Preparation and Storage Energy Density Based on Dielectric Properties of P(VDF-HFP)/PU/BNKT Thin Films

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Abstract. Novel electrical devices based on energy storage capacitor and energy conversion, have developed to advanced dielectric properties including electrical performance. In this work, three phases composite of poly(vinylidene fluoride hexafluoropropylene) (P(VDF-HFP)) blended with polyurethane (PU) and filled with Bi₀.₅(Na₀.₈-K₀.₂)₀.₅TiO₃ (BNKT) ceramic was studied on the dielectric, electrical properties and a storage energy density. All composite thin films are fabricated by the tape casting method in solution. Polarization-Electrical (P-E) loop of all composite thin films were also investigated relaxor-ferroelectric characteristic with the various electric fields. The recoverable energy density and energy efficiency from the loop were then analysed. As a result, the three phases composite of P(VDF-HFP)/PU/BNKT composites produce the highest dielectric constant as well as conductivity; however, they produce the lowest energy efficiency in this work. It seems that the interfacial polarization is easy switchable dipole moment in three phases more than one phase, resulting in high dielectric constant as well as conductivity. However, the larger conductivity seemingly generates larger dielectric loss, resulting in lower energy efficiency. Therefore, the comparison based on three and two phases can be used to predict in capability of electric capacitor devices in the future.

1. Introduction

The electric devices such as capacitor, transformer and cables were based on storage energy systems. The development on storage energy density has an important role for improvement of dielectric properties. Most of dielectric materials not only has high dielectric properties, but also has ferroelectric properties that recoverable energy density and high energy conversion efficiency [1]. Normally, there are two types of ferroelectric materials with electrical insulator: ceramic and polymer. For high dielectric properties but small electrical breakdown strength was devoted to ceramic, while the lower dielectric properties and larger electrical breakdown strength was found on polymer. The flexible on dielectric polymer with easy to fabricate and high electrical breakdown strength [2] were considered to main reason for thin film. The combination between ceramic as filler and polymer as matrix was carried out to finding the critical point on storage energy density performance. As reported by Gitanjali [3] and Feng [4], filling ferroelectric polarized ceramic to PVDF polymers is effective on optimizing energy storage by gaining its dielectric properties. In previous paper [5], we found that the three phases of PU which is high electrostrictive property blend with PANi and graphene fillers...
produced an advanced electrostrictive properties. In this paper, we make another contribution by using that different three phases of P(VDF-HFP) blend with PU BNKT filler for observing on storage energy density and dielectric properties as well. In this research, P(VDF-HFP) was blend with polyurethane (PU) by DMF solvent before filled with BNKT powder to be thin films. Afterward, final thin films were observed the dielectric properties and storage energy density.

2. Experiments

2.1. Materials preparation

Thin films were fabricated by tape casting method with 30 ± 5 µm thickness. Firstly, Bi$_{0.5}$(Na$_{0.8}$-K$_{0.2}$)$_{0.5}$TiO$_3$ (BNKT, synthesised by the conventional solid state reactions method) powder was dispersed in N, N-dimethylformamide (DMF, 99% purity, purchased from RCI Labscan Limited, Thailand) by using sonication for 25 min to be the homogeneous solution. Afterward, Polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP), Solef 11010/1001, purchased from Solvay Solexis, Belgium) powder and thermoplastic polyurethane elastomers (PU, DP 9370A, supplied from Covestro AG, Germany) granules were then dissolved and stirred 60 °C for 5 hours in the solution before removing bubble for 2 hours. Then, the composites solution was cast on the glass plate and dried in the oven at 80 °C for 24 hours. Finally, obtained films were taken off from the smooth glass plate. The pure P(VDF-HFP), P(VDF-HFP)/BNKT and P(VDF-HFP)/PU/BNKT composites were named from the ratio 10:0:0 wt% of P(VDF-HFP):PU:BNKT, 10:0:20 wt% of P(VDF-HFP)/PU/BNKT, and 8:2:20 wt% of P(VDF-HFP):PU:BNKT, respectively.

2.2. Dielectric properties

Electrical capacitor, dielectric loss on thin films were measured by LCR meter (IM 3533 HIOKI) at frequency range 10$^2$–10$^5$ Hz. Then, the dielectric constant and AC conductivity can be calculated from Equation (1) and (2), respectively. Where $\varepsilon_r$, $C_p$, $t$, $A$, $\varepsilon_0$, $\sigma_{ac}$, $f$ and $\varepsilon_r$ are dielectric constant, electrical capacitor, thickness of film, area of electrode, permittivity of air equalling 8.853 × 10$^{-12}$ F m$^{-1}$, AC conductivity, frequency, and dielectric loss, respectively.

$$\varepsilon_r = \frac{C_p t}{A \varepsilon_0}$$  \hspace{1cm} (1)

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \varepsilon_r^*$$  \hspace{1cm} (2)

2.3. Ferroelectric P-E loops properties

Polarization-Electric filed (P-E) loops were measured via a ferroelectric analyser under different electric fields at room temperature. Recoverable energy density ($U_e$) can be calculated from the curve of P-E loop as Equation (3). For loss energy density ($U_l$) can be calculated in the closed area in P-E loop [4-6]. Furthermore, energy conversion efficiency ($\eta$) was evaluated by using the ratio of $U_e$ and $U_l$ following in Equation (4) [6, 7]. Where $U_e$, $E$, $P$, $P_r$, $P_{max}$, and $\eta$ were recoverable energy density, electric field, polarization, remnant polarization, the maximum polarization, energy conversion efficiency, respectively.

$$U_e = \frac{P_{max}}{P_r} EdP$$ \hspace{1cm} (3)

$$\eta(\%) = \frac{U_e}{U_e+U_l} \times 100$$ \hspace{1cm} (4)

3. Results and discussion

3.1. Dielectric properties

All samples were measured for dielectric properties as showed in showed in Figure 1. In Figure 1 (A) showed the relationship between The dielectric constant ($\varepsilon_r$) in various frequencies (10$^2$ – 10$^5$ Hz) of
pure P(VDF-HFP), P(VDF-HFP)/BNKT and P(VDF-HFP)/PU/BNKT composites. It can be observed that all samples have high dielectric constant at the lowest frequency. The decrease of dielectric constant was observed when the frequency increases because of represents orientational polarizability, matching with prior study [8]. The dielectric constant increases with increasing phases materials from pure PVDF-HFP, two phases P(VDF-HFP)/BNKT, and three phases P(VDF-HFP)/PU/BNKT, respectively. The highest dielectric constant was devoted to 5.70 at 100 Hz for three phases P(VDF-HFP)/PU/BNKT. Similar trend with dielectric loss ($\varepsilon''$) and AC electrical conductivity ($\sigma_{ac}$), it showed in Figure 1 (B)-(C), respectively. Moreover, Figure 1 (B) showed the dielectric loss in function of frequency. It seems that the dielectric loss ($\varepsilon''$) hit a lowest peak at frequency around $10^3$-$10^4$ Hz. The highest loss was seemingly presented at the lowest (10$^2$ Hz) because range is interfacial polarization that easily switchable polarization under electric field. Moreover, the highest frequencies (10$^5$ Hz) also show the high dielectric loss. The dipole moment may hardly switchable, resulting in high dielectric loss. However, too much dielectric losses were undesirable for electronic devices. In addition, Figure 1 (C) exhibited the AC electrical conductivity ($\sigma_{ac}$) in function of frequency. This conductivity was related to the number of charges carries with electrical resistance. It can see that the conductivity was increased with increasing phases materials from pure P(VDF-HFP), P(VDF-HFP)/BNKT and P(VDF-HFP)/PU/BNKT. The three phases materials possible produce the highest charges carries that hop between phases. They gradually increase with frequency as described by the MWS model [9, 10].

Figure 1. (A) dielectric constant, (B) dielectric loss, and (C) AC conductivity of pure PVDF-HFP, two phases P(VDF-HFP)/BNKT, and three phases P(VDF-HFP)/PU/BNKT thin films at room temperature.
3.2. Ferroelectric P-E loops properties

![Polarization vs. Electric Field](image1)

![Loss Energy Density vs. Electric Field](image2)

![Energy Conversion Efficiency vs. Electric Field](image3)

Figure 2. The unipolar P-E loop of (A) pure P(VDF-HFP), (B) P(VDF-HFP)/BNKT composite, (C) P(VDF-HFP)/PU/BNKT composite. (D) recoverable energy density, (E) loss energy density, and (F) energy conversion efficiency of pure P(VDF-HFP), P(VDF-HFP)/BNKT, P(VDF-HFP)/PU/BNKT composites under different electric fields.

From Figure 2 showed the P-E loops and their storage energy density on pure P(VDF-HFP), P(VDF-HFP)/BNKT, and P(VDF-HFP)/PU/BNKT composites. The Figure 2 (A-C) display about the unipolar P-E loop of all samples. They were measured under electric filed from 40-110 MV/m at 10 Hz frequency with room temperature. It can be observed that the characteristic of P-E loops was bigger with applied electric field, resulting in larger \( P_r \) and \( P_{max} \). Considering at 110 MV/m, the lowest of \( P_{max} \) was belonged to pure P(VDF-HFP); while, the highest of \( P_{max} \) was devoted to three phases P(VDF-HFP)/PU/BNKT thin films, equaling 2.10 \( \mu \) C/cm\(^2\). As a result, the closed area of three phases produce the highest loss energy density as \( U_l \); while, the pure P(VDF-HFP) was the lowest one, equaling 28.35 J/cm\(^3\) as show in Figure 2 (E). This trend of \( U_l \) intensification with material phases was
seemly related with dielectric loss as show above. The $U_1$ seemly increase in exponential with the external force of electric filed as well as $U_e$ in Figure 2 (D). However, $U_e$ characteristic was slightly different. It can see that the highest $U_e$ was belonged to P(VDF-HFP)/BNKT; whereas, the lowest $U_e$ was still P(VDF-HFP)/PU/BNKT, equalling 26.54 J/cm³. In this case, it seems that BNKT was relaxor ferroelectric, resulting in slimmer loop and produce the highest $U_e$ on P(VDF-HFP)/BNKT composite. To more convenient for comparison, the energy conversion efficiency as $\eta$ was considered in Figure 2 (F). It can see that $\eta$ tends to decrease with electric field [11], and the lowest $\eta$ was devoted to three phases P(VDF-HFP)/PU/BNKT. The higher phases possibly produce a large charge carries, resulting in large dielectric loss, $U_1$, and $\eta$, respectively. The movement of interfacial polarization may have easily to move when considered in three phases, resulting in provide the highest dielectric constant [12]. However, the easily movement of the polarization produce the larger energy loss $U_1$ as well. Actually, PU has no ferroelectric properties as P-E loop although it exhibits high dielectric constant, resulting in the smallest $\eta$ in any electric fields.

4. Conclusion
The thin films of pure P(VDF-HFP), P(VDF-HFP)/BNKT, and P(VDF-HFP)/PU/BNKT composites were fabricated by tape casting method and compared electrical properties such as dielectric properties and ferroelectric P-E loops. The higher phases as three phases P(VDF-HFP)/PU/BNKT composites produce the best dielectric constant, whereas, the three phases provide the lowest ferroelectric P-E loop properties. The pure P(VDF-HFP) is suitable for energy conversion efficiency; while, the two phases P(VDF-HFP)/BNKT is suitable for recoverable energy density because of the relaxor BNKT characteristic. These new three phases relation on dielectric and ferroelectric properties will be able to design the advanced storage energy density in capacitors and electronic devices in future.

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