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# PHOSPHOTUNGSTIC ACID LOADED MIXED MATRIX BLEND MEMBRANES OF POLY(VINYL ALCOHOL)/GELLAN GUM FOR PERVAPORATION DEHYDRATION OF ISOPROPANOL

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## ABSTRACT

Mixed matrix blend membranes of Poly (vinyl alcohol) (PVA)/Gellan gum (GG) were prepared using solution casting method by incorporating 5, 10 and 15 Wt.% of phosphotungstic acid (PWA). These membranes were crosslinked with glutaraldehyde and tested for the pervaporation (PV) dehydration of isopropyl alcohol (IPA) at 30°C. These membranes were characterized by Fourier transform infrared spectroscopy (FTIR) to confirm crosslinking and assess the intermolecular interactions present between polymers and PWA. Thermal stability and crystallinity of these membranes were determined from thermo gravimetric analysis (TGA), Differential scanning calorimetry (DSC) and X-ray diffraction (X-RD) studies. The morphology of membranes was characterized by SEM studies, which indicated good compatibility of these membranes. Swelling studies were carried out to evaluate the extent of hydrophilicity with and without PWA particles and also based on their nature. The pervaporation performance was evaluated by varying experimental parameters such as feed composition, different polymer compositions, PWA content and found to be promising membrane for separation of water- isopropanol mixtures. From the results it was concluded that the phosphotungstic acid, with its hydrophilic nature as well as its molecular sieving effect and its favourable interaction with hydrophilic PVA and GG, was responsible to enhance the PV dehydration of isopropanol in terms of selectivity (α), flux (J), and pervaporation separation index (PSI).The results pertaining to the 15 wt% PWA loaded blend membrane had the highest selectivity 4,491 which was attributed to the combined effect of molecular adhesion between PWA and PVA-GG blend matrix as well as hydrophilicity.

**Keywords:** PV dehydration, Poly (vinyl alcohol), Gellan gum, Phosphotungstic acid.

## 1. INTRODUCTION

Among many separation and purification technologies available in the literature, polymer-membrane based pervaporation (PV) separation is considered to be one of the simplest unit operations to separate azeotropic mixtures, closely boiling liquid mixtures, heat sensitive biochemicals, liquid-liquid isomers, etc.[1-5]. PV is an energy saving and eco-friendly method when compared with other separation techniques including conventional distillation.

Even though research in this area has been actively pursued over many decades, yet achievement of a simultaneous increase in flux and selectivity to water has been a major challenge. Only a handful of polymeric membranes have been successful in commercial applications, yet research to develop newer membranes has been actively pursued using a variety of crosslinking agents and loading with zeolites and inorganic fillers to enhance membrane performance. In particular, the development of blend membranes has been an attractive area of PV study because one component of the blend provides the desired permeability characteristics and other improves the mechanical strength of the membranes [6-10]. Poly vinyl alcohol (PVA) has been the most widely used membrane for water-alcohol separation through pervaporation, but because PVA is a hydrophilic, it swells and thus hinders separation. Because of recent environmental concern and awareness in public sectors, new trends are moving in the direction of using environment-friendly polymers that can easily be degraded after their intended application. Blends of PVA with sodium alginate [11], chitosan [12] poly vinyl pyrrolidine or pectin [13] are reported in literature.

Gellan gum is a high molecular weight water soluble linear anionic polysaccharide produced by the fermentation of the organism sphingomonas elodea [14].

Gellan gum, obtained naturally, contains two acyl substituents, namely acetate and glycerate. Acylated gellan gum gives soft, very elastic and non-brittle gels whereas deacylated gellan gum gives hard, non-elastic and brittle gels under optimum gelling conditions. Because of its low thermal, mechanical and chemical stability [15], the applicability Gellan gum membrane is limited. Polymer membranes incorporated with inorganic fillers, clays are promising candidates to overcome these drawbacks, in which these added materials present a class of highly ordered, porous and crystalline silica containing materials with multipurpose character and a far better stability [16].

In order to improve Pervaporation separation characteristics of IPA-water mixtures, in this work, blending of PVA with Gellan gum is considered to limit the excessive swelling of PVA. Since PVA and Gellan gum polymers are completely miscible in all proportions, due to hydrogen bond formation between donor groups of PVA and acceptor groups of Gellan gum, in the blend system, favoring dehydration of isopropanol. As a part of our pervaporation studies [17-21] the PVA + Gellan gum blend membranes incorporated with PWA have been chosen in the present study as there were no reports in literature on this system.

For pervaporation studies through mixed matrix membranes using Phosphotungstic acid (PWA) as a filler there are rare reports [22, 23], in literature. In order to achieve extraordinary separation performance of mixed matrix membranes (MMMs) the strong interactions between the host polymers and PWA must be responsible. The PWA consists of Keggin unit as a primary structure, i.e., the polyanion $[PW12O40]^{3-}$, and a secondary structure, i.e., a regular three-dimensional assembly of the hetero polyanions with counter cations (protons) and additional water molecules [23]. This Keggin unit consists of a central $PO_4$ tetrahedron surrounded by four $W_3O_{13}$ sets, linked together through oxygen atoms of which, four types can be distinguished; the central oxygen atom belonging to $PO_4$ tetrahedron is shared by three tungsten atoms, while the edge-sharing oxygen atoms bridge two tungsten atoms of the same set. The corner-sharing oxygen atoms bridge two tungsten atoms of different sets and terminal oxygen atoms are associated with a single tungsten atom. The bridging and terminal oxygen atoms are on the periphery of the structure, which are available to associate with protons or water molecules to form hydrates that are thought to enhance selectivity to water. Also, hydrogen-bonding is likely to be established between PWA and the PVA/GG blend system. Due to these advantages, PWA-loaded PVA/GG blend membrane is selected to investigate the PV dehydration of isopropanol.

The MMMs developed were characterized by FTIR, X-RD, SEM, DSC, TGA and swelling studies. Effect of varying amounts of PWA particle loading on swelling and pervaporation performance have been investigated in order to achieve optimum performance of the developed MMMs of PVA / GG for the dehydration of isopropanol. PWA content and feed composition effect on pervaporation performance has been studied in terms of flux, selectivity and pervaporation separation index (PSI). Results of this study are discussed in terms of nature of polymer-filler interactions as well as solution-diffusion concept and the results are presented here.

## 2. MATERIALS & EXPERIMENTAL METHODS

### 2.1. Materials

Gellan Gum was purchased from Sisco Research laboratories, Taloja, Maharashtra, India, Poly (vinyl alcohol) (PVA) (molecular weight 80,000gm), Phosphotungstic acid, acetone, hydrochloric acid, and glutaraldehyde, were of reagent grade purity and were purchased from s.d. fine chemicals, Mumbai, India. Isopropanol (IPA) (AR-grade) was obtained from Qualigens fine chemicals, Mumbai, India and these chemicals were used without further purification. Deionised and distilled water prepared in the laboratory was used in this work.

### 2.2. Membrane preparation

By using solution casting method PVA/Gellan Gum blend membranes were prepared by incorporating with phosphotungestic acid in different amounts. 2g of Gellan gum was dissolved in 45mL distilled water at 30°C and 2gms of PVA was dissolved in 45ml of distilled water at 90°C. By constant stirring for 30min these two solutions were thoroughly mixed until it forms a homogeneous solution and was filtered to remove any suspended particles. The 5, 10, and 15 wt% of PWA particles ( with respect to the weight of the polymer ) dispersed in 10 ml distilled water separately by sonication for 30 min; these three solutions were separately added to the previously prepared blend solution (of 90 ml) and then the whole mixture was kept under stirring for another 24h. The blend solution was poured onto a preleveled glass plate in dust-free atmosphere to cast the membranes with uniform thickness. Membranes thus formed were allowed to dry at ambient temperature and then peeledoff from the glass plate and then crosslinked with glutaraldehyde [2.5ml] containing 85:10 Acetone:Water mixture in which 2.5ml HCl was added as activator and allowed for crosslinking reaction for 2h. Acetone being a non-solvent prevents the initial dissolution of the membrane and water present in the feed leading to swell the membrane thereby facilitating an easy penetration of GA into the membrane matrix for an effective crosslinking. Crosslinking reaction takes place between the –OH groups of PVA, GG, and –CHO groups of GA because of formation of ether linkages by eliminating water molecules. The crosslinked membranes were removed from crosslinking bath and washed repeatedly with distilled water to remove the adhered GA and unreacted molecules and then dried in hot air oven at 50°C to constant weight. The above prepared membranes were named as PG-0, PG-1, PG-2, and PG-3 where the PWA content is 0, 5, 10 & 15 wt % respectively. Using a micrometre screw gauge the membrane thickness was found to be around 35-40µm.

## 2.3. Membrane characterization

PWA loaded and unloaded blend membranes were scanned by FTIR spectrophotometer (Bomen MB-3000, Canada) between 400 to 4000 $cm^{-1}$. To prepare these samples KBr pellet method was used. PVA/GG blend membranes under different loadings of PWA were scanned using powder X-ray diffractometer (Siemens D5000) at room temperature. The X- ray source was Ni-filtered Cu Kα radiation (40kv, 30ma). The angle of diffraction (2θ) was varied from $0\text{-}60^0$ to identify any changes in crystal morphology and intermolecular distances between inter segmental chains of polymers. SEM micrographs of the membranes under study were obtained at different resolutions with a SEM (JEOL, Jsm-840A, Japan) at Jain University, Bangalore. The membranes were scanned using Differential scanning calorimeter Model-SDT Q600, (TA instrument, USA) at the heating rate of $10^0$C/min in a nitrogen atmosphere.

## 2.4. Swelling Studies

All the membranes under study were subjected to equilibrium sorption study gravimetrically at 10 to 40 wt % of water in IPA feed mixtures at 30°C. Initial weight of circularly cut membrane pieces (diameter in 2.5cm) were weighed on an electronic balance (Adaam 160L) with an accuracy of ±0.001mg. The membranes were weighed accurately and kept in different soaking mixtures for 48 h, after carefully blotting the surface-adhered excess water + isopropanol droplets, these membranes were accurately weighed to estimate the amount of liquid mixture sorbed by the membrane at the chosen time, t. The degree of swelling, (DS) was calculated as:

$$DS\% = \left(\frac{W_S - W_d}{W_d}\right) X100 \qquad \text{............(1)}$$

Where Ws and Wd are the mass of the swollen and dry membranes, respectively.

## 2.5. Pervaporation experiment

Pervaporation experiments were carried out using an indigenously designed apparatus described elsewhere [21]. It consists of a PV cell with two components, viz., feed cell with 500ml capacity and permeate cell separated by a membrane having an effective area of 34.43 $cm^2$ and the diameter of 7.4cm. The vacuum in the downstream side of the apparatus was maintained by a two-stage vacuum pump (Indvac, Model pvp-150, Peenya industrial area, Bangalore-58, India.) with a vacuum pressure as low as 1mm Hg. The test membrane was allowed to equilibrate for about 2 hrs while in contact with the feed mixture before starting the PV experiment. Weight of the feed mixture taken in the PV cell was around 70 gm and temperature of the feed mixture was maintained at 30±0.01°C by water through thermostatic water bath. After the steady state the permeate was collected in trap immersed in liquid nitrogen jar on the downstream side at a fixed time intervals. The water composition of the feed mixture was varied between 10 and 40 mass %. The flux was calculated by weighing permeate. The % composition of permeate was estimated by measuring refractive index of the mixture with an accuracy of ±0.0001 units, using a refractometer (Atago-3T, Japan), as calculated by using the previously established standard graph of refractive index versus known mixture composition.

Membrane performance in PV experiments was studied by calculating the total flux (Jp), separation factor ($\alpha_{sep}$) and pervaporation separation index (PSI). These were calculated, respectively using the following equations:

$$Jp = Wp/At \qquad \text{................(2)}$$

Where Wp represents the mass of water in permeate (kg), A is the membrane area ($m^2$) and t represents the permeation time (h).

$$\propto = \left\{\frac{Y_A}{1 - Y_A}\right\}\left\{\frac{1 - X_A}{X_A}\right\} \qquad \text{................(3)}$$

$$\mathrm{PSI} = \mathrm{J}(\propto - 1) \qquad \text{................(4)}$$

Where $X_A$ is Wt. % of water in the feed and $Y_A$ is Wt. % of water in the permeate. $Y_A$ and $X_A$ are weight factions of permeate and feed, respectively.

At least three independent measurements of flux and selectivity were made under the same conditions of temperature and feed composition to confirm the steady-state pervaporation. The results are reproducible to an accuracy of ±3% standard deviation, but average values were considered for calculation and graphical display.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of membrane

### *3.1.1. Fourier Transform Infrared Spectroscopy*

FTIR spectra of pure PWA-loaded blend membranes are shown in Fig. 1. The spectrum of PWA shown in Fig.1 shows three characterstics bonds around 1030 $cm^{-1}$, 940 $cm^{-1}$ and 845 $cm^{-1}$ that are respectively attributed to W-Od bonds, W-Ob-W bridges (inter bridges between corner-sharing octahedra). A strong and broad band appearing around 3400 $cm^{-1}$ corresponds to stretching vibrations of –OH groups of PWA.

The spectrum of unfilled PVA-GG blend membrane (PG-0) and those of MMMs (i.e.PG-1, PG-2 &PG-3) are shown in Fig.1(b-e) respectively. The spectrum of PVA-GG (PG-0) shows prominent peaks of C-H group at 2940 $cm^{-1}$, C=O stretching of the carboxylic group of Gellan gum, and characteristic free-OH is observed around 3188-3583 $cm^{-1}$. In case of PG-1, PG-2 and PG-3 membranes, no characteristic bands of PWA appeared, indicating homogeneous distribution of PWA particles in PVA/GG blend membranes. A similar observation was reported by Kittur et.al. from their pervaporation studies [24]. For PG-1, PG-2 and PG-3 the peak intensities corresponding to -OH shows a decrease in intensity compared to unfilled PG-0 membrane, indicating the interaction between PWA and blend membrane.

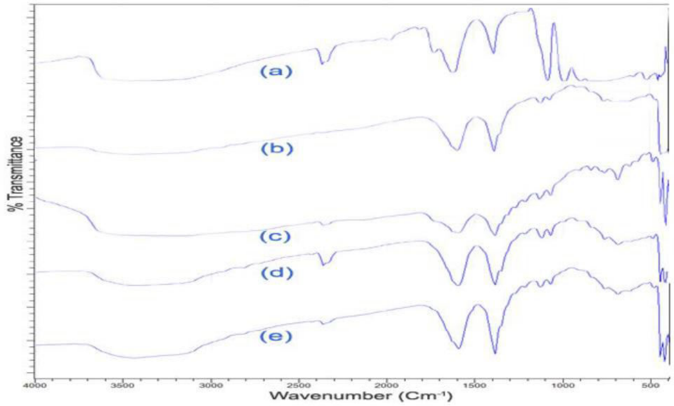

**Fig.1: FTIR spectra of (a) Pure PWA (b) PG-0, (c) PG-1, (d) PG-2 and (e) PG-3 membranes**

### *3.1.2. Differential Scanning Calorimetry (DSC)*

Fig. 2 shows the Differential Scanning Calorimetry thermograms of without PWA loaded PVA–Gellan gum blend membranes (PG-0) and PWA loaded blend membranes (PG-1& PG-2). From Fig.2, it is noticed that unfilled blend membrane (PG-0) shows a Tg of 79.4°C and this is shifted to 84.5°C for PG-1 & PG-2 respectively. The rise of Tg values can be attributed to the intermolecular hydrogen-bonding between PWA particles and PVA-Gellan gum blend particles. It can be seen from Fig. 2 that the Tg curves are quite identical, suggesting the compatibility between blend membranes and PWA filler particles. However the Tg of PG-1 & PG-2 are higher than PG-0 to the micro-phase separation during the membrane process.

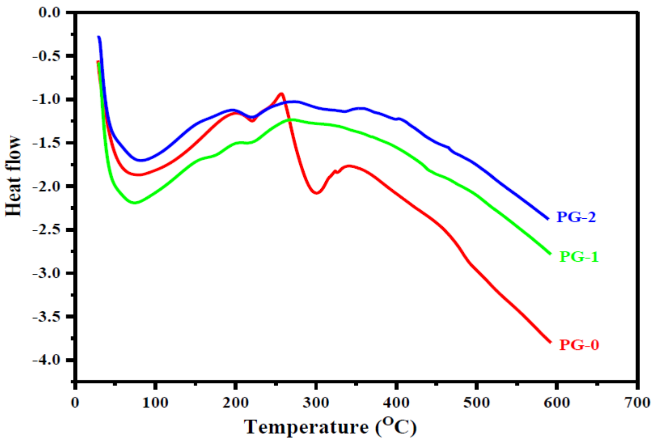

**Fig.2: DSC Thermograms of pure blend membrane of PVA/GG (PG-O) and PWA loaded MMMs (PG-1& PG-2).**

### *3.1.3. Thermo gravimetric analysis (TGA)*

TGA thermograms of without loaded PWA blend membrane (PG-0) and PWA loaded blend membranes (PG-1 & PG-2) are shown in Fig.3. These curves showed the thermal stability of the systems understudy. From Fig.3, it is noticed that single stage degradation was observed in case of unfilled blend membrane (PG-0) with an onset of degradation at 200°C. Thermal decomposition curves (between 200-450°C) were observed for filled in mixed matrix blend membranes (PG-1 & PG-2) and further these transitions have shifted to higher temperatures due to the presence of PWA particles compared to unfilled blend membrane (PG-0). It is also noticed that PG-1 & PG-2 MMMs are more stable than PG-0. This is again an evidence for the intermolecular hydrogen bonding between the functional groups of PWA particles and pure blend membranes. Again it is further noticed that the stability of the membranes are in the following order. PG-2> PG-1 >PG-0.

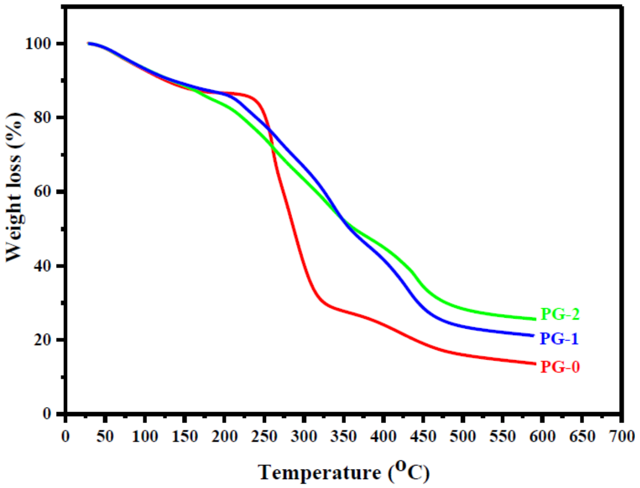

**Fig.3: TGA curves of PVA/GG membranes**

### 3.1.4. *X-Ray diffraction Studies:*

X-RD was employed to study the effect of PWA on the membrane morphology. X-Ray diffraction patterns of pure PWA (a) pristine blend membrane (b) and PWA filled blend membranes (c) are presented in Fig.4. Pure PWA X-RD graph (curve a) shows its characteristics peaks at 2θ= 22 to $35^0$ which indicates the crystalline nature of the PWA. The X-RD patterns of PWA unfilled blend membrane (curve b) shows characteristics peaks at 2θ= 18 to $25^0$. But in case of PWA loaded blend membrane (curve c) the peaks at 2θ is observed from 18 to $25^0$, which indicates the interactions of functional groups present in PWA with functional groups present in blend membrane. The X-Ray diffraction patterns of PWA peaks are not seen in curve C which indicates that PWA is uniformly dispersed in blend membrane. This also further supports the miscibility of the two polymers in the blend membrane.

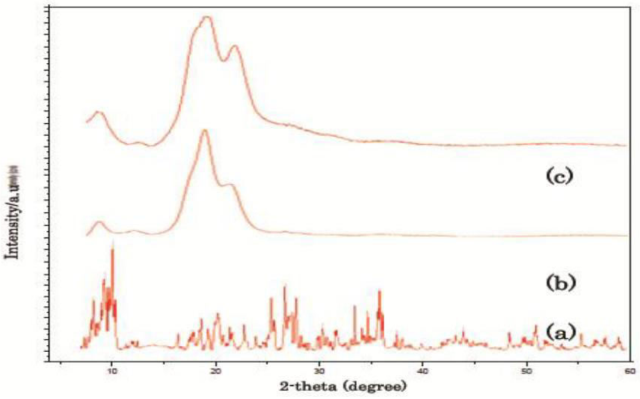

**Fig. 4: X-RD patterns of pure PWA (a) pristine blend membrane PG-O (b) and PWA filled blend membranes (c)**

### 3.1.5. *Scanning electron microscopy (SEM)*

Surface SEM images of PWA unloaded blend membranes (PG-0) are shown in Fig.5. at two different resolutions i.e. at 1000 (Fig.5a) and at 15000 (Fig.5b). Similarly PWA loaded blend membrane (PG-3) SEM images are shown in Fig.5 at two different resolutions i.e. at 5000 (Fig.5c) and at 10,000 (Fig.5 d). The SEM images of pristine blend membrane are smooth which indicates the complete miscibility of these polymers whereas in case of PWA loaded blend membranes the SEM images indicates a smooth surface with uniform distribution of PWA particles. Such a homogeneous mixing of PWA particles in the bulk of the polymer phase would facilitate higher water transport through the membrane due to the creation of channels that are more favorable to the transport of water molecules than IPA.

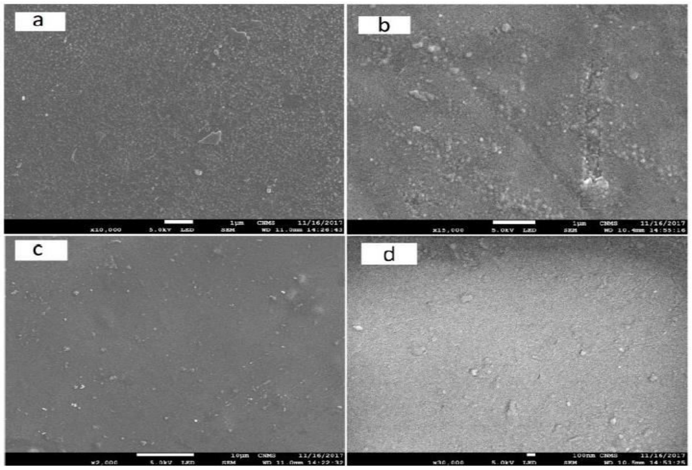

**Fig.5: Surface SEM images of without PWA loaded blend membrane (a&b) PG-0 and PWA loaded blend membrane(c&d)**

### 3.1.6. *Swelling Results*

The results of % of degree of swelling (DS %) of plain PVA-Gellan gum blend membrane (PG-0) and PWA loaded MMMs of the PG-1,PG-2 & PG-3 at 30°C and feed mixture from 10 to 40 wt% water in the feed are presented in Table.1. The degree of swelling (%) of the membranes are calculated and plotted as a function of wt. % of water in the feed mixture at 30 °C (Fig. 6).

It is observed that the higher PWA loaded blend membrane PG-3 is showing highest swelling at all feed water composition compared to other membranes understudy. Degree of swelling of the PG-3 increased to almost double, i.e., from 47.89 to 97.80 with increasing water concentration in the feed mixture from 10 to 40wt. %. These results support the higher values of flux observed in case of PG-3 when compared to PG-2, PG-1 and PG-0. The lowest degree of swelling for pristine blend membrane increased from 25.35 to 55.09, for 10 to 40 wt. % water content in the feed, because of the higher hydrophilic nature of the two polymers PVA/GG. The same trend is observed with regard to the flux values of the membranes in the chosen feed mixture. An increase in equilibrium swelling with increasing amount of PWA in blend membrane is due to the hydrophilic interaction of PWA and blend membrane. The equilibrium swelling results vary as per the sequence: PG-0 < PG-1 < PG-2 < PG-3, i.e., higher loading of PWA, higher will be the swelling which in turn shows the higher hydrophilic interaction of PWA with the hydrophilic polymers (PVA & GG) in the blend.

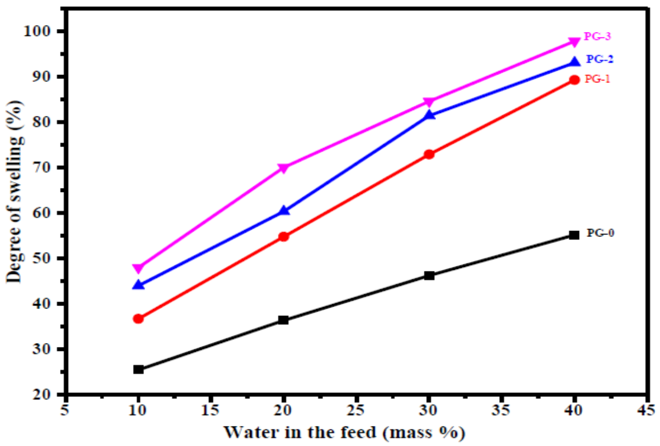

**Fig.6: Degree of swelling of pristine PVA/GG blend and MMMs of PG-1, PG-2, PG-3 Vs water in the feed (mass %).**

**Table 1: Percentage of swelling data of blend membranes in different % of water in the feed mixture of water/ IPA at 30°C.**

| % of water in the feed | % of Swelling | | | |
|---|---|---|---|---|
| | PG-0 | PG-1 | PG-2 | PG-3 |
| 10 | 25.35 | 36.61 | 43.90 | 47.89 |
| 20 | 36.24 | 54.71 | 60.28 | 69.97 |
| 30 | 46.16 | 72.08 | 81.38 | 84.56 |
| 40 | 55.09 | 89.25 | 93.06 | 97.80 |

## 3.2. Membrane Performance through PV Studies

The pervaporation results i.e. feed composition, permeate composition, selectivity, flux and PSI values for dehydration of isopropanol are given in Table.2.

### *3.2.1. Membrane Performance Interms of Flux and Selectivity*

Based on the solution-diffusion principles [26, 27], molecular transport occurs in pervaporation due to concentration existing between the feed and permeate mixture. In general first of all the permeating molecules dissolve on the upper side of the membrane and then diffuse through the membrane on the other side of it as a result of concentration gradient. In case of mixed matrix membranes of the present study, overall separation can be explained as due to the delicate balance of solvent properties, viz., its nature and affinity towards membrane, size and vapour pressure in addition to morphological set up of the membrane. Considering the PV separation of water-isopropanol mixtures, the relative affinity of either isopropanol or water molecules towards membrane could be assessed from the sorption (swelling) measurements. When the hydrophilic PWA filler is mixed with a hydrophilic polymer (PVA/GG) blend, the permeation flux of such membranes would be enhanced in proportion to the amount of filler added (see Table 2). In the present study when the filler amount is higher (i.e. at 15%) greater would be the degree of swelling which leads to higher permeation flux. Similarly the swelling of the membrane is also in the following order i.e. 10% 0f PWA >0% of PWA where the flux values also vary accordingly.

At low level of PWA loading, presumably the PWA spread around considerably within the blend bulk matrix, which would form the isolated islands within the matrix environment. Such a matrix is likely to absorb more of water molecules as compared to unfilled blend membrane matrix. The hydrogen-bond type inter-actions between hydrophilic PWA particles as well as blend polymer are responsible for higher values of flux and selectivity as compared to the pristine blend membrane. A substantial increase in selectivity and a moderate increase in permeation flux rate over that of pristine blend membrane (PG-0) for 5, 10 and 15 wt. % PWA loaded MMMs is due to the fact that in the swollen state, hydrophilic PWA would preferentially allow the water molecules to be sorbed faster than isopropanol, and this would increase the selectivity and flux values even at higher amounts of water in the feed. The importance of using filler-filled membranes in PV separation has been well documented in the earlier literature for a variety of polymer- filler combinations [28, 29]. The crystalline ordered structure of hydrophilic PWA with a narrow size distribution has a higher resistivity to organic liquids than water. Thus, by dispersing PWA particles into blend polymer matrix, the increase in permeation flux of the MMMs could be the result of preferential interaction of water molecules, which would accommodate higher amount of water than isopropanol. This could be possibly due to: (1) strong adsorptive hydrophilic interaction of water molecules onto PWA particles, (2) surface diffusion from cage to cage and (3) vaporization on the permeate side. Physical adsorption involves both vander Waals type dispersion-repulsive and electrostatic interactions due to polarization, as well as dipole and quadrupole type interactions. The complimentary effects of PWA on water transport would thus improve the membrane performance.

### *3.2.2. Effect of Feed Water Composition*

In the present work, we find that crosslink density increases by varying the amount of PWA in the PVA/GG blend, because the PWA particles will act as the reinforcing bridge between the polymer chain segments of PVA and GG, while the PWA will help to establish this bridge through the electrostatic interactions. Hence, all the MMMs of this study will exhibit higher selectivity than the pristine blend membrane (PVA/GG) alone. However, the fluxes of all the MMMs are higher even compared to pristine blend (PVA/GG) membrane at all the compositions of water in the feed mixture (Table 2).

**Table 2: Pervaporation data of IPA/water mixtures for different membranes at 30°C**

| Feed compositions |  | Permeate compositions |  |  |  |  |
|---|---|---|---|---|---|---|
| Water (x) | IPA (1-x) | (wt %) Water (y) | IPA (1-y) | Selectivity(α) | Flux (kg /m$^2$h) | PSI |
| PG-0 |  |  |  |  |  |  |
| 10 | 90 | 98.86 | 1.14 | 780.47 | 0.0600 | 46.82 |
| 20 | 80 | 98.75 | 1.25 | 316.00 | 0.1037 | 32.76 |
| 30 | 70 | 98.58 | 1.42 | 161.98 | 0.1623 | 26.28 |
| 40 | 60 | 98.12 | 1.88 | 78.28 | 0.3191 | 24.97 |
| PG-1 |  |  |  |  |  |  |
| 10 | 90 | 99.69 | 0.31 | 2894.22 | 0.0930 | 269.16 |
| 20 | 80 | 99.50 | 0.50 | 796.00 | 0.1597 | 127.12 |
| 30 | 70 | 99.32 | 0.68 | 340.79 | 0.2514 | 85.67 |
| 40 | 60 | 99.16 | 0.84 | 177.07 | 0.3838 | 67.95 |
| PG-2 |  |  |  |  |  |  |
| 10 | 90 | 99.78 | 0.22 | 4081.90 | 0.1120 | 457.17 |
| 20 | 80 | 99.58 | 0.42 | 948.38 | 0.1902 | 180.38 |
| 30 | 70 | 99.46 | 0.54 | 429.75 | 0.3188 | 137.00 |
| 40 | 60 | 99.24 | 0.76 | 195.86 | 0.5292 | 103.64 |
| PG-3 |  |  |  |  |  |  |
| 10 | 90 | 99.80 | 0.20 | 4491.00 | 0.1218 | 547.00 |
| 20 | 80 | 99.72 | 0.28 | 1424.00 | 0.2419 | 344.60 |
| 30 | 70 | 99.63 | 0.37 | 628.28 | 0.3634 | 228.31 |
| 40 | 60 | 99.45 | 0.55 | 271.22 | 0.5621 | 152.45 |

The variations of flux, selectivity and permeate composition with wt% of water in the feed are displayed in Figs. 7a, 7b and 7c respectively. The flux of pristine blend membrane has increased from 0.060 to 0.3191 kg/m$^2$h for feeds containing 10% of water to 40% of water. However, selectivity of the pristine blend decreased from 780.47 to a considerably smaller value of 78.28 when water in the feed mixture increased from 10 to 40%. Parallel to this effect, mass% of water in permeate also decreased from 98.86 to 98.12, water in permeate for pristine blend membrane, for 5% PWA loaded blend membrane ranged between 99.69 to 99.16 and, for 10 mass% PWA loaded blend membrane, it ranged between 99.78 to 99.24 %, while for 15% PWA loaded blend membrane, it ranged between 99.80 to 99.45 over the whole range of water compositions of the feed mixture. Since membranes used in this study are highly water selective, very small differences in these compositions may cause huge differences in selectivity. Therefore, sensitivity of water measurements plotted in Fig. 7c shows the exact composition of water in permeate as a function of water in feed for different loadings of PWA in blend membrane matrix. This could be due to hydrophilic nature of PWA, which might have exerted high affinity to water molecules than isopropanol, since water is more polar than isopropanol. Free channels in the structure of PWA cage as well as the polymer plasticization effect could also be responsible for this effect in addition to strong molecular sieving effect induced as a result of higher amount of PWA in the blend membrane. Thus, the observed higher selectivity and high flux values for 5,10 and 15 mass% of PWA loaded blend membranes as compared to the pristine blend membrane (PG-0) is quite possible.

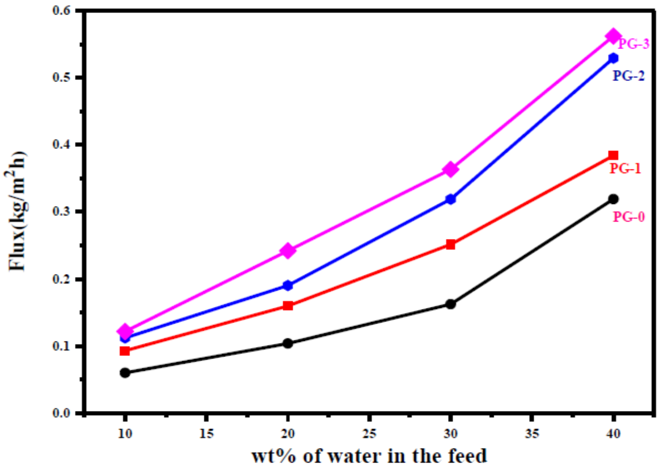

**Fig. 7a: Effect of wt% of water in the feed on flux for different blend membranes**

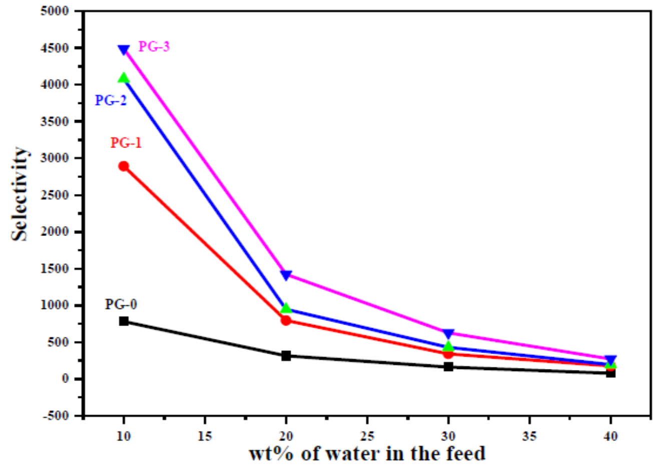

**Fig. 7b: Effect of wt% of water in the feed on selectivity for different blend membranes**

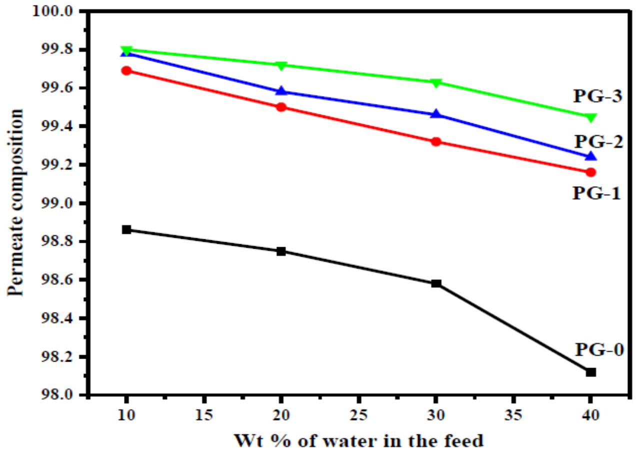

**Fig. 7c: Effect of wt% of water in the feed on water permeate for different blend membranes**

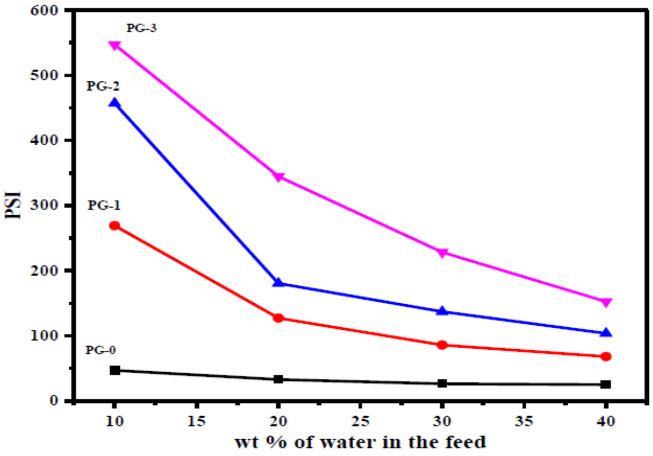

**Fig.7d: Effect of wt% of water in the feed on PSI for different blend membrane**

### *3.2.3. Effect of Pervaporation Separation Index*

The Pervaporation separation index (PSI), which is the product of total permeation rate and selectivity, which characterizes the performance of membranes. Pervaporation separation index (PSI) values are calculated (using eq No.4) with regard to pervaporation study of the present study and are included in Table 2. PV results are also discussed in terms of pervaporation separation index (PSI) at 30˚C as shown in Fig. 7d. The PSI values follow the same trends as in the case of selectivity and these values (PSI) decrease with increasing water concentration in the feed mixture. Pristine blend membrane exhibits the least PSI when compared to PWA loaded blend membranes. The increasing values of PSI from pristine blend membrane to PWA loaded blend membranes suggest an increase in the water content in permeate. The index can be used as a relative guideline for the design of new membranes for PV separation processes and also to select a membrane with an optimal combination of flux and selectivity. The simultaneous increase of separation factor and flux is difficult problem in PV separation, even though several studies have demonstrated this effect [30, 31]. The results in Table.2 indicate that PSI increased with PWA content in the membrane. This signified that the membrane incorporated with higher amount of PWA showed better performance for the separation of IPA and water mixtures. This is because the incorporation of PWA into the membrane matrix did not change only the membranes hydrophilicity but also its structure this may have had a significant effect on the diffusion. These results are particularly useful in membrane distillation processes during alcohol fermentation.

### *3.2.4. Influence of PWA Loading on PV Performance*

Membrane performance was studied by calculating flux and selectivity at different concentrations of PWA loaded blend, and their variations are shown in Figs. 8a and 8b respectively. The water flux for 5% PWA loaded blend membrane has increased from 0.093 to 0.3838 kg/m$^2$h, while the water flux for 10% PWA loaded blend membrane increased from 0.1120 to 0.5292 kg/m$^2$h, whereas in case of 15% PWA loaded blend membrane, water flux increased from 0.1218 to 0.5621 for all these 10, to 40% of water feed permeation in these MMMs flux increases with increasing amount of water in the feed from 10 to 15% of PWA. The flux values for all the MMMs are higher than the pristine blend membrane which can be clearly observed from the values of flux in Table 2 and also from the Fig. 8a. Mainly, selectivity of 5 wt.% PWA-containing membrane (i.e., PG-1) increased considerably compared to pristine PVA-GG blend membrane (PG-0). At the same time, it is observed from Fig. 8b that at higher concentrations of PWA i.e., PG-2, PG-3 membranes, the selectivity values also increased considerably compared to pristine blend membrane (PG-0) and 5% PWA loaded blend membrane (PG-0).

The decrease in selectivity for all the membranes with increasing water content of the feed depends upon the amount of filler added in the blend matrix. For instance, with PG-0 (PWA-5%) - filled membrane, selectivity dropped from 2894.22 for 10% water feed to 177.07 for 40% water feed, which is almost close to the value observed for pristine blend membrane and by this, it is evident that with a higher amount of PWA in blend membrane, the amount of water molecules could pass through the pores of PWA. For PG-2 (PWA-10%) - filled membrane, selectivity improved greatly, i.e., the observed value is 4081.90 for 10% water in the feed, which dropped steeply to 195.86 for 40% water in the feed. On the other hand, for the mixed matrix membrane containing 15% of PWA i.e. for PG-3 even though there was a slight improvement in flux, but selectivity values are quite higher over the entire range of feed mixture compositions. It is thus evident that the presence of higher amount of PWA in the blend membrane, higher number of water molecules would transport through the pores of PWA, thereby increasing its selectivity to water, but not for isopropanol.

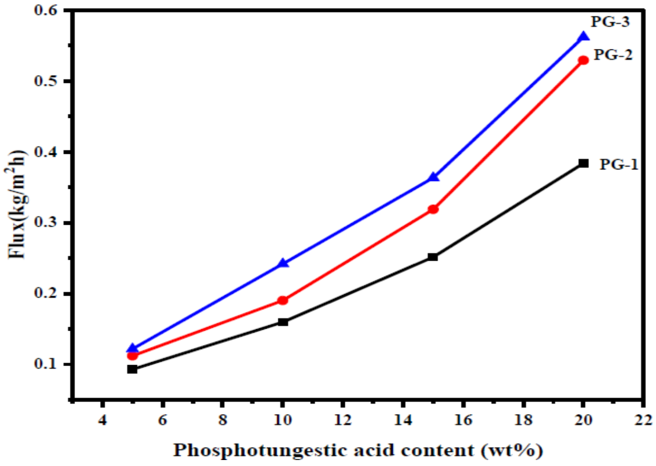

**Fig.8a: Effect of PWA content on flux at different wt% of water in the feed**

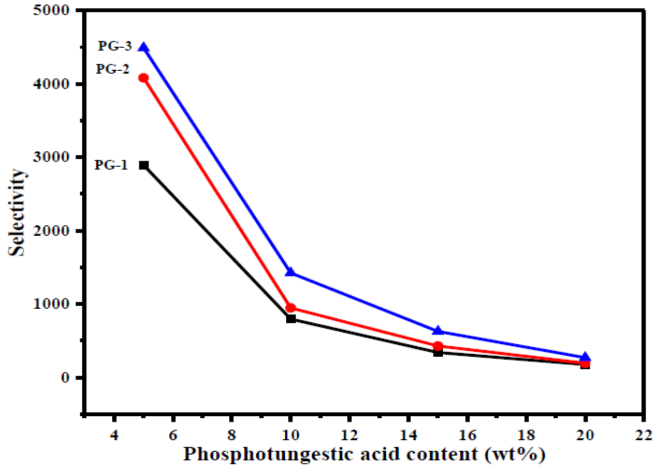

**Fig.8b: Effect of PWA content on selectivity at different wt% of water in the feed**

## 4. CONCLUSION

These investigations clearly demonstrate the effect that by incorporating PWA particles into PVA/GG blend host matrix, it is possible to enhance remarkably the pervaporation performance of the filled blend matrix membranes over that of unfilled PVA/GG blend membrane for isopropanol dehydration. However, higher loadings of PWA particles also showed an increase in hydrophilicty of the PVA/GG matrix which is responsible for an increase in flux and selectivity values. Membrane characterization was carried out by X-RD, SEM, DSC, FTIR and swelling studies. DSC analysis of the membranes indicated that the ordered association of pure blend membrane was decreased due to the presence of PWA. However, detailed mechanistic interpretation of pervaporation results require a consideration of both true micro cavity uptake as well as interstitially held water molecules between crystallites of the membrane matrix. Much research is yet to be done in these areas to understand such problems, particularly choosing different PWA filled polymeric membranes.

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