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Role of Polyvinlyppyrrolidone in Membrane Technologies

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Abstract : PVP, also known as polyvidone or povidone is a synthetic polymer consisting of linear 1-vinyl-2-yrrolidone groups. PVP is a versatile polymer with immense applications in pharmaceutical, biomedical and paper industry. This is due to the fact that PVP demonstrates a wide range of properties like water solubility, unique binding, high solubility in water as well as a broad range of liquid media, biocompatibility and good thermal resistance. Of late the use of PVP has been explored in the manufacturing of membranes for separation processes. This study reports the effect of PVP as a polymeric additive on the morphology, hydrophilicity and the performance of polymer membranes in general.

Introduction

PVP (Polyvinylpyrrolidone) is a versatile polymer with a wide range of applications, owing to its remarkable properties. Its unique combination of physical and chemical properties has made it suitable for a large number of applications like pharmaceutical industry and medicine, optical and electrical applications, membranes, adhesives, ceramics, paper manufacturing, coatings and inks, lithography and photography, textile industry, environmental applications [1].The most prominent field of application of PVP has been the pharmaceutical industry due to its biocompatible nature and ability to form stable association compounds with several active compounds [2]. It is commonly used for drug manufacture as a binder, adhesive, film coating, stabilizer, solubilizer, etc .

But over the past years, the use of PVP as an additive in polymeric membranes has also been explored due its properties of high compatibility, pore expansion capability [3] and improving the hydrophilic nature of the membranes [4]. PVP can be used in different concentrations and combinations to prepare membranes with varying structure, morphology and properties. This articles aims to provide an overview of the research involving the use of PVP in membrane preparation.

Structure , Synthesis and Properties of PVP

Structure PVP, also known as polyvidone or povidone[5], is a synthetic polymer consisting of linear 1-vinyl-2-yrrolidone groups. The PVP polymer has a carbon chain containing an amide group in the side substituent and having a poly-N-vinylamide structure (Fig. 1).

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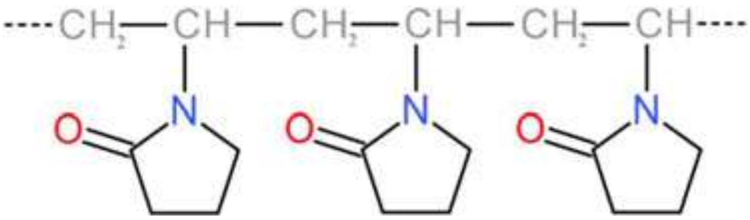

Fig. 1The chemical structure of poly(vinylpyrrolidone).

- **Synthesisof PVP**

PVP was first synthesised Walter Reppe by, a chemist from BASF in 1938 , as one of the numerous products of the acetylene chemistry discovered by him. The synthesis of the monomer N-vinylpyrrolidone (Fig. 2) was started with the reaction of acetylene with formaldehyde to obtain 1,4-butynediol, which was then hydrogenated to butane diol.

Butyrolactone is formed by oxidative cyclization; and, in reactionwith ammonia and the removal of water, pyrrolidone results. Finally, the vinyl group is introduced, as shown in Fig. 2, toform N-vinylpyrrolidone-2(1-(2-oxo-pyrrolidinyl)-ethylene)[6].

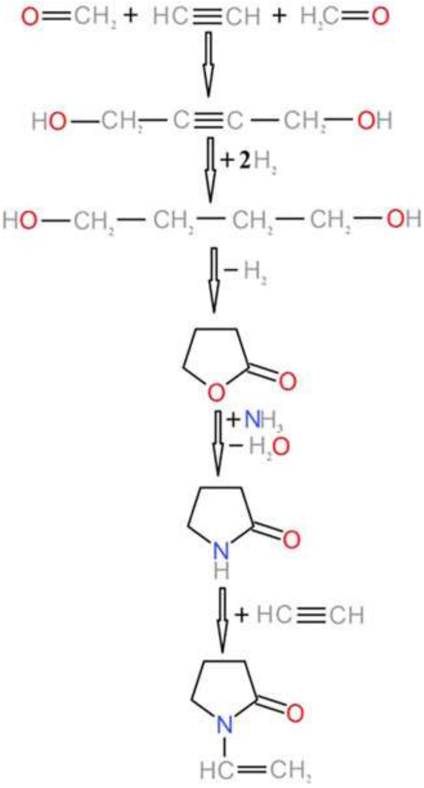

Fig. 2 Synthesis of N-vinylpyrrolidone from acetylene and formaldehyde.

The radical polymerization of N-vinylpyrrolidone (VP) canbe done either in bulk, in solution or in suspension, resultingpolymers with degrees of polymerization between 10 and105. The corresponding molecular weights are of 103–106g mol_1, but in industry are used mainly those polymers withmolecular weights of 2.5_103–106 g mol_1[3].

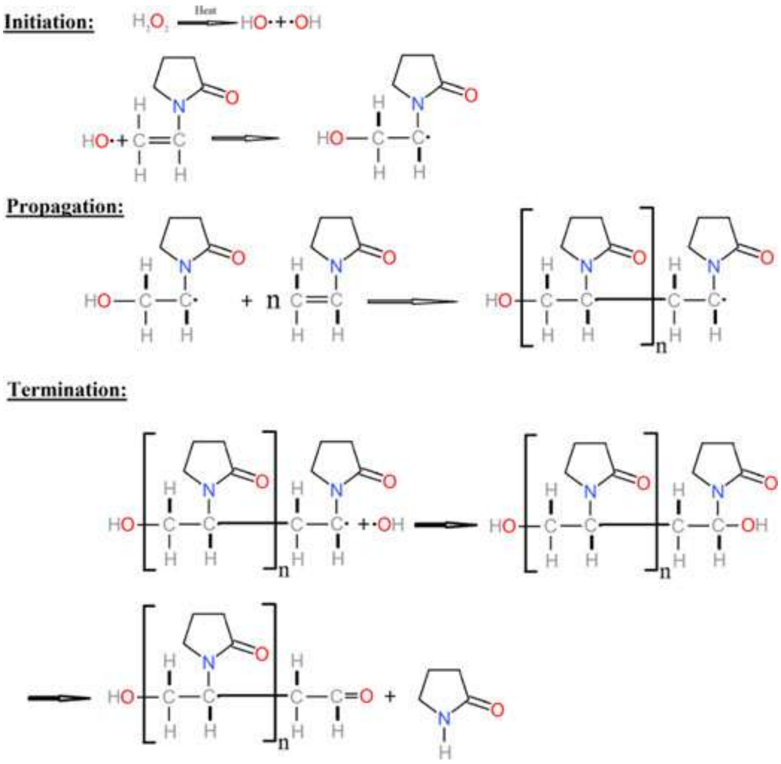

Fig. 3 Polymerization of VP in aqueous solution (adapted from ref.[3])

Highermolecular weight PVP samples are obtained in aqueoussolutions (Fig. 3), having hydroxyl and carbonyl end groups,and lower molecular weight polymers are produced by polymerization in organic solvents (Fig. 4), resulting in products with more stable end groups because solvents may act as chain transfer agents. The polymerization of VP in aqueous solution proceeds as shown in Fig. 3. Hydrogen peroxide, used as initiator, influences the molecular weight of the resulted polymer. Higher the concentration of hydrogen peroxide, the lower the molecular weight of the PVP samples. For obtaining PVP by VP polymerization in organic solvents (e.g., alcohols, toluene, etc.), follows a more complicated process, as described in Fig. 4.

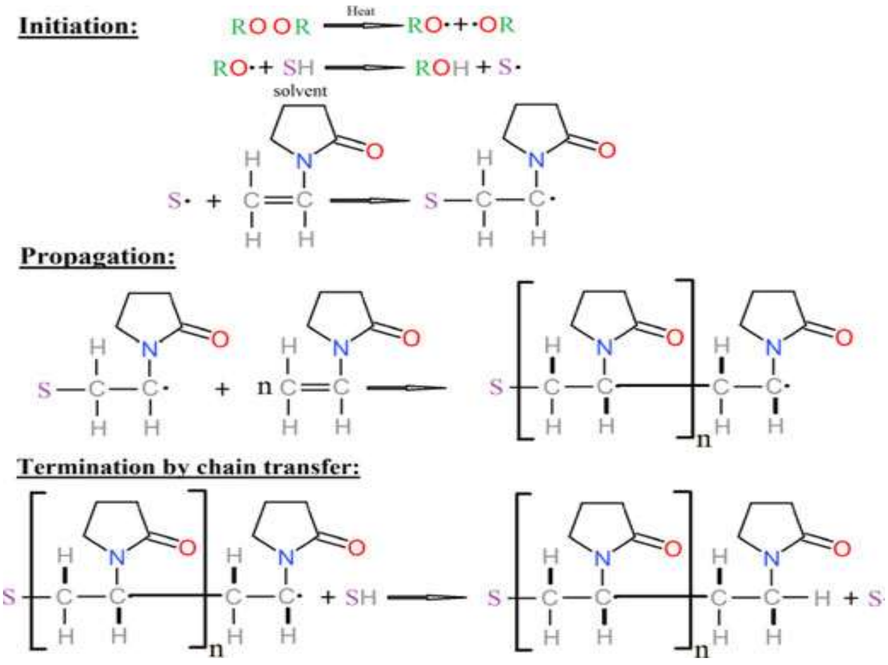

FIG. 4. Polymerization of VP in organic solution (adapted from ref[3]).

- **Properties**

PVP is water-soluble, nontoxic, biocompatible polymer[7], chemically inert, temperature-resistant, pH-stable, non-ionic and colourless[8]. In dry form, it is a light flaky white to yellowish white hygroscopic powder with different particle sizes [9], which absorbs up to 40% of water by its weight[2]. It has a very little taste of its own when dissolved in an aqueous solution [10].Depending on the average molecular weight the glass transition point (Tg) of PVP can range from 100°C (for Mw = $2.5*10^3$ g mol^{-1}) to 175°C (for Mw of 10^6 g mol^{-1})[11]. Tg values fall below 100°C at low molecular weights, and also the addition of small quantities of water may lead to sharply decreasing Tg values [12].

For the determination of the broad area of applications, the solubility of PVP is a deciding property. Since PVP has hydrophilic as well as hydrophobic functional groups, it is soluble in water and many organic solvents (alcohols,some chlorinated compounds such as chloroform, methylenechloride and ethylene dichloride, nitroparaffins, and amines)[12]. In the mentioned solvents, Povidone ispractically infinitely miscible in all proportions, althoughabove a certain concentration, the solution obtained is highlyviscous. To rapidly dissolve without forming lumps(especially for Povidone K 90, with high molecular weight, which dissolves more slowly than the low molecular weight), it is recommended that the powder is added slowly and in small proportions to the solvent, ensuring a strong stirring [13].PVP is resistant to thermal degradation in solution.

PVP can form fairly stable complexes and association compounds. Oneof the best known chemical complexes of PVP is povidoneiodine. It was discovered by H. A. Shelanski and M. V. Shelanski in 1955.It is used as a universally preferred iodine antiseptic[14].

Role of PVP in Membranes

- **Rejection Enhancing Agent**

Recent studies have shown that weak spots or defects (pin holes) are common on the membrane surface, which naturally tend to degrade membrane element rejection characteristics. Recent research has shown that the PA active layer thickness is characterized by great spatial non-uniformity, exhibiting variations of the porosity and charge across the layer [15,16,17]. Furthermore, it is established that due to periodic chemical cleaning, membrane ageing, and occasional chlorine attack, there is gradual membrane degradation [18].

This degradation is the manifestation of physico-chemical changes that occur in the active layer (i.e., agglomeration and clustering of polymeric species), which leads to reduced salt rejection. A recent study [19] confirmed that the performance of used membranes suffers significantly ,with a spatial non-uniformity of such performance degradation, that occurs due to defects of the active membrane surface layer. An efficient solution to this problem is to apply coatings that adheres onto the active layer to seal the defects.

Mitrouli et al [20] demonstrated the use of PVP as a Rejection Enhancing agent (REA). In the tests conducted, 3 year old brackish water polyamide membranes were treated with PVP. It was concluded that when PVP was used in the concentration range of 5 – 30 ppm, the salt rejected of the membrane increased by 21% to 36%. The treatment of the membrane with REAs in a cross-flow experimental system, without interrupting normal operation, suggests that the process is attractive for practical applications. The improved membrane performance remained unchanged over a period of one month, indicating towards the durability of the membrane and the increased lifetime of the membrane.

- **Swelling Agent**

Saljoughi et al [21] studied the changes in morphology and performance of Cellulose Acetate membranes caused due to addition of PVP. Asymmetric CA membranes were synthesized using the phase inversion technique. The phase inversion process induced by immersion precipitation is a well-known technique to prepare asymmetric polymeric membranes [22]. In this technique, technique, a cast film containing a polymer and its suitable solvent is immersed into a coagulation bath containing an non-solvent. Then precipitation starts due to the low miscibility between the polymer and the non-solvent, causing formation of nucleuses of polymer-poor phase. Due to continual diffusional flow, the mentioned nucleuses continue to grow until the polymer concentration at their boundaries becomes too high. Rate of the demixing process affects morphology of the CA membranes. Instantaneous demixing often leads to macrovoids formation in the membrane structure, while slow demixing results in denser structure[23-26]. The application of the membranes depends upon the morphology and permeability, which can be controlled by CBT and an additive, PVP in this case. Various membranes with different PVP concentrations and CBTs were prepared and their morphology and PWF were determined. It was found out that initial addition of PVP to the cast film solution (from 0 to 3 wt.%) results in increasing macrovoids formation and PWF. However, further addition of PVP (from 3 to 6 wt.%) results in suppression of macrovoids and reduction of PWF. Increasing CBT always results in increasing macrovoids formation. However, increasing CBT from 0 to 25 °C results in increasing PWF, whereas further increasing CBT from 25 to 50 °C, due to noticeable reduction of the membrane hydrophilicity, results in reduction of PWF.

The role of PVP as a swelling agent was reported by Lafrenigret et al [27] when the effect of PVP in the performance of Polyethersulfone membrane was studied by using different proportions of PVP in the casting solutions of membrane preparation. The PES ultrafiltration membranes were prepared using phase inversion technique and for different concentrations of PES in the casting solution and varying PVP/PES ratio, the percentage solute separation and product rate were found. It was observed that the highest product permeation rate was obtained at a PVP/PES weight ratio of unity when the PES concentration in the casting solution was 15-30% and A wider distribution of the pore size extending into greater values in the pore size is obtainable at the above PVP/PES ratio. The role of PVP as a non solvent swelling agent was identified during the preparation of the membranes. In the gelation process, water of the gelation bath turns to white due to the release of low MW PES but at the PVP/PES ratio at unity, the water coloration was least indicating stronger interaction between PES and PVP. The higher product rate shows that the entrapment of PVP in the membrane increases the hydrophilic nature and hence the permeation flux is increased. It was noted that the primary effect of PVP in the casting solution is on the structure of the casting solution and, asa consequence, on the pore size and the pore size distribution of the membrane. In effect, the N–C=O group, present in PVP, should interact with the more polar group, O=S=O, present in the PES. The interaction could be of donor/receptor type between N-C=O and the aromatic ring of PES, as probed by the viscoelastic behaviour of PES–PVP solutions reported by Lafreniere et al. [28] and by Miyano et al.

- **Pore Size Enhancer**

Marchese et al [29] studies the effect of PVP on the pore sizeof them membrane. The addition of PVP in PES produced not only a structural effect, it also lead to substantial changes in fouling or molecular adsorption on the pore surface of the membrane. Nevertheless, the entrapment of PVP should increase the hydrophilicity and the membranes increase their permeability adding PVP with very similar pore size distribution, [30]. This result can be due to three causes:

a. an increment in the pore density;
b. a decrease of the effective thickness of the dense layer due to macrovoids in the support layer;
c. an increment in the hydrophilicity of the surfaces on the membrane and inside the pores.

AFM results showed an increment in the surface roughness by PVP addition, and also an increment in the porosity; however, this last result is not decisive. It indicates that, certainly, the structure is modified by the PVP addition. But if the additive remained entrapped, it could also increase the hydrophilicity.In a previous study about the characterization of commercial polysulfone membranes with different pore sizes by XPS and phase contrast AFM [31], a correlation between the nitrogen content on the surface (not present in the polysulfone) and the pore size has been found. The existence of nitrogen, probably due to the addition of PVP during the manufacture of these membranes, shows that PVP could remain on the membrane surface. Marcheseet all made several polyethersulfone (PES) ultrafiltration membranes with small quantities of polyvinyl-pyrrolidone (PVP) of different molecular weights to increase the permeability without a significant reduction in selectivity and analysedcorresponding fouling mechanism and subsequent structural modifications havewhen in contact with bovine serum albumin (BSA) and dl-histidine (DLH).

- **Anti- Fouling Agent**

Membrane fouling is a process that foulants in feed water deposit or are adsorbed on the membrane surface [32], which causes flux decline and affects the quality of the water produced [33]. Therefore, it is necessary and meaningful to enhance the fouling resistance of the TFC polyamide RO membrane. It is known that membrane fouling is mainly determined by multiple interactions between membrane surface and foulants. The physic-chemical properties of RO membrane surface, such as hydrophilicity, roughness and charge, are closely related to the fouling . It is known that a more hydrophilic and smoother membrane surface with lower negative charge density exhibited better fouling resistance [34]. Therefore, a great deal of antifouling materials have been used for surface modification to tailor the hydrophilicity, roughness and charge of the RO membrane surface. For example, polyvinylalcohol(PVA) [35], poly(ethyleneglycol) (PEG) and its derivatives [36,37] and zwitterionicpolymers [38-40]are common anti fouling materials which have been introduced onto the RO membrane surface to enhance the fouling resistance. The membrane surface roughness and charge density were reduced in some cases, and generally the surface hydrophilicity of these modified RO membranes was enhanced. Higher surface hydrophilicity of the membrane contributes to forming a hydration layer on the surface, which prevents the adsorption or deposition of hydrophobic foulants. Infact, hydrophilic monomers or polymers are always preferred for the RO membrane surface modification for improvement of the hydrophilicity and fouling resistance [41-43]. PVP has a high affinity for water molecules because of the presence of the polar lactam group in the pyrrolidone moiety that increases the hydrophilicity of the polymer [44]. Actually, PVP has been widely used as the hydrophilic additive and pore-forming agent of casting solution to enhance the water flux and fouling resistance of ultrafiltration membranes [45,46]. Besides, surface modification PVP has been also extensively investigated to prevent the nonspecific protein adsorption on the microfiltration and ultrafiltration membranes [47-49]. Since there are no active functional groups in PVP, the surface modification of RO membrane is not easy to be performed by a “graft to” method. For the microfiltration and ultrafiltration membranes, the surface modification with PVP is usually performed by a “graft from” method using its monomer N-vinyl-2-pyrrolidone.Forexample,by low temperature plasma treatment, PVP was grafted on to the poly(ethersulfone) ultra filtration membrane surface. The PVP-modified membrane had higher filtration performance with less total and irreversible fouling [50]. Feng et al. [51] modified polypropylenene on-woven fabric (NWF)membrane with PVP via ozone surface activation and surface-initiated atom transfer radical polymerization(ATRP).The PVP-modified NWF membrane exhibited better fouling resistance against bacterial. However, PVP has not been used for the surface modification of RO membrane to improve the fouling resistance. It is difficult to immobilize PVP firmly on to a RO membrane surface..It has been reported that PVP is capable of adsorbing polyphenols compounds selectively through strong hydrogen bonding interactions [51-53]. In some cases, the strength of multiple hydrogen bonding interactions between lactam groups in PVP and phenolic hydroxyl groups in polyphenols is comparable to that of covalent interactions [52.53]. This is because PVP is a strong hydrogen acceptor, and compound containing large amounts of phenolic hydroxyl groups is usually a very strong hydrogen donator.

- **Macropore Supressing Agent**

Due to its excellent chemical resistance and good physical and thermal stability, PVDF industrial waste treatment including oily emulsion, organic/water separations, gas absorption and stripping, membrane distillation and ultrafiltration. PVDF membranes prepared were not of practical interest because of their low permeate fluxes [54]. In addition, they are nowadays too expensive to consider for environmental depolluting applications used widely. Blending is frequently used for improving the properties of polymeric membranes [55-57]. Low rejection and large pore size are caused by the fact that large molecular weight PVP tends to form thicker skin layer containing bigger pores [54-60]. Xu et al. studied the effect of PVP for different molecular weight on morphology of polyetherimide hollow fiber membrane. They found that the higher molecular weight of PVP was added, the bigger pore was made [61] on the other hand, Wienk et al. draw that PVP is an agent for suppressing Macropore formation in the phase inversion membranes. Thermodynamically, PVP works as a demixing enhancer that accelerates the phase inversion reduces α crystal structure resulting in reduction of the crystallinity of PVDF in membranes, contributing to the enlargement macrovoidstructure in the membranes, which improves the membrane flux. However, in further increment of PVP, kinetic impact is dominant. The demixing of the casting dope delayed and the crystallinity of PVDF increases, resulting in macrovoids being stretched down like a finger from the underneathof membrane skin to the bottom of a sublayer.PVP in the PVDF/TPU dope suppress macrovoid formation at high concentration. The flux is decreased rather than increased. It reveals that kinetic effect takes over thermodynamic enhancement [62].

- **Hydrophilicity Enhancer**

Qin et all [63] studied the effect of hypochlorite concentration on properties and morphology of the membranes treated for a fixed period of 48 h. The untreated membrane experienced low fouling tendency, but the treated membranes showed significant fouling tendency. The low fouling tendency could be attributed to the hydrophilicity of the untreated membrane due to the hydrophilic PVP blending with a hydrophobic polymer [64–68,69–74] and the high fouling tendency could be attributed to the reduced hydrophilicity of the treated membranes due to the removal of PVP after hypochlorite treatment, which was also supported by SEM images of the membranes. Hypochlorite treatment, therefore, appeared not only to remove residual PVP in the membranes, which reduced swelling of PVP in the pores, but also changed the membrane pore size or pore size distribution. The results also showed the untreated membrane experienced very low fouling tendency due to the hydrophilic PVP blending with PSU while the treated membrane showed significant fouling tendency due to much reduced hydrophilicity. SEM images showed that an inner dense skin layer of less than 0.4 _m could be clearly distinguished after hypochlorite treatment and PVP contents in the blend membrane could be removed by hypochlorite treatment.

- **Effect of Hypochlorite on PVP**

During the past decade, ultrafiltration has become extensively used in the production of high quality drinkingwater. However, it is now well established that fouling, resulting from reversible and irreversible adsorption, the accumulation and cake build-up of water matrix components at the membrane surface, is one of the major drawbacks of membrane filtration processes [75]. As a consequence, for on-site operations, membranes are periodically subjected to cleaning procedures using mostly sodium hypochlorite as oxidizing agent during back-washing and chemical cleaning [76].Aside from their effectiveness in removing irreversible pollutants for optimum restoration of the membrane flux and performance, chemical cleaning agents such as sodium hypochlorite can impact the physical/chemical characteristics of the membrane.The DMA analysis results suggested that the elastic property of membrane is affected by sodium hy- pochlorite exposure dose. In previous work, it was confirmed that hypochlorite exposure induces PVP radical degradation (involving PVP chain scissions) and dislodgement from the PES matrix, leading to an embrittlement of the membrane [77]

In a previous study it was confirmed that sodium hypochlorite affects the membrane materials in such a way that PVP is selectively removed from the membrane matrix. The reaction between hypochlorite and PVP involves chain scission of PVP according to a radical mechanism [78]. The results of SEM showed that many macro-voids formed in the membrane skin structure. According to DMA, TGA and ATR-FTIR analysis, we conclude that this phenomenon resulted from the degradation and dislodgment of the PVP within PVDF matrix which increases both the molecular mobility and the free volume of the polymer[79]

The mechanism of separation in non-porous membranes is based on solubility and diffusion, but the mechanism of separation in porous membrane is based on the differences between particles and pores size. Therefore, determination of the morphology of porous membranes is very important.Some researchers considered the effect of PVP on the performance of PVDF membranes [80,81]. The desire for becoming two phase in solution increase by adding additives to the polymer solution, also viscosity of the solution increases and mass transfer rate between solvent and non-solvent decreases, therefore using additives have two conflicting effect on the demixing process and precipitation rate.Safekordi et al [82] predicted the effect of TiO_2 and PVP on the morphology and performance of the membranes. When PVP wasused as additive with an amount up to 5%, permeability and porosity increased but both of them decreased a bit for higher concentration of PVP. By adding 1% PVP tothe PVDF/DMAc solution the morphology changed and finger like structure was obtained. By increasing the concentration of PVP, relative kinetic parameter increased and the morphology of the membrane changed.

- **Effect of PVP on Morphology**

To enhance the phase inversion method, additives can usually be added to the mixture of base polymer and solvent. Many research studies have been conducted to investigate the role of additives on the membrane preparation process [83–86]. Chakrabarty et al. [87] discussed the impact of PVP molecular weights on the structure and permeation properties of polysulfone (PSf) membranes fabricated using two different solvents (N-methyl-pyrrolidone, NMP and dimethylacetamide (DMAc). It was found that the membrane sublayer becomes denser and pure water flux decreases when higher molecular weight PVP was added to the casting solution. The relationshipbetween additive concentration on membrane performance and structural properties had already been studied by Ismail and Hassan [88]. Boom et al [89] investigated the effect of PVP on the formation of membranes and found that addition of PVP to the ternary system suppresses the formation of macrovoids in the sub-layer, which should be avoided for high pressure operation because of the reduced strength and greater chance of collapse that may occur. The formation phenomena of macrovoids, which are large elongated spaces belowthe upper surface of the membrane, have been discussed by many researchers[90-93]. Susanto and Ulbricht [94] compared the effect of three different macromolecular additives polyvinylpyrrolidone (PVP), polyethyleneglycol (PEG) and Pluronic on the membrane structure and their stability in the polymer membrane matrix of the PES membrane. They found that addition of Pluronic as a modifier agent showed the best performance and stability. Wang et al. [95] reported that the PVP-added PES membrane has a higher water flux, water adsorption, and lower water contact angle (CA) than the pure PES membrane. The contact angle decreased by 16% when the PVP content in the casting solution was 10 wt.%. Saljoughi et al. [96] reported that an increase of PVP concentration in the cast film from 0 to 1.5 wt.% resulted in the facilitation of macrovoid formation in the membrane sublayer, which increased pure water flux (PWF) and decreased the insulin rejection. However, in the samestudy, it was observed that an increase in PVP concentration from 1.5 to 3, 6 and 9wt.% resulted in a decrease in PWF, where the macrovoid had been suppressed gradually. Ochoa et al. [97]proved that the addition of small quantities of different molecular weight PVP to the casting solution increases the UF PES membrane permeability without significant changes in selectivity [97]. Amirilargani et al. [98] studied the influence of blending PVP with PES membranes. It was reported that PES membrane with 1 wt.% of PVP (15,000 g/mol) in casting solution had the best mechanical properties in term of tensile strength and elongation. However, addition of more PVP (3, 6 and 9%) to the casting solution led to a decline in mechanical strength. Cabasso et al. [99] found that the addition of PVP to PS membrane reduces their tensile strength. The main objective of this study is to investigate the effect of PVP concentration on the performance of PES membranes, where two different concentration of PES used to prepare the membranes with the variation in concentration of PVP. It was found that It has been found that addition of PVP to the casting solution strongly enhances the permeability of membrane to a specific point, after which high concentration of PVP may cause the top layer of membrane to become a denser structure leading to a decrease in the measured water permeability[100]. Mechanical property measurements revealed that addition of PVP causes a reduction in tensile strength and elongation properties of the membrane.

- **AG Capping Agent**

The role of PVP in Ag-capping has received considerable attention due to the chemical structure of PVP which contains N atom that protect Ag particles from growing and agglomerating [101]. A number of studies have reported that PVP plays an important role in enhancing flux by acting as 'pore-former' and suppress macrovoid [102,103]. Since PVP can be retained well in polymeric membrane structure the addition of PVP into dope formulation is expected to contribute to the Ag-entrapment on studied membrane surfaces, tailoring the antibacterial properties of membrane [104]. The influence of PVP of variousMWhas been reported by several authors. According to Jung et al., the higher the MW of PVP, the thicker the top layer formed on an asymmetric membrane [105]. The results also revealed that with the addition of higher content of PVP, more PVP materials were presented in membrane structure. Lee et al. quoted that the PVP chain length played an influential role in the formation of Ag particles in polystyrene. They discovered that PVP with mediumlength (MW 10,000) demonstrated the strongest reduction in Ag(0) formation [106]. Basri et al [107] synthesized antibacterial membrane by incorporating Ag with PVP in the membrane and observed in the study that the higher concentration of PVP, the more hydrophilic the membrane.

Conclusion

PVP is a very versatile polymer with a wide spectrum of uses. Since it was first sythesized in 1938, the number of applications have increased tremendously as new properties and uses are discovered. Endowed with properties like highhydrophilicity, pore expansion and highbiofouling resistance, PVP has tremendous potential for use in the membrane industry. This literature survey offers a useful compilation of the results obtained in research of use of PVP in membranes.

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