is the electrical breakdown strength (E_b) [3]. Ferroelectric materials like poly(vinylidene fluoride, PVDF) and its copolymer are intrinsically multifunctional. Blending between β-PVDF-base and copolymer was widely investigated in term of polarization and strong dipole interaction; however, they are still low E_b. For example, PVDF-TrFE/PVDF-TrFE-CTFE terpolymer was the E_b of 150 kV/mm [4]. The E_b of the polymer can be improved by blending with another polymer of high E_b, for instance, poly(methyl methacrylate) (PMMA), polystyrene (PS), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). In case, PVDF-HFP/42.6vol%PMMA blend was reported the electric field of 475 MV/m [5]. Poly(vinylidenefluoride-trifluoroethylenechlorotrifluoroethylene) (PVDF-TrFE-CTFE) terpolymer show the relaxor ferroelectric materials which provided high dielectric constant and high β-phase region but low E_b (300 V/μm). Such a low breakdown strength limited the applied electric field which make the modified terpolymer useless for electrical application. In the current, PVDF-HFP copolymer is more interesting due to its high dielectric constant, high E_b (400-700 V/μm), easy to preparation and
inexpensive. In this work, the PVDF-TrFE-CTFE blend with PVDF-HFP was prepared and studied on the dielectric properties and electrical breakdown strength.

2. Experimental

2.1. Material preparation
PVDF-TrFE-CTFE 63-033 from PolyK Technologies State College, filled with PVDF-HFP, Solef 11010/1001, purchased from Solvay Solexis, Belgium. The composite films were prepared by the tape casting solution method. Blending PVDF-TrFE-CTFE/PVDF-HFP in five different ratios (100/0, 70/30, 50/50, 30/70 and 0/100) was dissolved in N, N-dimethylformamide (DMF, 99% purity, purchased from RCI Labscan Limited, Thailand), and stirred for 6 h at 50 °C. After fully dissolved, the solutions were casted on the glass plate and annealed at 120 °C for 12 h for evaporation of the solvent. Subsequently, the films were taken off from the glass plate with deionized water.

2.2. Dielectric characterization
The dielectric constant, AC conductivity and dielectric loss factor of films were investigated by the LCR meter (IM 3533 HIOKI) with a frequency range 1 - 10^5 Hz at room condition. The dielectric constant and AC conductivity were calculated by equation (1) and (2), respectively:

\[ \varepsilon_r = \frac{C_p t}{\varepsilon_0 A} \]  

(1)

\[ \sigma = \frac{Gt}{A} \]  

(2)

where \( \varepsilon_r \) and \( \sigma \) are dielectric constant and AC conductivity and \( C_p, t, A, \varepsilon_0, G \) are electrical capacitor, the thickness of film (at 100 ± 5 µm in all case), the area of electrode, the permittivity of air (8.853 x 10^{-12} Fm^{-1}) and the conductance, respectively.

2.3. Electrical breakdown strength (E_b)
The films were under electric field between 0 and 10kV which measure the E_b by Dielectric Breakdown Test System (PolyK Technologies State College). 12 breakdown tests were performed on each sample and E_b was analysed by using the Weibull model which shown in equation (3):

\[ P(E) = 1 - \exp\left[-\left(E/E_b\right)^{k}\right] \]  

(3)

where P(E) is the breakdown probability of the material when the electric field E 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 at 63.2% [6].

3. Results and discussion
From table 1, the dielectric constant, dielectric loss and conductivity of all samples decreases with increasing the content of PVDF-HFP. For example, the dielectric constant of neat PVDF-TrFE-CTFE and PVDF-HFP films were 17.1350 and 3.7667, respectively. It was noted that neat PVDF-TrFE-CTFE terpolymer is higher than five-fold. The results showed that the dielectric constant of blend polymer decreased when PVDF-HFP copolymer was increased, according to mixing law. In general, the dielectric constant based on interfacial polarization significantly affects the heterostructure materials. In place of PVDF-TrFE-CTFE terpolymer is semi-crystalline polymer, which provided the main crystallinity phase as β-phase (high β-phase) that affects to dipole response electric field and amorphous phase as α-phase while PVDF-HFP copolymer was more α-phase polymer so the interfacial polarization of terpolymer lead to high dielectric value. It may be attributed that the decrement of the dielectric constant of blend polymer concerns with the crystalline phase when PVDF-HFP
copolymer was increased. Moreover, it was found that the dielectric loss significantly decreases with increasing the content of PVDF-HFP. In general, the dielectric loss or loss tangent of dielectric materials related to its conductivity. Thus, dielectric loss increased when the ratio of PVDF-HFP was decreased, which leads to the increment of AC conductivity of the sample. In fact, PVDF-TrFE-CTFE terpolymer was the high dielectric constant and more β-phase region that affects to dipole response electric field while PVDF-HFP copolymer was more α-phase polymer.

Table 1. The dielectric constant, dielectric loss and AC conductivity of all composite films with frequency at 1000Hz.

| Ratio of PVDF-TrFE-CTFE/PVDF-HFP | Dielectric constant | Dielectric loss | AC Conductivity (×10⁻¹¹S/m) |
|----------------------------------|--------------------|----------------|-----------------------------|
| 100/0                            | 17.1350            | 0.0530         | 4.2556                      |
| 70/30                            | 10.5043            | 0.0409         | 1.9636                      |
| 50/50                            | 9.5388             | 0.0361         | 1.5793                      |
| 30/70                            | 5.9279             | 0.0272         | 1.0306                      |
| 0/100                            | 3.7667             | 0.0194         | 0.9547                      |

Figure 1 shows the breakdown probability, P(E) of different PVDF-HFP loading in terpolymer. The E_b of 100/0, 70/30, 50/50, 30/70 and 0/100 are 316, 570, 423, 396 and 495 V/μm, respectively. Blending between terpolymer and copolymer enhanced the E_b when the ratio of terpolymer was adjusted. The E_b increases with increasing PVDF-HFP content. Moreover, it was found that the optimization of the E_b between the PVDF-TrFE-CTFE/PVDF-HFP is ratio of 70/30. From experimental results, it may be attributed that the crystalline region and crystalline size of terpolymer are significantly impacting on the E_b of materials. As previously reported that the enhancement of electrical breakdown strength can be contributed to the semi-crystalline terpolymer is biphasic material and the expanded interfacial region from PVDF-HFP [7-8].

4. Conclusion
This work, the PVDF-TrFE-CTFE blended with PVDF-HFP films was prepared by the solution casting method. The results showed that the dielectric constant of this polymer decreased as PVDF-HFP copolymer was increased, according to mixing law. While dielectric loss increased when the ratio of PVDF-HFP was decreased, which has the same trend with of AC conductivity or the electrical response.
of the sample. The enhancement of electrical breakdown strength by blending with the proportion of PVDF-TrFE-CTFE/PVDF-HFP (70/30) provided the highest $E_b$ (570 V/μm) and the dielectric constant of 10.5 at 1 kHz. It may be attributed that the changing of $E_b$ related to the crystallinity of PVDF-TrFE-CTFE composite films when PVDF-HFP copolymer was used.

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