Research article

Investigation of structural, dielectric and sensing properties of MgCl₂/PVDF composite films prepared via solution casting technique

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Abstract: This article investigates the effect of Mg insertion into the Polyvinylidene fluoride (PVDF). The composite films were prepared using solution casting technique. XRD, and FTIR characterizations were done to study the structural changes in the MgCl₂/PVDF composite films. The dielectric study reveals the improvement in the dielectric constant and conductivity with the insertion of Mg ions in the PVDF composite. The MgCl₂/PVDF composite has immense potential in sensing and actuator applications.

Keywords: PVDF composite; filler; dielectric constant; crystallinity

1. Introduction

Recently the Polyvinylidene fluoride (PVDF) is studied extensively due to its interesting piezoelectric and pyroelectric properties. PVDF based composites found application in lithium ion batteries, capacitors, hydrophones and variety of sensors [1,2,3]. The most attractive property of PVDF is polymorphism. It exists in five α, β, γ, δ, ε phases but the first two phases are dominate phases [4,5,6]. The piezoelectric and pyroelectric properties are mainly governed by α and β phase. So researchers are investigating the various methods to promote these phases. Fillers/dopants are used to make PVDF composite film so as to improve the dielectric, magnetic and mechanical properties. The addition of dopant in polymer enhances the physical properties, thus widening the application are of PVDF polymer. In various studies, the researchers confirm the changes in the morphology and crystalline structure of PVDF doped with different types of fillers/dopant [7,8]. For PVDF film having dominated α, and β phase the prepared films were to be mechanical stretched as well as poled [9]. This technique enhances the piezoelectric response which is desirable for sensing
applications. Plasma treatment was also used to enhance the hydrophilic property of PVDF membranes [10]. Different types of organic and inorganic fillers were utilized to investigate the effect on various physical and chemical properties of PVDF. The degree of crystallinity and electrical response of PVDF also depends upon the weight percentage of fillers [11]. Few researches have added nanoclay as filler to PVDF so as to study the changes in structure PVDF matrix [12,13]. Some groups focused on use of high polarity solvent used for casting the PVDF film. Recently Zeolite was actively used as filler to develop a Zeolilite/PVDF composite. Additions of Zeolite improve the tensile strength as well as mechanical properties of PVDF thin films, thus widening the application are of these composites [14]. Some of the common fillers used as dopant includes Ba, Co, Mn, Fe, Cr, Ti, Li and so on [15–18]. In this research work, the MgCl₂ is selected as dopant material. It was revealed that addition of MgCl₂ significantly modifies the crystalline structure and reduction in crystalline structure was observed. The other objective was to evaluate the effect of MgCl₂ on the dielectric constant and application of sensing properties of PVDF composite films.

2. Materials and Methods

2.1. Preparation of PVDF Composite Films

The PVDF composite films were prepared by solution casting technique. The MgCl₂ powder was dissolved in DMF for 30 minutes on magnetic stirrer. PVDF powder was dissolved in DMF for 60 minutes at temperature of 60 °C. Then the dopant solution is mixed with appropriate amount of PVDF solution. The mixed solution of MgCl₂/PVDF was again stirred continuously for 30 minutes. The solutions of different weight percentage were casted on the glass slides and placed in furnace for 6 hrs at temperature of 70 °C. PVDF composite films were then peeled off from the glass slides and washed with DI water to remove any solvent traces. Then the films of different wt% of MgCl₂ were coated with Al on both sides using vacuum coating unit and poled subsequently. The detailed regarding different weight percentage of MgCl₂ is given in Table 1.

| Table 1. Solution composition of MgCl₂/PVDF composite. |
|-----------|
| Solution | MgCl₂ wt% | PVDF wt% | DMF   |
|-----------|
| S₀        | 0%        | 10%      | 100 ml |
| S₁        | 2%        | 10%      | 100 ml |
| S₂        | 4%        | 10%      | 100 ml |
| S₃        | 6%        | 10%      | 100 ml |

2.2. Characterization and Measurement

The phase structure of MgCl₂/PVDF composite was analysed using X ray diffractometer (PANalytical). The FTIR spectra were carried out using spectrum 400 (Perkin Elmer). The dielectric parameters were measured using LCR meter (Hioki 3532). Vacuum coating unit were used to deposit Al on both sides of films. The sensor response was observed using Digital oscilloscope (Yokoga DL9140). The poling of PVDF samples were done using setup shown in Figure 1. Poling was done in two fold process. The samples were initially placed in temperature controlled furnace. Firstly 250
volts DC was applied at temperature of 70 °C for 1 hour. After 1 hour the temperature was brought down to the room temperature and electric field was still applied for another 30 minutes. After this two fold process the PVDF samples were removed from furnace for sensing and dielectric measurements.

![Figure 1. Schematic of PVDF Poling.](image)

3. Results and Discussion

3.1. XRD Analysis

The XRD scans of MgCl2/PVDF composite for pure and various wt% of dopant is shown in Figure 2. The pure PVDF exhibits the semi crystalline structure comprising of both amorphous and crystalline phase. The peaks at 18.40°, 26.50°, 38.60° corresponds to α phase. The peak at 20.2° indicates the presence of β phase [2,19]. As the concentration of filler increase to 6 wt%, all other peaks disappeared only one broader peak related to β phase remains present. The piezoelectric property of PVDF is affected by crystallinity appreciably. Without crystallinity, the PVDF would not exhibit any piezoelectric properties. The level of crystallinity is key parameter affecting the PVDF chemical, piezoelectric, mechanical and thermodynamic properties. The crystallinity is calculated using relation (1).

\[
X_c = \frac{K_c (A_1 + A_2)}{K_c (A_1 + A_2) + K_a (A_3)} \times 100
\]

Where \(A_3\) is the area concerned with amorphous hump, \(A_1 \) & \(A_2\) is area of two crystalline peaks as depicted in Figure 3. \(K_a\) & \(K_c\) are proptionallity constant for amorphous and crystalline phases [20,21]. The crystallinity of Pristine PVDF as determined from XRD is 51.8%. With the addition of MgCl2 into PVDF, the crystallinity decrease to 42.6%. The decrease in crystallinity indicates the modification in crystalline structure with the addition of MgCl2.
3.2. FTIR

The FTIR scans for pure and doped PVDF is shown in Figure 4. Most of the peaks at frequency corresponds to $\alpha$ and $\beta$ phase. The peaks at 610 cm$^{-1}$, 760 cm$^{-1}$ and 1420 cm$^{-1}$ belong to $\alpha$ phase [22,23]. The other peaks at 508 cm$^{-1}$ and 836 cm$^{-1}$ related to $\beta$ phase. With increase in dopant concentration to higher level, some of peaks intensity reduces to lower level.
3.3. Dielectric Constant and Force Sensing

The dielectric constant or permittivity $\varepsilon'(\omega)$ is a measure of the polarization of the medium between two charges when an electric field is applied. The dielectric constant of a
PVDF polymer depends on structural morphology and presence fillers in crystalline structure. The dielectric constant $\varepsilon'(\omega)$ was calculated using following equation:

$$
C_p = \varepsilon_0 \varepsilon' \frac{A}{D}
$$

Where, $\varepsilon_0$ is the dielectric constant/permittivity ($8.86 \times 10^{-12}$ F/cm) for free space, $d$ (in cm) is thickness and $A$ (in cm$^2$) is the cross sectional area of PVDF thin films. As the dopant wt% increase to 6 wt% (Figure 5), the dielectric constant increase indicating the large polarization in PVDF composite. As the frequency increase to higher level, the decrease in dielectric constant was observed. Figure 6(a) and 6(b) shows the output voltage from pristine and doped PVDF composite sensor when force of 19 N was applied to the surface.

Figure 6. Voltage output of (a) Pristine PVDF, (b) MgCl$_2$/PVDF sensor.
4. Conclusion

The present work shows the MgCl₂ has significantly affected the structural properties of the PVDF composite films. The reduction in crystallinity was also observed which confirms the modification in morphology of PVDF films. The enhancement in dielectric constant was observed as the dopant concentration reaches to higher level. This present study reveals the application of PVDF composite in sensing areas which includes tactile as well as pressure sensing.

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Conflict of Interest

The authors declare no conflicts of interest regarding this paper.

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