Preparation and characterization of flexible PVDF-HFP film for piezoelectric applications

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Abstract. We report on the preparation of electroactive β-phase in polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) without any electrical poling treatment. The PVDF-HFP film with various mass fractions (wt%) of magnesium chloride hexahydrate salt (MgCl₂·6H₂O) was fabricated by a solution casting technique. The morphological, mechanical, structural and dielectric properties were investigated. Results founded that the PVDF-HFP composite films show a large number of micro-pores on the top surface as a sponge-like structure. The Young’s modulus and crystallinity values tend to be linearly decreased with the MgCl₂·6H₂O concentration leading to enhance flexibility. The largest β-phase fraction of 87.2% is found in the composite with 1 wt% MgCl₂·6H₂O filler. The obtained value is 4 times higher than the value of unfilled PVDF-HFP. Moreover, the maximum value of dielectric constant is about 19.2 at 10 Hz for 4 wt% MgCl₂·6H₂O filler. Therefore, the modified composites with the excellent flexibility, dielectric constant and β-phase may be a promising material for applications in the field of piezoelectric energy conversion.

1. Introduction

Nowadays, the development of flexible polymer composites with high dielectric properties has been paid attention of researchers worldwide. These can be used in wide range applications such as low-power portable electronics, actuator and different types of sensors [1]. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) have been designed as a polymer matrix due to their light weight, flexibility, environmental compatibility and brilliant electroactive responses (including piezo-, pyro- and ferroelectric effects) [2]. P(VDF-HFP) exhibits four different crystalline phases namely α-, β-, δ-, and γ-phases depending on molecular conformation [3]. However, the α- and β-phases are widely considered for investigation. The most stable nonpolar phase of α polymorph is found inactive with electroactive responses. Another is the largest spontaneous polarization of β-phase[4, 5]. Consequently, a variety of strategies have been focused on the enhancement of α - to β - transformation with reorientation of the dipole moment such as mechanical stretching, electrical poling, electrospinning, spin coating and adding of different fillers, etc. [6]. In this work, magnesium chloride hexahydrate (MgCl₂·6H₂O) was employed as the active filler due to its easy process. It was found that the β-phase structure can be formed directly in the crystallization process by hydrogen bonding interaction between PVDF-HFP molecules and water in the MgCl₂ hydrated salts [7, 8]. The crystalline phase
transformation, dielectric property, surface morphology and mechanical behavior of the composite films were investigated using Fourier transform infrared spectroscopy, scanning electron microscopy, atomic force microscopy and tensile testing, respectively.

2. Materials and methods

PVDF-HFP (Solef 11010/1001) powder was chosen as the polymer matrix purchased from Solvay Solexis, Inc. MgCl$_2$·6H$_2$O (M2393) filler and N,N-dimethylformamide (DMF, D158550) solvent were obtained from Sigma-Aldrich. PVDF-HFP films with and without MgCl$_2$·6H$_2$O filler were prepared by a simple solution casting method. Briefly, 20 mg PVDF-HFP was initially dissolved in 100 ml DMF (i.e., the polymer to the solvent ratio of 1:5) at room temperature by magnetic stirring for 6 h. Thereafter, the MgCl$_2$·6H$_2$O filler was dispersed in 10 ml DMF at four concentrations (1, 2, 3, and 4 wt%) by using an ultrasonic bath for 10 min. The prepared MgCl$_2$·6H$_2$O solution with various concentrations was added to the previous PVDF-HFP solution under continuous stirring for 12 h. Afterward, the mixture with different salt contents were cast on a clean glass by adjustable film applicator (SH1102; Sheen) and dried at 80 °C for 12 h in an oven to evaporate completely the DMF solvent. Finally, the PVDF-HFP samples were obtained with an average thickness of 100 μm.

Scanning electron microscope (SEM; Quanta 400) and atomic force microscope (AFM; Nanosurf Easyscan2) were used to study the surface morphology of prepared PVDF-HFP samples. An average pore size of PVDF-HFP film can be analyzed from the SEM images via the Java image processing program. Moreover, this software can be used to determine a percentage of porosity of the films proposed by Bilad and coworkers [9]. Each PVDF-HFP film was investigated in a non-contact mode in order to determine the surface roughness in term of root-mean-square surface roughness ($S_q$). Mechanical property of all samples was investigated using a tensile testing machine (z010, Zwick Roell). Fourier transform infrared spectrometer (FTIR; Vertex70, Bruker) was recorded from 400 to 1000 cm$^{-1}$ in the Attenuated total reflectance (ATR) mode. The dielectric measurement was carried out on the samples by an LCR meter (IM 3533, HIOKI).

3. Results and discussion

3.1. Surface morphology

Figure 1 shows the SEM images of the PVDF-HFP films added with different concentrations of MgCl$_2$·6H$_2$O filler. It is shown a smooth surface in the bare PVDF-HFP sample. With loading MgCl$_2$ samples, a large number of micropores/cavities on the top surface is revealed as a sponge struture. As can be seen from table 1, both average pore size and porosity of uniform microporous film become increase with the MgCl$_2$ concentrations. This phenomenon may be the result of a low evaporation of the DMF solvent and water molecules of the MgCl$_2$·6H$_2$O filler in drying process, as was reported by Adhikary et al. [8]. The consistent distribution of micropores is attributed to the good compatibility between PVDF-HFP matrix and MgCl$_2$·6H$_2$O dopant resulting in a presence of the homogenous structure which is suitable for the fabrication of energy conversion devices. In addition, representative height images are also used to further investigate the surface topography of the samples. Figure 2 and table 1 are presented the 3D-AFM diagrams with a scanned area of 70 x 70 μm$^2$ and surface roughness values of as-prepared samples. The darkest and brightest regions are respectively assigned to the pores and film surface zones. It is confirmed that the pristine PVDF-HFP film represents a smoother surface compared to the others. Upon the addition of MgCl$_2$·6H$_2$O salt, the surface roughness of the samples are obviously increased with the filler contents agreed with the SEM results. Therefore, it can be indicated that the addition of MgCl$_2$·6H$_2$O salt causes a significant enhancement of pore size as well as roughness on the surface of PVDF-HFP films.
**Figure 1.** (a) SEM and (b) 3D-AFM images of PVDF-HFP film added with different concentrations of MgCl₂·6H₂O filler.
| PVDF-HFP sample | Pore size (μm) | Surface roughness (μm) | Porosity (%) |
|----------------|---------------|------------------------|--------------|
| 0%-MgCl\textsubscript{2} | N/A            | 0.0125                 | 0.54 ± 0.1   |
| 1%-MgCl\textsubscript{2} | 1.25 ± 0.12   | 0.225                  | 10.65 ± 0.5  |
| 2%-MgCl\textsubscript{2} | 2.02 ± 0.20   | 0.396                  | 21.39 ± 0.9  |
| 3%-MgCl\textsubscript{2} | 3.56 ± 0.25   | 0.604                  | 34.66 ± 1.5  |
| 4%-MgCl\textsubscript{2} | 5.68 ± 0.28   | 1.176                  | 40.22 ± 1.8  |

3.2. Young’s modulus

In order to study the mechanical property of PVDF-HFP film improved with MgCl\textsubscript{2}·6H\textsubscript{2}O, the stress-strain results of all prepared PVDF-HFP films are listed in table 2. The tensile strength, elongation at break of the samples steadily reduce with increasing of the MgCl\textsubscript{2}·6H\textsubscript{2}O concentrations. The potential reason may be due to plasticizing effect of MgCl\textsubscript{2}·6H\textsubscript{2}O filler. A large amount of MgCl\textsubscript{2} molecule significantly suppresses of PVDF-HFP polymer chain movement in crystallization process resulting in low crystallinity [10]. Another reason is the formation of the spongy structure with higher porosity (SEM images) of the samples resulting in a weak linkage between the polymer and filler [11]. In addition, Young’s modulus value tends to be linearly decreased with the MgCl\textsubscript{2}·6H\textsubscript{2}O concentrations. This leads to significantly develop in a greatly flexible film and easy deformation under applied force, which suggests that the composite sample is more favorable for the improvement in piezoelectric applications.

| sample | Tensile strength (Mpa) | Elongation at break (%) | Young's modulus (Gpa) |
|--------|------------------------|-------------------------|-----------------------|
| 0%-MgCl\textsubscript{2} | 23.7                   | 408.6                   | 1.56                  |
| 1%-MgCl\textsubscript{2} | 22.8                   | 347.0                   | 1.22                  |
| 2%-MgCl\textsubscript{2} | 20.8                   | 300.5                   | 0.87                  |
| 3%-MgCl\textsubscript{2} | 19.9                   | 236.4                   | 0.78                  |
| 4%-MgCl\textsubscript{2} | 15.2                   | 154.9                   | 0.33                  |

3.3. Phase structure

The FTIR spectra of the PVDF-HFP samples assigned to crystalline α- and β-phases are given in figure 2a. According to the literature, the vibrational bands at 431, 531, 614 and 763 cm\textsuperscript{-1} are identified as the characteristic nonpolar α-phase, while the polar β-phase is represented at 837 cm\textsuperscript{-1} [12]. It is revealed that the pure PVDF-HFP film appears all characteristic peaks of α-phase. After addition of the MgCl\textsubscript{2}·6H\textsubscript{2}O filler, these α-peaks become disappear and the β-peak is gradually increased with MgCl\textsubscript{2} contents. The all-trans conformation of β-phase may be formed by hydrogen bond interactions between -CH\textsubscript{2} dipole of PVDF-HFP and water molecules in the filler [13]. Moreover, these specific bands can be used for determining the β-phase fraction (%F(β)) and total β-phase fraction in crystalline region (%β) using equation (1).

\[ %F(\beta) = \frac{A_\beta}{1.26A_\alpha + A_\beta} \times 100\% \] (1)

where \( A_\beta \) and \( A_\alpha \) are the intensity peak at 837 and 763 cm\textsuperscript{-1}, respectively [14]. The %F(β) and %β (%β=[X,×F(β)]×100%) values of each sample are displayed in figure 2b. About 24.1% of %F(β) is obtained for the pure PVDF-HFP film. With the loading 1 wt% MgCl\textsubscript{2}·6H\textsubscript{2}O concentration in the PVDF-HFP matrix, maximum values of %F(β) and %β is about 87.2% and 38.7%. At higher doping concentrations, %F(β) almost saturates while %β gradually decreases. This is attributed to the reduction of crystalline degree with the increasing concentration of the filler.
3.4. Dielectric behaviors
The variation of dielectric property as a function of frequency in the PVDF-HFP films is illustrated in figure 3. The values of dielectric constant ($\varepsilon'$) and dielectric loss ($\tan \delta$) are given as; $\varepsilon' = C t / \varepsilon_0 A$ and $\tan \delta = \varepsilon'' / \varepsilon'$, where $C$ is the sample capacitance measured by the LCR meter. $A$ is an area of the sample, $t$ is the sample thickness and $\varepsilon_0$ is a constant representing permittivity of free space. $\varepsilon''$ and $\varepsilon'$ are the imaginary and real parts of permittivity, respectively [15]. From figure 3a, the dielectric constant of all samples slightly decreases with frequency. This behavior is caused by less enough time to arrange of dipole moment in electric field direction at high frequency [16]. It is also observed that dielectric constant linearly increases with MgCl$_2$·6H$_2$O concentration. The maximum value of dielectric constant is about 19.2 at 10 Hz for 4 wt% MgCl$_2$·6H$_2$O filler. This improvement of dielectric constant from hydrated MgCl$_2$ dopant results from several reasons. Firstly, the increase of hydrated MgCl$_2$ can induce large interfacial polarization formed by strong interaction between the water molecule of MgCl$_2$ filler and -CF$_2$ dipoles of polymer chains [8]. This interaction leads to transforming the $\beta$-phase structure described in the FTIR section. Secondly, the large accumulation of void charges at MgCl$_2$/PVDF-HFP interface may be formed as numerous micro-capacitors [17]. Moreover, a presence of micro-pores may be filled with air and separated by insulating dielectric polymer which is attributed to the property of a piezoelectric material [2]. From figure 3b, the dielectric loss is also gradually declined with increasing the applied frequency related to the interfacial polarization between the interface of hydrated MgCl$_2$ and polymer matrix [18]. The charge carriers accumulated on the interfaces have low mobility and need a long time interval to rotate in electric field direction [19]. Thus, maximum tangent loss of the samples presented at low frequencies (<1 kHz) is higher than that of ones at high frequencies. However, the dielectric loss value of all as-received samples remains relatively low (<0.5). The results suggest that the excellent piezoelectric properties of the samples with high dielectric constant and low dielectric loss may be used in modern electrical and electronic systems.

Figure 2. (a) FTIR spectra; and (b) $\beta$-phase fraction of PVDF-HFP film added with different contents of MgCl$_2$·6H$_2$O filler.

Figure 3. (a) Dielectric constant and (b) dielectric loss tangent of the PVDF-HFP film added with different concentrations of MgCl$_2$·6H$_2$O filler.
4. Conclusion
In this study, the MgCl$_2$·6H$_2$O/PVDF-HFP films were prepared by the solution casting technique. The results pointed out that the composites showed the surface microstructure like sponge. The surface roughness of films increased thanks to the increase of size and density of pores with raising the MgCl$_2$·6H$_2$O filler. The PVDF-HFP composites with high porosity also exhibited the low Young’s modulus. Furthermore, the MgCl$_2$·6H$_2$O filler played an important role in the $\beta$-phase transformation of films. The largest $\beta$-phase fraction of 87.2% was found in the composite with 1 wt% salt filler. The enhanced value was 3.6 times higher than the value of unfilled PVDF-HFP. The maximum dielectric constant and minimum Young’s modulus of the film could achieve 19.2 and 0.34 GPa for 4 wt% salt, respectively.

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