# Analytical Study of Solvent trapping nature of Biocomptable PVA Polymer 

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#### Abstract

Polyvinyl alcohol (PVA) is a fabulous, non-toxic, synthetic solvent swelling polymer having widespread novel applications for its biocompatible characteristics. However, water is an excellent solvent for PVA, except this, it is soluble in numerous polar, organic solvents such as DMSO, DMF, etc. The present study is associated with the synthesis of PVA polymeric membranes by using different solvents. The spectroscopic analysis both from density functional theory and experimental observations indicate the co-existence of solvents in the PVA polymeric membrane, where the solvents remain trapped inside the membrane and impossible to remove completely despite the application of higher temperature to the membrane, which helps to refute the basic concept of membrane technology of "solvent-free membrane" formation. The XRD patterns of membranes show a peculiar phase changing phenomenon after annealing the membranes at $125^{\circ} \mathrm{C}$. The FTIR and Raman spectroscopic studies showed a comprehensive perception on solubilization mechanism for the preparation of PVA membrane in different solvents with the variation in annealing temperatures and provided information regarding the polymer-solvent interactions during the formation of the polymeric membrane. The SEM images show the beautiful fish scale-like (spherulite) surface morphologies of the synthesized PVA-membranes.


Keywords: Polyvinyl Alcohol; FTIR; XRD; Solvent swollen,DMF,DMSO, SEM, Raman-Laser, Biomedical, Biocompatable

Introduction:
Polyvinyl alcohol (PVA), is a biodegradable polymer with excellent mechanical and acousto-optical properties. It has been used extensively in various fields such as medicals (drug delivery, contact lens, artificial blood vessel etc.), optoelectronics (polarization, retardation, optical filtration etc.), absorbants, membrane materials and other fields [1-3]. PVA consists of the basic recurrent unit $\left[-\mathrm{CH}_{2}-\mathrm{CH}(\mathrm{OH})-\right]_{\mathrm{n}}$, where a hydroxyl group is attached with each monomer as shown in the schematic diagram represented by Fig. 1. Within the macromolecular structure of PVA, there is a wide range of stereo-chemical
configurations. Due to its simple conformation, which indicates its isotactic character, it is generally consented to crystallization [4-6]. PVA is prepared by dissolving polyvinyl acetate in alcohol
in presence of an alkaline catalyst. PVA is a solvent swollen polymer and soluble in various polar protic and aprotic solvents. Generally, the solvents used are $\mathrm{H}_{2} \mathrm{O}$, DMSO, DMF, polyethylene glycol


Figure-1: The Schematic diagram of PVA monomer structure. solvent, at first the solvent diffuses into the polymeric network and swells the polymer, after that at a certain critical concentration of the solvent, the polymeric chain becomes disentangle, as a result the polymer dissolves in the solvent [9].

#  <br> DMF <br>  <br> DMSO <br>  <br> PEG <br>  

The PVA polymeric system, which is built in conjunction with water, is strongly influenced by temperature
changes during both the heating and cooling of the system, such that glass transition temperature changes and at the temperature below $\left(-10^{\circ} \mathrm{C}\right)$, the water molecules turn into fine ice crystals by freezing up. Association of water with PVA network shows the phenomena of phase transition, hydrogen bonding and entanglements respectively [10], above the crystallization point of water. In the water swollen PVA polymeric system, three distinct thermal phases of water can be observed such as free water, freezable bound water and nonfreezing water respectively. Free water exhibits the similar phase transition as bulk water. The freezable bound water reveals the phase transition during the interaction with the polymer chain. The nonfreezing water does not show any significant phase transition with the variation of temperature. However, partial crystalline and amorphous phases in PVA are influenced by the addition of water [11].

Dimethyl sulfoxide (DMSO) is a very proficient aprotic solvent, and has the ability to dissolve a wide spectrum of both the polar and nonpolar molecules [12]. The strong intra-interactions between sulfur ( S ) and oxygen ( 0 ) atoms, help to create the self-connected polymer chain in between DMSO molecules, which disarticulate with the rise in temperature [13]. At the molecular level, PVA easily disperses in DMSO such that no aggregation occurs during the dissolution process [14]. Due to the strong hydrogen bond accepting property [15], DMSO may also interact strongly with PVA molecules through O-H interactions.
$\mathrm{N}, \mathrm{N}$ - dimethyl formamide (DMF) is also an important polar aprotic solvent as DMSO [16]. DMF has a wide liquid temperature range with the boiling point $153^{\circ} \mathrm{C}$. It shows excellent thermal and chemical durability along with the wider spectrum of solubility for both organic and inorganic components [17]. It is a good solvent for PVA [18]. The 0-H interactions play a vital role during the reactions of DMF with PVA. It is very important to investigate the mechanism involved in PVA's response with various solvents. The vibrational spectroscopic studies are very much helpful in the comprehensive perception of
solubilization mechanisms for the preparation of PVA membrane. It also provides information regarding the polymer-solvent interactions during the formation of the polymeric membrane. X-ray diffraction (XRD) technique is very much useful to investigate the phase determination of the polymer after dissolving in a solvent. Through which it can provide more information about how the solvent interacts with the semicrystalline membrane of PVA. The surface morphology of the PVA membrane is characterized by the scanning electron microscopy.

In the present communication, we have studied the effect of thermal treatment on the solvent-polymer interactions and examined their behavioral responses. Spectral analysis of the polymeric matrices prepared in different solvents (water, DMSO and DMF) were used to correlate frequency and chemical shift.

## Experimental Details

## (a) Material Synthesis

Polyvinyl alcohol (PVA) polymer (molecular weight, M.W. $=98,000 \mathrm{~g} / \mathrm{mol}$, Across organics), dissolved in double distilled water; Dimethyl sulfoxide (DMSO) and Dimethyl formamide (DMF) solvents. The conventional solution cast technique has been used for the development of solid polymer membrane.
PVA was dissolved in 20 ml solvent to make 0.6 M PVA homogeneous solution. This $\sim 20-22 \mathrm{ml}$ solution was poured in the petri dish ( 10 cm diameter and 35 ml volume) and dried in controlled ambient ( $\mathrm{RH} \sim 65 \%$ and Temperature $\sim 32{ }^{\circ} \mathrm{C}$ ) condition. These completely dried membranes are used for further measurements.

## (b) Material Characterisation

Structural behavior of pure PVA, polymer electrolyte films with different solvents and different annealing temperatures were carried out by X-ray diffractometer (Philips X-Pert model) in the $2 \theta$ range ( $10^{\circ}$ to $75^{\circ}$ ). The SEM images of different electrolyte systems were recorded with the JEOL JXA-8100 EPMA instrument. For SEM imaging the polymeric membranes (size $\sim 2 \mathrm{~mm} x$ 2 mm ) were fixed on a stub with the help of double sided carbon tape and Carbon coating ( $\sim 10-15 \mathrm{~nm}$ ) was done on the membranes using Jeol vacuum evaporator JEE-420. The infrared spectrum was recorded on Bruker Alpha (Germany) FTIR with ATR spectrometer in a range $4000-500 \mathrm{~cm}^{-1}$ at the room temperature as well as various annealed temperatures. Raman spectra were collected with a Uniram confocal Raman spectrophotometer with laser sources at 785 nm with variable power in the spectral range ( $100-2000 \mathrm{~cm}^{-1}$ ).

## (c) Computational Method

Theoretical studies on PVA (considered the four different configurations i.e. monomer, dimer, trimer, and tetramer) and PVA membrane in different solvents are optimized by the Gaussian 09 Software Package [19] and Density functional theory (DFT) method B3LYP/6-31G** basis set [20-27]. With the help of these software packages, we have studied the theoretical behavior of PVA in different solvents. Theoretically calculated isotropic polarizability, enthalpy, entropy, thermal energy, specific heat, zero-point energy, dipole moment, and Gibbs free energy change are summarized in Table 1


Figure-4 FTIR spectra (range $1500 \mathrm{~cm}^{-1}-700 \mathrm{~cm}^{-1}$ ) of PVA membrane in $\mathrm{H}_{2} \mathrm{O}$ at different annealing temperatures (RT $-200^{\circ} \mathrm{C}$ ).

## Results and Discussion:

## FTIR Studies of PVA and PVA Membranes

The infrared spectra of PVA powder and PVA membranes at room temperature are shown in Fig. 3. In PVA powder the assignments of theoretical and experimental FT-IR prominent peaks are given in Table 2. Peak at $3285.62 \mathrm{~cm}^{-1}$ (broad) assigned to CH stretching and $\mathrm{CH}_{2}$ asymmetric stretching vibrations. A doublet at 2935.68 and $2909.69 \mathrm{~cm}^{-1}$ represent $0-\mathrm{H}$ stretching from the intramolecular H of $(\mathrm{OH})$ group in the vinyl alcohol unit, which is assured by the vibration of theoretical tetramolecular configuration in PVA. The strong peak corresponding to $1325.19 \mathrm{~cm}^{-1}$ is associated with C H in-plane bending, $\mathrm{C}=\mathrm{C}$ stretch, wherein from the theoretical aspect, the $0-\mathrm{H}$ bending vibration becomes weak gradually from mono to tetramolecular configuration. .The small peak at 1134.31 $\mathrm{cm}^{-1}$ is associated with $\mathrm{C}-\mathrm{O}$ stretching, $\mathrm{CH}_{2}$ in-plane rocking, and $\mathrm{O}-\mathrm{H}$ in-plane bending. Wherein, the presence of external $\mathrm{H}_{2} \mathrm{O}$ (adsorbed) molecules that influence PVA into several vibrations appears in the form of doublet peak at $1085.03 \mathrm{~cm}^{-1}$. However, in theoretical observations, this may be absent due to the influence of external /ambient water molecules.

The peak at $1023.00 \mathrm{~cm}^{-1}$ represents $\mathrm{CH}_{2}$ out of plane twisting, $\mathrm{C}-\mathrm{H}$, and $\mathrm{O}-\mathrm{H}$ out of plane bending vibrations. The peak at $942.43 \mathrm{~cm}^{-1}$ represents $\mathrm{CH}_{2}$ in-plane rocking, vibrations. Furthermore, $\mathrm{CH}_{2}$ out of plane wagging vibration also exists at $834.61 \mathrm{~cm}^{-1}$.

The variance of FT-IR spectra with annealing temperature for PVA polymeric membrane developed in various solvents are shown in Fig. 4, Fig. 5 and Fig. 6.
A comparative account of the temperature variance infrared spectral data and their assignments of PVA polymeric membrane developed experimentally in various solvents viz., PVA membrane in $\mathrm{H}_{2} \mathrm{O}$, PVA in DMSO and PVA in DMF with their corresponding theoretical peak are given in Table 3, Table 4 and Table 5.

After a vigorous study of the infrared spectral data from both theoretical and experimental aspects, it can be confirmed that the PVA


Figure-3: FTIR spectra (range $4000 \mathrm{~cm}^{-1}-500 \mathrm{~cm}^{-1}$ ) of PVA membrane in different solvents at room temperature.


Figure-5 FTIR spectra (range $1500 \mathrm{~cm}^{-1}-700 \mathrm{~cm}^{-1}$ ) of PVA membrane in DMSO at different annealing temperatures (RT $-200^{\circ} \mathrm{C}$ ).
membranes which are prepared using various solvents during solvent casting method, may not be completely free from solvents molecules at room temperature. Further, temperature variance infrared spectral studies were done to confirm whether it is possible to set up a solvent-free membrane or not through a thermal treatment of synthesized PVA membranes in various solvents.

All the major IR peaks observed in bare PVA show changes on interacting with various solvents, representing solute - solvent interactions in the polymeric membrane when subjected to the change in temperature, and very interesting changes especially in the peak region (Fig. 4-6) between 1480 $-880 \mathrm{~cm}^{-1}$. The most probable explanations are given accordingly system wise:

The peak at $1425 \mathrm{~cm}^{-1}$ at RT retained its character, and peak at $1421.60 \mathrm{~cm}^{-1}$ corresponds to the theoretical PVA peak, which emphasizes the scissoring vibrations of the in-plane $\mathrm{CH}_{2}$
group. Since PVA is a solvent swollen molecule [28], therefore due to the entangled solvent molecule's vibrations, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending vibrations of PVA along with weak $0-\mathrm{H}$ are affected leading to deformation in $\mathrm{H}_{2} \mathrm{O}$. It may give an assumption about the existence of $\mathrm{H}_{2} \mathrm{O}$ molecules inside PVA membrane. But the appearance of multiple peaks starts from annealing temperature $100^{\circ} \mathrm{C}$ to $125^{\circ} \mathrm{C}$ indicates some transitional changes in the polymer matrices. This emphasizes several increased vibrations of PVA accompanying with vibrations of deformed $\mathrm{H}_{2} \mathrm{O}$.

After applying heat treatment on the membrane, the peak does not shift but splits. Splitting may be due to the swelling of the PVA matrix incorporating slight change in the bond length, increasing the maximum possibility of interaction of the - OH group with $-\mathrm{CH}_{2}$ group of the matrix. It confirms the existence of $\mathrm{H}_{2} \mathrm{O}$ molecules inside the PVA membrane. After that from $150^{\circ} \mathrm{C}-$ $200^{\circ} \mathrm{C}$, the change in the structure may be reversed and get stabilized, indicated by the regaining the nature of the said peak in IR curve as it is in at $50^{\circ} \mathrm{C}$. At $200^{\circ} \mathrm{C}$, the vibrations may be due to the indication of the starting point of the melting of PVA. Slight changes in the IR curves in the region $1251-1239 \mathrm{~cm}^{-1}$ at $100^{\circ} \mathrm{C}$, responsible for $\mathrm{C}-\mathrm{O}$ asymmetric stretch in PVA may cause $\mathrm{O}-\mathrm{H}$ out of plane bending vibrations both in PVA and $\mathrm{H}_{2} \mathrm{O}$ molecules. As in the case of PVA- $\mathrm{H}_{2} \mathrm{O}$ system, the critical range for the changes observed in PVA-DMSO system lies in the region, from $1422-1455 \mathrm{~cm}^{-1}$. There occurs a blue shift and spiltting of doublet peak at $1441-1422 \mathrm{~cm}^{-1}$, to multiplet $1425-1455 \mathrm{~cm}^{-1}$ from $100^{\circ} \mathrm{C}-125^{\circ} \mathrm{C}$. After this critical temperature, the structural changes are recovered as reflecting from the curve , peak position at $1422 \mathrm{~cm}^{-1}$.

In the etherial group region of PVA, there occurs a slight red shift in the peak from 1088 to $1086 \mathrm{~cm}^{-1}$ indicating a slight increase in the bond length at $100^{\circ} \mathrm{C}-125^{\circ} \mathrm{C}$ range and a little blue shift of peak $1020 \mathrm{~cm}^{-1}$ to $1024 \mathrm{~cm}^{-1}$. This peak not only matches with the theoretical evidence for PVA-DMSO interactions but also matches with that for the PVA- $\mathrm{H}_{2} \mathrm{O}$ interactions, indicating the presence of some moisture along with DMSO and PVA inside the membrane matrices.

In this system, the peak at $1419.42 \mathrm{~cm}^{-1}$ shows a peculier characteristic. It gives a multiplet $\left(1396 \mathrm{~cm}^{-1}, 1416 \mathrm{~cm}^{-1}, 1432 \mathrm{~cm}^{-}\right.$ ${ }^{1}, 1456 \mathrm{~cm}^{-1}$ and $1474 \mathrm{~cm}^{-1}$ ) along with blue shift at specific temperature $125^{\circ} \mathrm{C}$. This behavior is not observed in the spectra taken at the temperatures above or below it. This peculiarity in the case of DMF may be attributed to the fact that, in case of DMF the functional group is an amide group, while in DMSO, sulphoxide group is there. Since the electro-negativity of nitrogen is much higher than sulphur, the polarity in DMF molecule is higher as reflected from their dipole moment values. Moreover, the polarity increases almost three times in its tetrameric structure, therefore, the structure of PVA dissolved in DMF is more stable with respect to $\mathrm{H}_{2} \mathrm{O}$ and DMSO. DMF as a solvent molecule coalesces with PVA during the formation of the membrane and also found inside the membrane in spite of the application of high temperature.

## Raman Study of PVA Membranes

The Raman spectra of PVA membrane in $\mathrm{H}_{2} \mathrm{O}$, PVA membrane in DMSO and PVA membrane in DMF at room temperature as well as $200^{\circ} \mathrm{C}$ (annealing temperature) are shown in Fig. 7. The main peaks obtained theoretically and experimentally in PVA powder is given in Table 6 and different membranes are summarized in Table 7, 8 and 9 respectively. Membrane developed in $\mathrm{H}_{2} \mathrm{O}$, at room temperature, the band at $1425.25 \mathrm{~cm}^{-1}$ is precisely similar to the theoretical peak $\left(1425.89 \mathrm{~cm}^{-1}\right.$ for PVA- $\mathrm{H}_{2} \mathrm{O}$ tetramer) and shifts to $1446.16 \mathrm{~cm}^{-1}$ at $200^{\circ} \mathrm{C}$. This peak represents the vibrations of $\mathrm{H}_{2} \mathrm{O}(\mathrm{O}-\mathrm{H}$ bending) accompanying with PVA, indicating the presence of $\mathrm{H}_{2} \mathrm{O}$ in the PVA membrane. The peak at $1276.13 \mathrm{~cm}^{-1}$, is closer to the theoretical Raman shift for the dimer configuration of PVA ( $1283.50 \mathrm{~cm}^{-1}$ represents the vibrations of PVA, disappears at the higher temperature.

The bands at $729.80 \mathrm{~cm}^{-1}, 846.84 \mathrm{~cm}^{-1}$, and $992.29 \mathrm{~cm}^{-1}$ represent the vibrations of PVA, which are absent in the annealed membrane. After annealing the membrane, a bulk structure is formed due to the cross-linking of the polymer chain. The bulk structure acquires a relatively high isotropic conductivity, and its polarizability is virtually dependent on poorly bound electrons. Due to this fact, some of the Raman bands existing at room temperature disappear at ambient temperature. At room temperature, the Raman band at $1162.93 \mathrm{~cm}^{-1}$ is similar to the theoretical band at $1168.16 \mathrm{~cm}^{-1}$ represents $\mathrm{C}-\mathrm{O}$ stretch, $\mathrm{CH}_{2}$ in-plane rocking and $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA along with the $\mathrm{O}-\mathrm{H}$ out of plane bending in $\mathrm{H}_{2} \mathrm{O}$ molecules. After annealing the membrane at $200^{\circ} \mathrm{C}$, this peak slightly shifts toward the higher wave number at $1166 \mathrm{~cm}^{-1}$, confirming the existence of $\mathrm{H}_{2} \mathrm{O}$ inside the PVA membrane. A new band is observed at 891 $\mathrm{cm}^{-1}$, due to the partial thermal decomposition of the polymeric membrane during annealing [29]. The peak at $895.43 \mathrm{~cm}^{-1}$ represents the $0-\mathrm{H}$ out of plane bending vibration of both PVA and $\mathrm{H}_{2} \mathrm{O}$ molecules, which assures the probable interaction between $\mathrm{H}_{2} \mathrm{O}$ and PVA indicates the presence of $\mathrm{H}_{2} \mathrm{O}$ as solvent inside the PVA membrane. The Raman band at $614 \mathrm{~cm}^{-1}$ (at RT) shifts to $608.27 \mathrm{~cm}^{-1}$ after the heating process. Due to heating, the peak at $444 \mathrm{~cm}^{-1}$ shifts to $439.16 \mathrm{~cm}^{-1}$, at $287.04 \mathrm{~cm}^{-1}$ changed to $284.84 \mathrm{~cm}^{-1}$ and at $210.06 \mathrm{~cm}^{-1}$ to $208.91 \mathrm{~cm}^{-1}$ respectively due to $0-\mathrm{H}$ interactions between $\mathrm{H}_{2} \mathrm{O}$ and PVA molecules. In the membrane developed in DMSO, most of the Raman peaks are at the same position at room temperature and high temperatures. The band at $1463.32 \mathrm{~cm}^{-1}$ representing DMSO's vibration in association with PVA is absent at high temperatures. After annealing some band shifts to lower wave number side represent the vibrations of DMSO in accompany with the vibrations of PVA. However, the Raman band at $732.29 \mathrm{~cm}^{-1}$ represents the vibration of PVA, which disappears at high temperatures. The Raman bands at


Figure-7 Raman spectra of PVA membrane in different solvents at room temperature and annealed mple at $200^{\circ} \mathrm{C}$
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Figure-8 XRD pattern (range $15^{\circ}-45^{\circ}$ ) of PVA membrane in different solvents at room temperature. 572.23 and $594.34 \mathrm{~cm}^{-1}$ represent DMSO's vibrations that shift at $511.54 \mathrm{~cm}^{-1}$ after annealing the membrane at the higher temperature.

The band at $511.54 \mathrm{~cm}^{-1}$, which generally represents DMSO's vibrations, may also influence the PVA to vibrate weakly. This band shifts to $390 \mathrm{~cm}^{-1}$ on increasing the temperature of the membrane at $200^{\circ} \mathrm{C}$, which relates to DMSO's vibrations. The precise exploration of the Raman bands of the PVA-DMSO membrane indicates DMSO's existence inside the membrane, despite the high temperature. This may be possible due to the strong interaction between PVA and DMSO during and after membrane formation. So, it can be inferred that it is difficult to complete removal of DMSO molecules from the PVA polymeric membrane even at $200^{\circ} \mathrm{C}$ heating.

The Raman spectra of PVA membrane developed in DMF shows the Raman bands at $177.39 \mathrm{~cm}^{-1}$, $231.41 \mathrm{~cm}^{-1}, 296.82 \mathrm{~cm}^{-1}, 467.99 \mathrm{~cm}^{-1}, 704.03$ $\mathrm{cm}^{-1}, 895.13 \mathrm{~cm}^{-1}, 982.30 \mathrm{~cm}^{-1}, 1099.09 \mathrm{~cm}^{-1}$, $1406.67 \mathrm{~cm}^{-1}$, and $1506.87 \mathrm{~cm}^{-1}$ respectively. At higher annealing temperature, some bands shift or disappear.

The band at room temperature at $213.41 \mathrm{~cm}^{-1}$ is shifted to $200.48 \mathrm{~cm}^{-1}$ at a higher temperature to represent the vibrations of DMF. It indicates the presence of DMF in the PVA membrane after annealing. Another band at $177.39 \mathrm{~cm}^{-1}$ is shifted to 226.55 $\mathrm{cm}^{-1}$ at a higher temperature to show simultaneous vibrations of both the DMF and PVA. The bands at 296.82 and $1506.87 \mathrm{~cm}^{-}$ ${ }^{1}$ are analogous to the theoretical peaks at $296.83 \mathrm{~cm}^{-1}$ and $1504.80 \mathrm{~cm}^{-1}$ for the tetramer configuration of PVA-DMF represent only the vibrations of DMF. The experimental band at $467.99 \mathrm{~cm}^{-1}$ indicates the existence of $\mathrm{H}_{2} \mathrm{O}$ that may come from ambient during or after the formation of the PVA membrane at room temperature. After annealing the membrane at $200^{\circ} \mathrm{C}$, this band disappears, indicating the removal of external $\mathrm{H}_{2} \mathrm{O}$ molecules that are loosely bound in the PVA membrane. At room temperature, there exist two bands at 895.13 and $982.30 \mathrm{~cm}^{-1}$, respectively, representing the vibrations of PVA. These bands remain absent after increasing the temperature of the membrane to $200^{\circ} \mathrm{C}$. At $200^{\circ} \mathrm{C}$, the experimental Raman bands at 448 $\mathrm{cm}^{-1}, 848 \mathrm{~cm}^{-1}$, and $596 \mathrm{~cm}^{-1}$ are similar to the theoretical peaks for PVA membrane in DMF. These bands imply the presence of partial DMF solvent in the PVA membrane even after the thermal treatment.

## XRD Study of PVA Powder and Membrane

The XRD pattern of PVA powder and membranes developed in various solvents viz. $\mathrm{H}_{2} \mathrm{O}$, DMSO and DMF are shown in Fig. 8. The characteristic peaks of PVA powder is $19.35^{\circ}, 22.5^{\circ}$ and $40.42^{\circ}$. The first two peaks show the semicrystalline and last show the amorphous nature of Polyvinyl alcohol [30]. The XRD pattern of PVA membrane synthesized by the phase inversion technique with different solvents at various annealing temperature are shown in Fig. 9, Fig. 10, Fig. 11 respectively, the main peaks position shifts at $2 \theta=19.61^{\circ}$ and $22.55^{\circ}-22.80^{\circ}$. A comparative study of these two peaks infer that peak at $2 \theta=19.61^{\circ}$ has higher intensity than the $2 \theta=22.55^{\circ}$ due to slow evaporation rate of water and DMSO from PVA matrix.

Some solvent gets trapped in the matrix and makes it swell. But in the case of DMF based membrane, this difference is very low because of the fast evaporation rate of solvent and making the membrane maximum/fully solvent free. In all the three cases, the peak height of two peaks at $2 \theta=19.61^{\circ}$ and $22.6^{\circ}$ continuously increases upto $100^{\circ} \mathrm{C}$. This increase is plausibly due to the added swelling of lattice and resulting in the increase in their bond lengths. Jamil et.al [31] reporting on the thermal study of PVA shows the endothermic nature of heat flow in PVA (temperature range $90-150{ }^{\circ} \mathrm{C}$ ) and minimum at $125-130{ }^{\circ} \mathrm{C}$. But the peak at $40.36^{\circ}$ fully vanishes in all cases.

Some Important facts are observed at $125^{\circ} \mathrm{C}$ XRD pattern as :
(i) The increase in the broadness of both the peaks at $2 \theta=19.61^{\circ}$ and $22.6^{\circ}$ means amorphosity of membrane increased;

In the water base membrane the height of $2 \theta=19.6^{\circ}$ decreases (crystallinity decreases $\sim 25 \%$ ) and height and broadness of $2 \theta=22.6^{\circ}$ increases. The amorphous peak at
 $40.35^{\circ}$ splits in a doublet ( $40.23^{\circ}$ and $43.17^{\circ}$ ). In the membrane developed in DMSO the height of $2 \theta=19.87^{\circ}$ decreased rapidly at $100^{\circ} \mathrm{C}$ and the second peak either remained the same or slightly grew. The peak at $2 \theta=40.6^{\circ}$ disappeared completely.
(ii) This is due to the swelling of PVA matrix and slight change in bonding pattern of $\mathrm{CH}_{2}$ group, ether group and CH phenyl group of PVA. This change is clearly observed in the IR spectra. At annealing temperature $200^{\circ} \mathrm{C}$, it tries to regain the lower temperature nature possibly due to the onset starting of melting.

In the case of DMF solvent, no such inversion in peaks is observed. but at $50^{\circ} \mathrm{C}$, the peak height of $2 \theta=19.61^{\circ}$ increased similarly to DMSO and $\mathrm{H}_{2} \mathrm{O}$ base membrane peak because the completely solvent free membrane based on DMF gets -OH from the ambient and results in the swelling of the membrane. Besides this, the solvent-cast PVA membrane holds a little amount of bound water (comes from the ambient), which escapes during annealing the membrane between $90^{\circ} \mathrm{C}$ to $170^{\circ} \mathrm{C}$ [32].This bound water can play a vital role by controlling the membrane's crystalline nature in between that temperature range during annealing. The peaks reflect this phenomenon at $2 \theta=26.57^{\circ}$ and $30.92^{\circ}$ in the XRD pattern of the PVA membrane at $125^{\circ} \mathrm{C}$.

## Degree of Crystallinity of PVA Membranes

Degree of crystallinity of PVA powder and PVA membranes are calculated by FT-IR and XRD data. For the degree of crystallinity, from FTIR spectra, we use the following formula:

$$
\begin{equation*}
\alpha(\%)=b+a \times(\mathrm{Ac} / \mathrm{Ar}) \tag{1}
\end{equation*}
$$

Where $a$ and $b$ are two constants, reported by Tretinnikov et al.[33], such as $b=-13.1, a=89.5$. Also, Ac and Ar represent the intensity of the crystallinity band and reference band at $1144 \mathrm{~cm}^{-1}$ and $1094 \mathrm{~cm}^{-1}$, respectively, for the absorption peaks. However, in the present study, the peaks mentioned earlier are found around $1141 \mathrm{~cm}^{-1}$ and $1088 \mathrm{~cm}^{-1}$, respectively, and the calculated degree of crystallinity with the variation of temperature are shown in the Fig. 12.

From the deconvolution of the XRD patterns, it became easier to find the crystalline and amorphous peak individually. The polymeric membranes' amorphous nature can be understood by calculating the percentage of crystallinity from the respective XRD patterns by
the equation given below.

Where, $A_{c}$ represents the intensity of the peak that indicates the crystalline phase, and $A_{a}$ the intensity of the broad peak that indicates the amorphous phase [34]. The variation in the percentage of crystallinity of the PVA membranes developed in different solvents is also shown in Fig. 12.

The crystallinity in the membrane depends upon both the PVA-solvent interactions as well as the nature of the solvent and process of membrane development. The crystalline nature of the annealed membranes also varies with temperature. After annealing the membranes above $100^{\circ} \mathrm{C}$, both the plots from XRD patterns and FTIR spectra show similar nature at $125^{\circ} \mathrm{C}$. The crystallinity change with temperature plot (in both cases from IR and XRD spectra) shows an almost similar pattern. Initially, crystallinity increases and becomes constant up to $100^{\circ} \mathrm{C}$, showing an irregular pattern in the temperature range from $100^{\circ} \mathrm{C}$ to $170^{\circ} \mathrm{C}$. This irregular pattern is due to the crystalline relaxation of the polymer chain. At $125^{\circ} \mathrm{C}$, the characteristic crystalline peak of PVA becomes broader in the PVA in $\mathrm{H}_{2} \mathrm{O}$ membrane and sharper in the PVA-DMF membrane. In the intermediate, the PVA-DMSO membrane shows a peculiar phenomenon such that along with the broadening, it also alters the position of the characteristic crystalline peak. Broader the peak represents the increase in amorphous nature, and sharper the peak indicates an increase of crystalline nature. So, a phase change occurs at $125^{\circ} \mathrm{C}$, different nature is seen in the XRD pattern for different membranes constructed with different solvents, where the solvents remain trapped in the membranes and play a vital role by controlling crystalline and amorphous nature in the membranes.

## SEM Analysis of the Synthesized PVA Membranes Developed in Different Solvent



Figure-12: (a) Percentage crystallinity from XRD patterns, and (b) Degree of crystallinity from FTIR spectra of PVA membrane in different solvents with variation of annealing temperature.

Fig. 13 shows SEM images of PVA polymeric membrane developed in three different solvents. At room temperature, the membranes' surface morphologies are almost similar and nearly homogeneous in structure. As it is clear that PVA is a solvent swollen polymer [35], during the development of the membrane, the solvent goes inside the polymer and is trapped in the matrix (as evident from the earlier experimental result) and swells it. During the annealing process, the solvent evaporates from the matrix and makes spherulite (or fish scale-like) boundaries in the membrane.

The SEM images of the PVA membranes after annealing at high temperature shows the exciting fish scale-like structure, arranged symmetrically in case of $\mathrm{H}_{2} \mathrm{O}$, but in DMSO and DMF solvent, such symmetrical structure get destroyed, and the membranes start to crack, although , in case of DMF, only some part of the membrane shows similar structure prominently like as for $\mathrm{H}_{2} \mathrm{O}$. Furthermore, the fish scale-like structure helps the membrane to become more flexible [36].

It is the probable reason for the flexibility of the membrane without any crack despite higher annealing temperature. That is why the membrane, which is associated with the $\mathrm{H}_{2} \mathrm{O}$ solvent, does not face any cracking and provides more flexibility than DMSO and DMF, respectively. With DMF solvent, the membrane shows better symmetry in structural configuration than that for the DMSO solvent. The fish scale structure consists of a periodic pattern which states a uniform deformation during the bending of the membrane, as a result of which the membrane becomes flexible.

## Conclusions

Experimental and theoretical studies of FTIR infers the presence of $\mathrm{H}_{2} \mathrm{O}$ in PVA bonded with strong hydrogen bond at the one site as well as in the form of free water molecules in clustered form exist between the crystallites and amorphous regions in PVA respectively. The presence of crystallinity inside the structural configuration controls PVA's physico-mechanical properties. The interaction of PVA with various solvents to form a solution, hydrogen bonds predominantly play a vital role. Experimental studies showed the partial existence of solvent in the membrane. The crystallinity of membrane depends on the process of solvent's evaporation while in synthesis of membrane, solvent-polymer interaction strength between solvent molecules and the intermolecular or intramolecular hydrogen bonds of OH groups, which are associated with monomers in
 PVA have a significant impact. It may also control the elastic properties in PVA and helps to stabilize its structural configuration. The theoretical studies show that the isotropic polarizability exhibits higher values for PVA-DMSO and PVA-DMF configurations compared to PVA- $\mathrm{H}_{2} \mathrm{O}$ configuration. The SEM images also support the solvent evaporation process and show unique structural morphologies of the PVA polymeric membranes in different solvent based membrane at different annealing temperature.

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Figure-13: SEM images of PVA membrane developed in $\mathrm{H}_{2} \mathrm{O}$ : (a), (b), (c) at room temperature and (d), (e), (f) at $200^{\circ} \mathrm{C}$; PVA membrane developed in DMSO: (g), ( h$)$, (i) at room temperature and (j), ( k ), (l) at $200^{\circ} \mathrm{C}$; PVA membrane developed in DMF: ( m ), ( n$)$, (o) at room temperature and $(\mathrm{p})$, ( q$)$, ( r$)$ at $200^{\circ} \mathrm{C}$, with the magnifications 200x, 500x and 1000x for each set respectively.

## References

1. Badr YA, Abd El-Kader KM, Khafagy RM (2004) Raman Spectroscopic Study of CdS, PVA Composite Films. J of Applied Polymer Science 92: 1984-1992. https://doi.org/10.1002/app. 20017
2. Duman O, Uğurlu H, Diker C Ö, Tunç S. (2022) Highly hydrophobic and super oleophilic agar/PVA aerogels forselective removal of oily substances from water. Carbohydrate Polymers.286:119275 https://doi.org/10.1016/j.carbpol.2022.119275
3. Duman O, Uğurlu H, Diker C Ö, Tunç S. .(2022) Fabrication of highly hydrophobic or superhydrophobicelectrospun PVA and agar/PVA membrane materials for efficient and selective oil/water separation Journal of Environmental Chemical Engineering. 10:107405-107416. https://doi.org/10.1016/j.jece.2022.107405
4. Arai K, Okuzono M, Shikata T. (2015) Reason for the high solubility of chemically modified poly (vinyl alcohol)s in aqueous solution. Macromolecules. 48:1573-1578. https://doi.org/10.1021/ma502602r
5. Kafle, N., Makita, Y., Zheng, Y., Schwarz, D., Kurosu, H., Pan, P., Eagan J. M., Nakama Y, Hayano S, Miyoshi,T., T. (2021). Roles of Conformational Flexibility in the Crystallization of Stereo irregular Polymers. Macromolecules, 54, 5705-5718. DOI:10.1021/acs.macromol.1c00888
6. Ohgi, H.; Sato, T.; Hu, S.; Horii, F. (2006) Highly isotactic poly(vinyl alcohol) derived from tert-butyl vinyl ether. Part IV. Some physical properties, structure and hydrogen bonding of highly isotactic poly(vinyl alcohol) films. Polymer, 47, 1324-1332. https://doi.org/10.1016 /j.polymer. 2005.12.036
7. Takahashi N, Kanaya T, Nishida K, Kaji K (2007) Gelation-Induced Phase Separation of Poly(vinyl alcohol) in Mixed Solvents of Dimethyl Sulfoxide and Water. Macromolecules 40: 8750-8755. https://doi.org/ 10.1021/ma071256t
8. Rangasamy V S, Thayumanasundaram S, Locquet J P, (2019) Solid polymer electrolytes with poly(vinyl alcohol) and piperidinium based ionic liquid for Li-ion batteries. Solid state Ionics 333: 76-82. https://doi.org/10.1016/j.ssi.2019.01.024
9. Narasimhan B, Snaar J E M, Bowtell R W, Morgan S, Melia CD, Peppas N A. (1999) Magnetic resonance imaging analysis of molecular mobility during dissolution of poly(vinyl alcohol) in water. Macromolecules. 32:704-710. https://doi.org/10.1021/ma981382k
10. Jia E,Wang C, Su L, Liu P, Xu J (2015) Influence of water on polyvinyl alcohol sol-gel transition and gel spinning, J Polym Res 22:69-75, DOI 10.1007/s10965-015-0717-3
11. Hodge R M. (1996) Water absorption and states of water in sernicrystalline poly(vinyl alcohol) films. Polymer 37:1371-1376. https://doi.org/10.1016/0032-3861(96)81134-7
12. Galvao J, Davis B, Tilley M, Normando E, Duchen MR, Cordeiro MF. (2014) Unexpected low dose toxicity of the universal solvent DMSO. The FASEB J. 28:1317-1330. https://doi.org/10.1096/fj.13-235440
13. Catala'n J, Dı́az C, García-Blanco F. (2001) Characterization of Binary Solvent Mixtures of DMSO with Water and Other Cosolvents. J Org Chem. 66:5846-5852. https://doi.org/10.1021/jo010415i
14. Tacx J C J F, Schoffeleers H M, Brands A G M, Teuwen L. (2000) Dissolution behavior and solution properties of poly vinyl alcohol as determined by viscometry and light scattering in DMSO, ethylene glycol and water. Polymer. 41:947957. https://doi.org/10.1016/S0032-3861(99)00220-7
15. Mc Garry PF, Jockusch S, Fujiwara Y, Kaprinidis NA, Turro N J.(1997) DMSO Solvent induced photochemistry in highly photo stable compounds. The role of intermolecular hydrogen bonding. J Phys Chem A. 101:764-767. https://doi.org/10.1021 / jp961382r
16. Xua A, Cao L, Wang B. (2015) Facile cellulose dissolution without heating in [ $\mathrm{C}_{4 \mathrm{mim}}$ ] [ $\left.\mathrm{CH}_{3} \mathrm{COO}\right] /$ DMF solvent. Carbohyd Poly. 125:249-254.

DOI: 10.1016/ j.carbpol.2015.02.045
17. Roy Chowdhury S, Roy P S, Bhattacharya S K. (2018) Room temperature synthesis of poly vinyl alcohol stabilized palladium nanoparticles: Solvent effect on shape and electro-catalytic activity. Nano Struc Nano Obj. 14:11-18. https://doi.org/ 10.1016/ j.nanoso. 2018.01.004
18. Melad O, Romiya M. (2015) Effect of Solvent on the Compatibility of Polyvinyl Alcohol and Poly methyl methacrylate by Dilute Solution Viscometry Method. Polymer Sci Ser A. 57:622-627. https://doi.org/10.1134/S0965545X15050144
19. Frisch MJ, Trucks GW, et al (2009) Gaussian 09, Revision A. 02.
20. Lee C, Yang W, Parr R G. (1988) Development of the Colle-Salvetti correlation-energy formula in to a functional of the electron density. Phys Rev B. 37:785-789.

DOI:10.1103/physrevb. 37.785
21. Becke AD. (1993) Density-functional thermo chemistry. III. The role of exact exchange. J Chem Phys. 98:5648-5652. https://doi.org/10.1063/1.464913
22. Hay P J, Wadt W R. (1985) Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J Chem Phys. 82: 299-310. https://doi.org/10.1063/1.448975
23. Hariharan P C, Pople J A. (1973) The influence of polarization functions on molecular orbital hydrogenation energies. Theo Chim Acta. 28:213-222. https://doi.org/10.1007 / BF00533485
24. Gordon MS. (1980) The isomers of silacyclopropane. Chem Phys Lett. 76:163-168. https://doi.org/10.1016/0009-2614(80)80628-2
25. Hariharan P C, Pople J. (1974) Accuracy of AH n equilibrium geometries by single determinant molecular orbital theory. Mol Phys. 27:209-214. https://doi.org/10.1080/ 00268977400100171
26. Hehre W J, Ditchfield R, Pople J A.(1972) Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J Chem Phys. 56:2257-2261. https://doi.org/10.1063/1.1677527
27. Ditchfield R, HehreW J, Pople J A. (1971)Self- Consistent Molecular- Orbital Methods. IX. An Extended Gaussian- Type Basis for Molecular- Orbital Studies of Organic Molecules. J Chem Phys. 54:724-728. https://doi.org/10.1063/1.1674902
28. Shinyashiki N., Shimomura M., Ushiyama T., Miyagawa T., Yagihara S. (2007) Dynamics of Water in Partially Crystallized Polymer/Water Mixtures Studied by Dielectric Spectroscopy. J. Phys. Chem. B.111:10079-10087. DOI: 10.1021/jp0730489.
29. Prosanov I Y, Matvienko A A. (2010) Study of PVA thermal destruction by means of IR and Raman Spectroscopy. Phys Sol Stat.52:2203-2206. https://doi.org/10.1134/ S1063783410100318
30. Aziz S.B., Modifying Poly(Vinyl Alcohol) (PVA) from Insulator to Small-Bandgap Polymer: A Novel Approach for Organic Solar Cells and Optoelectronic Devices J. Electron. Mater 2016,45,736-745. https://doi.org/ 10.1007/s11664-015-4191-9
31. Jamil N., Husin H., Alfid A.W., Aman Z and Hassan Z, (2018) Characterization and Preparation of Polyvinyl Alcohol (PVA) as Inhibitor in Formation of Hydrates, nt. J. Cur. Res. Eng. Sci. Tech. 1:578-584, DOI:10.30967/ijcrset.1.S1.2018.578-584
32. Thomas D, Cebe P. (2017)Self-nucleation and crystallization of polyvinyl alcohol. J Therm Anal Calorim. 127:885-894. doi:10.1007/s10973-016-5811-1
33. Tretinnikov 0 N, Zagorskaya S A. (2012) Determination of the degree of crystallinity of poly(vinyl alcohol) by FTIR spectroscopy. J Appl Spectro. 79:521-526. https:// doi.org/10.1007/s10812-012-9634-y
34. Gaidukov S, Danilenko I, Gaidukova G. (2015) Characterization of strong and crystalline polyvinyl alcohol/montmorillonite films prepared by layer-by-layer deposition method. Int J Poly Sci. 123469:1-8. https://doi.org/10.1155/2015/123469
35. Kamemaru K, Usui S, Harishima Y, Suzuki A. (2018) Irreversible Swelling behavior and reversible hysteresis in chemically cross linked poly(vinyl alcohol) gels. Gels 4, 45 (9p ages); doi:10.3390/gels4020045
36. Ehrlich, H. (2015). Materials Design Principles of Fish Scales and Armor, in Biological Materials of Marine Origin,237262. doi: 10.1007/978-94-007-5730-1_5.


Table 1: Various theoretical (calculated) parameters of PVA powder and membranes.

| Physical Parameter | Molecular configuration of PVA |  |  |  | Molecular configuration of PVA-$\mathrm{H}_{2} \mathrm{O}$ |  |  |  | Molecular configuration of PVADMSO |  |  |  | Molecular configuration of PVADMF |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Monom er | $\begin{array}{\|l\|} \hline \text { Dime } \\ \mathrm{r} \\ \hline \end{array}$ | $\begin{array}{\|l} \hline \text { Trim } \\ \text { er } \\ \hline \end{array}$ | $\begin{array}{\|l} \left\lvert\, \begin{array}{l} \text { Tetram } \\ \text { er } \end{array}\right. \\ \hline \end{array}$ | Monom er | Dimer | Trimer | Tetram er | Monom er | Dimer | $\begin{array}{\|l} \hline \text { Trime } \\ \mathrm{r} \\ \hline \end{array}$ | Tetram er | Monom er | $\begin{array}{\|l\|} \hline \text { Dime } \\ \mathrm{r} \\ \hline \end{array}$ | $\begin{array}{\|l\|} \hline \text { Trime } \\ \mathrm{r} \\ \hline \end{array}$ | Tetram er |
| Total Energy (a.u.) | -153.82 | $307.6$ | \|461.4 | -615.33 | -230.26 | -460.55 | -690.83 | -921.12 | -707.02 | $\begin{array}{\|l\|} \hline- \\ 1414.0 \\ 6 \end{array}$ | $2121.1$ | $\left\lvert\, \begin{aligned} & 2828.1 \\ & 6 \end{aligned}\right.$ | -402.36 | $\begin{array}{\|l\|} \hline- \\ 804.7 \\ 3 \\ \hline \end{array}$ | $\left[\begin{array}{l} - \\ 1207.1 \\ 1 \end{array}\right.$ | $\left\lvert\, \begin{aligned} & 1609.1 \\ & 8 \end{aligned}\right.$ |
| Dipole moment (Debey) | 1.13 | 3.17 | 0.12 | 0.02 | 4.97 | 1.41 | 0.94 | 1.14 | 5.20 | 2.97 | 5.09 | 2.82 | 6.00 | 0.169 | 4.96 | 17.47 |
| Isotropic polarizabil ity | 30.35 | 62.84 | 97.85 | 131.22 | 40.71 | 83.59 | 124.23 | 168.37 | 86.90 | 174.50 | 262.95 | 351.39 | 83.05 | $\begin{aligned} & 165.4 \\ & 2 \end{aligned}$ | 250.14 | 288.57 |
| $\begin{aligned} & \text { Enthalpy } \\ & \text { (a.u.) } \\ & \hline \end{aligned}$ | 0.0600 | $\begin{array}{\|l\|} \hline 0.124 \\ 0 \\ \hline \end{array}$ | 0.186 | 0.2494 | $\begin{aligned} & \hline 0.0883 \\ & 8 \\ & \hline \end{aligned}$ | $\begin{array}{\|l\|} \hline 0.1783 \\ 46 \\ \hline \end{array}$ | $\begin{array}{\|l\|} \hline 0.2685 \\ 28 \\ \hline \end{array}$ | $\begin{array}{\|l\|} \hline 0.3575 \\ 79 \\ \hline \end{array}$ | 0.1474 | 0.2979 | 0.4463 | 0.5983 | 0.1724 | $\begin{array}{\|l} \hline 0.347 \\ 2 \\ \hline \end{array}$ | 0.5218 | 0.6912 |
| Gibbs energy (a.u.) | 0.031 | $\begin{aligned} & 0.809 \\ & 9 \end{aligned}$ | 0.131 | 0.1836 | $\begin{aligned} & 0.0509 \\ & 4 \end{aligned}$ | $\begin{aligned} & \hline 0.1254 \\ & 89 \end{aligned}$ | $\begin{aligned} & \hline 0.2005 \\ & 96 \end{aligned}$ | $\begin{aligned} & \hline 0.2708 \\ & 80 \end{aligned}$ | 0.1005 | 0.2240 | 0.3439 | 0.4651 | 0.1235 | $\begin{aligned} & 0.268 \\ & 5 \end{aligned}$ | 0.4129 | 0.5626 |
| Entropy (Cal/molK) | 60.96 | 90.61 | $\begin{aligned} & 116.3 \\ & 7 \end{aligned}$ | 138.46 | 78.81 | $\begin{aligned} & 111.24 \\ & 7 \end{aligned}$ | 142.97 | 182.47 | 98.68 | 154.93 | 215.32 | 280.36 | 102.90 | $\begin{aligned} & 165.4 \\ & 6 \end{aligned}$ | 229.14 | 270.83 |
| Thermal Energy (Kcal/mol) | 37.54 | 77.24 | $\begin{aligned} & 116.6 \\ & 9 \end{aligned}$ | 155.92 | 54.87 | $\begin{aligned} & 111.32 \\ & 1 \end{aligned}$ | 167.91 | 223.79 | 91.92 | 186.16 | 279.46 | 374.90 | 107.61 | $\begin{aligned} & 217.2 \\ & 8 \end{aligned}$ | 326.88 | 433.19 |
| Specific Heat (Cal/molK) | 11.35 | 27.64 | 42.98 | 57.77 | 21.03 | 42.50 | 65.18 | 86.54 | 36.04 | 77.14 | 118.44 | 158.39 | 36.07 | 77.39 | 118.53 | 152.75 |
| Zero point energy (a.u.) | 0.056 | $\begin{aligned} & \hline 0.114 \\ & 7 \end{aligned}$ | 0.173 | 0.2311 | $\begin{aligned} & 0.0807 \\ & 84 \end{aligned}$ | $\begin{aligned} & 0.1648 \\ & 83 \end{aligned}$ | $\begin{aligned} & \hline 0.2485 \\ & 88 \end{aligned}$ | $\begin{array}{\|l\|} \hline 0.3309 \\ 58 \end{array}$ | 0.1360 | 0.2745 | 0.4109 | 0.5507 | 0.1606 | $\begin{aligned} & \hline 0.323 \\ & 0 \end{aligned}$ | 0.4851 | 0.6456 |

Table 2: Comparison of experimental and theoretically calculated IR peaks with their assignments of PVA powder at room temperature.

| Theoretical IR peak position of PVA Powder | Experimental IR peak position of PVA powder | Assignments |
| :---: | :---: | :---: |
| 3666.13 | - | O-H stretching |
| 3273.56 | 3285.60 | $\mathrm{H}-\mathrm{C}-\mathrm{H}$ asymmetric stretching, $\mathrm{C}-\mathrm{H}$ stretching |
| $2902.32$ | $\begin{aligned} & \hline 2935.68 \\ & 2909.69 \end{aligned}$ | O-H stretching |
| $\begin{aligned} & \hline 1705.00 \\ & 1683.11 \\ & \hline \end{aligned}$ | $\begin{aligned} & 1717.01 \\ & 1653.74 \\ & \hline \end{aligned}$ | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bend, $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching |
| 1527.54 | 1564.31 | $\mathrm{CH}_{2}$ in-plane scissoring, O-H in-plane bend. |
| 1410.38 | 1422.09 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bend. |
| 1389.64 | 1371.15 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{O}-\mathrm{H}$ and $\mathrm{C}-\mathrm{H}$ in-plane bend, $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching. |
| 1334.34 | 1325.19 | C-H in-plane bend, $\mathrm{C}=\mathrm{C}$ stretching. |
| - | 1241.23 | Presence of external $\mathrm{H}_{2} \mathrm{O}$ molecules in PVA. |
| 1136.67 | 1134.31 | $\mathrm{C}-\mathrm{O}$ stretching, $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{O}-\mathrm{H}$ in-plane bend. |
| - | 1085.03 | Presence of external $\mathrm{H}_{2} \mathrm{O}$ molecules that influences PVA into several vibrations. |
| $\begin{aligned} & 1025.46 \\ & 1021.63 \\ & \hline \end{aligned}$ | 1023.00 | $\mathrm{O}-\mathrm{H}$ and C-H out of plane bending, $\mathrm{CH}_{2}$ out of plane twisting. |
| 929.81 | 942.43 | $\mathrm{CH}_{2}$ in-plane rocking, C-H in-plane bending, $\mathrm{C}-\mathrm{O}$ stretching. |
| 859.54 | 834.61 | $\mathrm{CH}_{2}$ out of plane wagging in PVA. |

Table 3: The IR peaks and their assignments of PVA membrane synthesised in $\mathrm{H}_{2} \mathrm{O}$ at different temperatures.

| Theoretical Peaks of PVA membrane (in $\mathrm{cm}^{-1}$ ) | Experimental Peaks of PVA membrane synthesised in $\mathrm{H}_{2} \mathrm{O}$ (in $\mathrm{cm}^{-1}$ ) |  |  |  |  |  | Assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| RT | RT | $50^{\circ} \mathrm{C}$ | $100^{\circ} \mathrm{C}$ | $125^{\circ} \mathrm{C}$ | $150^{\circ} \mathrm{C}$ | $200^{\circ} \mathrm{C}$ |  |
| 3824.95 | - | - | - | $\begin{aligned} & \hline 3858.53 \\ & 3844.18 \end{aligned}$ | $\begin{aligned} & 3858.89 \\ & 3844.08 \end{aligned}$ | $\begin{aligned} & \hline 3858.47 \\ & 3844.05 \end{aligned}$ | $\mathrm{O}-\mathrm{H}$ stretch in $\mathrm{H}_{2} \mathrm{O}$ |
| 3771.76 | - | - | 3742.18 | 3742.08 | 3742.08 | 3742.08 | O-H stretch in $\mathrm{H}_{2} \mathrm{O}$ |
| 3272.88 | 3285.27 | 3283.35 | 3292.47 | 3294.82 | 3294.71 | 3305.21 | H-C-H asymmetric stretch, C-H stretch in PVA |
| 2938.55 | 2935.70 2912.37 | $\begin{aligned} & 2933.62 \\ & 291307 \end{aligned}$ | 2934.05 <br> 2911.63 | 2934.00 2911.05 | $\begin{aligned} & 2933.79 \\ & 2909.67 \end{aligned}$ | $\begin{aligned} & \hline 2934.08 \\ & 2909.56 \end{aligned}$ | O-H stretch in PVA, O-H stretch in $\mathrm{H}_{2} \mathrm{O}$ |
| ${ }^{-}$ | 2094.46 | 2090.51 | 2084.75 | 2090.39 | $\begin{aligned} & 2086.40 \\ & 2065.38 \\ & \hline \end{aligned}$ | $\begin{aligned} & 2088.84 \\ & 2067.54 \\ & \hline \end{aligned}$ | O-H stretch in PVA, $\mathrm{H}_{2} \mathrm{O}$ in-plane scissoring |
| 1752.02 | 1728.46 | 1729.08 | 1730.25 | 1732.27 | 1732.071 | 1730.73 | $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching, $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ inplane bending in PVA |
| 1672.09 | 1655.13 | 1656.14 | - | 1652.50 | 1652.29 | 1651.15 | $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching, $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ inplane bending in PVA, $\mathrm{H}-\mathrm{O}-\mathrm{H}$ in-plane scissoring in $\mathrm{H}_{2} \mathrm{O}$. |
| 1597.09 |  |  |  |  |  |  | $\mathrm{H}-\mathrm{O}-\mathrm{H}$ in-plane scissoring in $\mathrm{H}_{2} \mathrm{O}$ |
| $\begin{aligned} & 1574.76 \\ & 1509.08 \\ & \hline \end{aligned}$ | 1567.09 | 1564.47 | 1560.75 | $\begin{aligned} & 1540.60 \\ & 1514.01 \\ & \hline \end{aligned}$ | $\begin{aligned} & 1542.27 \\ & 1514.05 \\ & \hline \end{aligned}$ | $\begin{aligned} & 1541.97 \\ & 1514.01 \\ & \hline \end{aligned}$ | O-H in-plane bending, weak $\mathrm{CH}_{2}$ in-plane scissoring and C-H in-plane bending, weak $\mathrm{C}=\mathrm{C}$ stretch in PVA. $\mathrm{H}-\mathrm{O}-\mathrm{H}$ in-plane scissoring in $\mathrm{H}_{2} \mathrm{O}$. |
| 1425.89 | 1421.60 | 1423.65 | 1425.04 | 1425.26 | 1425.58 | 1425.12 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. Weak $\mathrm{O}-\mathrm{H}$ bending in $\mathrm{H}_{2} \mathrm{O}$. |
| 1397.86 | 1371.31 | 1371.14 | 1371.14 | 1371.08 | 1371.06 | 1371.11 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{C}=\mathrm{C}$ and $\mathrm{C}-\mathrm{O}$ stretching in PVA. |
| 1251.78 | 1242.50 | 1240.54 | 1239.56 | 1240.11 | 1239.91 | 1239.53 | $\mathrm{O}-\mathrm{H}$ out of plane bending in $\mathrm{H}_{2} \mathrm{O}$ molecules. $\mathrm{O}-\mathrm{H}$ out of plane bending in PVA. |
| 1071.06 | 1087.56 | 1085.52 | 1085.47 | 1085.72 | 1085.55 | 1086.31 | O-H out of plane bending both in $\mathrm{H}_{2} \mathrm{O}$ and PVA. |
| 1003.65 | 1020.20 | 1022.22 | 1024.27 | 1024.23 | 1024.22 | 1024.29 | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ out of plane bending, $\mathrm{CH}_{2}$ out of plane twisting in PVA. |
| 949.65 | 946.69 | 944.74 | 942.72 | 942.89 | 942.77 | 942.77 | $\mathrm{CH}_{2}$ in-plane rocking, C-H in-plane bending, C-O stretching in PVA. |
| 852.82 | 840.65 | 840.60 | 840.61 | 839.78 | 840.69 | 840.91 | $\mathrm{CH}_{2}$ out of plane wagging in PVA |

Table 4: The IR peaks and their assignments of PVA membrane synthesised in DMSO at different temperature.

| Theoretical peak of PVA membrane (in | Experimental Peaks of PVA membrane synthesised in DMSO (in $\mathrm{cm}^{-1}$ ) |  |  |  |  |  | Assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| RT | RT | $50^{\circ} \mathrm{C}$ | $100^{\circ} \mathrm{C}$ | $125^{\circ} \mathrm{C}$ | $150^{\circ} \mathrm{C}$ | $200^{\circ} \mathrm{C}$ |  |
|  |  | $\begin{aligned} & 3858.66 \\ & 3844.31 \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline 3858.51 \\ & 3844.31 \\ & \hline \end{aligned}$ | - | - | $\begin{aligned} & 3858.66 \\ & 3844.31 \end{aligned}$ | O-H stretch in external $\mathrm{H}_{2} \mathrm{O}$. (Presence of external $\mathrm{H}_{2} \mathrm{O}$ ) |
|  |  | 3741.51 | 3742.00 | - | 3784.29 | 3741.51 | $\mathrm{O}-\mathrm{H}$ stretch in $\mathrm{H}_{2} \mathrm{O}$. (Presence of external $\mathrm{H}_{2} \mathrm{O}$ ) |
| 3273.70 | 3286.41 | 3300.45 | 3283.14 | 3286.85 | 3292.55 | 3300.45 | $\mathrm{H}-\mathrm{C}-\mathrm{H}$ asymmetric stretching and C-H stretching in PVA. |
| 3011.99 | $\begin{aligned} & 2935.96 \\ & 2913.94 \end{aligned}$ | $\begin{aligned} & 2934.29 \\ & 2912.57 \end{aligned}$ | $\begin{aligned} & 2934.31 \\ & 2910.19 \end{aligned}$ | $\begin{aligned} & 2933.29 \\ & 2910.62 \end{aligned}$ | $\begin{aligned} & 2931.92 \\ & 2909.78 \end{aligned}$ | $\begin{aligned} & 2934.29 \\ & 2912.57 \end{aligned}$ | O-H stretch in PVA, O-H stretch in external $\mathrm{H}_{2} \mathrm{O}$. |
| 2803.23 | - | 2856.32 | - | - | - | 2856.32 | O-H stretching in PVA. |
| - | - | $\begin{aligned} & \hline 2356.93 \\ & 2318.62 \end{aligned}$ | $\begin{aligned} & \hline 2369.35 \\ & 2320.70 \end{aligned}$ | - | $\begin{aligned} & \hline 2359.30 \\ & 2326.80 \end{aligned}$ | $\begin{aligned} & \hline 2356.93 \\ & 2318.62 \end{aligned}$ | O-H stretching in PVA. <br> $\mathrm{H}-\mathrm{O}-\mathrm{H}$ symmetric stretch in $\mathrm{H}_{2} \mathrm{O}$. |
| 2342.17 | 2341.04 |  |  |  |  |  | $\mathrm{H}-\mathrm{C}-\mathrm{H}$ asymmetric stretching and C-H stretching in PVA. |
| $\begin{aligned} & 1700.86 \\ & 1676.95 \end{aligned}$ | $\begin{aligned} & 1726.11 \\ & 1658.83 \end{aligned}$ | $\begin{aligned} & 1714.64 \\ & 1650.59 \end{aligned}$ | $\begin{aligned} & 1731.01 \\ & 1650.71 \end{aligned}$ | 1717.92 | $1715.38$ | $\begin{aligned} & 1714.64 \\ & 1650.59 \end{aligned}$ | $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching, $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. |
| 1519.73 | 1568.47 | $\begin{aligned} & 1538.71 \\ & 1514.66 \end{aligned}$ | $\begin{aligned} & 1540.93 \\ & 1515.85 \\ & \hline \end{aligned}$ | - | 1588.74 | $\begin{aligned} & 1538.71 \\ & 1514.66 \\ & \hline \end{aligned}$ | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}=\mathrm{C}$ stretch in PVA. $\mathrm{H}-\mathrm{O}-$ H in-plane scissoring inexternal $\mathrm{H}_{2} \mathrm{O}$. |
| 1409.60 | 1422.42 | 1423.92 | 1425.23 | 1424.42 | 1421.83 | 1423.92 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. Weak $\mathrm{O}-\mathrm{H}$ bending in external $\mathrm{H}_{2} \mathrm{O}$. |
| 1382.02 | 1371.89 | 1371.00 | 1371.20 | 1371.53 | 1373.09 | 1371.00 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching in PVA. |
| 1333.47 | 1325.69 | 1322.38 | 1322.24 | 1324.59 | 1325.04 | 1322.38 | C-H in-plane bending, $\mathrm{C}=\mathrm{C}$ stretch in PVA. |
| 1230.65 | 1242.19 | 1241.58 | 1240.33 | 1241.75 | 1243.47 | 1241.58 | $\mathrm{CH}_{2}$ out of plane twisting and $\mathrm{O}-\mathrm{H}$ out of plane bending in DMSO |
| 1138.34 | - | 1136.50 | 1133.74 | 1136.35 | 1136.35 | 1136.50 | $\mathrm{C}-\mathrm{O}$ stretch, $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. |
| 1065.30 | 1087.64 | 1087.37 | 1086.41 | 1086.84 | 1086.60 | 1087.37 | $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. <br> $\mathrm{O}-\mathrm{H}$ out of plane bending in external $\mathrm{H}_{2} \mathrm{O}$. |
| 1021.00 | 1020.31 | 1024.11 | 1024.18 | 1024.30 | 1025.59 | 1024.11 | $\mathrm{CH}_{2}$ out of plane twisting, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ out of plane bending in PVA. |
| $\begin{aligned} & 933.60 \\ & 930.19 \\ & \hline \end{aligned}$ | 946.81 | 943.17 | 943.99 | 943.08 | 941.61 | 943.17 | $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{C}-\mathrm{H}$ in-plane bending, $\mathrm{C}-\mathrm{O}$ stretch in PVA |
| 855.10 | 840.37 | 842.06 | 840.16 | 840.63 | 840.68 | 842.06 | $\mathrm{CH}_{2}$ out of plane wagging in PVA. |

Table 5: The IR peaks and their assignments of PVA membrane synthesised in DMF at different temperature.

| Theoretical peak of PVA membrane (in $\mathrm{cm}^{-1}$ ) | Experimental Peaks of PVA membrane synthesised in DMF (in |  |  |  |  |  | Assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| RT | RT | $50^{\circ} \mathrm{C}$ | $100^{\circ} \mathrm{C}$ | $125{ }^{\circ} \mathrm{C}$ | $150^{\circ} \mathrm{C}$ | $200^{\circ} \mathrm{C}$ |  |
|  | - | - | - | $\begin{aligned} & \hline 3858.37 \\ & 3843.85 \\ & \hline \end{aligned}$ | - | - | O-H stretch in external $\mathrm{H}_{2} \mathrm{O}$. (Presence of external $\mathrm{H}_{2} \mathrm{O}$ ) |
| 3283.60 | 3280.22 | 3280.82 | 3284.91 | 3285.75 | 3287.06 | 3305.61 | $\mathrm{H}-\mathrm{C}-\mathrm{H}$ asymmetric stretching and $\mathrm{C}-\mathrm{H}$ stretching in PVA. |
| - | $\begin{aligned} & 2936.03 \\ & 2913.94 \end{aligned}$ | $\begin{aligned} & 2936.76 \\ & 2914.04 \end{aligned}$ | $\begin{aligned} & 2935.31 \\ & 2911.80 \end{aligned}$ | $\begin{aligned} & 2935.21 \\ & 2910.66 \end{aligned}$ | $\begin{aligned} & 2935.24 \\ & 2910.66 \end{aligned}$ | $\begin{aligned} & 2934.40 \\ & 2909.73 \end{aligned}$ | O-H stretch in PVA, O-H stretch in external $\mathrm{H}_{2} \mathrm{O}$. |
| 2455.58 | $\begin{aligned} & \hline 2361.03 \\ & 2329.12 \end{aligned}$ | - | - | $\begin{aligned} & \hline 2369.70 \\ & 2319.35 \end{aligned}$ | $\begin{aligned} & \hline 2361.88 \\ & 2325.13 \end{aligned}$ | $\begin{aligned} & \hline 2362.75 \\ & 2327.92 \end{aligned}$ | O-H stretch in PVA. <br> $\mathrm{H}-\mathrm{O}-\mathrm{H}$ symmetric stretch in $\mathrm{H}_{2} \mathrm{O}$. <br> (PVA interacts with water) |
| 2067.32 | 2106.30 | 2113.57 | 2108.62 | $\begin{array}{r} 2109.85 \\ 2085.41 \\ \hline \end{array}$ | 2108.86 | 2110.26 | $\mathrm{O}-\mathrm{H}$ stretch in PVA, $\mathrm{H}_{2} \mathrm{O}$ in-plane scissoring. (External $\mathrm{H}_{2} \mathrm{O}$ interacts with PVA.) |
| $\begin{aligned} & \hline 1704.39 \\ & 1649.42 \\ & \hline \end{aligned}$ | $\begin{aligned} & 1718.11 \\ & 1659.35 \\ & \hline \end{aligned}$ | $\begin{aligned} & 1716.95 \\ & 1656.85 \\ & \hline \end{aligned}$ | 1723.91 | $\begin{aligned} & 1730.55 \\ & 1651.25 \\ & \hline \end{aligned}$ | $1726.50$ | $1716.18$ | $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching, $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ inplane bending in PVA. |
| 1573.59 | 1589.17 | 1587.28 | 1591.66 |  | 1594.65 | 1590.57 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{C}-\mathrm{O}, \mathrm{C}=\mathrm{O}$ and $\mathrm{C}-\mathrm{C}$ stretch, $\mathrm{H}-\mathrm{O}-\mathrm{H}$ out of plane twisting in PVA. <br> $\mathrm{CH}_{3}$ asymmetric deformation and $\mathrm{C}=\mathrm{N}$ stretch in DMF |
| 1542.97 |  |  |  | 1541.48 |  |  | $\mathrm{CH}_{3}$ asymmetric deformation, $\mathrm{C}-\mathrm{H}$ in plane bending, $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}-\mathrm{N}$ stretch in DMF. |
| 1516.66 |  |  |  | 1515.27 |  |  | $\mathrm{CH}_{3}$ asymmetric deformation |
| 1419.42 | 1422.73 | 1423.07 | 1425.00 | 1425.31 | 1426.01 | 1425.70 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}-\mathrm{C}$ stretch in PVA. <br> Weak $\mathrm{O}-\mathrm{H}$ bending of external $\mathrm{H}_{2} \mathrm{O}$. |
| 1388.00 | 1373.36 | 1373.07 | 1371.13 | 1370.77 | 1371.16 | 1371.01 | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{CH}_{2}$ out of plane twisting, weak $\mathrm{CH}_{2}$ inplane scissoring, C-C-O asymmetric stretch in PVA. |
| 1328.53 | 1327.63 | 1328.02 | 1326.71 | $\begin{aligned} & \hline 1330.87 \\ & 1322.37 \\ & \hline \end{aligned}$ | 1325.62 | 1324.35 | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{C}=\mathrm{C}$ stretch, weak $\mathrm{CH}_{2}$ out of plane twisting and wagging, weak C-C stretch in PVA. |
| $\begin{aligned} & 1254.11 \\ & 1246.62 \end{aligned}$ | 1246.36 | 1245.92 | 1241.91 | 1240.66 | 1240.70 | 1241.58 | C-N-C asymmetric stretch, $\mathrm{CH}_{3}$ asymmetric deformation, C-H in-plane bending, $\mathrm{C}=0$ stretch in DMF |
| 1146.89 |  |  |  |  | $\cdots$ |  | $\mathrm{C}-\mathrm{O}$ and $\mathrm{C}-\mathrm{C}$ stretch, $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. <br> $\mathrm{CH}_{3}$ asymmetric deformation in DMF. |


| 1136.49 | - | - | 1136.45 | 1134.72 | 1136.07 | 1136.02 | $\mathrm{CH}_{3}$ asymmetric deformation, C-N and C- N stretch, C- N-C <br> asymmetric stretch, C-H out of plane bending in DMF. C-O stretch, CH2 <br> in-plane rocking, O-H in-plane bend in PVA |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :--- |
| 1075.63 | 1087.52 | 1087.41 | 1086.88 | 1087.31 | 1086.89 | 1087.38 | $\mathrm{CH}_{3}$ asymmetric deformation, C-N-C asymmetric stretch in DMF. |
| 1031.53 | 1025.23 | 1025.43 | 1024.48 | 1024.12 | 1023.90 | 1023.38 | O-H and C-H out of plane bending, CH2 out of plane twisting in PVA. <br> C-H out of plane bending in DMF. |
| 938.56 | 944.71 | 944.46 | 943.22 | 943.35 | 944.33 | 944.66 | $\mathrm{CH}_{2}$ in-plane rocking, C-H in-plane bending, C-O and C-C stretch in <br> $\mathrm{PVA.}^{2}$ |
| 821.46 | 837.44 | 837.76 | 840.50 | 839.60 | 840.53 | 840.77 | $\mathrm{CH}_{2}$ out of plane wagging, CH2 out of plane rocking, C-H and O-H out of <br> plane bending, C-O and C-C stretch in PVA. |

Table 6: Comparison of experimental and theoretically calculated Raman peaks with their assignments PVA at room temperature.

| Theoretical peak position of PVA Powder | Experimental <br> peak position of PVA powder | Assignments |
| :---: | :---: | :---: |
| 3666.13 | - | O-H stretching |
| 3273.56 | 3285.60 | H-C-H asymmetric stretching, C-H stretching |
| $2902.32$ | $\begin{aligned} & 2935.68 \\ & 2909.69 \end{aligned}$ | O-H stretching |
| $\begin{aligned} & \hline 1705.00 \\ & 1683.11 \end{aligned}$ | $\begin{aligned} & 1717.01 \\ & 1653.74 \end{aligned}$ | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bend, $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching |
| 1527.54 | 1564.31 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{O}-\mathrm{H}$ in-plane bend. |
| 1410.38 | 1422.09 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bend. |
| 1389.64 | 1371.15 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{O}-\mathrm{H}$ and $\mathrm{C}-\mathrm{H}$ in-plane bend, $\mathrm{C}=\mathrm{C}-\mathrm{O}$ asymmetric stretching. |
| 1334.34 | 1325.19 | C-H in-plane bend, $\mathrm{C}=\mathrm{C}$ stretching. |
| - | 1241.23 | Presence of external $\mathrm{H}_{2} \mathrm{O}$ molecules in PVA. |
| 1136.67 | 1134.31 | $\mathrm{C}-\mathrm{O}$ stretching, $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{O}-\mathrm{H}$ in-plane bend. |
| - | 1085.03 | Presence of external $\mathrm{H}_{2} \mathrm{O}$ molecules that influences PVA into several vibrations. |
| $\begin{aligned} & \hline 1025.46 \\ & 1021.63 \end{aligned}$ | 1023.00 | $\mathrm{O}-\mathrm{H}$ and $\mathrm{C}-\mathrm{H}$ out of plane bending, $\mathrm{CH}_{2}$ out of plane twisting. |
| 929.81 | 942.43 | $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{C}-\mathrm{H}$ in-plane bending, $\mathrm{C}-\mathrm{O}$ stretching. |
| 859.54 | 834.61 | $\mathrm{CH}_{2}$ out of plane wagging in PVA. |

Table 7: The Raman peaks and their assignments of PVA membrane synthesised in $\mathrm{H}_{2} \mathrm{O}$ at different temperature.

| ```Theoretical peak of PVA membrane (in cm-1)``` | Experimental Raman Peaks of PVA membrane synthesised in $\mathrm{H}_{2} \mathrm{O}$ (in $\mathrm{cm}^{-1}$ ) |  | Assignments |
| :---: | :---: | :---: | :---: |
| RT | RT | $200^{\circ} \mathrm{C}$ |  |
| 281.94 | 287.04 | 284.84 | -H of -OH group in PVA try to interact with each other, $\mathrm{H}_{2} \mathrm{O}$ molecules try to interact |
| 216.70 | 210.06 | 208.91 | with each other, O of $\mathrm{H}_{2} \mathrm{O}$ molecules interact toward $\mathrm{O}-\mathrm{H}$ group in PVA. |
| 314.33 | - | - | O-H out of plane bending in $\mathrm{H}_{2} \mathrm{O} . \mathrm{CH}_{2}$ in-plane rocking in PVA. |
| 428.67 | 444.00 | 439.16 | O of $\mathrm{H}_{2} \mathrm{O}$ molecules interact toward O-H group of PVA |
| 466.47 | - | - | $\mathrm{O}-\mathrm{H}$ out of plane bending in $\mathrm{H}_{2} \mathrm{O}$. |
| 609.08 | 614.50 | 608.27 | $\mathrm{H}-\mathrm{O}-\mathrm{H}$ in-plane rocking in $\mathrm{H}_{2} \mathrm{O}$. |
| 718.41 | 729.80 | - | $\mathrm{CH}_{2}$ out of plane twisting in PVA |
| 895.43 | - | 891.39 | O-H out of plane bending both in $\mathrm{H}_{2} \mathrm{O}$ and PVA. |
| 852.82 | 846.84 | - | $\mathrm{CH}_{2}$ out of plane wagging in PVA. |
| 1003.65 | 992.29 | - | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ out of plane bending, $\mathrm{CH}_{2}$ out of plane twisting in PVA. |
| 1168.16 | 1162.93 | 1166.15 | $\mathrm{C}-\mathrm{O}$ stretch, $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. $0-\mathrm{H}$ out of plane bending in $\mathrm{H}_{2} \mathrm{O}$. |
| 1251.78 | - | - | O-H out of plane bending in PVA. O-H out of plane bending in $\mathrm{H}_{2} \mathrm{O}$. |
| - | 1276.13 | - | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending, $\mathrm{CH}_{2}$ in-plane rocking, $\mathrm{C}-\mathrm{O}$ stretch. |
| 1425.89 | 1425.25 | 1446.16 | $\mathrm{CH}_{2}$ in-plane scissoring, $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ in-plane bending in PVA. $\mathrm{O}-\mathrm{H}$ bending in $\mathrm{H}_{2} \mathrm{O}$. |
| 281.94 | 287.04 | $284.84$ | H of OH group in PVA try to interact with each other, $\mathrm{H}_{2} \mathrm{O}$ molecules try to interact with |
| 216.70 | 210.06 | $208.91$ | each other, O of $\mathrm{H}_{2} \mathrm{O}$ molecules interact toward $\mathrm{O}-\mathrm{H}$ group in PVA. |

Table 8: The Raman peaks and their assignments of PVA membrane synthesised in DMF at RT and annealed temperature $200^{\circ} \mathrm{C}$.

| Theoretical Peak of PVA membrane (in $\mathrm{cm}^{-1}$ ) | Experimental Raman Peak of PVA membrane synthesised in DMF <br> (in cm ${ }^{-1}$ ) |  | Assignments |
| :---: | :---: | :---: | :---: |
| RT | RT | $200^{\circ} \mathrm{C}$ |  |
| 178.06 | 177.39 | - | $\mathrm{CH}_{2}$ and $\mathrm{H}-\mathrm{C}-\mathrm{O}$ out of plane twisting in PVA. $\mathrm{CH}_{3}$ asymmetric deformation in DMF. |
| $\begin{aligned} & 202.40 \\ & 212.81 \\ & \hline \end{aligned}$ | 213.41 | 200.48 | $\mathrm{CH}_{3}$ asymmetric deformation in DMF. |
| 225.51 | - | 226.55 | $\mathrm{H}-\mathrm{C}=0$ out of plane twisting in PVA. $\mathrm{CH}_{3}$ asymmetric deformation in DMF. |
| 296.83 | 296.82 | - | $\mathrm{C}-\mathrm{N}$ and $\mathrm{C}-\mathrm{C}$ in-plane bending in DMF. |
| 320.13 | - | - | C-H out of plane bending in PVA. |
| - | - | 301.61 | O-H out of plane bending in $\mathrm{H}_{2} \mathrm{O} . \mathrm{CH}_{2}$ in-plane rocking in PVA. |
| 434.71 | - | 448.79 | C-H out of plane bending in PVA. C-H out of plane bending and C-N in plane bending in DMF. |
| - | 467.99 | - | O-H out of plane bending vibrations of external $\mathrm{H}_{2} \mathrm{O}$. |
| 602.21 | -- | 596.12 | $\mathrm{CH}_{3}$ asymmetric deformation, $\mathrm{N}-\mathrm{H}$ out of plane bending in DMF. |
| 691.92 | 704.03 | 716.17 | $\mathrm{CH}_{2}$ out of plane twisting, $\mathrm{C}-\mathrm{H}$ out of plane bending in PVA. |
| 851.73 | - | 848.69 | $\mathrm{O}-\mathrm{H}$ and C-H out of plane bending in PVA. C-N-C symmetric stretch in DMF. |
| 889.34 | 895.13 | - | $\mathrm{CH}_{2}$ out of plane wagging and $\mathrm{O}-\mathrm{H}$ out of plane bending in PVA. |
| 987.44 | 982.30 | - | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ out of plane bending in PVA. |
| 1098.94 | 1099.09 | - | C-N stretch and weak $\mathrm{CH}_{3}$ asymmetric deformation in DMF. C-O stretch, O-H inplane bending and $\mathrm{CH}_{2}$ in-plane rocking in PVA. |

Table 9: The Raman peaks and their assignments of PVA membrane synthesised in DMSO at RT and annealing temperature $200^{\circ} \mathrm{C}$.

| Theoretical peak of PVA memb-rane (in $\mathrm{cm}^{-1}$ ) | Experimental Raman Peaks of PVA membrane synthesised in DMSO (in cm ${ }^{-1}$ ) |  | Assignments |
| :---: | :---: | :---: | :---: |
| RT | RT | $200{ }^{\circ} \mathrm{C}$ |  |
| $\begin{aligned} & 149.36 \\ & 176.32 \\ & \hline \end{aligned}$ | 178.63 | $148.04$ | $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. $\mathrm{CH}_{2}$ out of plane twisting and C-H out of plane bending in PVA. |
| 223.42 | - | 223.51 | $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. $\mathrm{CH}_{2}$ out of plane twisting, $\mathrm{C}-\mathrm{H}$ out of plane bending in PVA. |
| 270.37 | 271.53 | - | C-S-C in-plane scissoring and $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. $\mathrm{CH}_{2}$ out of plane twisting, $\mathrm{C}-\mathrm{H}$ out of plane bending in PVA. |
| 371.90 | 453.19 | 390.77 | $\mathrm{S}=0$ bending, $\mathrm{C}-\mathrm{S}$ bending and $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. |
| 512.69 | - | 511.54 | $\mathrm{S}=0$ stretch and C-S stretch in DMSO. Weak $\mathrm{CH}_{2}$ in-plane rocking in PVA. |
| 572.39 | 572.23 | - | C-S stretch in DMSO. |
| 586.17 | 594.34 | - | C-S stretch in DMSO. |
| 718.41 | 732.29 | - | $\mathrm{CH}_{2}$ out of plane twisting and C-H out of plane bending in PVA |
| - | - | 807.71 | O-H out of plane bending in PVA |
| 940.70 | - | 938.14 | $\mathrm{C}-\mathrm{H}$ and $\mathrm{O}-\mathrm{H}$ out of plane bending in PVA. $\mathrm{CH}_{3}$ asymmetric deformation in DMSO |
| 1000.83 | 999.14 | - | $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. C-H and O-H out of plane bending in PVA. |
| 1441.82 | 1463.32 | $\bigcirc$ | $\mathrm{CH}_{3}$ asymmetric deformation in DMSO. $\mathrm{CH}_{2}$ in-plane scissoring, C-H and O-H out of plane bending in PVA. |

