Preparation and ferroelectric properties of poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) filled with graphene-nanoplatelets film composites

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Abstract. The poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP composite films with addition graphene-nanoplatelets (GPN) was prepared by using the tape casting solution method. The obtained composite films were stretched with help from thermal stretching machine at 80 °C with 5 mm/min rate. Dielectric constant and hysteresis loop (PE-loop) between the stretching and non-stretching films at different fillers percentage were compared in this study. Dielectric constant was investigated by the LCR meter. The PE-loop was measured by the ferroelectric polarization loop test system. The experimental results showed that the dielectric constant of all samples increases with increasing fillers content, regardless of frequency. The dielectric constant of stretching composite films was higher than non-stretching composite films. In addition, the PE-loop shapes of the stretching films have slimmer than the non-stretching films regardless of filler content. However, the PE-loop produced the shape to be bigger loop with increasing filler content. The energy efficiency of obtained PVDF-HFP composite films will be discussed on their dielectric constant, dielectric loss, AC conductivity, and polarization performances for electric–capacitor materials applications.

1. Introduction
Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) is widely investigated due to its exceptional ferroelectric properties. These properties are at the origin of various applications, especially in the field of sensor, transducers, actuator devices, and electric–capacitor materials [1],[2]. The β-phase of P(VDF-HFP) exhibited the strongest ferroelectric properties. The increasing of β-phase transition of polymer has been investigated on several techniques. Stretching films at a temperature below the crystal phase transition temperature resulted in a significant increase in the β–phase [3]. However, the dipolar moments of polymer are randomly oriented. The poling field will induce a preferred orientation of the dipoles along the field direction that can generate the β–phase regions. On the other hand, the β-phase can be enhanced by conductive particle fillers [4]. Graphene-nanoplatelets (GPN) have been recognized due to its excellent conductivity, thermal, mechanical, electrical properties, and its possibility of mass production at low cost. In fact, GPN are layered graphene nano - crystals in the structure of platelets stacked by van der Waal’s forces. Thus, the ferroelectric and dielectric properties of PVDF-HFP can be enhanced with increasing GPN content. In this work, the PVDF-HFP blend with GPN in DMF solvent was prepared and synthesized film by the solution casting method. The dielectric constant, AC conductivity, dielectric loss factor, PE-loop and energy efficiency were
assessed by using LCR meter and the ferroelectric polarization loop test system. The obtained PVDF-HFP composites with and without stretching various content fillers was studied and discussed on the dielectric and ferroelectric properties.

2. Experimental

2.1 Material preparation
Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP, Solef 11010/1001, purchased from Solvay Solexis, Belgium) filled with graphene-nanoplatelets (GPN, 806633 from Sigma-Aldrich). The polymeric films were prepared by the solution casting method. Firstly, the GPN (conditions of 1, 2, 3 and 4 %wt.) was dissolved and homogenized in N, N-dimethylformamide (DMF, 99% purity, purchased from RCI Labscan Limited, Thailand), and dispersed by the ultrasonic probe (Hielscher UP400S) for 20 min. Subsequently, the obtained GPN was mixed with PVDF-HFP solution and continuously stirred for 3h at room temperature. The solutions were cashed on the glass plate and annealed at 80°C for 12 h for evaporation of the solvent. And then, the films were taken off from the glass plate. Finally, the composite films were stretched with the thermal stretching machine at 80°C with rate of 5 mm/min.

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 frequency of 1 - 105 Hz at room condition. The dielectric constant and AC conductivity were calculated by equation (1) and (2), respectively:

\[ \varepsilon_r = \frac{C_{Pr} \times t}{\varepsilon_0 A} \]  
\[ \sigma = \frac{G t}{A} \]

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 (Samples thickness is 100 ± 3 µm in all case), the area of electrode, the permittivity of air (8.853 x 10^-12 F m^-1) and the conductance, respectively.

2.3 Ferroelectric characterization: Au electrodes were sputtered on the both surface of films. The ferroelectric properties was analysed by Polarization-Electric filed (P-E) loop test system with the electric fields range of -40 to 40 MV/m at room temperature. The energy density (\( U_e \)), and energy efficiency (\( \eta \)) can be calculated from the curve of PE-loop as Equation (3) and (4) [5], respectively. For loss energy density (\( U_l \)) was calculated in the closed area in PE-loop:

\[ U_e = \int_{Pr}^{P_{max}} EdP \]  
\[ \eta(\%) = \left( \frac{U_e}{U_e + U_l} \right) \times 100 \]

where \( E \), \( P_r \) and \( P_{max} \) were the electric field, the remnant polarization, the maximum polarization, respectively.

3. Results and discussion

3.1 Dielectric properties: In Figure 1(a) shows the dielectric constant of all samples increases with increasing content of fillers. The dielectric constant of stretching PVDF-HFP films is higher that of non-stretching films, regardless of used content of fillers. For examples, the dielectric constant of stretching and non-stretching PVDF-HFP with GPN 4%wt was 2.99 and 1.86, respectively. The micro-polarization contributions in case of the heterostructure can be increased which is strongly relevant to the interfacial polarization between polymer matrix and fillers. In fact, the GPN exhibited the good conductivity, thus there are enhancement of charge accumulation in polymer matrix when the GPN was used as fillers.
Furthermore, it may be attributed that its crystallinity of polymer chain was increased when the composites films were stretched, lead to enhancement of the $\beta$ – phase region. While, the AC conductivity of stretching PVDF-HFP films is not more change when compared with non – stretching films. Figure 1(b-c) exhibited the AC conductivity of PVDF-HFP composites increases with increasing GPN content. The dielectric loss factor had the same trend with the AC conductivity, can assume by, the dielectric loss factor (tan$\delta$) depends on AC conductivity ($\sigma$) [6].

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \cdot \frac{\sigma}{\varepsilon_f}$$

![Figure 1](image1)

**Figure 1.** (a) The dielectric constant, (b) AC conductivity and (c) The dielectric loss factor of PVDF-HFP filled with GPN compared between stretching film (S: Red square symbol) and non-stretching film (NS: Black circle symbol) at 1000Hz.

![Figure 2](image2)

**Figure 2.** PE-loop under electric field of (a) Pure PVDF-HFP and filled with GPN at (b) 1%, (c) 2%, (d) 3%, (e) 4% compared between stretching film (S: Red line) and non-stretching film (NS: Black line).

### 3.2 Ferroelectric properties

The shape of the hysteresis loop (PE-loop) as shown in Figure 2(a-e). The loss energy density ($U_l$) of the stretching films have less than the non-stretching films, regardless of filler content. From PE-loop can evaluate the energy efficiency ($\eta$) from equation (4). the $\eta$ of stretching film is higher than non-stretching film. However, the neat film stretched had the highest efficiency at 77% (Figure 3). It may be attributed that the addition of GPN related to crystalline size
of PVDF-HFP composite films [7]. Agglomerate of GPN particle resulted in increasing of $U_i$ and reduction $U_e$, so the $\eta$ of the composite film had the decreasing trend.

Figure 3. The energy efficiency of pure PVDF-HFP and PVDF-HFP filled with GPN 1%, 2%, 3% and 4% compared between stretching film (S) and non-stretching film (NS).

4. Conclusions
This work demonstrates the enhancement of the dielectric constant, AC conductivity and dielectric loss factor of the stretching PVDF-HFP film by GNP particle. In addition, the shape and volume of the hysteresis loop or the loss energy density of the stretching films have less than the non-stretching films, regardless of filler content. It may be attributed that the changing of hysteresis loop related to the crystallinity of PVDF-HFP composite films when GNP fillers was used.

5. References
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