The enhancement of high dielectric properties for pure PVDF-HFP by using the suitable stirred temperature and time

A Salea¹, K Jehlaeh¹ and C Putson¹*  
¹Materials physics laboratory, Physics department, Faculty of Science, Prince of Songkla University, Songkhla, 90112, Thailand  
*Email: chatchai.p@psu.ac.th

Abstract. A novel light-weight electronic device from the dielectric polymer is so remarkable as the actuators, sensors, energy storage device and energy conversion. For this work, the thin film electroactive polymer is fabricated by casting technique which PVDF-HFP dissolve in N,N-dimethylformamide (DMF). The three stirred temperatures (30, 55 and 80 °C) and two stirred times (6 and 12 h) are completely considering. The highest polarization as the β phase is also considered for dielectric properties improvement. The FTIR, LCR and DSC equipment are used to measure the electroactive improvement. As a result, the 12 h stirred time with 30 °C stirred temperature is the best condition. The 0.25 g/ml concentration is also the suitable condition. The better dielectric properties are the requisite condition for a novel energy storage device in the future.

1. Introduction
The flexibility, light-weight, easy to process and high breakdown strength of dielectric polymer have to be the main reason to apply in such the novel applications as the energy storage, electrostriction, pyroelectric and electrocaloric [1, 2]. These advantages of the polymer are so interesting to improve dielectric properties as much as dielectric ceramic materials. Polyvinylidien fluoride-hexafluoropropylene (PVDF-HFP) is a semi-crystalline polymer which is one of high dielectric properties. The improvement of dielectric properties has to controllable PVDF-HFP chain structure to be the highest net-dipolemoment as called β phase. The β phases are -[CH₂- CF₃]- structure that arranged to the opposite site between two C-H and two C-F, which is bonding up and down perpendicular to carbon backbone causing to produce the highest net-dipolemoment per unit cell compared with another phases such as α, γ and δ [3, 4]. The stretching and poling techniques are able to response the β phases to enhance including dielectric properties [5]. The controllable PVDF-HFP structure is able to improve β phases according to 511, 837, 1234 and 1275 cm⁻¹ vibrational peak in FTIR [6]. Several reported papers tried to improve dielectric properties by using composites powder for dispersion in the polymer matrix but they lack observed the suitable stirred temperature and stirred time especially in the pure PVDF-HFP polymer. The suitable stirred temperature and stirred time might able to create the higher β phase transformation causing to enlargeable dielectric properties.

2. Materials and method
Polyvinylidien fluoride-hexafluoropropylene (P(VDF-HFP) powder, purchased from Solvay Solexis, Belgium) is dissolved in 99% purity N,N-dimethylformamide (DMF, purchased from RCI Labscan Limited, Thailand). And it is then stirred 12 h in different temperatures (30, 55 and 80 °C) to be
homogeneous solution before cast on the smooth class plate. They are directly dried in the oven at 80 °C for 24 h to become 100 μm thin film as showed in Figure 1 (a). Afterward, their electroactive β phase and dielectric properties are analysed by using FTIR technique and LCR meter in frequency from 1 to 10^5 Hz followed by using the equation (1) and (2), respectively. Moreover, it is suddenly confirmed the melting temperature by using DSC technique. In addition, the best condition is altered the stirred time to be 6 h (from 12 h). Finally, the best condition is observed the surface morphology by using SEM with EDX for observing the atomic distribution.

3. Results and discussion

3.1. The electroactive β phases transformation

Fourier Transform Infrared Spectra (FTIR), (Vertext70, Bruker, Germany), is scientific equipment that is able to classify PVDF-HFP structure. Figure 1 (b-c) represented to the electroactive β phase including with α and γ (figure 2 a). The transformation of β phases are confirmed in the growing β phase intensity by using Lambert-Beer law the equation (1) which is a ratio between α and β phase at the wavenumber of 767 and 837 cm⁻¹ respectively.

\[
F(\beta) = \frac{A_\beta}{K_\alpha A_\alpha + A_\beta}
\]  

Where, \( A_\alpha \) is the absorbance at 767 cm⁻¹ and \( A_\beta \) is the absorbance at 837 cm⁻¹ and \( K_\alpha (6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}) \) and \( K_\beta (7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}) \) are the absorption coefficients at respective wavenumber [7]. The absorbance of wavenumber around 830 - 840 cm⁻¹ is able to obviously seem that the β phase decrease when they are increased the stirred temperature to 55 and 80 °C, respectively. The highest β phase is showed at 30 °C. The β phase is calculated and plotted in different stirred temperature as showed in figure 2 (b). The higher temperature might be the disturbing the β phase conformation to be another phases as α or γ.

![Figure 1](image)

Figure 1 (a) film preparation by casting technique, (b) absorbance FTIR spectra (c) their absorbance β phase intensity of 30, 55 and 80 °C stirred temperatures in pure PVDF-HFP.

3.2. Dielectric properties and thermoanalytical analysis

The LCR meter (IM 3533 HIOKI) is dielectric measurement equipment to measure such dielectric properties as dielectric constant (\( \varepsilon_r \)) and dielectric loss (\( \varepsilon'_r \)) in various frequencies (1 - 10^5 Hz). The samples are applied 1 V ac voltage pass through the sample by two electrodes. And then they are measured surface charge (\( C \), in F) and calculated to be \( \varepsilon_r \) as showed an Equation (2).

\[
\varepsilon_r = \frac{Cd}{\varepsilon_0 A}
\]  

(2)
Where $d$ is sample thickness (m), $A$ is electrode area (m$^2$), and $\epsilon_0$ is free space permittivity with value 8.853 x 10$^{-12}$ F m$^{-1}$[8]. Figure 2 (a-b) showed the dielectric properties. The dielectric constant is decreased with increasing the frequency in any conditions as showed in figure 3 (a) which can be explained by Maxwell-Wagner-Sillars (MWS) interfacial polarization [9]. Moreover, as dielectric constant with different temperatures, the dielectric constant decreases when the temperature is increased because of the disturbing $\beta$ phase from heat following FTIR result. In addition, the dielectric loss in figure 3 (b) is insignificantly different that the loss at the lowest frequency (1 Hz) produces unsteady transient because the lower frequency make easy to rearrange chain polarization or unsteady loss and it might fluctuate polarization.

Differential Scanning Calorimetry (DSC), Simultaneous Thermal Analyser, STA8000, Perkin Elmer, USA, is thermoanalytical technique to measure the absorbed heat energy of the sample from 30 °C (room temperature, RT) to 200 °C in the air atmosphere as showed Figure 2 (c). The increasing stirred temperature is able to ship the melting temperature ($T_m$) referred to the changing of crystallinity to be lower temperature from 160.68 to 159.55 and 159.07 °C for 30, 55 and 80 °C, respectively. This result can also confirm the previous data that the hotter stirred temperature might able to destroy net polarization from the $\beta$ phase to be another.

The stirred time of the best solution (RT) is decreased from 120 h to 6 h to find the minimum time for the suitable stirred time with measure dielectric properties as showed Figure 2 (d-e). It can seem that the dielectric constant increase when the stirred time is increase from 6 to 12 h because it have time to rearrange and increase the $\beta$ phase to be greater as well as their dielectric loss.

**Figure 2** Dielectric constant (a), dielectric loss (b) and DSC-thermograph (c) of 30, 55 and 80 °C three stirred temperatures (d) dielectric constant and (f) dielectric loss of 6 and 12 h stirred times in pure PVDF-HFP

3.3. Surface morphology, atomic distribution and the thickness with various concentrations.
Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDX), FEI, Quanta 400, SEM-Quanta, is electron microscope that not only produces the image by electron scattering but also detects several atomic elements which distribute on the sample surface as showed in **Figure 3** (a-d). The surface morphology of the sample is also slightly rough of porous which might come from the evaporated solvent as showed in figure 4(a). The carbon (C) and fluorine (F) atoms are detected for PVDF-HFP structure which distributed on that surface as showed in figure 4 (b-c). The structure of PVDF-HFP is shown in figure 4 (d) which related to the ratio of both two elements. The PVDF-HFP with DMF is proportionated to 0.20, 0.25 and 0.30 g/ml as called concentration with measure thickness in various blade sizes (1.2, 1.4 and 1.6 mm) and figure out the relationship as showed in **Figure 3** (e). It can seem that the thickness size of samples is increased with
increasing concentration and blade sized because DMF are evaporated due to heat. The 0.25 g/ml concentration, 1.2 blade size and 100 µm thickness size is suitable for this work due to dissolvable and savable amount of DMF.

![Figure 3](image-url)

**Figure 3** Surface morphology on pure PVDF-HFP; SEM image (a), with EDX signals of C (b) and F (c) elements, the percent atomic weight with PVDF-HFP structure, (d) relationship between thickness sizes with three concentrations in different blade sizes.

4. Conclusion
The 0.25 g/ml of PVDF-HFP in DMF is the suitable concentration for this work. It is cast on the smooth glass to adjust the thickness for characterization. The highest polarization as β phase is a critical dielectric properties term. The three stirred temperatures and two stirred time are considered. FTIR, Dielectric properties including with DSC are analysed. The best condition in this work is 12 h stirred time and 30 °C stirred temperature. The highest dielectric properties are applicable to be energy storage devices applications including a novel light-weight battery.

Acknowledgments
We would like to thanks the Thailand Center of Excellence in Physics (ThEP-61-PIP-PSU3), Science Achievement Scholarship of Thailand (SAST), including Physics Department, Faculty of Science, and Prince of Songkla University, Songkhla, Thailand.

References
[1] Lallart M, Thetpraphi K and Capsal J-F. 2018 *Phys. Lett. A* 382 449-54
[2] Yang L, Qian XS, Koo C, Hou Y, Zhang T, Zhou Y, Lin MR, Qiu JH and Zhang QM. 2016 *Nano Energy* 22 461-7
[3] Chen S, Yao K, Tay FEH and Liow CL. 2007 *J. Appl. Phys.* 102 104108
[4] Martins P, Costa CM, Benelmekki M, Botelho G and Lanceros-Mendez S. 2012 *CrystEngComm* 14 2807-11
[5] Kepler RG and Anderson RA. 1978 *J. Appl. Phys.* 49 1232-5
[6] Parangusan H, Ponnamma D and Al-Maadeed MAA. 2018 *Sci. Rep.* 8 754
[7] Thakur P, Kool A, Bagchi B, Das S and Nandy P. 2015 *Phys. Chem. Chem. Phys.* 17 1368-78
[8] Zhong K and Li B 2017 *Polymer Nanocomposites for Dielectrics* (Singapore: Pan Stanford Publishing Pte. Ltd) p 208
[9] Tsangaris GM, Psarras GC and Kouloumbi N. 1998 *J. Mater. Sci.* 33 2027-37