

Dielectric Spectroscopy of Ferroelectric Crossbred PVDF-ZnO Polymer Composite Thin Films

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Polyvinylidene fluoride (PVDF), a semi-crystalline ferroelectric polymer with a range of interesting properties, shows potential to be used in a variety of technological applications. Flexible thin films of PVDF and its composites have made the progress in electronic properties mainly due to the dielectric response. In this paper, we report the synthesis, characterization, and dielectric properties of PVDF-ZnO composite in thin film form. PVDF-ZnO polymer composites with various concentrations of ZnO as filler in PVDF matrix were synthesized by solution mixing method using Dimethylformamide (DMF) as a solvent. The phase transformation and surface morphology of the prepared ferroelectric polymer composites were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively. The XRD patterns confirm the formation of the tetragonal perovskite structure of ferroelectric β -phase of PVDF and β -phase shifts towards a lower value of 2θ that is influenced by uniform mixing of ZnO particles. Further, the crystallinity of the composites with ZnO composition in the PVDF matrix was found to be enhanced. The SEM micrograph depicts an increase in the structural density with ZnO composition in the PVDF matrix. The FTIR spectrum of the composites shows absorption peaks characteristic of α and β phases and an increase in their intensity due to ZnO, indicating the wurtzite phase. The dielectric constant of PVDF-ZnO is an anomaly at low frequencies and decreases with increasing frequency, validating the Maxwell-Wagner type of interfacial polarization, and was found to be in agreement with Koop's phenomenological theory.

Keywords: PVDF, PVDF-ZnO, XRD, SEM, FTIR, Dielectric constant.

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1. INTRODUCTION

Ferroelectric composite films based on polyvinylidene fluoride (PVDF) matrix facilitate further research to achieve tunable dielectric properties such as outstanding durability, high permittivity, low dielectric loss and high flexibility [1-3]. Many organic-inorganic types of filler are used in polymeric materials to enhance their characteristic properties. The metal oxide particles filled with a polymer matrix have considerably improved dielectric properties [4]. The polymer PVDF composites are easy to prepare in any desired form by techniques such as compression molding, hot press, ball milling and solvent cast methods. According to the requirements, the properties can be adapted by varying the composition of the constituents. The combination of components with a high degree of dispersion in composites provides better performance and finds potential application in photoelectron-chemical devices, electrochemical devices, nonlinear optical systems, and so on [5-7].

The dielectric properties of organic-inorganic composites are attracting more and more attention due to their flexibility and the need as a sensing component in several essential electronic devices. Generally, high dielectric constant inorganic materials are dispersed in a polymer to enhance the dielectric response of composites. Hence, it is necessary to carefully select inorganic

filler with a high dielectric constant, so that uniform dispersion in a polymer is done for the development of a composite film. PVDF, a semi-crystalline ferroelectric polymer with chemical formula $[-(\text{CH}_2-\text{CF}_2)-]_n$, has an excellent mechanical and chemical properties with thermal stability. PVDF polymer crystallizes into four forms, namely α , β , γ and δ which depend on the preparation conditions [8-10].

Semiconductor material ZnO has a direct band gap energy of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [11]. Hexagonal wurtzite and cubic zinc blende are two crystalline forms of ZnO that exhibit a hexagonal wurtzite structure with the lattice constants $a = 0.32498$ nm, $b = 0.32498$ nm and $c = 5.2066$ nm (JCPDS card No. 36-1451) under general conditions. ZnO particles are useful in a variety of solar cells, sensors, photocatalysis, and transparent thin film transistors due to many excellent properties of ZnO [12]. Since ZnO has piezo-, pyroelectric and nonlinear optical properties, while PVDF has ferro-, pyro- and piezoelectric properties, it would be interesting to fabricate a PVDF-ZnO composite for better and improved dielectric spectroscopy.

In this article, we report on the synthesis of PVDF-ZnO ferroelectric composite thin films, characterization techniques, and their properties. PVDF-ZnO composite films were synthesized by solution mixing method using N N Dimethylformamide (DMF) as a solvent. De-

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tailed structural studies were done using XRD, SEM and FTIR analysis. The dielectric properties of polymer composite films as a function of frequency were computed using an impedance analyzer that confirms the Maxwell-Wagner type of interfacial polarization in accordance with Koop's phenomenological theory.

2. EXPERIMENTAL

2.1 Materials

Granular PVDF with a molecular weight of 534000 was supplied by Sigma Aldrich, India. To prepare PVDF composite thin films we used AR grade ZnO and N N Dimethylformamide (DMF) as a solvent supplied by Hi Media Lab. Pvt. Ltd., Mumbai, India. X-ray diffraction, surface morphology study and FTIR spectra of the ferroelectric polymer and its composite thin films were carried out using XRD unit Rigaku Miniflex (5th generation), field-emission scanning electron microscopy (FESEM, Zeiss Sigma), and Perkin Elmer Spectrophotometer, respectively, at Manipal Academy of Higher education, Mangalore. The electrical properties such as dielectric behavior via capacitance have been measured using LCR meter (Hioki, Japan IM3536) at the Department of Physics BKIT, Bhalki.

3. PREPARATION OF PVDF AND PVDF-ZnO COMPOSITE FILMS

Pristine PVDF and PVDF-ZnO composite thin films were blended by economical solution mixing method. An appropriate amount of PVDF granules was dissolved in 50 ml of DMF solvent and heat-treated at 60 °C using a magnetic stirrer, so that a transparent and homogenous solution was obtained. The solution was then poured into a petridish and dried under a light source for 24 h. The PVDF film was peeled-off from the petridish. A standardized PVDF-ZnO solution was obtained by adding ZnO powder in the weight % ratio of 2, 4, 6, 8 and 10 % into PVDF/DMF solution. To uniformly disperse the particles in the polymer matrix, the solution was sonicated for half an hour and the solution was poured into the petridish. After drying, the composite films were peeled-off and used for further studies [13].

4. RESULTS AND DISCUSSION

4.1 XRD Analysis

XRD patterns obtained for pure PVDF and PVDF-ZnO composite films with different wt. % are shown in Fig. 1 and Fig. 2, respectively. From Fig. 1, it is seen that 2θ peaks nearly at 19.90° and 20.90° confirm the existence of (110), (110) and (200) planes, which proves the presence of α and β phases of pure PVDF. Fig. 2 shows reflections corresponding to (100), (002), (101), (102) and (110), (103), (200), which are very similar to the standard diffraction pattern of ZnO (JCPDS file No. 79-0208). An increase in the intensity of prominent peaks of ZnO particles is observed when the concentration of the composition varies from 2 to 10 wt. %. The peak value of pristine PVDF observed at $2\theta = 20.20$ decreases in intensity with increasing concentration and shifts towards lower values as ZnO particles are immersed and remains constant with increasing wt. %

of ZnO in PVDF. The crystallinity of the composites is enhanced due to the formation of cationic complexes with the functional group of PVDF, which confirms the intercalation of ZnO with the PVDF polymer system.

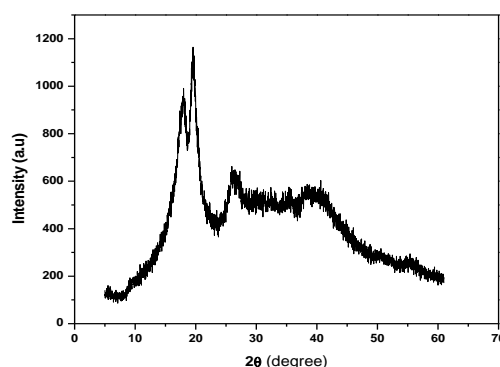


Fig. 1 – XRD pattern of pure PVDF film

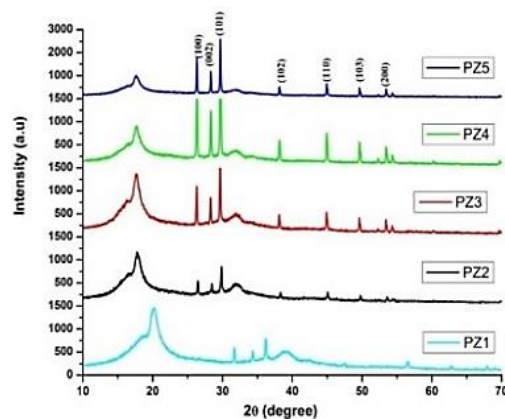


Fig. 2 – XRD analysis of PVDF-ZnO composites

4.2 SEM Analysis

SEM micrographs of PVDF-ZnO are shown in Fig. 3 for 4 to 10 wt. % variation of ZnO in PVDF, respectively. Cellular porosity of the PVDF matrix can be examined very systematically, and the images also show a change in pore size with variation in ZnO concentration i.e., the size of PVDF pores reduces as ZnO particles begin to occupy the pores. This means that the addition of ZnO to PVDF affects the surface morphology, which leads to variations in the dependent parameters of different properties of PVDF. Moreover, the appearance of the films shows an increase in the structural density as the concentration of ZnO in the film increases.

4.3 FTIR Studies

The results of the FTIR spectra of PVDF-ZnO composites are shown in Fig. 4. The peaks at 622 , 782 and 930 cm^{-1} represent the vibration modes of the PVDF powder due to the α -phase, and the peak at 851 cm^{-1} shows the IR vibration modes of the β -phase. These exhibit the existence of α and β phases in PVDF-ZnO composites [14-16]. Because of rocking and asymmetric stretching of CH_2 and CF_2 in the β -phase, the peak at 851 cm^{-1} appears in the FTIR spectra. Whereas peaks at 622 and 782 cm^{-1} are due to bending of CF_2 and skeletal bending of $-\text{C}(\text{F})-\text{C}(\text{H})-\text{C}(\text{F})-$ of the α -phase of

PVDF and the peak at 930 cm^{-1} represents CH_2 bending mode of the α -phase of PVDF. The FTIR spectra of PVDF-ZnO composites confirm the existence of both α and β phases of PVDF. The peaks at 412, 450, 580 and 820 cm^{-1} theoretically confirm the presence of the wurtzite structure of ZnO as infrared active mode, stretching vibrations of the Zn-O bond [17]. A comparison of the FTIR spectra of PVDF-ZnO composites shows that the absorption bands characteristic of α and β phase absorption peaks increase in intensity as a result of ZnO and also indicate the wurtzite phase of ZnO.

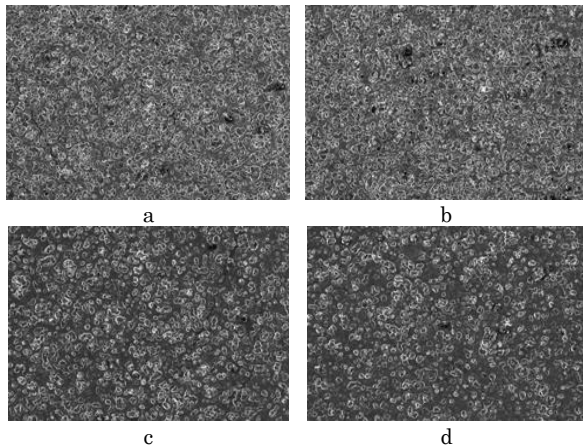


Fig. 3 – SEM micrographs of PVDF-ZnO composite films: a) 4 wt. %, b) 6 wt. %, c) 8 wt. %, d) 10 wt. % of ZnO in PVDF

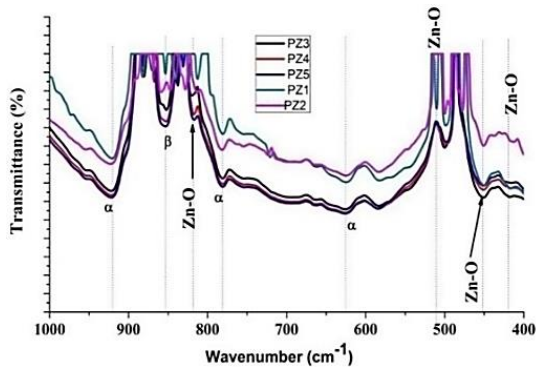


Fig. 4 – FTIR spectra of PVDF-ZnO composites

5. DIELECTRIC SPECTROSCOPY OF PVDF COMPOSITE FILMS

The deviation of the dielectric constant with frequency for pristine PVDF and PVDF-ZnO with 2, 4, 6, 8, and 10 wt. % of ZnO in PVDF is shown in Fig. 5. The dielectric constant of PVDF-ZnO is an anomaly at low frequencies and decreases with increasing frequency, validating the Maxwell-Wagner type of interfacial polarization in accordance with Koop's phenomenological theory. Dielectric constant with frequency follows the usual nature of a dielectric material. At low frequencies, the dielectric constant is found to be higher, and it decreases with higher frequencies. At low frequencies, the value of the dielectric constant is found to be in good agreement with the literature value, and it increases with increasing wt. % of ZnO fillers in the PVDF matrix [18, 19]. For a sample with 10 wt. % of ZnO in PVDF, at 50 Hz, a broaden skew peak of the dielectric constant

and a 180-fold jump in the dielectric constant compared to pristine PVDF are observed. The resulting high dielectric constant at short frequencies contributes to all possible polarization mechanisms, namely, electronic, ionic, orientation and space charge polarizations. All of them can be active at low frequencies, and variations of the dielectric constant with frequency indicate the type of contributions that are present in them. However, a decrease in the dielectric constant at high frequencies is caused by a slight depolarization of the dipoles that exist in weakly bonded interfaces and boundary regions. Mainly, orientation polarization is the main factor that restricts the dielectric constant at higher frequencies. PVDF is a ferroelectric polymer, and as the frequency increases, the dipoles find themselves unable to keep pace with a fast-changing field. A large value of the dielectric constant at low frequencies is due to the presence of space charge as well. The introduction of ZnO fillers into the PVDF polymer matrix enhances the dielectric constant of the composite films, since electrically conductive ZnO induces extra charge carriers in the composite material. As the content of the ZnO filler increases, the dielectric constant increases further, and so, loss tends to increase, which is mainly explained by means of interfacial space charge polarization [20].

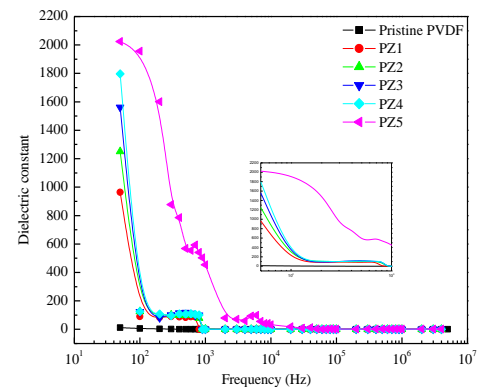


Fig. 5 – Variation of the dielectric constant with frequency for pristine PVDF and the composition of ZnO

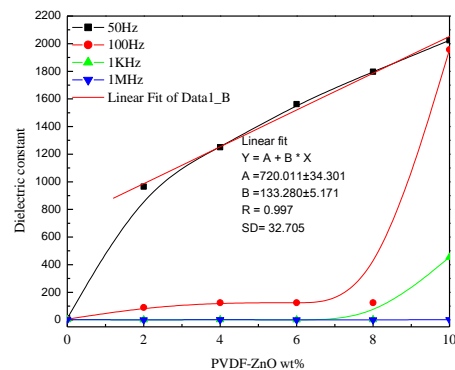


Fig. 6 – Variation of the dielectric constant with wt. % of ZnO in PVDF

The variation of the dielectric constant with wt. % of ZnO in PVDF for selected frequencies of 50 Hz, 100 Hz, 1 kHz, and 1 MHz is shown in Fig. 6. It is observed that the dielectric constant at 50 Hz maintains a linear dependence on wt. % of the additive ZnO component. However, for frequencies between 100 Hz and

1 kHz it is independent of the composition up to 6 wt. %. Thereafter, the dielectric constant increases exponentially with an increase in the ZnO concentration for compositions of 8 and 10 wt. %. No considerable variation in the dielectric constant is observed beyond 1 MHz. Changes observed for 8 and 10 wt. % at 100 Hz to 1 kHz can contribute to the harmonization of space charge polarization due to the homogenous mixture of fillers in the matrix, as depicted in the SEM images. Saturation of the dielectric constant beyond 1 MHz is due to pinning and freezing of polarization. Thus, broadband dielectric measurements provided evidence of interfacial polarization in the films, and the decrease in the dielectric constant with increasing frequency is due to the constraints of orientation polarization, which confirmed the dipole-dipole interaction in hybrid polymer PVDF-ZnO composite films.

6. CONCLUSIONS

The solution mixing method was used to prepare PVDF and PVDF-ZnO composite films. XRD and SEM

images confirmed the incorporation of ZnO into the PVDF matrix. SEM micrographs depict an increase in the structural density with the ZnO composition in the PVDF matrix, and the FTIR spectrum indicates the presence of the wurtzite phase. The improvement in the dielectric constant values of composites due to doping with ZnO in the polymer may be due to the fact that electrically conductive ZnO induces additional charge carriers in the composite material. A wide range of frequency band dielectric spectroscopy measurements provided evidence of interfacial polarization in the films, and the decrease in the dielectric constant with increasing frequency is associated with restrictions on orientation polarization, which confirms the presence of dipoles in hybrid composite films.

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Діелектрична спектроскопія сегнетоелектричних гібридних полімерних композиційних тонких плівок PVDF-ZnO

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Полівініліденфторид (PVDF), який є напівкристалічним сегнетоелектричним полімером з рядом цікавих властивостей, має потенціал для використання в різних технологічних додатках. Гнучкі тонкі плівки PVDF та його композитів поліпшили свої електронні властивості в основному за рахунок діелектричного відгуку. У роботі ми повідомляємо про синтез, характеристики та діелектричні властивості композиту PVDF-ZnO у формі тонкої плівки. Полімерні композити PVDF-ZnO з різними концентраціями ZnO як наповнювача в матриці PVDF синтезували методом змішування розчину з використанням діметилформадиду (DMF) як розчинника. Фазові перетворення та морфологія поверхні отриманих сегнетоелектричних полімерних композитів характеризувались рентгенівською дифракцією

(XRD) та скануючою електронною мікроскопією (SEM) відповідно. Дифрактограми підтверджують формування тетрагональної перовскітної структури сегнетоелектричної β -фази PVDF та зсуви ліній β -фази у бік менших значень 2θ , на що впливає рівномірне змішування частинок ZnO. Крім того, встановлено підвищення кристалічності композитів із вмістом ZnO в матриці PVDF. Мікрофотографії SEM демонструють збільшення структурної густини зі складом ZnO в матриці PVDF. Спектр FTIR композитів показує піки поглинання, характерні для α і β фаз, та збільшення їх інтенсивності за рахунок ZnO, що вказує на фазу вюрциту. Діелектрична проникність PVDF-ZnO є аномалією при низьких частотах і зменшується зі збільшенням частоти, підтверджуючи тип міжфазної поляризації Максвелла-Вагнера, і було встановлено, що вона узгоджується з феноменологічною теорією Купа.

Ключові слова: PVDF, PVDF-ZnO, XRD, SEM, FTIR, Діелектрична проникність.