Preparation, Characterization and Application Studies of PVDF-PS Ultrafiltration Membranes

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Abstract

Polyvinyledenefluoride–polystyrene (PVDF/PS) blend ultrafiltration membranes were prepared using phase inversion technique. Casting solutions were prepared with different compositions of polyvinylidene fluoride (PVDF) and polystyrene (PS) both in the presence and absence of the additive, polyvinylpyrolidone (PVP) using di- methylacetamide as solvent. The effects of compositions of PS and concentrations of PVP on shrinkage ratio, pure water flux, percentage of water content and porosity of the blend ultrafiltration membranes were studied and results are discussed. It was found that with the increase in PS and PVP in the blend, the shrinkage ratio decreased while the pure water flux, water content and porosity of the membrane increased. The morphology of the blend membranes were obtained by scanning electron microscope . Further, the application of the PVDF/PS blend membranes in separation of toxic heavy metal ions from aqueous streams were also attempted and the results are discussed.

Keyword: Polyvinylidene fluoride, polyvinylpyrolidone, polystyrene, ultrafiltration membranes ,shrinkage ratio, metal ions.

1. INTRODUCTION

There is an increasing demand for developing ultrafiltration(UF) membranes with high performance to price ratio for various Industrial applications. Generally the best and extensively used method for preparation of the UF asymmetric membrane is based on the finding of Loeb Sourirajan's method [1]. The polymer–solvent interactions, solvent–nonsolvent interactions and interfacial stability play key role in the membrane performance. Thus, the material selection such as polymers, solvents, and nonsolvents is very important for the fabrication of asymmetric membranes, according to its applications [2].

Polyvinylidene fluoride (PVDF) is a polymer with increasing scientific attention and industrial importance because of its, durability and biocompatibility and high chemical resistance to many acids and alkalis. This polymer is widely used in food and medicine field for ultrafiltration [3].

These properties make PVDF as an attractive membrane material [4]. Its crystalline phase provides thermal stability while the amorphous phase provides the desired membrane flexibility. However, the crystallinity in PVDF has a detrimental effect on the final membrane transport properties by decreasing both the free volume and amorphous region available for species transport.[5]. Being a hydrophobic polymer PVDF has a high shrinkage ratio which would affect the porosity of the membrane which in turn would reduce the pure water flux.

To over come the defects of the PVDF membranes, it requires modification. Blending of polymers in the membrane casting solution is an useful technique for modifying the properties of the prepared membrane and considerable a cost-effective method. In the present investigation commercially available polystyrene was blended with PVDF in the presence of additive polyvinylpyrolidone (PVP). PS was chosen due to their high mechanical, thermal and chemical resistance properties[6]. It is an amorphous polymer having wide variety of application in fuel cells, pervaporation and gas separation applications.

2 MATERIALS AND METHODS
2.1 MATERIALS

Polyvinylidene fluoride (Kynar grade 760, M_w 444,000) was obtained from ARKEMA, Singapore. Polystyrene was procured from Supreme Petrochemicals Private Limited, India. The solvent, Dimethylacetamide (DMAc) and the surfactant, Sodium Lauryl Sulphate (SLS) of AR grade were purchased from M/s. Sisco Research Laboratories Private Limited, India. Acetone and Polyvinylpyrolidone (PVP) (M_w 40,000) were supplied by Hi-Pure Pvt Ltd India.

2.2. MEMBRANE PREPARATION

The UF membranes were prepared by the phase inversion method using immersion precipitation technique. The blends of PVDF and

PS polymers were prepared by dissolving two polymers at different compositions in DMAc as solvent by thoroughly mixing for 4h at room temperature both in the presence and absence of PVP at various concentrations as pore former. The detailed description of the preparation of the membranes are explained elsewhere [7].   The membranes were prepared by casting this blend solution on a glass plate followed by evaporation for definite time in a non-solvent water bath which was kept at 10° C.

2.3 SHRINKAGE RATIO

A piece of wet membrane immersed in the glycerin solution was cut into square shape. The length and width were measured with a square caliper and the average value was obtained after measuring the dimension three times. The membrane was dried at 75^0C for 3 h. [8] .The shrinkage ratio was calculated using the formula as follows:

Shrinkage ratio (%) = [1 – (ab/ a_o b_o)]x 100

where **a_o and b_o** are the length and breath of the wet membrane, cm

a and b are the length and breath of the dry membrane, cm

2.4 WATER CONTENT

The membranes were soaked in distilled water for 24h.. The soaked membranes were mopped with the blotting paper and weighed with an electronic balance with 0.0001g accuracy. The wet membrane samples were placed in the dryer at 75^oCfor 48h and cooled it to room temperature in the desiccators and then the dry weights were measured [9] The percentage water content was determined as follows

$$\% \text{ Water Content } = \frac{(W_1 W_2)}{W_1} \times 100$$

where,
W_1 - Wet membrane weight (g)
W_2 - Dry membrane weight (g)

2,5   PURE WATER FLUX (PWF)

Membranes after compaction, were subjected to pure water flux at a trans-membrane pressure of 345 kPa. The permeate was measured under steady state flow. Pure water flux was calculated from the equation

$$J_w = Q/(A \, \Delta t)$$

Where

Q   - quantity of permeate collected, l

J_W - the pure water flux, $lm^{-2}h^{-1}$

Δt - Sampling time, h

A   - Area of the membrane, m^2.

2.6 METAL-ION REJECTION STUDIES

Aqueous solutions of Zn^{2+} and Cu^{2+} with an approximate 1000 ppm concentration were prepared in 1 wt% solution of Polyvinylalcohol (PVA) in deionized water. The pH of these aqueous solutions were adjusted to 6.25 by adding small amount of either 0.1M HCl or 0.1M NaOH. Solutions containing PVA and individual metal ions or metal chelates were thoroughly mixed and left standing for 5 days for complete binding [10,11].

The chelate-metal ion containing solutions were filled in the feed reservoir. For each run, the first few ml of the permeate was discarded. The permeate flux was measured by collecting the permeate at a pressure of 345 kPa. The concentration of each metal ion in feed and permeate was measured by using Atomic Absorption Spectrophotometer (Perkin Elmer-2380). The pH of feed and permeate were measured with Elico pH meter.
The % metal ion rejection (%SR) was evaluated from the concentrations of the feed and permeate using equation

$$\% \, SR = \left(1 - \frac{C_p}{C_f}\right) X \; 100$$

where,

C_p - Concentration of metal ion in permeate

C_f - Concentration of metal ion in feed

3. RESULTS AND DISCUSSION

3.1 EFFECT OF POLYMER BLEND COMPOSITION AND ADDITIVE CONCENTRATION ON THE SHRINKAGE RATIO OF THE MEMBRANES.

Shrinkage ratio plays a vital role on the porosity of the membrane. Above 30% shrinkage will bring much negative effect on porosity and mean pore size of membranes[8]. Higher shrinkage tendency will result in tension in the membrane and this has the strong influence on the structure [12]. The casting solution was prepared from PVDF and PS polymers at a total polymer concentration of 17.5 wt%. The composition of polystyrene in the casting solution was varied and its effect on the shrinkage ratio was studied. It can be seen from the Fig 1 that the pure PVDF has the highest shrinkage ratio of

20.8% which attributes to its hydrophobic nature[13]. The possible mechanism would be the contraction of the polymer-rich phase after phase separation, which tends to pull the polymer together toward the bulk, like gel syneresis [14]

However, the addition of PS in the blend reduces the shrinkage ratio sharply . Thus, the addition of both PS and PVP to the blend decreases the shrinkage ratio. This could be explained on the basis that the cast solution containing polymer in its concentrated form leads to entanglement among the macromolecular chains due to their molecular interactions. When the cast membrane is dipped in the nonsolvent bath the flow of nonsolvent tends to align the sections of chains between the coupling points. Hence elastic energy will be stored in the section of chains between entanglements. The energy will be released after certain times when the flow stops [13]. The membrane formation is so short that there is hardly time for the release of energy. Hence much stress is fixed between the entanglements in the cast films. The stress will be released when the temperature rises during drying process, thus resulting in the shrinkage of the membrane. However, due to high glass transition temperature of PS (80°C) the macromolecular chain becomes less flexible at room temperature due to the glassy nature of PS. It implies that the PS chain segment could not change their position freely at room temperature. Due to this reason PS acts as reinforcement in the blend membrane which prevents the blend from shrinking and hence the observed results [8]. However, the existence of the high supersaturation degree between the casting solution and nonsolvent results in comparative high shrinkage ratio in the absence of the additive. The supersaturation degree decreases with the addition of PVP to the casting solution which is due to the hydrophilic nature of the PVP[12]. Which explains the low shrinkage ratio with thw addition of PVP to the blend.

3.2 EFFECT OF POLYMER BLEND COMPOSITION AND ADDITIVE CONCENTRATION ON WATER CONTENT OF THE MEMBRANE

Effect of water content of the membrane is shown in the Fig2. The water content of pure PVDF was found to be 59.9% in the absence of both PS and additive PVP. Since PVDF is a polar polymer it is possible that the electrostatic repulsion will impede the bundling of the polymer which could give rise to larger pores or interconnected pores as observed by Bowen et al [15]. However, with the increase in the content of PS from 5 to 25 wt% in the blend, the water content also increased from 60.6% to 82.1%. This increase in the water content is due to the poor miscibility between the two polymer which substantially and systematically decreases the mean addition between the two components which further advances the repulsion between the polymer leading to larger pores and subsequently increases the water content of the membrane [15]. The addition of of PVP increases the ratio of non solvent inflow to solvent outflow by increasing the viscosity of the casting solution, which according to the theory proposed by Young and Chen [16], results in more porous membranes resulting in higher water content with increase in PVP.

3.3 EFFECT OF POLYMER BLEND COMPOSITION AND ADDITIVE CONCENTRATION ON PURE WATER FLUX OF THE MEMBRANE

The effect of blend composition on pure water flux is shown in the Fig. 3.The pure PVDF membrane in the absence of PS and the additive exhibited the lowest flux of 7.39 $lm^{-2}h^{-1}$. The addition of 5wt% of PS to the blend, increased the flux to 8.87 $lm^{-2}h^{-1}$ and at 25wt% of PS concentration in the blend the flux further increased to 14.79 $lm^{-2}h^{-1}$. Thus, the increase in flux is a direct consequence of the presence of PS in the blend.

This might be due to the fact that with the increase in the PS content in the blend the nucleation decreases drastically. This indicated that PS addition reduces the energy to form critical size nucleus of PVDF [17] which is expected to reduce the crystalline nature of PVDF resulting in the improved flux. Hence, PS forms a dispersed phase in continuous matrix of PVDF. Further the weak interactions between PVDF and PS chains also lead to larger distance between the two kinds of chains and resulting in increase in the pore size and hence increase in the pure water flux of the system [8]. Moreover, there is a high interaction between the additive PVP and PVDF [18]. Hence, the thorough mixing between PVDF and amorphous PVP there by further reducing the crystalline nature of the PVDF which has also aided in the increase of flux with the increase of additive concentration.

3.4 METAL ION REJECTION STUDIES

Ultrafiltration processes cannot be directly applied for ionic level rejection owing to the larger pore size of the membranes . Hence to apply this membrane in metal ion rejection, the size of the metal ions need to be enlarged there by enhancing the rejection of the metal ions. In this study, a water soluble chelating polymer, PVA, was used as the complexing agent for the metal ions Cu^{2+} and Zn^{2+} and were subsequently rejected individually from the aqueous stream by using PVDF/PS blend ultrafiltration membranes at 345 kPa.

3.4.1 ROLE OF POLYMER BLEND AND ADDITIVE CONCENTRATION COMPOSITION

The rejection of the metal ions using PVDF/PS blend membranes in the absence of the additive, was carried out individually after the metal ions were complexed by PVA and the results are shown in the Figs 7 and 8.

Thus, the pure PVDF membrane in the absence of additive yielded a highest separation of 99.6% for Zn^{2+} and 99.4% for Cu^{2+}. It was observed that in the case of PVDF/PS blend membranes, the separation of Zn^{2+} remained constant at 99.6% when the PS content was increased from 5 to 25 wt% in the blend in the absence of additive. Similarly the rejection for Cu^{2+} also remained constant at 99.4% with the increase of PS in the blend from 5 to 25wt%. Moreover, there was no significant change in the percentage of rejection with the addition of PVP to the blend. As explained already the addition of PS in the blend decreases the shrinkage ratio. Decrease in the shrinkage has high impact on the porosity of the membrane. With the increase in the PS in the polymer blend the pure water flux increases while there is no effect on the rejection of the metal ion. Thus from the rejection behavior of the membrane, it could be concluded that the porosity of the membrane has increased with the increase in PS in the blend. Moreover, the polystyrene being non adsorptive to electrolyte [19] the presence of PS in the membrane will not aid the passage of metal ion resulting in higher percentage of rejection.

4. CONCLUSION :

Ultrafiltration membranes are widely used in the chemical process industries for separation and removal of wide variety of chemicals due to its high efficiency, low energy requirements and its compact nature. The ultrafiltration membranes were prepared using PVDF and PS blend membranes in absence and presence of additive PVP in the solvent DMAc. By adding certain amount of PS into PVDF , the flux of membranes increased greatly while maintaining the retention ratio nearly unchanged. The shrinkage ratio is high in the case of pure PVDF membrane and an addition of PS in the blend enhances the flux of the membrane and decreases the shrinkage ratio of the membrane which establishes that an addition of PS in the blend not only decreases the shrinkage ratio but also enhances the flux of the membrane by increasing the porosity of the membrane .

Figure
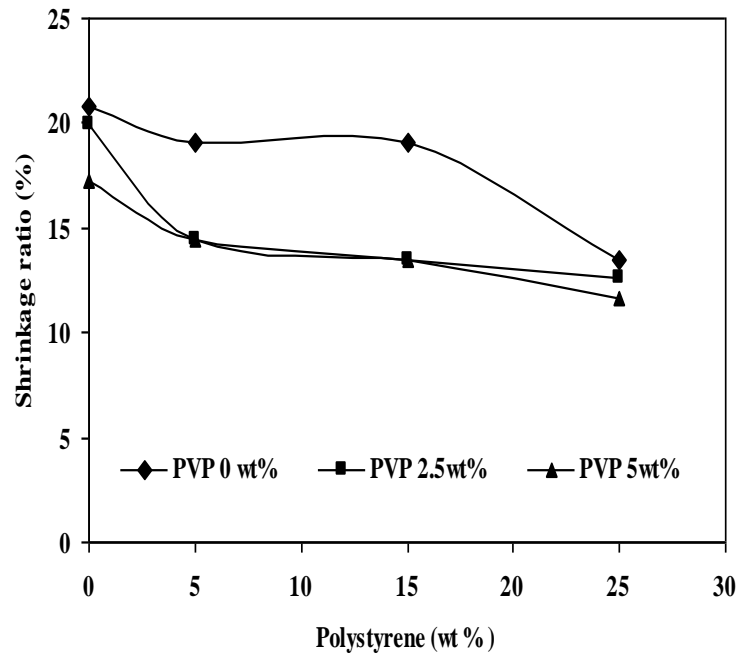**1. Shrinkage Ratio of PVDF/ PS blend membranes**

Fig 1 Effect of PS and PVP on the shrinkage ratio of– PVDF/PS blend membranes

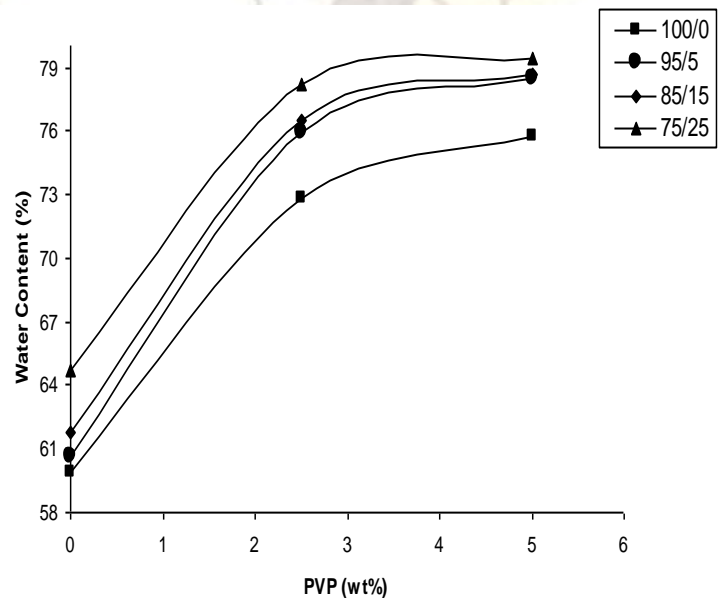**2. Water Content PVDF/ PS blend membranes**

Fig 2. Effect of PVP on the water content of– PVDF/PS blend membranes
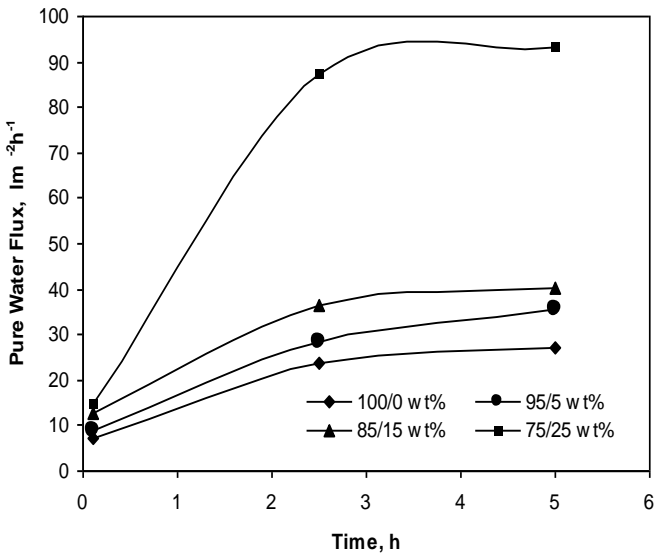**3. Pure water flux (PWF) PVDF/ PS blend membranes**

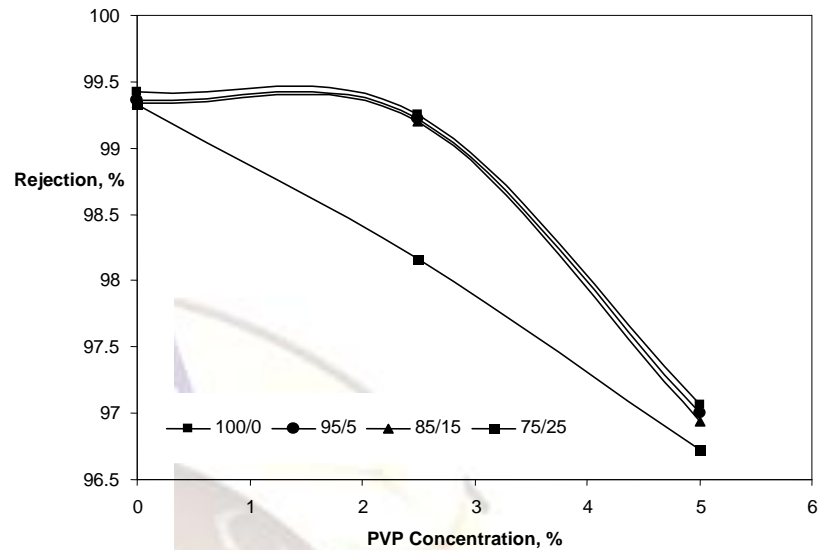**Fig 3 Effect of PVP on the PWF of– PVDF/PS blend membranes**

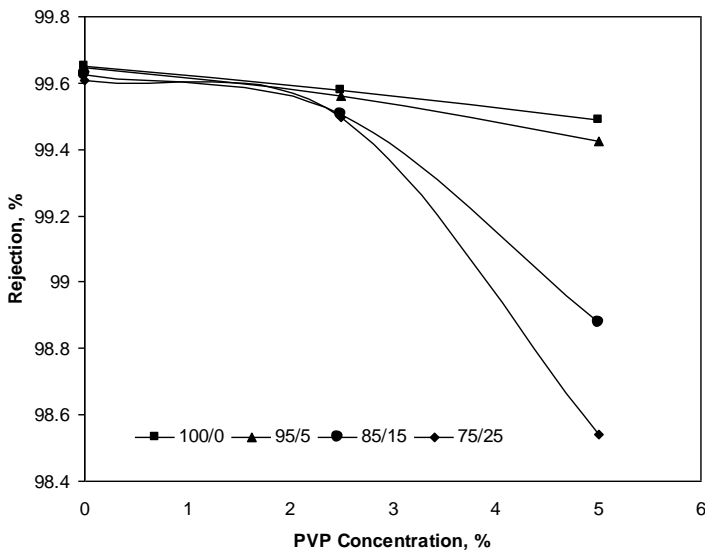### 4. Zn2+ ion rejection PVDF/ PS blend membranes

Fig 4 E**ffect of PVP concentration on rejection of Zn2+ metal ions**
PVDF/PS blend membranes

5. Cu2+ ion rejection PVDF/ PS blend membranes

Fig 5 E**ffect of PVP concentration on rejection of Cu2+ metal ions**
PVDF/PS blend membranes

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