Phase Transformation, Surface Morphology and Dielectric Property of P(VDF-HFP)/MgCl₂·6H₂O Nanocomposites

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Abstract. Nanocomposite piezoelectric films based on the blend of poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and magnesium chloride hexahydrate (MgCl₂·6H₂O) have been investigated in this work. The films incorporated with 0.5 wt% MgCl₂·6H₂O were prepared using a solution casting technique and uniaxially stretched at various ratios from 2 to 6 times in order to characterize phase transformation, surface morphology and dielectric behaviour. The piezoelectric β phase transformation and crystallinity of the stretched films were identified by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). A scanning electron microscopy (SEM) was conducted to observe the surface microstructure and porosity. The frequency dependence of dielectric properties was also measured by LCR meter at room temperature. The stretched films show the larger the stretching ratio, the greater the microdefects appearance. This leads to a decrease of dielectric constant with stretching ratio. Nevertheless, the P(VDF-HFP) nanocomposites with stretching ratio of 4 times display a higher β phase fraction of 90% than the unstretched films. Thus, this result points out that the β phase transformation of the composite films can be enhanced by mechanically stretching process.

1. Introduction
Poly(vinylidene fluoride) (PVDF) and its copolymer with hexafluoropropylene (P(VDF-HFP)) have been extensively utilized as piezoelectric components such as sensors, actuators and harvesters due to their excellent piezoelectricity, high flexibility, nontoxicity, and light weight [1]. PVDF is a typical semicrystalline polymer composed of α, δ, β, and γ crystalline phases relied on the molecular configurations. The α phase is the most stable phase of PVDF with a TGTG’ formation resulting in the non-polar crystal structure. Another β phase is the most beneficial phase for piezoelectric characteristic due to large polarization with all TTTT conformation. [2, 3] Accordingly, the reliable methods of the α-β phase transformation is essential for piezoelectric property enlargement. The well-known technique is to apply the mechanical stretching and electrical poling to the α-phase film. Recent years, the large β phase formation without the electrical poling can be obtained from adding some hydrated salts in PVDF or P(VDF-HFP). [4] In the present study, the P(VDF-HFP)/MgCl₂·6H₂O nanocomposite film is therefore stretched at various ratios and characterized according to the preferred properties, i.e., crystalline phase structure, surface morphology and dielectric behaviour.
2. Experimental details

2.1. Sample Preparation

The hydrated-salt P(VDF-HFP) nanocomposite film was prepared by solution casting technique as shown in figure 1. The P(VDF-HFP) powder (MW=450,000 g/mol, Sigma-Aldrich) was dissolved and stirred in N,N-Dimethyformamide solvent (DMF, D158550, Sigma-Aldrich) with a weight ratio of 1:4 at room temperature until it was homogenous. Subsequently, the magnesium chloride hexahydrate (MgCl₂·6H₂O, M2393, Sigma-Aldrich) with 0.5 wt% was added in the solution and continuously stirred for 12 h. The clear solution was casted on a glass substrate using Doctor Blade Applicator and evaporated the solvent at 80 °C for a day. Finally, the as-prepared nanocomposite film with thickness around 150 m was uniaxially drawn in a homemade tensile machine at 100 °C. Stretching velocity was kept constant at 5 µm/s. Drawing ratios (R = L_{final}/L_{initial}) were chosen from 1 to 6 times.

![Figure 1 Fabrication process of the stretched nanocomposite film.](image)

2.2. Measurement

The crystalline phase structure of the stretched nanocomposite film was characterized by Fourier transform infrared spectrometer (FTIR; Vertex70, Bruker, Germany) and X-ray diffractometer (XRD; X’Pert MPD, PHILIPS, Netherlands). Furthermore, the fraction of β phase (F(β)) and the percentage crystalline degree (X_c) can be calculated according to equation (1) and equation (2), respectively [5, 6].

$$ F(\beta) = \frac{A_\beta}{1.26A_\alpha + A_\beta} $$  \hspace{1cm} (1)

$$ X_c = \frac{\sum A_{cr}}{\sum A_{cr} + \sum A_{arm}} \times 100\% $$  \hspace{1cm} (2)

Where $A_\alpha$ and $A_\beta$ are the absorption peaks of the crystalline phase at 766 and 840 cm⁻¹, respectively. The number 1.26 is the ratio of absorption coefficients at 763 and 840 cm⁻¹.

The surface morphology of the film was imaged with a scanning electron microscope (SEM; Quanta 400, FEI, Czech Republic). In order to study the dielectric property, the conductance of all samples was measured by an impedance analyzer (IM 3533, HIOKI, Japan) at room temperature. The dielectric constants can be evaluated as the following relationships:

$$ \varepsilon_r = \frac{tC}{\varepsilon_0 A} $$  \hspace{1cm} (3)

where $\varepsilon_0$ is the vacuum permittivity (8.854×10⁻¹² F/m). t and A are the film thickness (m) and electrode area (m²), respectively [7].

3. Results and Discussion

The crystalline β phase formation of the stretched P(VDF-HFP)/MgCl₂·6H₂O nanocomposite films was identified by FTIR and XRD analyses. As observed FTIR spectra in figure 2(a), the characteristic absorption bands are presented at 488, 615, 766, and 976 cm⁻¹ related to the nonpolar α phase and 511, 840, 1280 and 1431 cm⁻¹ corresponded to the polar β phase [8]. It is obviously seen that the pure P(VDF-HFP) sample displays all the absorption peaks of α phase. For the nanocomposite samples, the absorption bands of α phase gradually decrease while the bands of β phase become increase with enlargement of the drawing ratios (1 to 6 times). Moreover, the evaluated value of β phase fraction of the samples reach a maximum of about 90% at 4 times of the ratios as depicted in figure 2(b).
XRD patterns as shown in figure 3(a) can also assist in the phase structure identification. The diffraction peaks at 17.7°, 18.3°, 19.9° and 26.6° are attributed to the α crystalline phase existing in the pure P(VDF-HFP) [9]. It is clearly found in case of the nanocomposite specimens that the XRD peak intensities at 20.6° gradually increase with an increase in the drawing ratios indicating the β phase enhancement. From figure 3(b), the degree of crystallinity rapidly reduces during addition of 0.5% MgCl₂·6H₂O. These values can be however improved by increasing the drawing ratios. The largest value of the degree of crystallinity is found in the nanocomposite film stretched with 6 times.

Figure 2 (a) FTIR spectra and (b) β phase fraction of the samples drawn at various drawing ratios.

Figure 3 (a) XRD patterns and (b) crystalline degree of the samples drawn at various drawing ratios.

Figure 4 SEM images showing the surface morphology of the samples drawn at various drawing ratios.
The surface morphology of the drawn nanocomposites is clearly seen in figure 4. Clear grain crystalline structure is displayed in the pristine nanocomposite or non-stretched film, whereas the stretched films (R = 2 to 6 times) show wrinkle and pore structure in the force direction which is attributed to an arrangement of the crystalline β phase.

In case of the dielectric property, figure 5 shows the dielectric constant and dielectric loss as a function of frequency for all the nanocomposite films. It is found that the dielectric constant and dielectric loss of the samples continuously decrease with applied frequency. The dielectric constant of the stretched films reduces with stretching ratio, while the dielectric loss increases with stretched ratios due to extended wrinkle and pore on the surface.

Figure 5 (a) Dielectric constant and (b) dielectric loss of the samples drawn at various drawing ratios.

4. Conclusion

In summary, the P(VDF-HFP)/MgCl$_2$·6H$_2$O nanocomposites is prepared. The stretched films exhibit an increase of microdefects on the surface with the stretching ratio resulting in a reduction of dielectric constant. Nonetheless, stretching process can enhance the β phase fraction reaching 90% and the degree of crystallinity of 52%. These results indicate that mechanical stretching is the effective process for the piezoelectric phase transformation of the nanocomposite films.

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