Fabrication and Characterization of PVDF Thin Film

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Abstract. In this study, the fabrication of polyvinylidene fluoride (PVDF) composite films enhances the fraction of β-phase. A simple and effective method is used to obtain crystallization of β-phase in PVDF directly from the melt. PVDF was used to dissolve with DMF, adding ionic liquid (IL) and casting at a specific temperature and time. IL can ultimately stimulate the PVDF crystallization during melting in the piezoelectric β-phase. PVDF composite films were immersed in hot water to remove IL. It found that piezoelectric properties were significantly increased while increasing the temperature of hot water. XRD investigates the characteristics of PVDF film composites. The PVDF composite's surface morphology and structure were examined using AFM and SEM. The output voltage response of the PVDF thin film sensor was measured for indicator performance.

Keywords: PVDF, Ionic Liquid, piezoelectric coefficient, PVDF film sensor

1 Introduction

PVDF as a piezoelectric material has been extensively used for various application fields, for instance, sensors, actuators, and power harvesting, because it has a good piezoelectric, ferroelectric, and pyroelectric response compared to other polymers. How to improve the content of β-phase on the polymer is always of great concern and has become an exciting and imperative research subject recently. As is known, increasing the content of β-phases to improve the piezoelectricity can be achieved by using the conventional methods of stretching and poling processes. In this article, PVDF thin film is fabricated using mixed mechanical and chemical processes with an appropriate percentage of solvents under certain operating conditions instead of using the above methods. As reported in our previous work [1-3], stretching, poling, and electrode pattern design are essential parameters in fabricating PVDF as thin film sensors.

Ionic Liquid (IL), used as an effective nano structuration agent, can interact with PVDF chains and contribute to the formation of the polar crystalline phases (β and γ] [4]. Previous studies have shown a new method to obtain pure beta-PVDF directly using IL from the melt [4] without stretching, annealing at high temperatures, and hot pressing. Ionic liquids are more popular

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solvents for practical application due to having high conductivity, good thermal, electrochemical, chemical stability, and low volatility [5]. The IL in the PVDF would significantly promote beta phase content due to the strong electrostatic interaction [6] upon melt crystallization [7]. Different from the conventional methods of using stretching or hot pressing, and so on, an attempt to develop a fast and straightforward way of producing high-quality PVDF thin film using DMF as solvent and IL as filler under specific ratios and operating conditions. Also, the effect of annealing treatment is significant and influences the performance.

2 Material and Method

The commercial PVDF (Kynar PVDF®740, Mw=180.000 g/mol, Tg=-40ºC, Tm=168ºC, diameter pellet = 3~5 mm, was purchased from Sigma-Aldrich). N-dimethylformamide (DMF, 99.5%, Sigma-Aldrich) was used as a solvent. The Ion Liquid (IL) 1-Ethyl-3-methylimidazolium tetrafluoroborate [C6H11BF4N2] with stated purity of 98%. PVDF was dissolved in DMF with a concentration of 20% wt. Then, IL 10%wt was added to the solution (PVDF/DMF) still under magnetic stirring at 80ºC with a rotation speed of 200 rpm for 12 hr until its homogeneous dissolution. After that, the solution was cast on a glass substrate using a blade coater with various thicknesses and put in an oven vacuum for 12 hr at 90oC for solvent evaporation to remove the solvent from the material. In the next step, the material was removed from the oven vacuum and placed in an open space to reach room temperature. The last step was performed by immersing PVDF film in a hot water bath to remove the content of IL at various temperatures (25 to 70ºC) for 2 hr by air drying. Figure 1 shows the PVDF composite film fabrication process using the solution casting method.

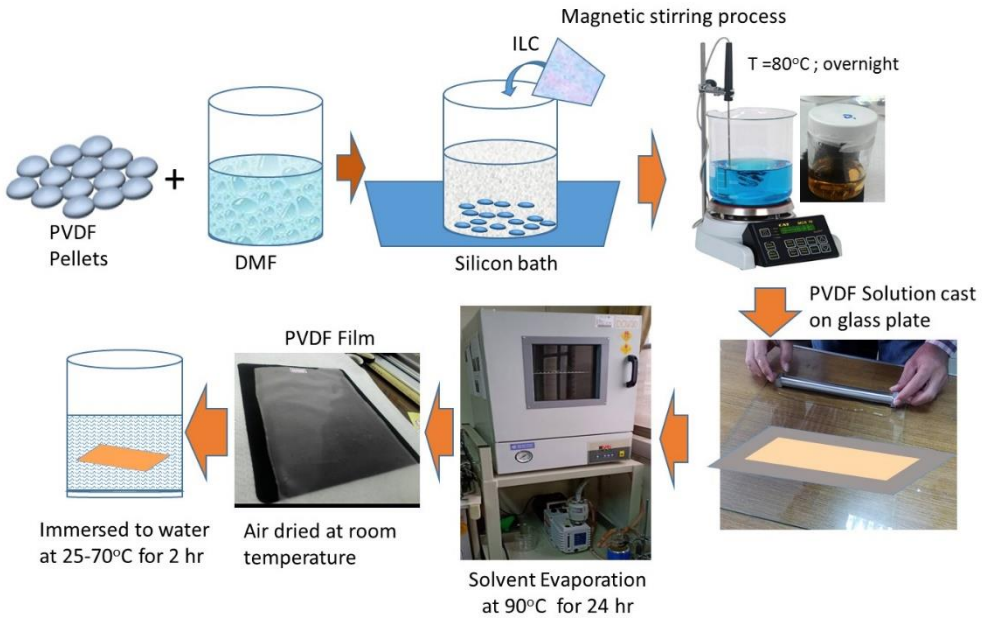

Fig. 1. Schematic representation of the fabrication process for PVDF film specimens [3].

3 Measurements and characterization

In this study, PVDF film is fabricated by using the solution-casting method. It is mixed with the solvent DMF and the filler ionic liquid. Furthermore, after casting and evaporation, the composite film is immersed in hot water for annealing treatment. Analyses of characteristics were carried out using Optical Image, SEM, XRD, and Atomic Force Microscopy (AFM) to examine the effect of IL in PVDF/DMF and annealing treatment at different temperatures. A series of PVDF tests thin films made by PVDF/DMF/IL (PDI) to compare pure PVDF and composite PDI film. The thickness of PDI produced was around 20–25 mm, making them suitable for thin film sensor application purposes. AFM was used to identify the surface roughness and surface morphology of the pure PVDF and PDI composite film samples. AFM observed surface image morphology and grain size of samples with a scanned area of 5x5 mm2 with 512x512 points of pixel resolution. The contact frequency of the cantilever probe of AFM was around 285 kHz, with a spring constant of the rectangular cantilever of around 26 N/m used during the observation. The differences in crystal structure and degree of crystallinity of pure PVDF and PDI composite films were analyzed using XRD.

4 Result and Discussion

Optical images of PDI composite film without and after treatment are shown in Figure 2. Generally, all the PDI composite films display good homogeneity. This condition is reflected through to transparency, softness, and flexibility. The specific feature of pure PVDF and PDI composite film also display.

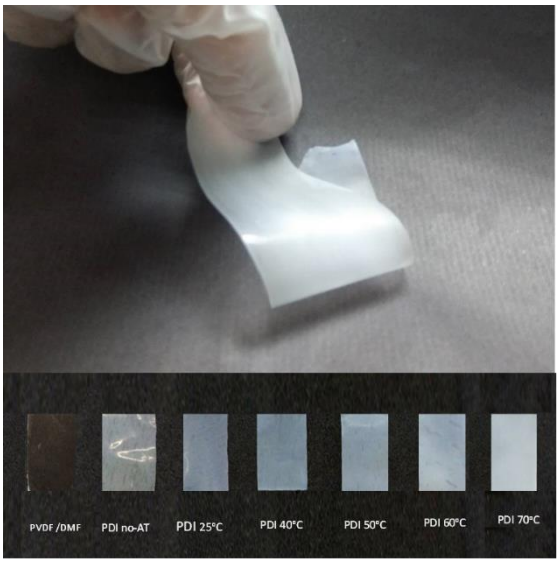

Fig. 2. Optical Image of PDI Composite film was immersed in hot water at temperature (a). No Treatment (b) 25ºC (c) 40ºC(d) 50ºC(e) 60ºC (f) 70ºC.

The surface morphology and microstructure images are shown in Fig. 3 provided by SEM model PhenomTM G2. The SEM measurements were made with a magnification range of 2000 to 45000 times at room temperature and under a 5 kV acceleration voltage. PVDF film samples were coated with a layer of gold with a thickness of around 2~3nm along the 60s under pressure 1Am~0.001mB to enhance the electronic conductivity by magnetron sputtering with a sputter coater. The surface of PVDF film morphology samples crystallized was observed on the top surface of the film samples. Fig. 3.a shows the granular structure of the top surface of PVDF/DMF film in the α phase, which shows a spherulitic structure with porosity when crystalized from solution or the melt. The presence of pores on the surface of films will hamper the deposition of electrodes. It causes difficulties in the poling process and reduces the electrical response of PVDF films.

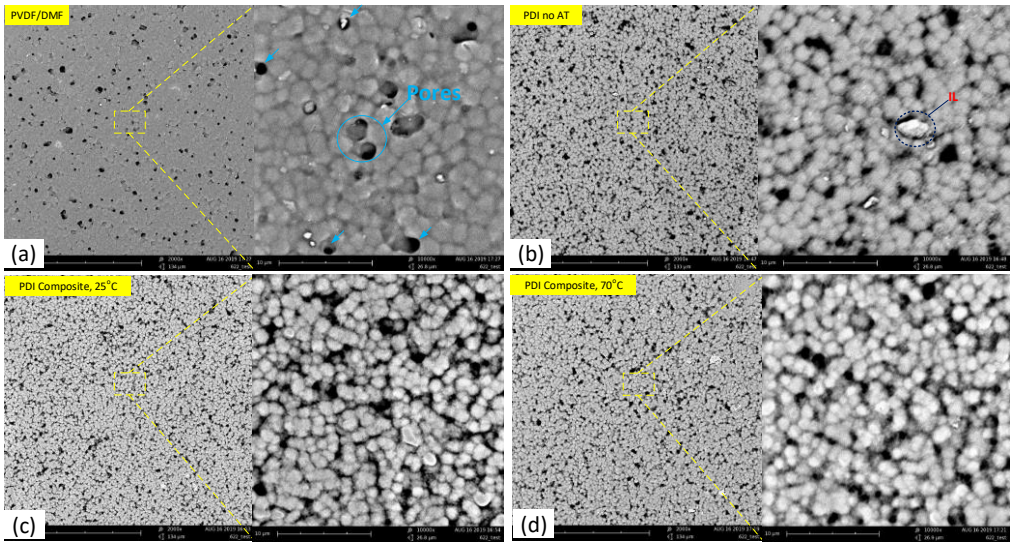

Fig. 3. SEM Images (a) PVDF/DMF film (b) PDI no AT (c-d) PDI composite was immersed at 25°C to 70°C, respectively.

4.1 Analysis of Crystallinity Structure by Using X-Ray Diffraction (XRD)

The XRD measurement by the solution casting method is clearly shown in Fig. 4. for composites of PVDF with 80%wt, 20%wt, and 10%wt of DMF, PVDF, and IL, respectively. The PVDF composite films were immersed in water at 25 °C, 40 °C, 50 °C, 60 °C, and 70 °C for 2 hrs. Previous studies showed that the effect of IL in solution (PVDF/DMF) could enhance the fraction of the β-phase. To identify the IL in solution PVDF/DMF impact on the PVDF crystal structure form after being immersed in hot water at different temperatures, the dominantly crystalline peak at the 2θ values around 20.10 to 20.26, which is explicitly attributed to the presence of PVDF-phase.[7-9].

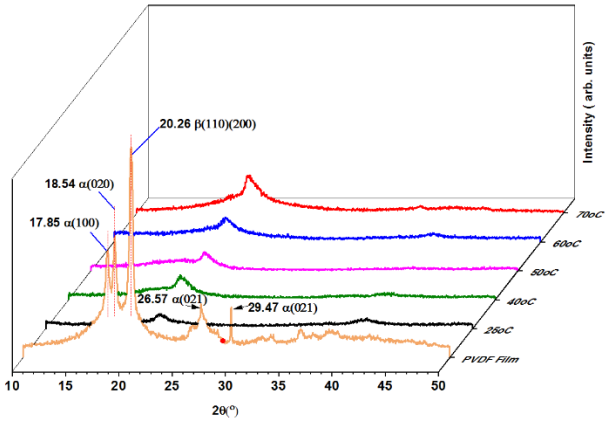

Fig.4. X-ray diffraction pattern of PVDF film composites.

4.2 Output Voltage Response of PDI Composite Film

In this study, the performance of the PVDF composite film sensor to define impact force is investigated. Fig.5 (a) shows the schematic of the dropped steel ball test using various weights and heights. The impact force of the steel ball in the impact process was calculated by the conservation principle of kinetic and potential energy by assuming all mechanical potential energy was transformed to impact kinetic energy[10]. It can be seen from Fig.5 (b) that the output voltage of the PDI composite film sensor is found to be increased with the increase linearly in the mass and height of the steel ball dropped.

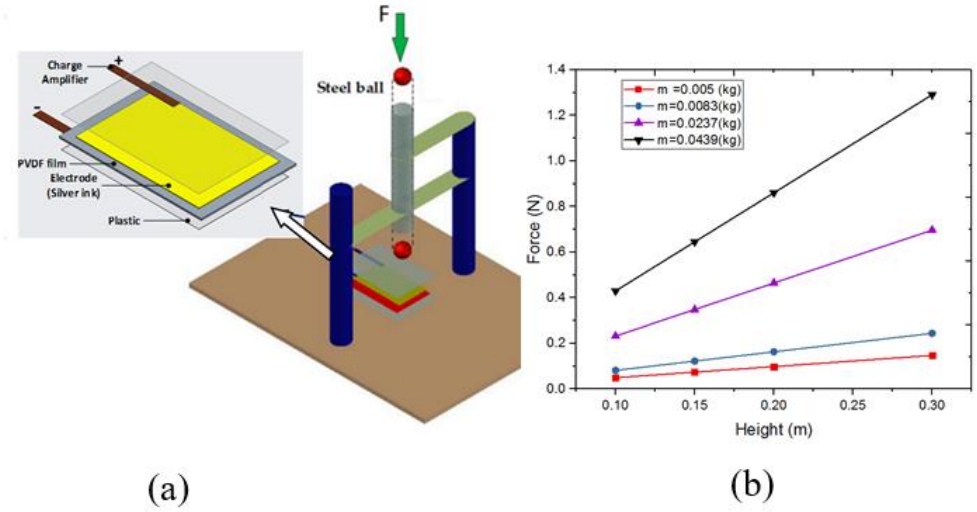

Fig. 5. (a) Impact Test (b) Response output voltage with different mass and height.

Figure 6. The output voltage response of 20wt% PVDF, 80wt% DMF, and 10wt% IL was immersed in water (a) 25 ^{o}C (b). 70 ^{o}C.

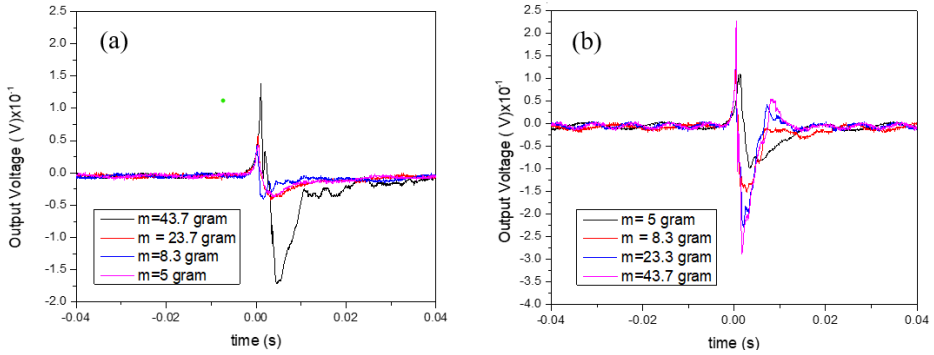

Fig. 6. The output voltage response of 20wt% PVDF, 80wt% DMF, and 10wt% IL was immersed in water (a) 25 ºC (b). 70 ºC.

Fig. 6. (a) and (b) show the output voltage response of the PDI composite thin film sensor with various masses and heights. The sample PDI composite film was selected for poling after the PVDF sample immersion in water at 25ºC and 70ºC. As a result, the output voltage response's growth rate will gradually increase linearly when the impact force increases.

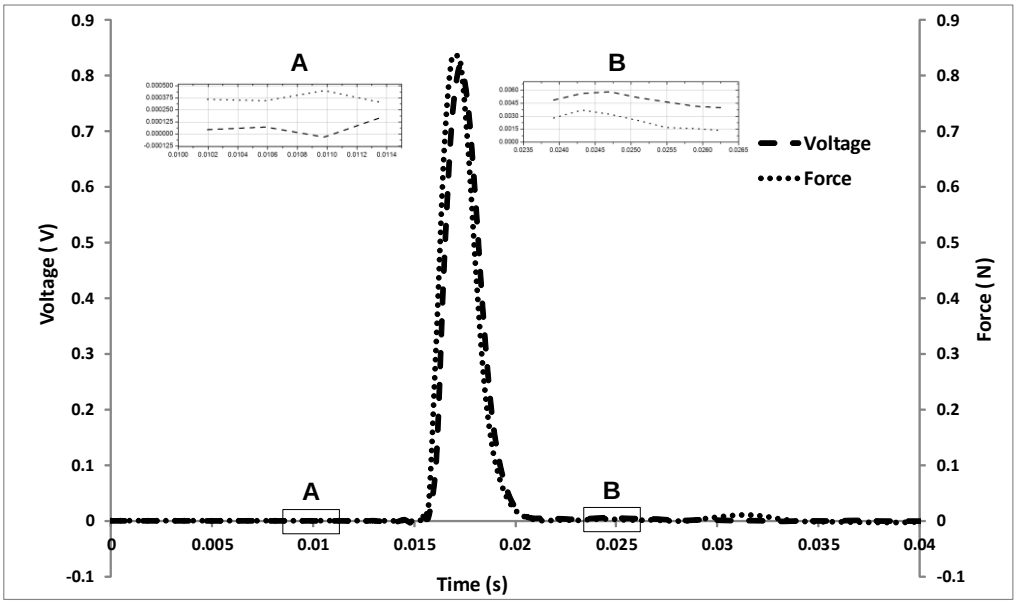

Fig. 7. Resonance frequency of PDI Composite film sensor

Fig. 7 shows that a PDI composite film sensor's resonance frequency response force and voltage are measured to verify the sensor's performance. PCB piezotronics 086E80, a small impulse hammer measurement system, is used for frequency response testing. As seen in Fig. 7, the natural frequency response occurs at around 60 Hz, consistent with previous work [11, 12].

4.3 Surface Morphology Analysis

AFM topography and grain size images were used to examine the annealing process's effect on the sample's surface roughness. Fig. 8a shows two-dimension (2D) surface image morphology of PVDF composites was carried out by Atomic Force Microscopy (AFM). Fig. 8.a shows the dark-color and bright-color domains, which represent the valley (depth) and peak (height) on the surface of PVDF sheet film samples, respectively [1]. The brightest colour can indicate the good response of piezoelectricity. In grain analysis shows in figure 8b, the red colour represents high contrast, while the blue colour represents low contrast [13], which indicates that the domain direction with downward and upward orientation.

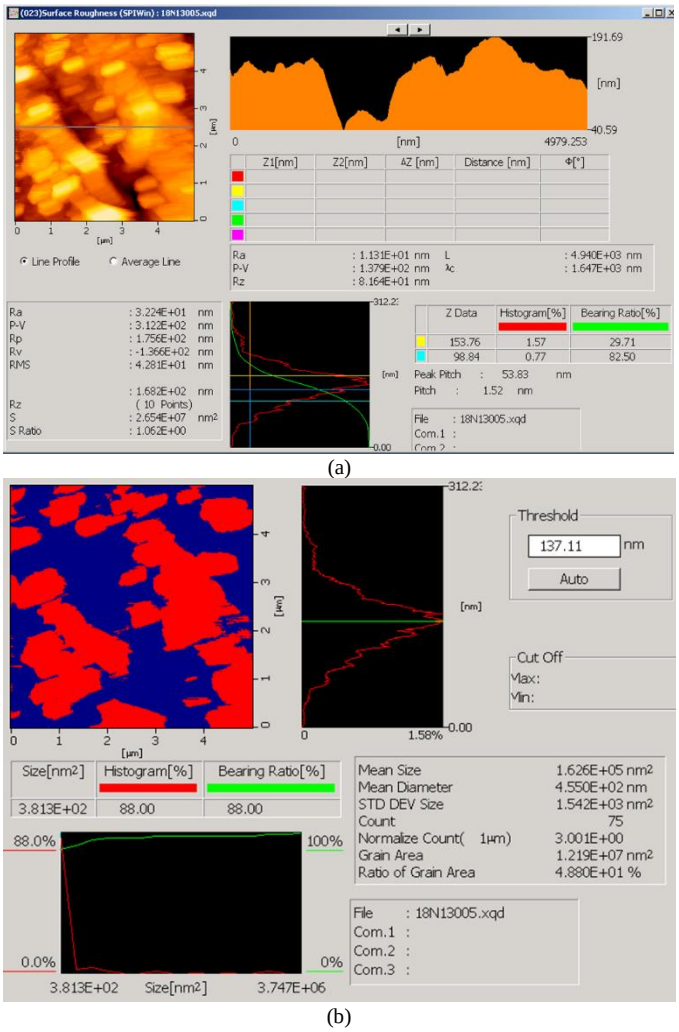

Fig. 8. AFM Images (a) Topography Image (b) Grain Size image.

4 Conclusions

In this study, PVDF composite films were prepared using the solution-casting method, and the influence of the processing parameters on PVDF film was investigated. XRD, SEM, and AFM were used to examine the influence of removed ionic liquid on PVDF/DMF by immersion of PDI composite films in hot water at different temperatures. From the study, the following results were obtained Ionic Liquid (IL) as a solvent in solution PVDF/DMF shows significant effects on the characteristics and dielectric properties of PVDF film. Adding IL to PVDF/DMF would enhance the phase of the β-phase content.

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