Preparation, Structural and Dielectric Properties of Solution Grown Polyvinyl Alcohol (PVA) Film

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Abstract: Flexible dielectrics with high permittivity have been investigated extensively due to their applications in electronic industry. In this work, structural and electrical characteristics of polymer based film have been analysed. Poly vinyl alcohol (PVA) film was prepared by solution casting method. X-ray diffraction (XRD) characterization technique is used to investigate the structural properties. The semi-crystalline nature has been determined by the analysis of the obtained XRD pattern. Electrical properties of the synthesized film have been analysed from the C-V and I-V curves obtained at various frequencies and temperatures. Low conductivity values confirm the insulating behaviour of the film. However, it is found that conductivity increases with temperature. Also, the dielectric permittivity is found to be higher at lower frequencies and higher temperatures, that proves PVA to be an excellent dielectric material which can be used in interface electronics. Dielectric behaviour of the film has been explained based on dipole orientations to slow and fast varying electric field. However further engineering can be done to modulate the structural, electrical properties of the film.

Keywords: organic electronics, dielectrics, Poly vinyl alcohol, capacitance-voltage, dielectric permittivity, Polymer thin films.

1. Introduction
Dielectric constant is related to the permittivity of the material. The permittivity is the ability of a material to get polarized with electric field. It is the ratio of the permittivity of the dielectric to the permittivity of vacuum. Traditionally dielectrics are made from inorganic substances e.g. mica and silicon dioxide [1]. Dielectrics with high permittivity are widely used in electronic industry. With the advancement of flexible electronics, high permittivity dielectric materials with excellent flexibility are in demand [3]. As compared to conventional dielectrics like ceramics, polymers are widely being used as dielectric materials when polymers exhibit better properties, like relatively high electric breakdown field, processing ease, mechanical flexibility etc [2]. Moreover, their properties can be modified by incorporating inorganic materials into it [5, 6, 8]. Many polymers like PVP, PVA, PMMA has been studied for their electrical and dielectric properties [11]. However, PVA is the most studied polymeric dielectric material due to its versatile properties like high solubility in water, low cost, easily processable, non-toxicity, good film forming, great insulating properties and the most important high dielectric permittivity. The above properties qualify PVA as a favourable organic material for interlayer dielectrics. PVA is produced by the hydrolysis of Polyvinyl acetate that is obtained by polymerization of vinyl acetate monomer [4]. The aim of the work presented here is to characterize...
the polymeric film of PVA for its structural and electrical properties and explore its application as an insulating and dielectric layer in electronic devices.

Polymer thin films find wide range of technological applications such as coatings, adhesives, lithography, sensors and as solid state electrochemical cells and as an insulating layer in electronic devices [11,10].

2. Materials and Preparation
A very simple method was used to cast thin PVA polymer film. Film was prepared as follows: To prepare 5% w/w solution of PVA in water, 5 gm of PVA powder (-C2H4O)n (Polyvinyl Alcohol, Sigma Aldrich, polymerization degree 1700-1800, hydrolysis degree 98-99 mol%) is preheated at 40°C in oven. 95ml of double distilled water is preheated at 80°C at hot plate without stirring. Preheated 5g PVA was dissolved in preheated 95mL double distilled water to make 100ml solution. A constant magnetic stirring is done at 70°C for 2.5 h till the complete dissolution of PVA to obtain 5% w/w PVA solution. Finally, 5ml of hot aqueous homogenous solution was cast into glass petri dishes (diameter 5 cm) and were dried in hot air oven at 60°C for 24h. The thin films of pure PVA were peeled off from the petri dishes and the synthesized films were kept in zip lock pouches in a silica gel desiccator to avoid the moisture effect. The obtained film was of nearly 100um uniform thickness. The thickness of these films was measured by micrometre.

3. Instruments and Characterization
Structural properties of the films have been studied through various measurement techniques. Structural features of the films have been determined using analytical method of X-ray diffraction (XRD) using Bruker’s D8 advance X-ray diffractometer using CuKα (λ=1.5406Å) radiation in the 2theta range from 10° to 70°.

For electrical characterization of the polymer film, a computer controlled Keithley electrometer was used to measure current–voltage (I–V) characteristics with variable temperature and a HIOKI 3532-50 LCR Hi Tester was used for capacitance–voltage (C–V) measurements with variable frequency.

4. Results and Discussion
4.1. X-ray diffraction
X-ray diffraction is a technique to characterize any material for its crystallinity [5]. The interpretation of the XRD pattern obtained of film shows limited crystallinity due to the hydrogen bond interaction among the hydroxyl groups present in polymeric chain. The broad diffractions occurred at 2Theta angles (~19.6°, 25.5° and 41.5°). The two broad humps between 15 and 30 indicate the semi-crystalline nature of the polymer PVA, which contains both the crystalline and amorphous regions.

Figure I: XRD pattern of synthesized PVA film
4.2. I-V characteristics and DC conductivity
The current-voltage, I-V characteristics of the polymer film were recorded at different temperatures (20-70°C) in the voltage range 0-10V. The film was coated with high conductivity silver paste to achieve circular ohmic contact. The sample was put inside an electrical furnace to heat at different temperatures. A digital thermometer measures the temperature. The DC conductivity of the films was calculated using the well-known relation [15]:

\[ \sigma_{dc} = \frac{d}{R \cdot A} \]  \hspace{1cm} \text{(1)}

where \( d \) is the sample thickness in m, \( R \) is its resistance in \( \Omega \) and \( A \) is contact area in \( m^2 \).

Figure 2 presents the DC insulation response of the synthesized PVA film at three different temperatures. The I-V characteristics of the film at some temperatures are shown. At lower applied potential difference (V), the current (I) is very small. However, with increasing V and temperature T current increases.

In a semi-crystalline polymer, the charge transport is mainly because of the amorphous region. The crystalline region does not play any major role in charge transport [7].

Figure 2: I-V Characteristics of PVA film at different temperatures

Figure 3 shows the dependence of \( \sigma_{dc} \) of the film on T. Numerical values of conductivity reveal the insulating behaviour of the polymer. However, conductivity increase with increasing T.

Figure 3: DC conductivity of PVA film versus temperature
4.3. C-V Characteristics and Dielectric permittivity

The dielectric measurements were carried out using C-V characteristics obtained at various frequencies (100Hz-100KHz) at room temperature. The dielectric permittivity of sample was calculated as [12]

\[ \varepsilon = \frac{dC}{\varepsilon_r A} \]  

(2)

Where C is the capacitance of the film and \( \varepsilon_r \) is the permittivity of free space (\( \varepsilon_r = 8.854 \times 10^{-12} \) F/m).

Figure 4: C-V Characteristics of PVA film at different frequencies (at 30C)

Figure 4 shows the C-V curves of the studied film at different frequencies. Capacitance decreases with the increase in frequency. Figure 5 shows the variation of dielectric permittivity of PVA film versus temperature and frequency. As shown, dielectric response decreases with the increase of frequency while increases with the increase of temperature. The same trend has also been observed by [13, 14,16]. High dielectric permittivity of polymer at lower frequencies may be because the dipoles have sufficient time to get align to the electric field. Decrease in dielectric permittivity at higher frequencies may be associated with the inability of dipoles to align rapidly with the rapidly changing applied field.

Similarly, at highertemperatures, the dipoles become comparatively free to respond to the applied electric field. That results in higher polarization and thus increased dielectric response. Higher hydrolysis degree is also a reason for high dielectric constant [4]as hydroxyl groups function as strong permanent dipoles that align themselves to the applied field, resulting in increased polarization and thus dielectric constant. The dielectric constants obtained are in agreement with the results reported in [4,14,15].
5. Conclusion

We have demonstrated the synthesis and characterization of PVA thin film as a dielectric material. PVA is a promising candidate to be used as a dielectric layer in electronic devices due to its suitable properties such as low leakage current, high dielectric permittivity, easily processable and good film forming properties [4]. Insulating and dielectric property of the polymer are inversely proportional; the increase of one result in decrease of the other.

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