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Research article

Investigation of structural, dielectric and sensing properties of $MgCl_2$/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 $MgCl_2$/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 $MgCl_2$/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 pyroelctric 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 pyrolectric 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 improvise 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 $MgCl_2$ is selected as dopant material. It was revealed that addition of $MgCl_2$ significantly modifies the crystalline structure and reduction in crystalline structure was observed. The other objective was to evaluate the effect of $MgCl_2$ 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 $MgCl_2$ 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 $MgCl_2$/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 $MgCl_2$ were coated with Al on both sides using vacuum coating unit and poled subsequently. The detailed regarding different weight percentage of $MgCl_2$ is given in Table 1.

Table 1. Solution composition of $MgCl_2$/PVDF composite.

Solution	$MgCl_2$ wt%	PVDF wt%	DMF
S_0	0%	10%	100 ml
S_1	2%	10%	100 ml
S_2	4%	10%	100 ml
S_3	6%	10%	100 ml

2.2. Characterization and Measurement

The phase structure of $MgCl_2$/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.

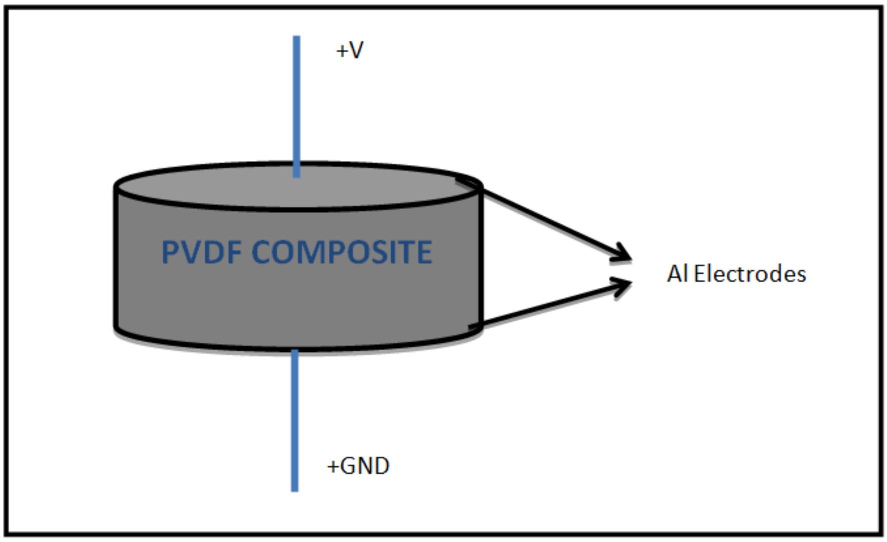

Figure 1. Schematic of PVDF Poling.

3. Results and Discussion

3.1. XRD Analysis

The XRD scans of $MgCl_2$/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).

$$X_c = \frac{K_c(A_1 + A_2)}{K_c(A_1 + A_2) + K_a(A_3)} \times 100 \qquad (1)$$

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 $MgCl_2$ into PVDF, the crystallinity decrease to 42.6%. The decrease in crystallinity indicates the modification in crystalline structure with the addition of $MgCl_2$.

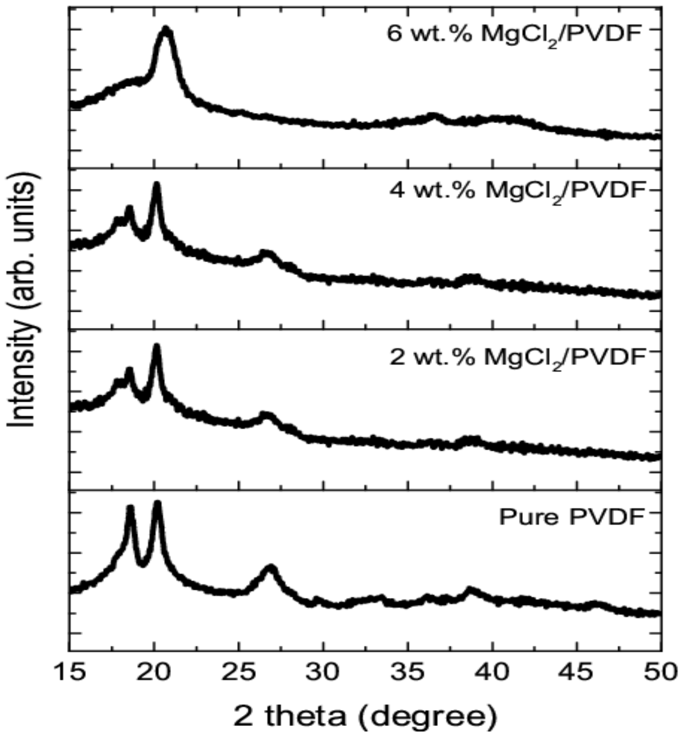

Figure 2. XRD scans of Pure and $MgCl_2$ doped PVDF.

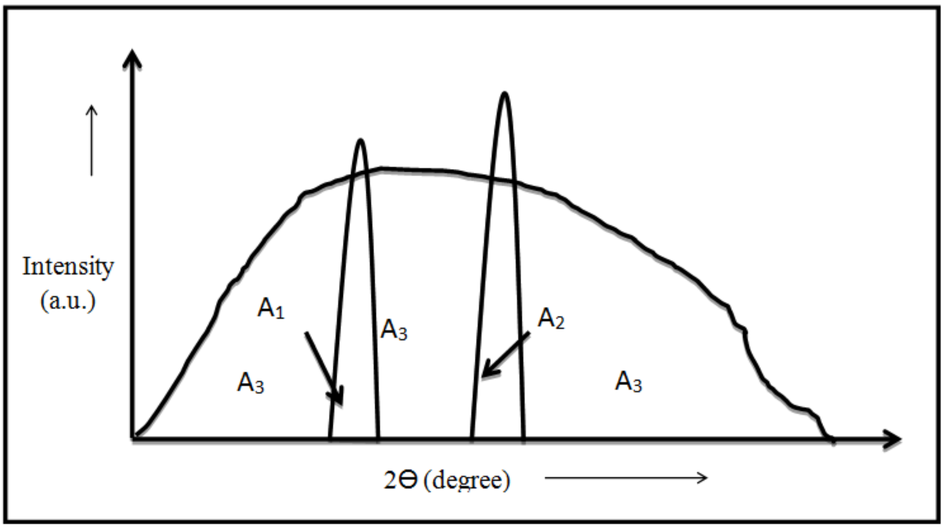

Figure 3. XRD pattern illustrating calculation of crystallinity.

3.2. FTIR

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

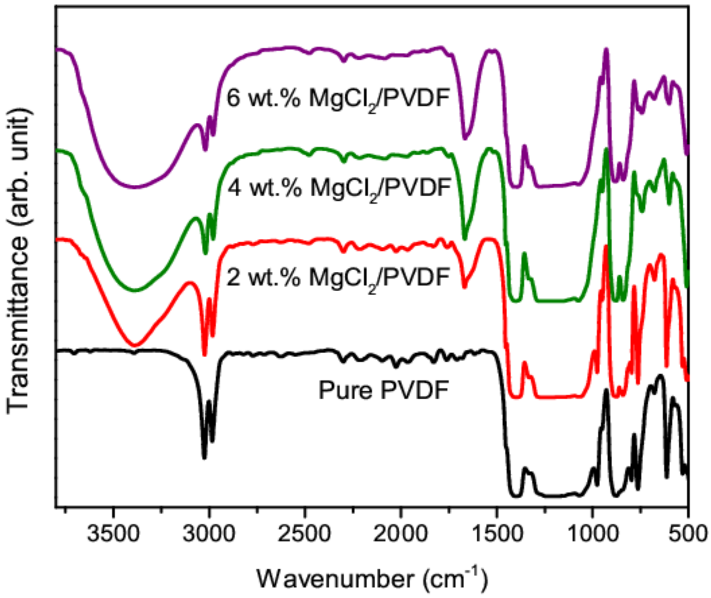

Figure 4. FTIR Spectra of Pure and doped PVDF composite.

3.3. Dielectric Constant and Force Sensing

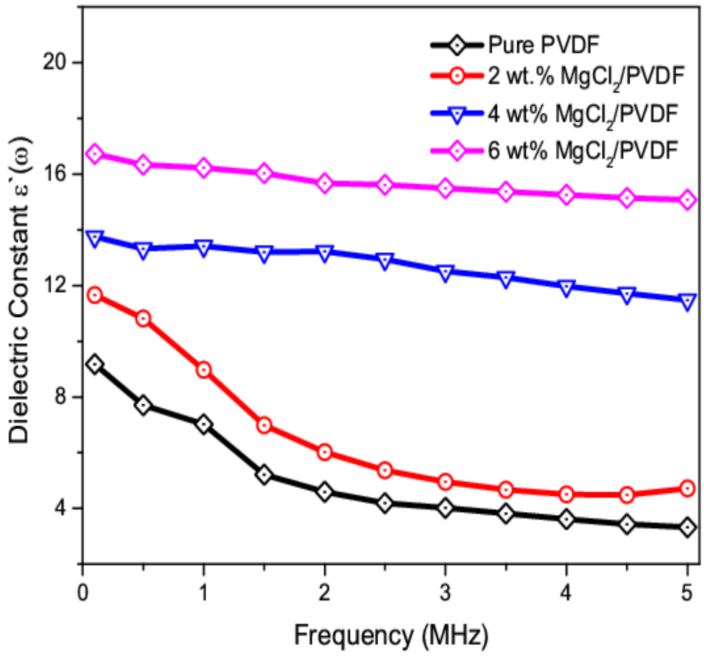

Figure 5. Dielectric constant vs. frequency.

The dielectric constant or permittivity *ε'(ω)* 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 *ε′(ω)* was calculated using following equation:

$$C_p = \varepsilon_0 \varepsilon' \frac{A}{D} \quad (2)$$

Where, ε_0 is the dielectric constant/permittivity (8.86 × 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.

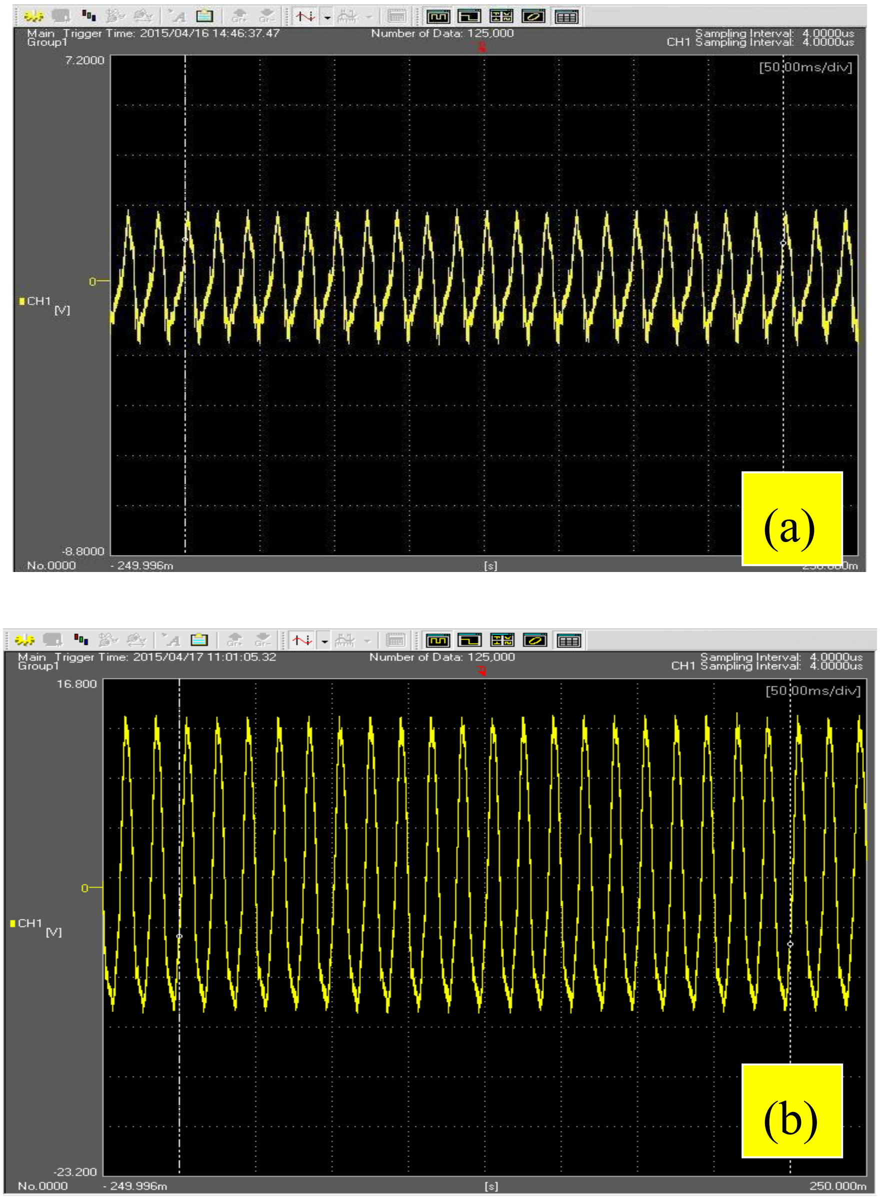

Figure 6. Voltage output of (a) Pristine PVDF, (b) $MgCl_2$/PVDF sensor.

4. Conclusion

The present work shows the $MgCl_2$ 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.

Acknowledgments

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Conflict of Interest

The authors declare no conflicts of interest regarding this paper.

References

1. Tao M, Liu F, Ma B, et al. (2013) Effect of solvent power on PVDF membrane polymorphism during phase inversion. *Desalination* 316: 137–145.
2. Gaur AM, Rana DS (2015) Structural, optical and electrical properties of $MgCl_2$ doped polyvinylidene fluoride (PVDF) composites. *J Mater Sci Mater Electron* 26: 1246–1251.
3. Gaur AM, Rana DS (2016) Effect of $CoCl_2$-$BaCl_2$ fillers on morphology, dielectric constant and conductivity of PVDF composite for pressure sensing application. *J Mater Sci Mater Electron* 27: 2293–2299.
4. Kadiroglu U, Abaci U, Guney HY (2014) Effects of B_2O_3 addition on structural and dielectric properties of PVDF. *Poly Eng Sci* 54: 2536–2543.
5. Low YKA, Tan LY, Tan LP, et al. (2013) Increasing solvent polarity and addition of salts promote β-phase Poly(vinylidene fluoride) formation. *J Apll Polym Sci* 128: 2902–2910.
6. Jung Y, Kwak J, Lee YH, et al. (2014) Development of a multi-channel piezoelectric acoustic sensor based on an artificial basilar membrane. *Sensors* 14: 117–128.
7. Li YC, Tjong SC, Li RKY (2011) Dielectric properties of binary polyvinylidene fluoride/barium titanate nanocomposites and their nanographite doped hybrids. *Express Polym Lett* 5: 526–534.
8. Mendes SF, Costa CM, Caparros C, et al. (2012) Effect of filler size and concentration on the structure and properties of poly(vinylidene fluoride)/$BaTiO_3$ nanocomposites. *J Mater Sci* 47: 1378–1388.
9. Tawansi A, Oraby AH, Abdelrazek EM, et al. (1999) Structural and electrical properties of $MgCl_2$-filled PVDF Films. *Polym Test* 18: 569–579.
10. Correiaa DM, Ribeiroa C, Sencadas V, et al. (2015) Influence of oxygen plasma treatment parameters on poly(vinylidenefluoride) electrospun fiber mats wettability. *Prog Org Coat* 85: 151–158.
11. Silva AB, Arjmand M, Sundarara U, et al. (2014) Novel composites of copper nanowire/PVDF with superior dielectric properties. *Polymer* 55: 226–234.

12. Lai CY, Groth A, Gray S, et al. (2014) Preparation and characterization of poly(vinylidene fluoride)/nanoclay nanocomposite flat sheet membranes for abrasion resistance. *Water Res* 57: 56–66.
13. Loan TV, Giannelis EP (2007) Compatibilizing Poly(vinylidene fluoride)/Nylon-6 Blends with Nanoclay. *Macromolecules* 40: 8271–8276.
14. Kang DH, Kang HW (2016) Surface energy characteristics of zeolite embedded PVDF nanofiberfilms with electrospinning process. *Appl Surf Sci* 387: 82–88.
15. Low, YKA, Tan LY, Tan LP, et al. (2013) Increasing solvent polarity and addition of salts promote β-phase poly (vinylidene fluoride) formation. *J Apll Polym Sci* 128: 2902–2910.
16. Jayalakshmy MS, Philip J (2014) Pyroelectric figures of merit and associated properties of $LiTaO_3$/poly vinylidene difluoride nanocomposites for thermal/infrared sensing. *Sensor Actuat A-Phys* 206: 121–126.
17. Abdelaziz M, Abdelrazek EM (2004) Effect of equal amounts of Mn and Co dopant addition on the structural, electrical and magnetic properties of PVDF films. *Physica B* 349: 84–91.
18. Elashmawi IS, Abdelrazek EM, Ragab HM, et al. (2010) Structural, optical and dielectric behavior of PVDF films filled with different concentrations of iodine. *Physica B* 405: 94–98.
19. Martins P, Lopes AC, Mendez SL (2014) Electroactive phases of poly(vinylidene fluoride): Determination, processing and applications. *Prog Poly Sci* 39: 683–706.
20. Rana DS, Chaturvedi DK, Quamara JK (2011) XRD and SEM investigation of swift heavy ion-irradiated polyvinylidene fluoride thin films. *J Mater Eng Perform* 20: 276–282.
21. Rana DS, Chaturvedi DK, Quamara JK (2009) Morphology, crystalline structure, and chemical properties of 100 MeV Ag-ion beam irradiated polyvinylidene fluoride (PVDF) thin film. *J Optoelectron Adv Mater* 11: 705–712.
22. He F, Fan J, Chan LH (2014) Preparation and characterization of electrospun poly(vinylidene fluoride)/poly(methyl methacrylate) membrane, *High Perform Poly* 26: 817–825.
23. Costa PMCM, Benelmekki M, Botelho G, et al. (2012) On the origin of the electroactive poly(vinylidene fluoride) β-phase nucleation by ferrite nanoparticles via surface electrostatic interactions. *Cryst Eng Comm* 14: 2807–2811.