# Effect of PVP Concentration on PVDF-$TiO_2$-PVP Mixed Matrix-Membrane Properties and Performance

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## ABSTRACT

PVDF-$TiO_2$-PVP flat sheet mixed matrix membranes were prepared using non-solvent phase inversion method. This research examined how the PVP concentration (1-5 %wt) as a pore-generating agent affects membrane characteristics. The membrane performance was evaluated by measuring the water flux, permeate flux, and BSA rejection. The hydrophilic membrane with the least contact angle was 65.79o, achieved with 2%wt PVP, whereas the most significant contact angle was 83.07o, obtained with 5%wt PVP. FESEM-EDX of a membrane containing 2%wt PVP reveals the presence of PVDF and $TiO_2$. The highest PVP weight percentage resulted in the most excellent permeate flux. The highest water flux measured was 182.38 L/m2h, and the highest BSA flux measured was 160.98 L/m2h. PVP at 5% weight led to the lowest BSA rejection (50.84%). This study found that the PVP weight percentage substantially impacts membrane characteristics and performance.

Keywords: PVDF; TiO2; PVP; mixed-matrix membranes; phase inversion; NIPS; flat-sheet; BSA

## 1. Introduction

Water is a necessary component of life, yet only a small fraction of the world's water supply is drinkable due to pollution and other factors [1], [2]. High-efficiency, user-friendly, and low-energy-consumption membrane separation procedures are gaining popularity as an alternative to traditional treatment methods due to their high energy demand and restricted reusability [3].

Polymeric membranes, which offer high design flexibility, are among today's most popular membranes for water purification [4]. Polyvinylidene fluoride (PVDF) is an excellent material choice for fabricating polymeric membranes used in ultrafiltration (UF) due to its remarkable chemical resistance, thermal stability, and mechanical strength. PVDF membranes exhibit lower hydrophilicity than other types of membranes, making them more prone to fouling by proteins and organic substances in wastewater treatment. Ghadiri et al. [5] found that membrane fouling decreases membrane life and water flux while increasing energy expenses. Consequently, the hydrophilicity of membranes experiences a significant decrease [3]. These membranes' hydrophilicity and antifouling characteristics can be enhanced using several techniques. One such approach involves incorporating inorganic nanoparticles into the membrane matrix [2].

To boost membrane efficiency, metal oxide nanoparticles are a common additive [6]. Several research [7], [8] reveal that $TiO_2$ has the greatest impact on membrane performance regarding metal ion removal. Hydrophilicity increases, and surface charge decreases when 1.0 wt% $TiO_2$ is included in the membrane matrix structure. $TiO_2$ nanoparticles can be used as an effective component to modify PVDF-PVP membranes due to the membrane separation technology's potential, $TiO_2$ exhibits a notable affinity for heavy metals and possesses the capability to enhance the hydrophilic properties of membranes [4][9].

Polyvinylpyrrolidone (PVP) exhibits a higher preference level than alternative organic additives. This preference is primarily attributed to its exceptional ability to produce pores and its extensive range of molecular weight (Mw) [10]. The increase in membrane water flux that occurs when PVP is introduced is often attributed to the formation of finger-like or sponge-like structures inside the sublayer of the membrane. A prior investigation has demonstrated that using a higher molecular weight (Mw) of PVP effectively inhibits the development of large spaces and leads to a more compact epidermal layer, hence diminishing the flux of water [11]. According to research by Sadrzadeh et al. [11], PVP reduced macro-void production throughout a broad MW range. Depending on the solvent, PVP shrank or enlarged the macro-voids [12][13].

It has not been previously described how incorporating titanium dioxide ($TiO_2$) nanoparticles and PVP into a polyvinylidene fluoride (PVDF) membrane affects its characteristics and performance. Given this curiosity, the current investigation employs the phase inversion technique to create a composite membrane containing a blend of PVP at different concentrations. FESEM, EDX, porosity, and contact angle measurements were all taken on the produced fibers. The flux and the rejection effectiveness for Bovine Serum Albumin (BSA) were analyzed.

## 2. Material and Methods

### 2.1. Materials

PVDF utilized in this investigation was provided by Arkema Inc., a company based in Philadelphia, USA. Merck supplied N, N-dimethylacetamide (DMAc) with a purity level exceeding 99%. Evonik GmbH, a German company, supplied $TiO_2$ nanoparticles (Degussa P25). Bovine serum albumin (BSA) and polyvinylpyrrolidone (PVP) were procured from Sigma Aldrich.

### 2.2. Membrane Preparation

Non-solvent phase inversion method was employed to prepare the flatsheet PVDF-$TiO_2$-PVP membranes. The solution containing the PVP additive was created by dissolving it in the DMAc solvent. Subsequently, 1%wt of $TiO_2$ was dispersed into the solution. The PVDF pellets were pre-dried for 1 day at 50 $^oC$. The PVDF (16 g) was added to the solution, and the mixture was agitated at 60 $^oC$ at 500 rpm for 24 hours. After the dope had completely dissolved, any remaining air bubbles were sucked out using an ultrasonicator for 25 minutes [14]. After waiting 24 hours in the dope solution for the membrane, it was cast and then soaked in water for a whole day. The membrane's performance was assessed through the quantification of the pure water flux, permeate flux, and BSA rejection [15]. The various PVP concentrations used in the dope solution are listed in Table 1.

Table 1: Compositions of Membrane Dope Solutions

| PVDF (%.wt) | $TiO_2$ (%.wt) | PVP (%.wt) | DMAc (%.wt) |
|---|---|---|---|
| 16 | 1 | 1 | 82 |
| 16 | 1 | 2 | 81 |
| 16 | 1 | 3 | 80 |
| 16 | 1 | 4 | 79 |
| 16 | 1 | 5 | 78 |

### 2.3. Filtration Analysis

The filtration efficiency of the membranes was determined by performing permeability experiments on flat sheet membrane testing equipment. The feed was a Bovine Serum Albumin solution at a concentration of 1000 g/L in reverse osmosis water. The membrane was then crushed in a membrane cell for 30 minutes. The permeation volume was measured after 20 minutes for 2 hours, and 1 bar of pressure. The flux of pure water, the flux of BSA, and the rejection of BSA were all measured in the permeation testing unit [16].

### 2.4. The Properties of Flatsheet Membranes

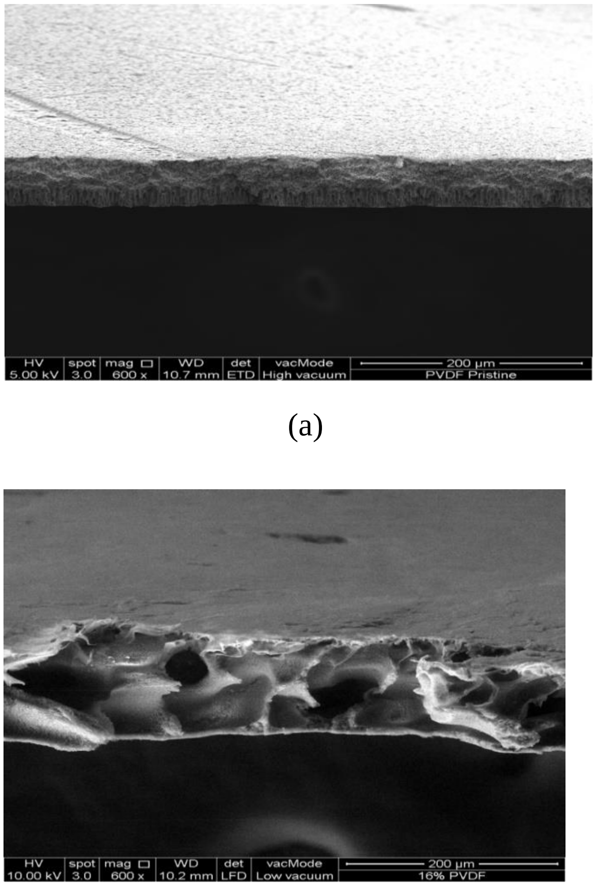
The membranes' surface components were identified using Energy Dispersive X-Ray (EDX), and the membranes' morphology was studied using a Field Electron Scanning Electron Microscope (FESEM). The membrane's hydrophilicity was also analyzed using contact angle measurements. Pore volume as a percentage of total membrane volume defines membrane porosity [16] [10] [17] [18].

## 3. Result and Discussion

### 3.1. Membrane Characterization

### 3.1.1. FESEM-EDX Result

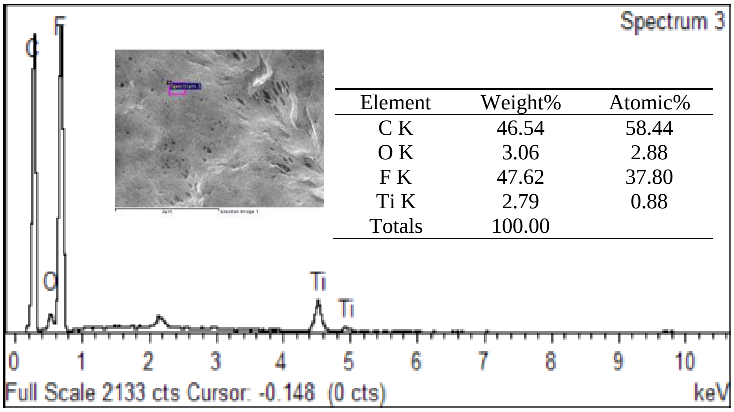
Figure 1 displays the FESEM images of PVDF and PVDF-$TiO_2$-PVP (2%wt). The macro-voids observed in the polyvinylpyrrolidone-modified membrane's sublayer were noticeably larger than those macro-voids observed in the pristine PVDF membrane. Upon increasing the molecular weight (MW) of the PVP, it was observed that finger-like macro voids developed on both the outer and inner surface layers [10]. Including PVP in the spinning solution improves the permeability of the non-solvent (water) into the polymer solution, hence facilitating the formation of noticeable macroscopic voids during the spinning process.



(a)

(b)

Figure 1: FESEM of a) Neat PVDF; b) PVDF-$TiO_2$-PVP Membrane (2%wt PVP)



| Element | Weight% | Atomic% |
|---|---|---|
| C K | 46.54 | 58.44 |
| O K | 3.06 | 2.88 |
| F K | 47.62 | 37.80 |
| Ti K | 2.79 | 0.88 |
| Totals | 100.00 | |

Figure 2: EDX of PVDF-$TiO_2$-PVP Membrane (2%wt)

The prepared flat sheet membrane and its matrix structure are shown in Figure 2. Elements C, O, F, and Ti were detected in the PVDF-$TiO_2$-PVP membrane (46%wt Carbon, 48%wt Florin, 3%wt Oxygen, and 3%wt Titanium). These compositions confirmed the mixed-matrix membrane's composition, which included PVDF and $TiO_2$.

### 3.1.2. Membrane Porosity

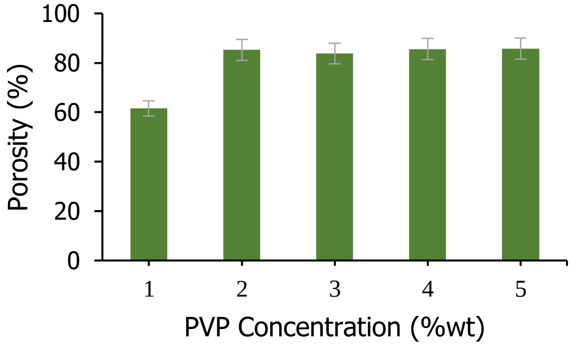


Figure 3: Porosity of PVDF-PVP-$TiO_2$ Membranes

The porosity membranes made of a mixed matrix with varying amounts of PVP is shown in Figure 3. The membrane generated with the minimum concentration of PVP (1 wt%) had the lowest porosity, at 61.51%. Maximum porosity of 85.74 percent was achieved by using a PVP concentration of 5 percent by weight (wt) in the membrane. Due to its inherent hydrophilicity, the utilization of PVP significantly facilitates the dispersion of polymer solvents and non-solvents, including water, during the process, thereby enhancing the size of the pores [19]. The porosity decreased due to the increased viscosity of the solution and the pore-blocking phenomenon [2].

### *3.1.3. Contact Angle Measurement*

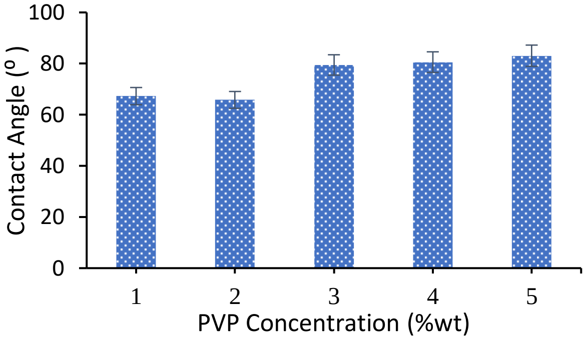


Figure 4: Contact Angle of Membranes

Water contact analysis (shown in Figure 4) illustrates the surface hydrophilicity of membranes with a mixed matrix of PVDF membranes and varying concentrations of PVP. The more hydrophilic a membrane is, its contact angle will be smaller [2]. The PVDF-$TiO_2$-PVP membrane with 2 wt% PVP was hydrophilic since its contact angle was the least (65.79°). The measured contact angle increases, indicating a decrease in hydrophilicity when the concentration of PVP rises from 3 to 5%wt. Adding 1% wt PVP results in a contact angle of roughly 67.3°, whereas adding 5% wt PVP increases the angle to 83.07°. This is feasible because agglomeration in dope solution is more likely the higher the concentration of PVP. Increased hydrophilicity of membranes has been attributed to PVP, a water-soluble polar molecule [20].

### *3.1.4 Membrane Performance Test*

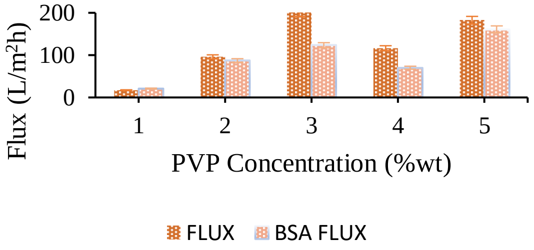


Figure 6: Pure Water Flux and BSA Flux of Membranes

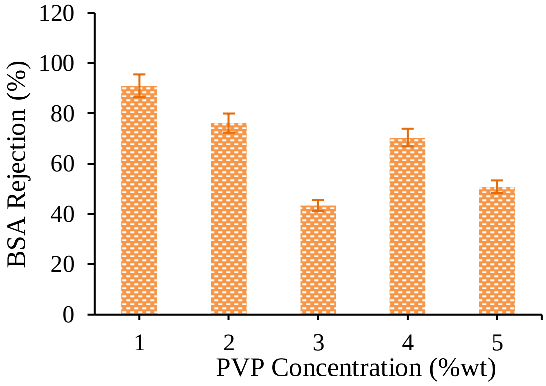


Figure 6: BSA Rejection of Membranes

The water flux and BSA flux of the PVDF-$TiO_2$-PVP nanocomposite membranes are shown in Figure 5. The highest PVP weight percentage (5 wt%) resulted in the greatest membrane flux. Based on the findings, it can be observed that the membrane exhibiting the highest PVP concentration demonstrated the most substantial flow (182 L/m$^2$h for pure water flux and 160 L/m$^2$h for BSA flux. The lowest fluxes were obtained with the smallest PVP concentration (1 wt%) (17 L/m$^2$h for pure water and 20 L/m$^2$h for BSA). The reason for this phenomenon is that PVP, acting as a pore-forming agent, amplifies the level of porosity and hydrophilicity[21]. As shown in Figure 6, 1%wt PVP resulted in the highest BSA rejection (90.99%), while 5%wt PVP resulted in the lowest BSA rejection (50.84%). The observed augmentation in the removal of BSA by the membranes may be attributed to the influence of incorporating $TiO_2$ into the matrix of the membranes [22].

A surface that exhibits hydrophilicity can attract and adhere to water molecules, creating a layer of hydration. The presence of this layer serves as a hindrance, impeding the rate of adsorption of pollutants onto the membrane [23]. Various factors contribute to the high pure water flux of PVDF-$TiO_2$-PVP membranes. First, the $TiO_2$ nanoparticles in the membrane create a hydrophilic surface, which allows water molecules to interact with the membrane more easily. Second, the PVP polymer in the membrane aids in the formation of a more open pore structure, allowing water molecules to move through more easily. Due to their high pure water flux, PVDF-$TiO_2$-PVP membranes are a good contender for various applications, including water purification, wastewater treatment, and food processing.

## 4. Conclusion

Non-solvent phase inversion was used to create PVDF-$TiO_2$-PVP mixed matrix membranes. This study investigated how the PVP concentration (1-5 %wt) as pore forming agent affect the membrane properties. The membrane performance assessment was conducted by measuring water flux, permeate flux, and the rejection of BSA in a membrane permeation system. The membrane exhibiting the highest hydrophilicity, as indicated by the shortest contact angle of 65°, was achieved using a 2% weight concentration of PVP, while the largest contact angle was 83.07° with the highest PVP concentration (5%wt). FESEM-EDX of membrane with 2%wt of PVP also showed the presence of PVDF and $TiO_2$. The highest weight percentage of PVP gave the most significant flux of membranes. The largest water flux was 182.38 $L/m^2h$ and the largest BSA flux was 160.98 $L/m^2h$. 5%wt of PVP resulted in the smallest BSA rejection (50.84%). This study demonstrated that the PVP weight percentage significantly affect the membrane properties and performance.

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