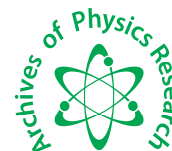




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Archives of Physics Research, 2015, 6 (4):1-6
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CODEN (USA): APRRC7

Investigations on spin coated poly(vinylidene fluoride) flexible films

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ABSTRACT

PVDF is a widely studied polymer due to its piezoelectric, ferroelectric and pyroelectric properties. Flexible PVDF films were prepared by spin coating technique which were in α phase. Polar β phase has been obtained by mechanically stretching the film. Investigations of the films was done using XRD, which indicated amorphous nature in α phase giving rise to much broader background scattering and the spectra contained sharp peaks due to crystallites in β phase. Values of the peaks obtained from FTIR studies indicate the transformation of the films from α to β phase. Micro structural study was done using SEM. Granular structure was observed in α phase and fibres in β phase. EDX indicated the presence of the elements of PVDF. The UV-Vis spectra of the developed film has been co-related to optical band gap using Tauc's expression. The Dielectric permittivity has almost remained a constant in the frequency range of 100 Hz to 1 MHz. The stretched film was exposed to high electric field wherein the molecular dipoles get oriented in the direction of the field and net polarization is formed. Piezoelectric properties were measured using piezometer. These results may be exploited in the development of sensors.

INTRODUCTION

Nowadays, with the rapid development of polymer processing methods and synthetic technology, industrial materials used in various manufacturing fields are being changed to polymers which have better properties than those materials previously used in many industrial areas [1]. Since polymers have superior properties, for example flexibility and easy process control, compared with previous materials, they are suitable materials for replacing the current materials widely used in industry. Also, in the case of sensor materials such as ceramics, attempts to utilize the flexibility and the lightness of polymer have been energetically made in the field of material engineering [2]. Especially, extensive studies of PVDF thin films for maximizing the advantages of piezoelectricity and pyroelectricity are currently being pursued by many research groups [3].

PVDF is a long chain, semicrystalline polymer having the repeat unit ($\text{CH}_2\text{-CF}_2$) [4]. This polymer can crystallize at least in five crystal forms α , β , ϵ , γ and δ depending upon crystallization conditions and can be converted from one to the other by various processes such as mechanical deformation, poling under large electric fields, annealing or crystallization at high temperatures. However, the most known are α and β forms. In the crystal form α chains are packed in the in the unit cell in such a way that the molecular dipoles are antiparallel and there is no net dipole. In crystal form β the chains are packed in the unit cell in such a way that the dipoles associated with individual molecules are parallel, leading to nonzero dipole moment of the crystal (Figure 1). Then, the crystal presents a large spontaneous polarization in its unit cell and when oriented and then poled under an electric field exhibits high piezoelectric properties [5]. The piezoelectric responses of PVDF are the highest known for any homopolymer and this is partly related to its high dielectric constant.

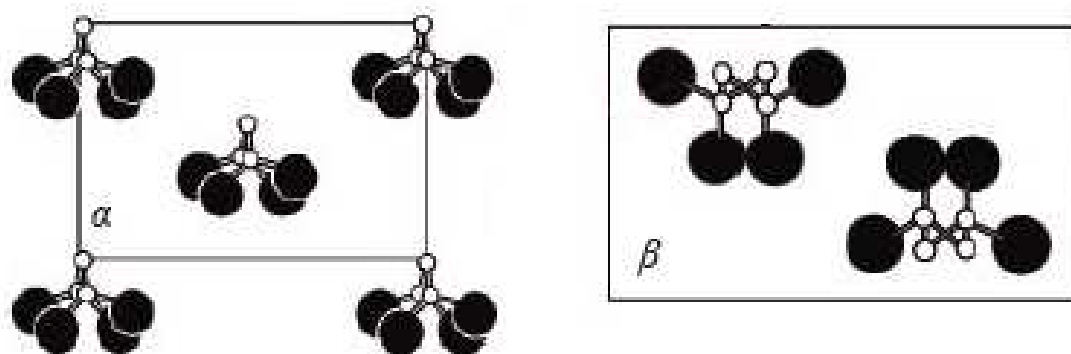


Figure 1. Crystalline structure of forms α and β of PVDF unit cell. Fluorine atoms are shown as large circles, carbon atoms as small circles and hydrogen atoms are omitted. [6]

The advantages of PVDF over piezoceramics include lower cost, larger area coverage, flexibility, low acoustic impedance and high frequency operation. Moreover, very thin, self supporting films are easily produced, electrodes can be attached on the film in a virtually unlimited variety of patterns, the polymer is very flexible and tough, and hence can be molded or stretched to conform to a surface [4]. In this work, we report the development of flexible PVDF film by spin coating which were in α phase. Mechanical stretching was done to obtain β phase and poling, for net polarization to be formed. To analyse the crystallinity of the PVDF thin film, techniques such as XRD, microscopy, infrared spectroscopy methods were employed in this research. Also optical and dielectric properties were studied. The film thus developed exhibited piezoelectric property which can be exploited for the design of sensors.

1. Preparation of PVDF film :

PVDF polymer is commercially available as pellets or granules. With a melting temperature of approximately 170°C and reasonable melt viscosity it is suitable for melt processing without the need for processing aids, stabilizers and additives. For research, PVDF pellets ($M_w \approx 534,000$, Aldrich) were dissolved in a polar solvent namely dimethyl formamide (DMF) purchased from Merck. A stir along with a hotplate was used to ease dissolution. The homogenous solution formed is poured onto a glass plate and then spun. The film thus formed is dried in an oven for the evaporation of the solvent. According to the described procedure, free standing flexible, opaque, milky white thick films ($100\text{-}130\ \mu\text{m}$) in α phase were obtained. α phase is then transformed to β phase by hot stretching of the film to four times its original length [7]. During this hot stretching process, the temperature was maintained at 80°C . It causes chain packaging of molecules into β crystalline phase. Dipole moments are randomly oriented and results in a zero net polarization. Opaque thick PVDF films of α phase were transformed into translucent films ($30\ \mu\text{m}$) of β phase. The homogenous β phase films were electroded with silver paste and poled by method of Corona Poling under an electric field of 80 kV/mm . This aligns the dipoles of the crystalline regions in the field direction. Piezoelectric properties were measured using piezometer and the charge coefficient was found to be 25 pC/nN

2. Investigations on PVDF films:

One of the most important parameters affecting the piezoelectric properties of PVDF is the level of crystallinity. Without crystallinity or defined morphology, PVDF would not exhibit any piezoelectric properties since it could not sustain a net dipole. Crystallinity also defines the mechanical, chemical and thermal properties of semicrystalline polymers(4). To analyse the crystallinity of formed PVDF thin film and evaluate its quality, a wide range of techniques were used in this research including XRD, SEM and infrared spectroscopy methods.

3.1 X-ray analysis :

The diffraction pattern created when X-rays impinge on a polymer sample can be used to determine the crystalline phases and also the level of absolute crystallinity. XRD spectra usually contain sharp peaks due to the crystallites, while the amorphous regions give rise to a much broader scattering. For the study the diffractograms of PVDF samples were acquired using an XPERT-PRO Diffractometer (Philips, Netherlands) using $\text{Cu K}\alpha$ radiation ($\lambda=0.154056\text{ nm}$).

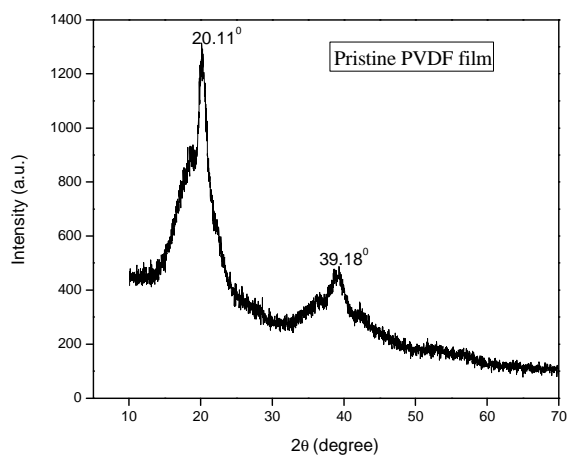


Figure 2a: X-ray diffractogram of PVDF in α phase

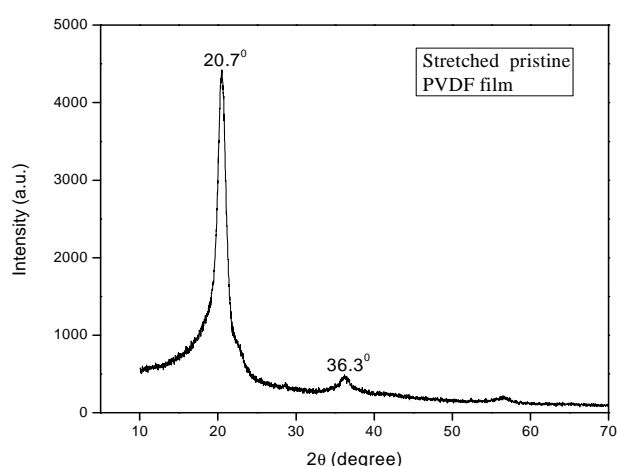


Figure 2b: X-ray diffractogram of PVDF in β phase

X-ray diffraction patterns obtained for pristine PVDF films before and after stretching are as shown in Figures 2a and 2b respectively. Table 1 shows PVDF crystal phases along with corresponding 2θ values. The sharp peak in Figure 2a of stretched pristine PVDF film indicates the formation of β phase and stretching has induced changes in the intensity of X-ray reflections towards reorientation of the crystal planes [7]. This confirms the piezoelectric property in stretched pristine PVDF film.

Table 1: Phases of PVDF along with crystal planes

Phases	$2\theta(^{\circ})$	Crystal planes (hkl)
α (fig)	20.11	(110)
	39.18	(002)
β (Fig)	20.7	(200)
	36.3	(310)

3.2 FTIR spectra

The formation of different phases was also confirmed by FTIR spectra, obtained by means of FTIR Spectrometer [Perkin Elmer]. The FTIR spectrometer allowed spectral measurements in the band of 400 to 1500cm^{-1} . In Figure 3a intensive absorption band at 532 , 609 , 891 and 1394cm^{-1} correspond to α phase, whereas peaks at 509 , 839 , 1050 and 1431cm^{-1} indicates β phase in Figure 3b. These results comply well with those described in literature [8]

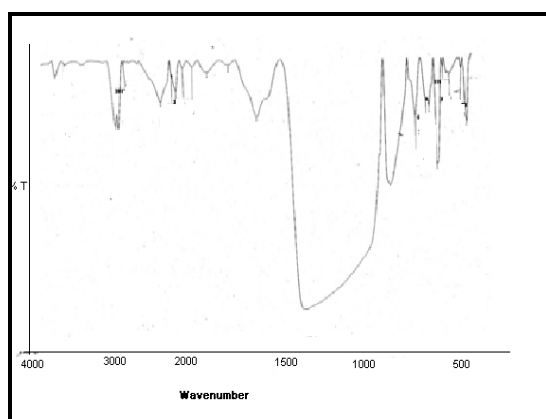


Figure 3a. FTIR of PVDF in α phase

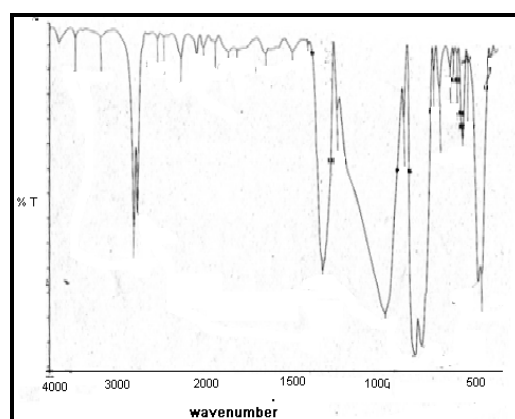


Figure 3b. FTIR of PVDF in β phase

3.3 Morphology and EDX study by SEM

The microstructure and morphology of the pristine PVDF samples are characterized using Scanning electron microscope equipped with an Energy Dispersive X-ray spectroscopy (EDX) using FEI Thermal Field Emission SEM Sirion. Figure 4a indicates the granular structure of the PVDF film in α phase. In α phase, the polymer

crystals are very small and arranged as spherically symmetric polycrystalline aggregates called spherulites that have no net polarization. Figure 4b indicates fibre like structure of PVDF in β phase because mechanical stretching of the sample has caused a breakdown of the spherulites and orientation of the molecular chains.

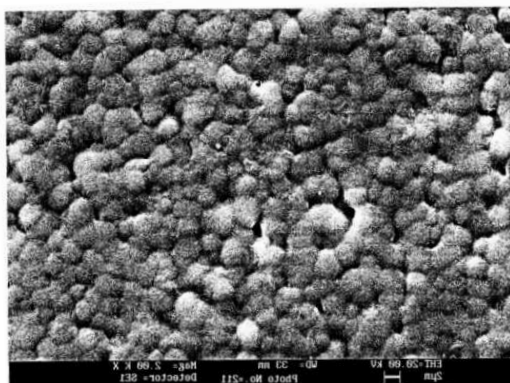


Figure 4a. SEM image of PVDF in α phase

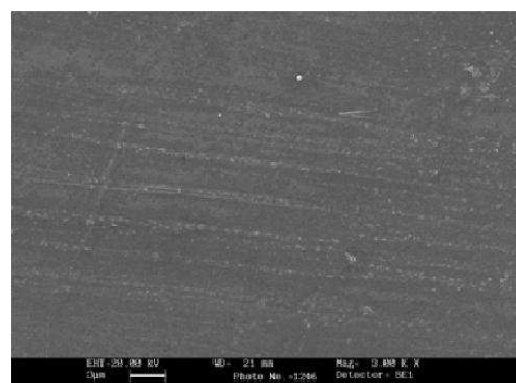


Figure 4b. SEM image of PVDF in β phase



Figure 5. EDX Analysis of Pristine PVDF

The EDX spectrum in Fig. 5 confirms the composition of the pristine PVDF film. Carbon and Fluorine originating from PVDF and trace amounts of Nitrogen and Oxygen are the impurities present in the sample.

3.4. Optical studies

The UV-Visible absorption spectroscopy is a powerful tool for the investigation of optical properties of the material. Ultra violet and visible absorption spectra was using Perlin Elmer UV-Vis spectrophotometer.

3.4.1 UV Vis absorption spectroscopy

Optical absorption spectra is recorded over the range 200-1500 nm as shown in the Figure 6. The absorption edge is around 204 nm for pristine PVDF and this sharp edge indicates the semicrystalline nature of PVDF [9].

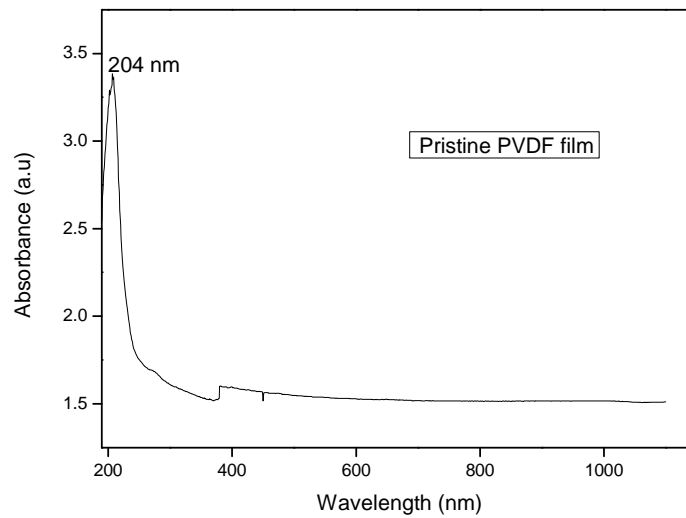


Figure 6. UV-Vis absorption spectra of Pristine PVDF

3.4.2 Optical band gap energy

The common and perhaps most direct method for probing the band structure of the polymer film is to measure its absorption spectra. The optical absorption edge can be analysed by the following equation [10]

$$\alpha h\nu = A(h\nu - E_g)^m \dots\dots\dots(1)$$

where A is constant and the exponent $m=2$ for allowed direct transitions. The variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ for pristine PVDF film is presented in Figure 7. The intercept (extrapolations) of the best fit line on energy axis gives the value of direct optical band gap energy. It is found to be 4.9 eV for pristine PVDF film. This value is comparable to that reported in literature [11]

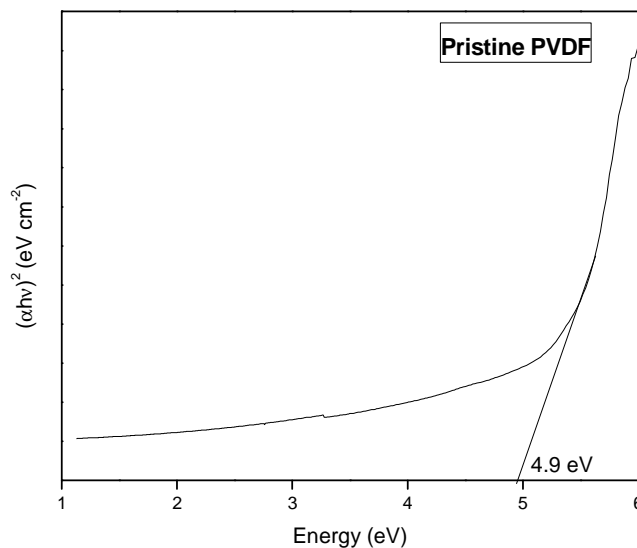


Figure 7. Optical band gap energy of Pristine PVDF

3.5 Dielectric Spectroscopy

The dielectric behaviour of the prepared pristine PVDF film is studied and the results are analysed in terms of different parameters. This analysis reflects the collective response of microscopic polarization process under an external electric field. The dielectric studies were conducted using Dielectric impedance analyser - Novocontrol Technologies, Germany.

3.5.1 Dielectric behaviour

On the application of alternating field, frequency dispersion or dielectric relaxation is observed due to different polarization mechanisms within the material. Typical spectroscopic plots of dielectric constant (ϵ^1) versus frequency for pristine PVDF is as shown in the Figure 8.

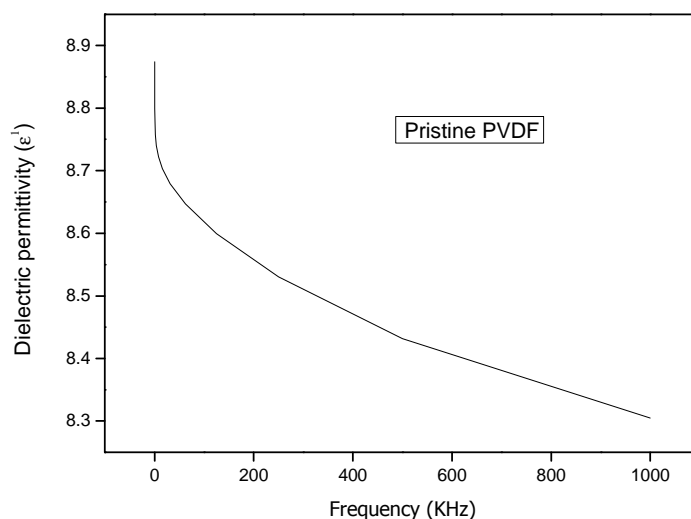


Figure 8. Dielectric permittivity versus Frequency for Pristine PVDF film

From literature it is observed that PVDF has a dielectric permittivity value of 6 [8]. Practically our pristine PVDF films prepared by spin coating has shown a value close to 8.9 and it is also observed from the above plot that the dielectric constant remains almost constant with increase in frequency. This property plays a vital role in the design of sensors for diverse applications.

CONCLUSION

This paper presents the results of the fabricated piezoelectric PVDF flexible film. The quality of the obtained films and their material characteristics are evaluated by means of X-ray and Infrared analysis as well as Scanning electron microscopy which indicated a phase transformation from α to β phase due to mechanical stretching of the film. Optical band gap value of 4.9eV comply well with literature. The dielectric permittivity remained constant within the frequency range of 100 Hz to 1 MHz. The qualitative films can be exploited for the design of sensors for diverse applications.

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