Original Article

Preparation and electrical studies on pure and oxygen plasma treated polyvinyl alcohol films

P. Sumithraj Premkumar

Post Graduate and Research Department of Physics, St. John’s College, Palayamkottai, Tirunelveli, Tamilnadu 627002, India

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ABSTRACT

In the present work, pure polyvinyl alcohol (PVA) film was prepared by solution-casting method. The smooth and uniform surface of pure PVA films was treated by oxygen plasma with a power of 30 W and by varying time. The structural and electrical properties of plasma treated and untreated PVA films were studied by XRD, FTIR and electrochemical impedance analysis respectively. X-ray studies revealed that all the pure and oxygen plasma treated PVA films are semi crystalline nature. The functional groups of pure and oxygen plasma treated PVA films were recorded using FTIR analysis. The impedance of all the pure and oxygen plasma treated PVA films were measured in the frequency range 1 Hz to 100 kHz at ambient to 110 °C temperature. The conductivity of pure PVA film exhibited the highest conductivity when compared to oxygen plasma treated PVA films. The activation energy of all the samples was determined by plotting the graph between ln(σ) and 1/T and is found to be nearly 0.5 eV. The dielectric constant and dielectric loss of pure and oxygen plasma treated PVA films were determined. The results are discussed.

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1. Introduction

PVA is a polymer with exceptional properties such as water solubility, biodegradability, biocompatibility, non-toxicity and non-carcinogenic that possesses the capability to form hydrogels by chemical or physical methods [1-3]. The excellent chemical resistance, physical properties and complete biodegradability of PVA resins have led to their broad practical applications [4-6]. Poly vinyl alcohol films have high tensile strength and abrasion resistance and hence used as binder in electrochemical windows, blood prosthetic devices, fuel cells and double layer capacitors, etc. [7,8].

Recently, the surface modification of metal oxides, nanoparticles and polymers has received great attention because it affects the physical and chemical properties such as hydrophilicity, roughness, dispersion, wettability and adhesive property of materials [9]. Different methodologies such as chemical treatment, ozone treatment, irradiation methods, corona discharge and plasma treatment were employed for surface modification of various polymers [10]. Among these methods, plasma treatment is attractive as it modifies only
the surface without affecting the bulk properties and inserts new functional groups on the surface [11].

Plasma, a quasi-neutral gas, is referred to as the fourth state of matter. It consists of a collection of electrons and ions as well as neutral, atomic and molecular species that exhibit a collective behavior in the presence of an electromagnetic field. Plasma is normally generated by providing energy to gaseous molecules. When energy is supplied, the gas molecules get ionized to form equal number of positive or negatively charged ions by the dissociation of chemical bonds. The supplied energy may be in the form of thermal, electrical or electromagnetic. The plasma is electrically neutral and the presence of large number of ions makes plasma electrically conductive.

Plasma is used for the modification of surface of different materials like polymers and nanomaterials for different applications [12]. The plasma irradiation induces the degradation of the initial structure by scission and emission of atoms, molecules and molecular fragments [13]. It generates a number of charged species, ions, free radicals and induces either scission or cross-linking or both. This leads to changes in density, solubility, molecular weight as well as optical and electrical properties. Surface modification of mesoporous TiO$_2$ by various chemical and physical methods like TiCl$_4$, Ozone and HNO$_3$ are attempted to improve the DSSC performance [14–16]. The structural, morphological and other applications of pure, γ-radiation, ion beam radiation and electron beam radiation on PVA polymer have been reported [17,18]. However, the effect of plasma treatment on PVA films especially on structural and electrical properties is not well understood. But, it is expected that the plasma irradiation on the PVA films lead to the changes in the physical and chemical properties.

Therefore in the present work, uniform and thin PVA films were prepared and an attempt has been made to irradiate the PVA films by oxygen plasma source with different power and time. The effect of oxygen plasma on the pure polyvinyl alcohol film with respect to time and power in the structural and electrical performance were studied in detail.

2. Materials and methods

Polyvinyl alcohol and de-ionized water were used in present work for the preparation of pure PVA films. RF plasma source was used to preparation for the oxygen plasma treated PVA films.

Pure polyvinyl alcohol (PVA) films were prepared using solution casting technique. 2 g analytical grade reagent of PVA was dissolved in 20 ml of de-ionized water and the samples were stirred at room temperature for 10–12 h. The stirred solution was cast on to polypropylene dishes and allowed to evaporate slowly at room temperature in the dust free environment. After some time solid polymer layers are formed as thin films with a thickness of 200 μm at the bottom of dishes. These films were dried completely in a high vacuum (10$^{-3}$ Torr) to eliminate the residual traces of water. Finally films were carefully separated from the dishes.

The plain and uniform surface of pure PVA films were selected and subjected to the plasma treatment. The plasma ion source employed in the present work is based on the literature [19]. The PVA films were introduced to the quartz plasma chamber and evacuated by rotor pump. Then, oxygen gas was introduced in to the chamber with a pressure of 1.5 × 10$^{-7}$ mbar. The oxygen plasma was generated by passing radiofrequency to the gas molecules through copper coils. Two oxygen plasma treated PVA films were prepared by different ratios of power and time as 30 W:10 min and 30 W:15 min separately.

X-ray diffraction of pure and oxygen plasma treated PVA films were recorded between 10$^\circ$ and 80 $^\circ$. Fourier transform infra red spectra of pure and oxygen plasma treated PVA films were recorded using JASCO 4100 LE model in the range 4000–400 cm$^{-1}$. Impedance analyzer (IM 6 ZAHNER) was used to measure the impedance of the pure and oxygen plasma treated PVA films.

3. Result and discussion

The XRD patterns of pure, 30 W:10 min and 30 W:15 min oxygen plasma treated PVA films are presented in Fig. 1.

Fig. 1 – XRD pattern of (a) pure PVA (b) 30 W:10 min and (c) 30 W:15 min oxygen plasma treated PVA film.

The characteristic peaks of pure PVA film were observed at 19.59$^\circ$ corresponding to an orthorhombic lattice which indicates the partial crystalline nature. Similar observations are reported in the literature [18,20]. In case of plasma treated PVA films, the maximum peak is noted at 19.77$^\circ$ and 19.21$^\circ$ for 30 W:10 min and 30 W:15 min plasma treated PVA films respectively. Additionally, it was noted that the intensity of the peaks
FTIR spectra exhibit the typical characteristic absorption bands of PVA which can be assigned to vibrations of the C–O–C, C–H, C–O, C=O and OH bonds. The broad absorption band in the region 3468–3046 cm\(^{-1}\) is assigned to H bonding OH stretching, mostly due to the intrinsic structure of the hydroxyl groups. The absorption peak at 2978, 1710, 1656, 1024 cm\(^{-1}\) are assigned to C–H asymmetric, C–O stretching, C=O stretching, C–O stretching mode respectively. The peak at, 1413 and 852 cm\(^{-1}\) indicates the presence of CH\(_2\) bending and C–C stretching respectively. Compared with pure PVA film, in the spectrum of the oxygen plasma treated PVA films there can be observed slight shift in the bands originating from oxygen irradiation.

The real and imaginary impedance with frequency range of 1 Hz to 100 kHz at different temperatures were measured. Fig. 3 shows the complex impedance plots of pure, 30 W:10 min and 30 W:15 min oxygen plasma treated PVA films at room temperature. The extrapolation of intercept of the semicircular arc with real axis (Z\(_{\text{in}}\)) at low frequency gives rise to the bulk resistance (R\(_{\text{b}}\)) of the polymer system and it is found that the R\(_{\text{b}}\) increases with increase the energy and time of oxygen plasma treatment to the pure PVA films.

The conductivity (\(\sigma_{\text{dc}}\)) of polymer films has been calculated by the following standard relation,

\[
\sigma_{\text{dc}} = \frac{d}{R_{\text{b}}} A
\]

where d and A are the thickness and area of the sample. The electrical conductivity (\(\sigma_{\text{dc}}\)) is found to increase with increase in temperature. The conductivity of pure PVA film exhibits the highest conductivity when compared to oxygen plasma treated PVA films. Also, a decrease in conductivity of oxygen plasma treated PVA films was found with increase in irradiation time.

The increase in ionic conductivity with temperature, as depicted in Fig. 4, obeys the Arrhenius type thermally activated process represented by

\[
\sigma_{\text{dc}} = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)
\]

where \(\sigma_0\) is the pre-exponential factor, E\(_a\) is the activation energy, k is the Boltzmann constant and T is the absolute temperature. The activation energy of all the samples is found to be nearly 0.5 eV. The Arrhenius plot of pure, 30 W:10 min and 30 W:15 min oxygen plasma treated PVA film is shown in Fig. 5.

The calculated activation energy of pure and oxygen plasma treated PVA film is tabulated in Table 2. The activation energy of oxygen plasma treated PVA film is slightly higher than the pure PVA films. It indicates the densification of polymer films due to cross-linking of the surface groups by plasma treatment which restricts the movement of ions through the polymer chains. The activation energy increases with increasing the irradiation time of oxygen plasma to the PVA films. The long exposure of plasma leads to cross-linking of polymer chains which leads to lower ionic diffusion which in turn decreases the ionic conductivity of the PVA films. Also Fig. 5 illustrates that the conductivity versus temperature plots follow non linear behavior. Such features are generally observed for amorphous polymeric systems. So they cannot

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**Table 1 – FTIR band assignment of pure and oxygen plasma treated PVA films.**

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Pure (cm(^{-1}))</th>
<th>30 W:10 min (cm(^{-1}))</th>
<th>30 W:15 min (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H stretching</td>
<td>3468–3046</td>
<td>3496.27–3038.84</td>
<td>3476.12–3058.99</td>
</tr>
<tr>
<td>C–H asymmetric</td>
<td>2978</td>
<td>2942.75</td>
<td>2997.97</td>
</tr>
<tr>
<td>C=C stretching</td>
<td>1656</td>
<td>1655.70</td>
<td>1657.35</td>
</tr>
<tr>
<td>CH(_2) bending</td>
<td>1413</td>
<td>1427.49</td>
<td>1446.46</td>
</tr>
<tr>
<td>C–O stretching</td>
<td>1024</td>
<td>1043.86</td>
<td>1039.51</td>
</tr>
<tr>
<td>C–C stretching</td>
<td>852</td>
<td>817.87</td>
<td>883.69</td>
</tr>
</tbody>
</table>

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around 11\(^\circ\) and 40\(^\circ\) were decreased in the oxygen plasma treated PVA films indicating the increasing the amorphous nature. These peaks may be contributed to small changes in the molecular chain on account of irradiation by the oxygen plasma ions. In case of \(\gamma\)-irradiation on PVA films, there is a partial scission of the main chain and removal of –OH groups [18]. However, there is no significant variation in the structure of the plasma treated PVA film when compared to the pure PVA films.

FT-IR spectroscopy is a sensitive and affective technique of detecting the chemical bonds of materials. Fourier transform infra red spectrum of pure and oxygen plasma treated PVA films are presented in Fig. 2. The peak positions corresponding to certain important chemical bonds are listed in Table 1.
be described by Arrhenius relationship alone. This non-linear dependence obtained suggesting that proton conduction is due to the Vogel-Tamman-Fulcher (VTF) mechanism. Thus the non-linearity of the plots suggests that the ionic transport is dependent on the polymer segmental motion [21].

The prepared film was placed between the electrodes of the experimental cell. The experimental cell consists of two electrodes made up of stainless steel coated with silver and having a diameter the same as the film and kept parallel to each other similar to a parallel plate capacitor. The experimental cell was electrically shielded and was placed in an electric oven for temperature variation.

The dielectric constant of pure and oxygen plasma treated PVA films measured at different temperatures from ambient to 110 °C in the frequency range 1 Hz to 100 kHz. The variation of dielectric constant and dielectric loss with different frequencies of pure PVA film is presented in Figs. 6 and 7 respectively. Fig. 6 indicates that the dielectric constant of pure and oxygen plasma treated PVA films are independent of frequency at low range and it is dependent at higher frequency range for ambient to 110 °C temperature. From the graphs, it is understood that the increase of dielectric for pure and oxygen plasma treated films when increase the frequency for the temperature between 30° and 110 °C. Also, the dielectric constant

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**Fig. 3** – Complex impedance plots of pure and oxygen plasma treated PVA films at room temperature.

**Fig. 4** – Variation of conductivity with temperature of pure and oxygen plasma treated PVA films.

**Fig. 5** – Arrhenius plot of pure and oxygen plasma treated PVA films.

**Table 2** – Arrhenius energy of pure and oxygen plasma treated PVA films.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pure</td>
<td>0.4844</td>
</tr>
<tr>
<td>2.</td>
<td>30 W:10 min</td>
<td>0.4954</td>
</tr>
<tr>
<td>3.</td>
<td>30 W:15 min</td>
<td>0.5100</td>
</tr>
</tbody>
</table>
reach the minimum value when the applied frequency above 100 Hz. This is because, when a frequency is increased the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations will begin to lag behind those of the field. In a low frequency region electronic, ionic dipolar and space charge polarization plays a dominant role in determining the dielectric properties of the materials.

From the plot between dielectric loss and frequency at different temperatures, we observed that the dielectric loss decreases when the frequency increases from 1 Hz to 100 kHz at the temperature ranges 30°C and 110°C. The variation of loss tangent with frequency can be arranged to the dipole
alignment when the field is applied. At low frequencies, the dipoles can be easily switch alignment with the changing field. As the frequency increases the dipoles are less able to rotate and maintain phase with applied field, thus they reduce their contribution to the polarization field. From this, it is clearly understood that the synthesized sample of plasma treated PVA films are the perfect dielectric material.

4. Conclusion

Pure PVA films were prepared by solution casting techniques and the prepared films were irradiated with 30 W oxygen plasma for 10 and 15 min. X-ray diffraction analysis of pure and oxygen plasma treated PVA films showed the partially crystalline nature and additional peaks were observed in plasma treated films due to small changes in the molecular chain. The FTIR spectrum revealed that the expected functional groups are present in the films.

The ac conductivity of pure and oxygen plasma treated PVA films are found to be decreased with increase in irradiation time. The activation energy of the pure and oxygen plasma treated PVA films was determined using Arrhenius equation and found to be in the range of 0.5 eV. Frequency dependent dielectric constant and dielectric loss factor at various temperatures from 30 °C to 110 °C suggests that the dielectric constant and loss factor is independent at lower frequency and dependent at higher frequencies for all the temperature.

Conflict of interest

The authors declare no conflicts of interest.

REFERENCES