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Title:

**Preparation of poly(butylene succinate)/poly(vinyl
pyrrolidone) blend membrane for utilization in
pervaporation process**

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Abstract

In the present research, polybutylene succinate (PBS) was applied for the first time in fabrication of pervaporation (PV) membranes and novel PBS/polyvinyl pyrrolidone (PVP) blend membranes were prepared and assessed for dehydration of acetone/water mixture. The influence of PVP concentration on membrane morphology, chemical structure, relative hydrophilicity/hydrophobicity, and mechanical properties was studied through field emission scanning electron microscopy (FESEM), Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, water contact angle measurement, and tensile test, respectively. Moreover, membrane swelling was determined and the performance of the prepared PBS/PVP membranes in PV dehydration of acetone/water mixture was compared via determination of acetone and water fluxes, total permeation flux, separation factor, and pervaporation separation index (PSI). Characterization of the prepared membranes implied that the surface and cross sectional structure of the pure PBS and PBS/PVP membranes was non-porous. Moreover, the presence of PVP in the polymer blend was confirmed via FTIR. The decreased water contact angle and increased swelling degree at higher PVP concentration were observed due to the presence of the hydrophilic PVP additive. Furthermore, tensile strength increased and elongation at break decreased with PVP introduction into the PBS matrix. Performance characterization indicated that blending the PBS solution with 3 wt. % PVP resulted in the best performance and brought about 3, 6.4, and 21 fold increase in total flux, separation factor, and PSI, respectively, compared to those of the pure PBS membrane.

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Preface

Membrane technology is now regarded as a promising separation method in various industrial processes including food, pharmaceutical and biotechnological industries; pure water production; and water and wastewater treatment. Polymers are still the main materials applied in membrane preparation due to their suitable properties. Therefore, the usage of biodegradable polymers in membrane preparation seems crucial since the biodegradable membranes can be well discarded to the environment after passing the service life. It can be expected that this type of novel membranes can be an interesting substitute for the common membranes, such as cellulose acetate (CA), polysulfone (PSf), and polyethersulfone (PES), provided that the final membrane is comparable in different specifications such as mechanical properties, permeability, and selectivity [1].

The aim of the present study was the novel application of PBS as a biodegradable polymer for the preparation of environmentally friendly PV dehydration membranes. In order to enhance the hydrophilicity of PBS and improve its PV dehydration performance, polyvinylpyrrolidone (PVP) was added to the membrane casting solution as a hydrophilic polymeric additive in small amount in order not to disrupt the biodegradable nature of PBS. The influence of PVP addition as well as its concentration in the polymer blend on the characteristics of the membrane was studied via field emission scanning electron

microscopy (FESEM), attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy, determination of membrane water contact angle and swelling degree, tensile test, and PV dehydration of acetone/water mixture. Chapter one deals with an introduction to PV, PV membrane materials and, various techniques for modification of PV dehydration membranes. Chapter two aims to discuss the properties of PBS and PVP as the utilized membrane materials in the present study and their application in preparation of PV membranes in previous literature. The detailed specification of the materials and experimental procedure as well as characterization techniques are mentioned in chapter three. Chapter four provides the obtained results along with the discussion and interpretation of them. Finally, a summary of the results and suggestions for future work are provided in chapter five.

Chapter One

Pervaporation dehydration membranes

1.1 Introduction

PV is one of the most recent membrane separation technologies. Numerous plants are being installed worldwide, the market size is expanding and process innovations are being made. Currently, PV research is focused on novel membrane materials, which exhibit high selectivity and high permeate fluxes. Therefore, the present chapter involves an introduction to PV, PV membrane materials and modification methods.

1.2 Introduction to PV

Membranes are successfully used in separation industries as selective barriers to prevent unwanted solutes from permeating through. Thus the impurity is separated from the target. Separation is based on pore sizes and hence the membranes got their characteristic names as microfiltration, ultrafiltration, and nanofiltration membranes (Fig. 1). Membranes are either porous or nonporous and in the separation based on sizes, usually porous membranes are used. PV is the distinction class among above membranes as the separation criteria are different. PV membranes have been widely employed for separating liquid mixtures. The separation feature is based on affinity with membrane materials and hence the molecule having higher affinity is adsorbed and diffuses through the membrane while the membrane retains molecules having low affinity [2].

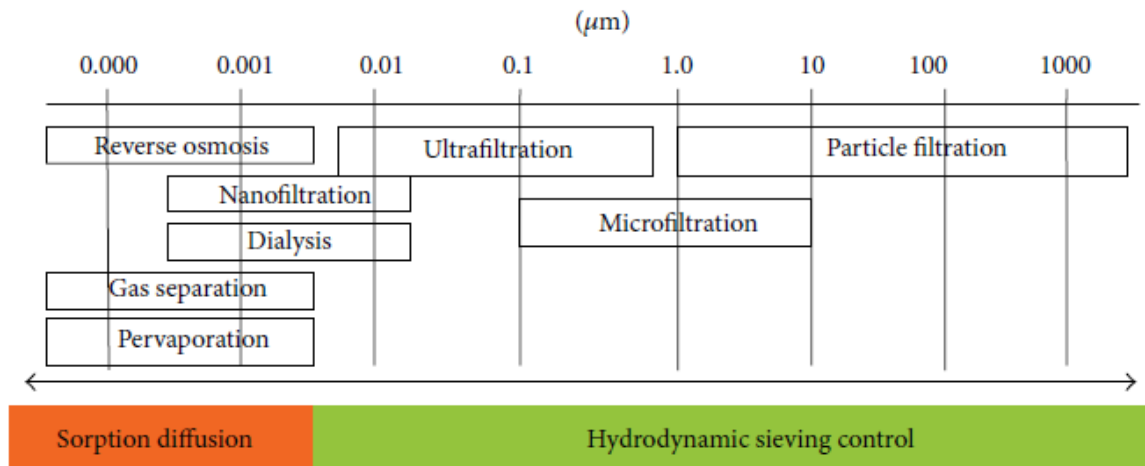


Fig. 1.1 The choice of membrane with respect to the size of particles encountered [2]

PV combines membrane permeation and evaporation for selective separation of liquid molecule mixtures. A general process of PV consists of the following steps: (i) liquid mixture flows through the upstream side of the membrane. (ii) Components in feed pass through the membrane driven by chemical potential difference which can be obtained by vacuumizing, gas sweeping or making thermal difference at the downstream side of the membrane. (iii) Permeate vapor desorbs from the downstream side of the membrane [3].

The mass transport process in PV membranes is generally described by solution-diffusion mechanism and facilitated transport mechanism. Although the phase change from liquid to vapor takes place in PV, only the latent heat of evaporation is required. Therefore, PV is considered as a more energy-saving process compared with broadly utilized distillation operation. Besides, no additives (the third components like entrainers or extractants) are required, which determines PV a more environmentally friendly separation process than azeotropic distillation and extractive distillation [3].

In theory, three effects often exist in PV process, namely, coupling effect, swelling effect and concentration polarization effect. Coupling effect lies in the fact that the rate of

diffusion of one permeant is not independent from that of the others. Attractive molecular interactions among liquid components can result in the formation of associated molecules which are partially immobilized in the membrane, thus causing a mutual drag among them. Coupling effect can be mitigated by improving the preferential affinity between membranes and the desired permeate. Swelling effect derives from the strong interactions between liquid components and the membrane matrix. Excessive swelling of membranes leads to a change in the structure of the membranes over time and hence a decrease in the mechanical strength and the permselectivity. Increasing the content of rigid fillers in polymer matrix is an effective way to decrease the swelling degree of membranes. As for concentration polarization effect, the rejected components are carried to the surface by the flux of the desired permeate, and cannot be balanced by back diffusion of rejected component, thus further forming excessive build-up. Concentration polarization effect can provide additional resistance to the permeation of the desired permeate. Increasing the flow velocity of feed which leads to an accelerated molecular motion can facilitate the diffusion of rejected component between the membrane surface and the bulk feed, thus significantly suppressing concentration polarization effect [3].

1.3 PV applications

In the last two decades, PV is finding wide range of areas for its application such as liquid hydrocarbons separations (petrochemical application, alcohol/ether separations), removal of volatile organic compounds (VOCs) from water, removal of water from glycerin, and dehydration to intensify esterification reaction [2].

PV can be integrated with either distillation or a chemical production step to provide intensification and energy integration. PV-distillation hybrid system leads to a clean technology and offer potential savings in energy because of reduced thermal and pressure

requirements. When integrated with reactions, it offers the opportunity to shift the chemical equilibrium by removing the product of the reaction. Reactor PV hybrid method overcomes the inhibition of the chemical equilibrium of the process and therefore leads to an increased productivity. This process also allows one to use heat of the chemical reaction to increase the efficiency of the PV process and leads consequently to potential savings in energy costs. [2]

The breakthrough of PV in industrial applications was realized in 1982 by GFT (Gesellschaft für Trenntechnik, Hamburg, Germany) with the first PV apparatus established in Brazil to separate ethanol/water azeotropic mixtures. After that, PV developed rapidly in large scale applications. Several companies including PolyAn GmbH in Germany, Sulzer Chemtech in Switzerland and SMART Chemical Company Ltd. in UK can produce commercial PV membranes. Currently, more than one hundred PV apparatuses have been worldwide established and a majority of them are for separation of water from organic-aqueous mixtures. Besides, PV has also found promising applications in another two areas: separation of organics from organic-aqueous mixtures and separation of organics from organic mixtures, which has been proved much more challenging [3].

In general, PV process can be categorized into hydrophilic PV process and organophilic PV process. The application of hydrophilic PV refers to separation of water from organic-aqueous mixtures, such as ethanol dehydration for fuel ethanol and isopropanol dehydration. The application of organophilic PV can further split into sub-sections based on their respective separation mixtures, which include separation of organics from organic-aqueous mixtures (i.e. organic removal from groundwater or drinking water, alcohol removal from beer and wine) and separation of organics from organic-organic mixtures (i.e. gasoline desulfurization and benzene/cyclohexane separation) [3].

1.3.1 Separation of water from organic-aqueous mixtures

In many industries, pure organics are indispensable as both solvents and reactants, and the existence of water in organics goes against production of high quality and efficiency. Separation of water from organic-aqueous mixtures deals with the following systems [3]:

- 1) Water and organic compound can form the azeotrope such as water/ethanol and water/isopropanol, etc.
- 2) Water occupies little amount in the separation system such as water/benzene, etc.

Some researchers coupled PV with chemical reactors by selectively removing the byproduct-water from the esterification reaction unit to enhance conversion performance [3].

1.3.2 Separation of organics from organic-aqueous mixtures

Industrial chemical reaction or biosynthetic processes rarely yield pure products. Thus, the organophilic PV (OPV) technology could be introduced into separation of organics from organic-aqueous mixtures for recycling organic products and for the treatment of wastewater. It has been reported that pervaporative method is more economical than conventional approaches in the environmental industry. The OPV technology is applicable in treating toward bio-alcohols, in particular, isobutanol (next generation biofuels). It is highlighted that the preferential adsorption of a permeating organic species determines to a large extent its overall selectivity for OPV [3].

1.3.3 Separation of organics from organic mixtures

Separation of organics from organic mixtures by the membranes represents the huge challenging application for the PV process since the strong interactions between organic

molecules. The vast majority of liquid pairs in this category are very important in industry, such as benzene/n-hexane, methanol/MTBE, benzene/cyclohexane and so on [3].

1.4 PV membrane structure

Membranes used in the process of PV possess have porous or non-porous structures. Membranes with or without pores in their structure are called porous and non-porous membranes, respectively. Difference of their pores size, shapes and distribution are the factors which determine PV efficiency and selectivity of the membranes. In porous membranes, the permeation is often carried out by size selection or exclusion. In permeating through the pores by diffusing process, such as separating water from organic solution using PV, a significant amount of water permeates across the membrane. Hence, a higher flux and lower selectivity are observed in the porous membranes [4].

The non-porous membranes function by first partitioning the molecule and then under a concentration gradient allowing it to diffuse through the solid material. So, in the non-porous membrane the partition coefficient and diffusivity affect the separation of components, therefore, this type of membrane is used for PV processes with high selectivity [4].

1.5 PV membrane materials

Most of the membrane materials used in PV techniques are usable in laboratory scale, but not in industrial applications. Thus, there is a need to survey more membrane materials possibilities which is important in order to overcome drawbacks in current membranes [4]. In general, there are three types of membrane materials for PV: polymeric, inorganic, and hybrid materials [3]. Moreover, PV membranes can be categorized in to main groups including hydrophobic and hydrophilic membranes.

1.5.1 Hydrophobic membranes

Hydrophobic membranes used as PV membranes are used to separate volatile organic compounds from the body of water. Hydrophobic membrane systems utilize membranes made from proprietary polymeric hollow fiber membranes. The membrane only permits the volatile organic compound and rejects water molecule due to its hydrophobic nature. Hence, PV integrated with membrane separation technology serves as an interesting subject for the separation of organic compounds such as pollutants and high-value products like aroma compounds. Here the membranes employed are polymeric in nature. Rarely, ceramic membranes can also be used. However, when it comes to recovering volatile polar organics from their very dilute solutions in water, the selectivity exhibited by polymeric membranes, as well as ceramic membranes, is not high. [2]

One of the most applied polymeric materials for organic separation is polydimethylsiloxane (PDMS). PDMS exhibits high selectivity and permeability towards organic substances because of the flexible structure and therefore is preferred for the removal of organic compounds from water [2].

1.5.2 Hydrophilic membranes

For PV, the hydrophilic membranes were the first one to achieve the industrial applications and were used for the organic solvent dehydration. The main industrial applications in PV even today are almost the same as before, which is the dehydration of organic liquids. Commercially available hydrophilic membranes are made of polymeric membrane materials such as polyvinyl alcohol (PVA), polyimides, polymaleimides, and polyacrylonitrile (PAN) [2].

Presently there have been a number of investigators concerning research and development of the hydrophilic membrane, which can be divided into organic, inorganic, and organic-inorganic hybrid membranes.

Since the objective of the present research is the preparation and characterization of a blend polymeric membrane for PV dehydration, the polymeric PV dehydration membranes are introduced in the following sections.

1.6 Polymeric PV dehydration membranes

Polymers are firstly and most widely used as PV membrane materials owing to their low cost, easy processing, good mechanical stability, and tuneable transport properties [3].

Ionic polymers contain ionic groups that are neutralized by counterions. They may be viewed as crosslinked polyelectrolytes. Ionic membranes, which can be subdivided into cationic and anionic, are normally water selective due to their affinity to water. Ionic polysaccharides have been shown to be potential materials for making dehydration membranes [5].

A membrane with low hydrophilicity generally exhibits a low water flux in dehydration, but some membranes made of polymers with very high hydrophilicity such as PVA and poly(acrylic acid) (PAA) need cross-linking for improved stability and selectivity. The polymer materials for dehydration membranes should maintain a proper balance of hydrophilicity and hydrophobicity. Improvement in membrane performance can often be achieved by polymer modification, for which several techniques have been developed, including cross-linking, grafting, blending, copolymerization, and incorporation of adsorbent materials [5].

Interpenetrating polymer networks (IPN's) are a unique type of polymer blend. IPN membranes of hydrophilic/hydrophobic, cationic/anionic, and glassy/ rubbery constituents offer another way of improving membrane performance. Such membranes can be prepared either by simultaneous polymerization of both networks or by sequential polymerization in which a polymer is swollen in a monomer followed by in situ polymerization of the monomer. Many polymers that can be formed into membranes have been investigated in terms of PV properties, and the list of polymer membrane materials is virtually endless insofar as possible chemical varieties are concerned. To improve permselectivity, it has been attempted to fill the membrane with organophilic adsorbent. As such, the sorption capacity and/or sorption selectivity will be enhanced due to the adsorbent fillers. However, strong adsorption will cause immobilization of the permeating species, leading to a reduction in permeation flux. Thus, suitable adsorbent filler should have proper organophilicity, hydrophobicity, and pore size characteristics. Poly(1-(trimethylsilyl)- 1-propyne) is an extraordinary glassy polymer. It has ~25% voids which may be linked through chain-to-chain gaps at least ~3 Å wide. Gas permeabilities through the polymer are orders of magnitude larger than in other glassy polymers due to its loose microstructure and high mobility of the pendant groups. However, during PV operations, both permeability and selectivity decline with operation time. The problem associated with membrane stability sustained applicability of this unique material for producing industrial PV membranes. For making dehydration membranes, PVA- and PAA-based polymers are the most widely used materials, while chitosan and aromatic polyimide materials are attracting great interest. PVA is a 1,3-diglycol polymer whose hydroxyl groups have strong interactions with water through hydrogen bonding. It is one of the very few high-molecular-weight water-soluble resins and can easily be cross-linked either chemically or thermally. Of all the membranes for PV separation of aqueous organic mixtures, PVA-

based membranes have been studied most intensively. Most of the research is centered on modification of PVA for improved permselectivity and stability and performance testing for various perspective applications. The commercial membrane of GFT Co. for solvent dehydration is made from chemically cross-linked PVA [5].

PAA is another polymer suitable for preparing water selective membranes. It has a high charge density based on the carboxyl groups, which are readily available for cross-linking and salt formation with alkaline metals. Multivalent cations such as Al^{3+} , Cr^{3+} , Ca^{2+} , and Mg^{2+} can be used to induce ionic cross-linking for improved resistance of PAA to dissociation in aqueous solutions. Alternatively, PAA can undergo ionization. It has been observed that by converting the acidic form of PAA to an alkali-metal salt form, both permeability and selectivity can be enhanced. However, the membrane suffers from the problem of long-term stability due to elution of the alkaline-metal ions out of the membrane, which leads to regeneration of polyacrylate to its acid form. Maintaining an appropriate pH of feed solution would immobilize the alkaline-metal ions in the membrane, but this method has limited applicability from an application point of view. Another way to stabilize the polyacrylate membrane is to use certain polycations, instead of alkali metals, to form a stable polyion complex. This method has been shown to be quite effective. BP International of the U.K. and Daicel Chemical of Japan are developing PAA-based membranes for solvent dehydration. Chitosan is the N-deacetylated product of chitin, the second most abundant natural polymer next to cellulose. It is a linear polymer comprised primarily of glucosamine. The reactive amino groups and the primary and secondary hydroxyl groups can be used for chemical modifications. Chitosan is considered as a versatile material for various applications partly due to the large variety of useful forms that either are commercially available or can be readily obtained in the laboratory.

Chitosan membranes have high water permselectivity and solvent stability. Chitosan in its free amine form is insoluble in water at neutral H's. However, in some acidic solutions (e.g., acetic acid), the free amino groups (NH_2) become protonated to form water-soluble chitosan- acid salts. Treatment of the latter with an alkaline solution converts the cationic amine groups (NH_3^+) into the NH_2 form, thereby accomplishing regeneration of chitosan to the free amine form. Therefore, chitosan membranes can be prepared by casting an aqueous solution of an appropriate chitosan acid salt, followed by neutralization with an alkaline solution [5].

1.7 Membrane modification for PV dehydration

According to the solution-diffusion model, membrane permeability is determined by diffusivity and solubility, and thus, membrane selectivity is determined by sorption selectivity and diffusion selectivity. While smaller permeating molecules normally exhibit larger diffusivity, the solubility is often influenced by the chemical affinity of the permeating species to the membrane material. Consider the separation of aqueous-organic mixtures where the water molecules are smaller than organic compounds. A hydrophilic membrane favors both solubility and diffusivity for selective permeation of water, while an organophilic membrane must have a large solubility to the organic compound in order to permeate the organic compound preferentially because of the unfavorable diffusion selectivity. This may be the reason that many polymers are selective to water permeation, while only a few are selective to the permeation of organic compounds [5].

It was previously stated that in order to prevent a low water flux in dehydration, the use of membranes with low hydrophilicity should be avoided. Therefore, polymer modification should be conducted for improving the membrane performance through techniques such as

cross-linking, grafting, blending, copolymerization, and incorporation of adsorbent materials [5].

It is reported that the smooth, mechanically resistant films are preferable for the manufacturing of PV membranes. In most cases, the films should also maintain a proper hydrophilic-hydrophobic balance because the introduction of hydrophilic groups swells the membranes significantly under aqueous mixture due to its plasticization action which results in poor selectivity [6].

The feasibility of a membrane process depends largely on the characteristics of the membrane material. In the PV process, it is desirable to have a polymeric membrane with the combined characteristics of high permeation and good selectivity. Usually, a membrane with high flux gives a low selectivity, and vice versa, so that an optimal combination of flux and selectivity should be determined by adjusting and controlling hydrophilic-hydrophobic balance properties of a membrane [6].

Since usually a single polymer does not possess the optimum properties for a given separation, new membrane materials are essential and have to be developed to achieve the desired balance of PV properties. Over the years, numerous membrane materials have been developed in order to create a polymer material whose properties correspond to the separation purposes. Most of the works have been focused at balancing the hydrophilicity-hydrophobicity of the polymer materials by incorporating some special groups into the polymer structure. In order to adjust and control the hydrophobic and hydrophilic balance of a polymer membrane, various modification techniques including copolymerization, polymer blending, and crosslinking have been investigated [6].

1.7.1 Copolymerization

Two or more different monomers can be polymerized to produce polymers that are covalent bonded. In general, the purpose is to blend the properties of each polymer that would occur if each monomer was individually polymerized. One of the monomer units may impart the structural integrity and mechanical property to the polymer chain. The second monomer unit may interact with the desired component of the feed. For example, the monomer and feed component may have similar solubility parameters. The monomer unit may be soluble in one feed component but not in the other component. Therefore, copolymerization can tailor the polymer to dilute too strong an interaction between feed and membrane that would be detrimental to membrane structural integrity. There are three structural types of copolymers [6]:

- 1) Random copolymer: the structural units are completely irregularly distributed and its properties are strongly dependent on the ratio of the structural unit;
- 2) Block copolymer: each monomer unit is distributed in blocks throughout the polymer chain and because of the miscibility of different oligomer blocks, phase separation might occur;
- 3) Graft copolymer: it consists of a regular main chain with irregular distribution of side chains of different monomer blocks. These monomer blocks can be covalently bonded to the main chain by chemical reaction or by irradiation.

Much attention has been directed toward graft polymerization processes as a means of the preparation of PV membranes. By graft copolymerization, much higher permselective layers can be introduced into the separation membrane without dissolution to the solvents. In addition to such characteristics, this procedure has the following advantages [6]:

- 1) The permselective layer composed of graft polymers is chemically bonded to the substrate film, and therefore mechanically stable;
- 2) Graft polymers can be further modified to improve the permselectivity, e.g., by metal-ionization, coupling, and other chemical reactions without causing faults on the substrates.

Among the methods for the initiation of graft polymerization, irradiation-induced grafting is the most popular and has been applied to improve significantly the membrane performance [6]. Most of the radiation grafted membranes have hydrophilic nature and therefore they have been found most suitable for removal of water from organic mixtures [7].

Plasma graft copolymerization, which is initiated by the surface-specific activation by glow discharge plasmas, is another hopeful means for the preparation of PV membranes. As the effects of plasmas are formed generally in a surface-specific manner, the bulk chemical structure and therefore its properties can be preserved [6].

In the PV dehydration process, the interaction of hydrogen bonding between the membrane material and water plays an important role in enhancing the permselectivity of water. One component of the feed mixture may be preferentially sorbed at the interface, and the strong interaction of the functional group increases the permselectivity [8].

In a research conducted by Lai et al. [8], by addressing the problem associated with the hydrolysis of PVA, its hydrophilic nature was used to improve the hydrophilicity of a polyamide membrane for PV process. To avoid such a defect, membranes were modified by irradiation grafting of vinyl acetate (VAc) onto a Nylon membrane to obtain the PVA-grafted Nylon membranes [8].

1.7.2 Crosslinking

In general, crosslinking is used to enhance resistance of a polymer material to its environment. In membrane technology, there are two reasons why a polymer is crosslinked. The first reason is to make the polymer insoluble for the feed mixture and the second reason is to decrease the degree of swelling of a polymer to maintain selectivity, especially for hydrophilic polymers such as PVA and PAA. A good example is the chemically crosslinked PVA top layer of the GFT¹ composite membranes which show excellent resistance to many solvents [6].

Crosslinking can be achieved by chemical reaction of a compound connecting two polymer chains, by irradiation, or by ionization. The degree of crosslinking is important; too low a level of crosslinking would allow excessive swelling and loss of selectivity, while too high a level of crosslinking reduces flux and may cause brittleness and mechanical failure [6].

1.7.3 Polymer blending

Polymer properties can also be blended at a molecular level by blending one polymer with another. A mixture of two or more polymers which are not covalently bonded is called a polymer blend. Polymer blending is a convenient technique for studying the influence of the modifications of the membrane nature on its PV characteristics [6].

In general, two kinds of blends can be distinguished [6]:

- 1) Homogeneous blends, in which the two polymers are miscible on a molecular scale for all compositions;
- 2) Heterogeneous blends, in which the two polymers are not totally miscible.

¹ Gesellschaft für Trenntechnik (GFT) Co., Germany

The properties of a homogeneous blend differ substantially from those of a heterogeneous blend. The properties of the individual polymers disappear in a homogeneous blend and often the properties of the blend lie between those of the two polymers. Since the homogeneous polymer blends are compatible at the molecular level, the new distinctive polymeric material thus combines the properties of the polymeric components [6]. Having said that, the properties of both materials are still present in a heterogeneous blend. In this case, heterogeneous blends are comparable to random copolymers where domains of one polymer within the matrix of the other polymer can be observed [6].

As potential membrane materials, only homogeneous blends are considered because heterogeneous blends will not give enough mechanical strength to the thin membrane. Two polymers mix homogeneously when the free energy of mixing, ΔG_m is negative [6]:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1-1)$$

The entropy of mixing, ΔS_m , is very small for polymers, which makes the influence of $T\Delta S_m$ very small, too. This means that the enthalpy of mixing, ΔH_m , must be smaller than $T\Delta S_m$ or even negative to produce a homogeneous polymer blend. Specific intermolecular interactions such as hydrogen bonding, are often necessary to ensure compatibility [6].

Polymer blends represent an attractive low-cost alternative to the synthesis of entirely new macromolecules and polymer blend technology has gained increasing interest from both the scientific and industrial communities [6].

Chapter Two

Literature review

2.1 Introduction

It was stated in Chapter 1 that the performance optimization of a membrane material is possible through a variety of techniques such as crosslinking, blending, copolymerization, etc. [5]. Among various modification methods, polymer blending is an attractive low-cost alternative to the synthesis of entirely new macromolecules which has gained increasing interest from both the scientific and industrial communities [6].

In the present research, polybutylene succinate (PBS) was utilized as the main polymer for preparation of PV dehydration membranes and membrane modification was accomplished through blending PBS with polyvinylpyrrolidone (PVP). In the following sections, the properties of PBS and PVP are summarized. Then a review on the published literature on preparation and characterization of PV membranes prepared from either PBS or PVP is conducted.

2.2 Polymers utilized in the present study

2.2.1 Polybutylene succinate (PBS)

Due to increasing concerns on sustainable development and the impact of materials on the environment, biodegradable materials have attracted intensive interest in the past decades. Among them, PBS synthesized from succinic acid and 1,4-butanediol (BDO) exhibits

balanced performance in thermal and mechanical properties as well as thermoplastic processability compared with other common plastics [9], as shown in Table 1.

Table 2.1 Physical properties of PBS compared with polylactic acid (PLA) and some commodity plastics [9]

Items	PLA (LACEA)	PBS (Bionolle) #1000	PP¹ MA210	HDPE²	LDPE³ F082
Glass transition temperature (°C)	55	-32	-5	-120	-120
Melting point (°C)	170-180	114	163	129	110
Heat distortion temperature (°C)	55	97	110	82	49
Tensile strength (MPa)	66	34	33	28	10
Elongation at break (%)	4	560	415	700	300

Via copolymerization with other dicarboxylic acids or diols, the properties of PBS can be varied in a wide range, which is a promising advantage for various applications. Massive efforts have been devoted to investigate the synthesis and properties of PBS and its copolymers. Due to the limitation of fossil resources and the concern on the corresponding emission of CO₂, the feedstocks derived from renewable resources have been candidates for synthesis of PBS and its copolymers [9].

¹ Polypropylene

² High-density polyethylene

³ Low-density polyethylene

Among the family of aliphatic poly(alkylene dicarboxylate) polyesters, poly(ethylene oxalate), poly(ethylene succinate) and poly(butylene succinate) demonstrate melting points exceeding 100 °C, which is crucial for applications at a high temperature range. Though poly(ethylene oxalate) has an equilibrium melting point of 177 °C, it attracts less attention due to its low thermal stability [9].

PBS is a highly crystalline polyester with its melting point at around 115 °C and heat distortion temperature at 97 °C. The tensile yield strength of unoriented specimens reaches up to 30–35 MPa, which is comparable to that of polypropylene. PBS is flexible with Young's modulus in the range of 300–500 MPa, depending on the degree of crystallinity [9].

To tailor design the physical properties of PBS, random copolymerization with different types of comonomer units has been examined, including adipic acid, terephthalic acid, methyl succinic acid, 2,2-dimethyl succinic acid, benzyl succinic acid, ethylene glycol and 1,3-propanediol, etc. It should be noted that random copolymerization usually results in a decreased melting point, degree of crystallinity, heat distortion temperature, and tensile strength. On the other hand, the elongation at break and impact strength usually rise with copolymerization [9].

As stated before, one of the interesting features of PBS is its biodegradability. PBS and its copolymers are biodegradable in lipase solution, soil burial, water, activated sludge and compost. Enzymatic degradation of PBS and its copolymers is faster than hydrolysis at neutral pH without enzyme [9].

2.2.2 Polyvinylpyrrolidone (PVP)

PVP is a widely applied polymer with highly interesting properties. Its unique combination of extraordinary physical and chemical properties (biocompatibility, nontoxicity, chemical stability, good solubility in water and many organic solvents, affinity to complex both hydrophobic and hydrophilic substances) made it suitable as a biomaterial in numerous significant medical and nonmedical applications (pharmaceutical industry and medicine, optical and electrical applications, membranes, adhesives, ceramics, paper, coatings and inks, household, industrial and institutional, lithography and photography, fibers and textiles, environmental applications) [10].

Pharmaceutical industry and medicine is the first and probably the most recognized field who benefited from the use of PVP, due to its excellent biocompatibility and capability to form stable association compounds and complexes with many active substances. Starting as a blood plasma expander, now the polymer is a common ingredient in drug manufacture, leading to all kinds of tablets, granules, pellets, soft gelatine capsules, gels, hydrogels, films and coatings, membranes and mats of nanofibers, powders, syrups, oral or injectable solutions, coatings for medical devices, contact lenses, and many others [10].

Its good electrical properties opened the path for PVP in various uses in electrical and optical applications, such as screens, printed circuit boards, cathode ray tubes, energy storage devices, solar cells, etc [10].

Nontoxic and soluble in water and many organic solvents, this polymer is an additive and a pore-former agent in membrane fabrication for biomedical applications, water purification, wastewater treatment, desalination, food processing (e.g., beer and wine filtration), gas separation, etc [10].

Adhesive properties of PVP have been exploited for many years for different uses in skin adhesives, hot-melt adhesives, glue sticks, etc. A wide range of paper products (copying paper, printing paper, electric insulating paper, thermal paper, etc.) and office supplies have been reported to use this polymer. Very broad prospects of application in cosmetics and toiletries, detergents and soaps, and many other household, industrial and institutional products are highlighted. Even the fibers and textile industry are included, where PVP is used in fiber production, dyeing and finishing treatment [10].

PVP is water-soluble, nontoxic, biocompatible polymer, chemically inert, temperature-resistant, pH-stable, nonionic and colorless. In dry form, it is a light flaky white to yellowish white hygroscopic powder with different particle sizes, which absorbs up to 40% of water by its weight. Dissolved in an aqueous solution, it has a very little taste of its own. Depending on the average molecular weight, the glass transition point (T_g) of PVP can range from 100°C (for $M_w=2.5\times 10^3$ g/mol) to 175°C (for $M_w\sim 10^6$ g/mol). T_g values fall below 100°C at low molecular weights [10].

Solubility of PVP is one of its most important properties, determining the broad area of applications. Due to the fact that PVP has hydrophilic as well as hydrophobic functional groups, it interacts with various solvents (readily soluble in cold water, also soluble in many organic solvents, including alcohols, some chlorinated compounds such as chloroform, methylene chloride and ethylene dichloride, nitroparaffins, and amines) [10]. Table 2.2 indicates the solubility of PVP in various solvents.

Table 2.2 Solubility of PVP in various solvents [10]

Soluble in		Insoluble in	
Water	Di(ethylene glycol)	Ethyl acetate	Carbon tetrachloride
Methanol	Poly(ethylene glycol) 400	Acetone	Light petroleum
Ethanol	Propylene glycol	Dioxane	Toluene
Propanol	1,4-Butanediol	Diethyl ether	Xylene
Butanol	Glycerol	Pentane	Liquid paraffin
Cyclohexanol	N-Vinylpyrrolidone	Cyclohexane	Mineral oil
Chloroform	Triethanolamine	Cyclohexanol	Nitromethane/Water
Dichloromethane	Formic acid		
1,2-Dichloroethane	Acetic acid		
N-Methylpyrrolidone	Propionic acid		
Ethylenediamine	Nitromethane		

2.3 Literature review on application of PBS and PVP polymers in PV membranes

With respect to the biodegradability of PBS, its application in preparation of biodegradable filtration membranes has been studied so far in a few number of researches [1, 11, 12]. As stated before, blending two different polymers is a promising method to improve the material performance [9]. Accordingly, a number of researches were conducted on blending PBS with PES/polyethylene glycol (PEG) [1], CA [11], and CA/dextran [12] to prepare biodegradable membranes for filtration of aqueous media. However, despite the interesting characteristics of PBS, it has not been employed in fabrication of PV membranes, yet.

On the other hand, as a nontoxic polymer, soluble in water and organic solvents, PVP is one of the best polymeric additives in ultra-, macro-, micro- and nanofiltration membrane fabrication. It is utilized as a pore former and to control the membrane structure, for: biomedical applications (e.g., hemodialysis), water purification, wastewater treatment, desalination, food processing, gas separation, selective permeability, hollow fiber membranes, and many others. Among the multiple functions that this polymer has in membrane applications, there can be mentioned: it adjusts pore size and pore size distribution, antifouling properties, good compatibility with a broad variety of compounds, ability to form hydrophilic membrane increases membrane permeability, strong polar character and hydrophilicity improves selective material separation properties, high biocompatibility, especially with blood, and toxicologically safe. The main uses are in polysulfone (PS), polyethersulfone (PES), polyphenylene oxide (PPO) and polyvinylidene fluoride (PVDF) membranes [10]. The application of PVP in PV process was reported by a number of researchers in separation of organic-organic mixtures [13, 14] or dehydration of organic-water mixtures [15-20]. A summary of the reported literature is given in Table 2.3.

Regarding PV application, some researchers reported the application of PVP in polymer blends for organic-organic separation. In a research conducted by Wu et al. [13], modified CA membranes for PV separation of methanol/methyl tert-butyl ether (MTBE) mixtures were prepared. Given the compact structure of the membrane, the permeation flux of pure CA membrane prepared by using dimethylformamide (DMF) as a solvent is reported to be relatively low for the separation of methanol/MTBE mixtures. However, PVP was chosen as the additive to blend with CA, with the aim of increasing the permeation flux without appreciably reducing the selectivity [13].

Table 2.3 Summary of the literature reported on application of PVP in preparation of PV membranes

Separation field	Membrane material	Detailed application	Reference
PV separation of organic-organic mixtures	CA/PVP	Separation of methanol/MTBE ¹	[13]
	PLA/PVP	Separation of ethanol/cyclohexane	[21]
	PLA/PVP	Separation of ethanol/ETBE ²	[14]
PV dehydration of organic-water mixtures	Chitosan/PVP	Dehydration of ethyl acetate/ethanol	[17]
	Chitosan/PVP	Dehydration of THF	[16]
	PVA/PVP/PMA ³ particles	Dehydration of ethanol	[15]
	PVA/PVP/PMA particles	Dehydration of isopropanol	[18]
	PAN ⁴ /PVP	Dehydration of THF	[19]
	NaAlg ⁵ /PVP on PAN support	Dehydration of caprolactam	[20]

PVP is soluble in water and most common organic solvents; however it is difficult to dissolve in ethers including MTBE and ETBE. The fact that the miscibility between PVP and methanol is much stronger than that between PVP and MTBE makes it reasonable to suppose that the PV performance of pure CA membrane may be enhanced by incorporating PVP into the CA matrix. Therefore, CA/PVP blend membranes with different PVP

¹ methyl tert-butyl ether

² ethyl tert-butyl ether

³ Phosphomolybdic acid

⁴ Polyacrylonitrile

⁵ Sodium alginate

contents were prepared for the PV separation of methanol/MTBE mixtures. The effect of PVP content in the blend membranes on the PV performance was discussed in terms of the sorption and diffusion behavior. The permeation flux was increased by the addition of PVP and the separation factor was also increased when the PVP content was in the range of 10-15 wt. %. Among all the fabricated blend membranes, the membrane containing 85 wt. % CA and 15 wt. % PVP showed the highest separation factor with a value of 411 and a permeation flux of 430 g/m²h for a feed composed of 20 wt. % methanol. It was demonstrated that the incorporation of PVP into CA matrix distinctly increased the permeation flux. Analysis of the sorption selectivity and diffusion selectivity revealed that the permeating process was governed by diffusion rather than sorption [13].

In another study, the successful use of a natural source polymer, polylactic acid (PLA), in combination with PVP, in PV separation of ethanol/cyclohexane azeotropic mixture was demonstrated. The membranes were able to selectively separate ethanol from the feed. Although all the membranes were ethanol selective, even a low amount of PVP in the PLA membrane could significantly increase the selectivity from 7.5 to 47.4. Due to the polarity of hydroxyl group in ethanol, a higher affinity was observed as the PVP content of the membranes increased. Adding up to around 11 wt. % PVP, the highest separation factor (around 120) was obtained, with no significant increase at higher PVP concentrations. On the other hand, the fluxes were continuously increased at higher PVP contents from 20 to 50 kg/m²h due to the higher affinity to ethanol, together with the more porous structure obtained. Furthermore, swelling experiments confirmed the same affinity to ethanol at higher PVP contents. All the membranes preferably absorb ethanol in their matrix, particularly at higher PVP contents, resulting in a higher degree of swelling up to 51.19% [21].

The same research group studied the PV properties of PLA, in another apolar/non-polar case study. PLA/PVP blend membranes were prepared containing different PVP contents and evaluated in ethanol/ethyl tert-butyl ether (ETBE) azeotropic separation. SEM cross-sectional images showed a porous structure at higher PVP concentrations. All the studied membranes selectively separated ethanol from ETBE. Compared to the literature, the obtained separation factors were not satisfactory. However, the fluxes were well in the range. The degree of swelling as well as the permeation flux ($0.05\text{--}1.36\text{ kg/m}^2\text{h}$) gradually increased when the PVP amount increased to 21 wt. %. On the other hand, the ethanol separation factor initially raised to 16 using 3 wt. % PVP and then decreased to 3 using 21 wt. % PVP. The continuously decreasing water contact angle confirmed higher hydrophilicity and ethanol affinity at higher PVP contents. However, the more porous morphology and the plasticization effect resulted in selectivity decrease [14].

In addition to the literature involving the preparation on PVP blend membranes for PV separation of organic-organic mixtures, a number of researches reported the introduction of PVP to the polymeric matrices for preparation of PV dehydration membranes. A summary of these studies is provided below.

Zhang et al. [17] prepared chitosan/PVP blend membranes crosslinked by glutaraldehyde for the separation of ethyl acetate/ethanol/water azeotrope by PV. The PV properties of the membranes were investigated through dehydration of the azeotrope. Crosslinking by GA and annealing could efficiently control the swelling of the membranes to ensure a high separation factor. Moreover, the addition of a certain amount of PVP could enhance the hydrophilicity of the membranes which was in favor of increasing permeation flux. However, the separation factor increased with increasing GA content, whereas the flux

decreased. The results showed that the membranes with PVP content of 10 wt% exhibited excellent PV properties with a flux of 953 g/m²h and separation factor of 746 [17].

Another study aimed PV dehydration of THF using the blend membranes of chitosan/PVP. Membranes were physically blended and crosslinked with glutaraldehyde as well as with sulfuric acid in methanol/sulfuric acid mixture bath to enhance their selectivity and mechanical strength properties. Sorption studies were carried out in pure as well as in different compositions of THF/water mixtures to assess polymer-liquid interactions. The membrane exhibited a high selectivity of 1025 with a reasonably high water flux value of 99.5 g/m²h at the azeotropic feed composition (94.31 wt. % of THF). It was demonstrated that blending CS with PVP reduced crystallinity, improved the permeability and selectivity to water. FTIR spectroscopy revealed the interaction between PVP and CS. The membranes of this study showed an adequate thermal stability to withstand the PV experimental conditions [16].

Mixed matrix blend membranes of PVA/PVP loaded with various concentrations of phosphomolybdic acid (PMA) were prepared and characterized. It was demonstrated that after incorporating 4 wt. % of PMA particles into PVA/PVP blend matrix, the PV performance of the filled matrix membranes was enhanced during ethanol dehydration. However, higher loadings (8 and 12 wt. %) of PMA particles did not result in any improvement of PV performance. Membrane characterization by DSC and DMTA revealed an adequate thermal and mechanical stability of the membranes. Sorption selectivity of such membranes being much higher than diffusion selectivity, favored the water separation selectivity during ethanol dehydration since the process was dominated by sorption mechanism. Sorption selectivity at 4 wt. % PMA was higher than the membrane prepared at 8 and 12 wt. % PMA, due to better compatibility of PMA particles into the

membrane at 4 wt. % loading. Selective sorption by the filler particles increased the preferentially permeating water molecules from ethanol-containing mixtures [15].

Preparation of mixed matrix membranes of PVA/PVP blends loaded with PMA was reported by another research group, Mali et al. [18]. They were fabricated and studied in terms of PV performance in PV dehydration of isopropanol. Membrane performance showed a dependence on the extent of PMA loading. The 4 wt. % PMA-loaded blend membrane had the highest separation factor, which declined considerably at higher loading. The flux of 4 wt. % PMA-loaded membrane was lower than that of unloaded blend membrane. Solubility selectivity being higher than diffusion selectivity, suggests that separation is dominated by solubility rather than diffusion selectivity. Degree of swelling was smaller after PMA loading exhibiting better separation ability. The near azeotropic composition of water/isopropanol mixture (10 wt. % water) could be efficiently separated using the obtained membrane [18].

In a previous study, membranes were made by blending polyacrylonitrile (PAN) and PVP in DMF, followed by an evaporation-coagulation phase to solidify the blends. Membranes of different structures were obtained by changing the preparation conditions: asymmetric membranes with finger-like macrovoids (low PVP content in the polymer and low solvent content in the precipitant bath), asymmetric membranes with honeycomb-like sub-structure, unskinned, granulous membranes (long precipitation in tetrahydrofuran (THF)), and dense film membranes (long evaporation time). The formation of these structures was interpreted on the basis of known mechanisms, except in the case of unskinned granulous membranes, where other hypotheses were proposed. Only dense membranes were sufficiently selective for the dehydration of water-organic liquid mixtures. Highest selectivity was obtained at a 1:1 composition of the blend. This type of membrane showed

good performance with water/THF mixtures. Its selectivity was lower but its permeability was higher with water-ethanol mixtures. The entanglement of PVP chains by PAN macromolecules produced a membrane sufficiently stable to withstand 50 hours of PV without being modified [19].

To develop a new caprolactam dehydration process, PV separation of caprolactam/water solutions was investigated using a composite membrane consisting of a selective sodium alginate (NaAlg)/PVP blend membrane as top layer and a PAN ultrafiltration (UF) membrane as substrate. The selective layer was physically blended and crosslinked with glutaraldehyde. The effect of PVP content in the blend membranes on the PV performance was investigated. The blend membranes showed good performance in PV dehydration of caprolactam aqueous solutions. It was demonstrated that introducing PVP could enhance the hydrophilicity of the membranes and was in favor of increasing permeation flux. Especially, as the PVP content in blend membranes increased from 0 to 20 wt.%, the separation factor also increased. The blend membrane containing 20 wt. % PVP exhibited excellent PV properties with a flux of 1634.4 g/(m²h) and separation factor of 1610.6 at 323 K, for 50 wt. % caprolactam. The evaluated results revealed that the separation performances of NaAlg–PVP composite membranes were strongly related to their intrinsic hydrophilic/hydrophobic nature as well as the operating parameters [20].

2.4 Purpose of the present study

According to the literature review, the preparation of PBS membranes for application in PV process has not been reported, yet. Moreover, a few number of researchers previously reported the modification of PV membranes via blending with PVP. Indeed, the positive influence of PVP introduction into the polymer matrix on PV dehydration performance of the blend membrane was reported in some previous researches. Therefore, the aim of the

present study is the preparation of PBS PV membranes for dehydration of organic-water mixture. Furthermore, the membrane performance is enhanced through blending with PVP.

Chapter Three

Materials and methods

3.1 Introduction

In the present study, PBS/PVP membranes were prepared and investigated for PV dehydration of acetone/water mixtures. Field emission scanning electron microscopy (FESEM) was conducted for morphological studies of the membrane. Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and water contact angle measurement were applied to study the chemical structure of the membranes and their relative hydrophilic/hydrophobic property, respectively. Moreover, membrane swelling was determined and the mechanical properties of the membranes were investigated via tensile test. In addition, PV performance of the membranes was compared during PV dehydration of acetone/water mixtures. The specifications of the utilized materials along with the detailed procedure of membrane preparation and characterization are provided in the following sections.

3.2 Materials

Polybutylene succinate (PBS) (density=1.3 g/ml and $T_m=120^\circ\text{C}$) extended with 1,6-diisocyanatohexane was purchased from Sigma-Aldrich and applied as the main polymer. Polyvinylpyrrolidone (PVP) K 25 (average $M_w\sim 24,000$) was also obtained from Sigma-Aldrich and used as the polymeric additive in preparation of membranes. N-methyl-2-pyrrolidone (NMP) (density=1.03 g/ml and purity $\geq 99.5\%$) was supplied by Daejung and

used as solvent in the membrane casting solution. Acetone (density=0.784 g/ml and purity \geq 99%) was obtained from Dr. Mojalali Industrial Chemical Complex Co. and used as the main feed component. Distilled water was utilized in preparation of the feed in PV experiments.

3.3 Membrane preparation

Pure PBS casting solution was prepared by dissolving 15.5 wt. % PBS in NMP via stirring at 70 °C for 3 h. Blend PBS/PVP casting solutions were obtained by addition of specified amount of PVP in previously obtained PBS solution followed by stirring at 70 °C for additional 3 h. The concentration of PBS in the final solutions was kept constant at 15.5 wt. % while the PVP concentration was varied at 0, 1, 2, and 3 wt. %. In order to prevent the appearance of defects in the membrane structure, the resultant solutions were left for 2 h at 70 °C without stirring to remove air bubbles. The composition of the final casting solutions is tabulated in Table 3.1.

Table 3.1 Compositions of the PBS and PBS/PVP casting solutions

No.	PBS Conc. (wt. %)	PVP Conc. (wt. %)	NMP Conc. (wt. %)
1	15.5	0	84.5
2	15.5	1	83.5
3	15.5	2	82.5
4	15.5	3	81.5

PBS membranes were obtained through solvent evaporation technique. After preparation of the solutions, they were subsequently poured onto clean glass plates and distributed via a manual film applicator at 250 μ m nominal thickness. Prior to membrane casting, the film

applicator and the glass plate were heated in an oven (KM-55, Pras Azma, Iran) at 80 °C for 20 min. The resultant film together with the glass plate was put in an oven at 80 °C for 1.5 h to accomplish the solvent removal and then immersed in a 50 °C water bath to facilitate the removal of the membrane from the plate. The final membrane was stored at room temperature overnight for drying.

3.4 Membrane characterization

3.4.1 Morphological studies

The surface and cross sectional morphology of the obtained membranes was studied through FESEM (TESCAN MIRA3-FEG, Czech Republic) after being Au sputtered in a Q150R ES coater (Quorum, England). Prior to analysis of the membrane cross section, the membrane samples were fractured in liquid nitrogen.

3.4.2 ATR-FTIR spectroscopy

The membrane chemical structure was investigated via ATR-FTIR characterization. ATR-FTIR spectra of the PBS membrane and the PBS/PVP membrane prepared at 3 wt. % PVP were collected using a Thermo Nicolet Avatar 370 spectrometer (USA). The analysis was conducted in the wavenumber range of 400–4000 cm^{-1} in transmission mode.

3.4.3 Determination of water contact angle

The water contact angle of the pure PBS membrane and the PBS/PVP membranes prepared at different PVP concentrations was measured by taking the optical images of small distilled water droplets dispensed on the membrane surface. Images of the droplets were taken at room temperature using an Olympus DP71 camera mounted on an Olympus

SZH10 stereo microscope. The test was repeated four times for each sample followed by analysis of the images. Then, the average of the measured angles was reported.

3.4.4 Determination of swelling degree

The degree of membrane swelling was determined for the PBS membrane and PBS/PVP membranes prepared at different PVP concentration. To study the degree of swelling, membrane sample was dried and weighted using an electronic balance with an accuracy of 0.001 g and then immersed in acetone water mixture at 85/15 weight ratio in a sealed vessel at room temperature. The sample was taken out of the solution every day and weighted immediately after removal of the superficial liquid with a filter paper. A constant weight was ensured by repeating the test during 4 days period. The following equation was used for calculation of the degree of swelling (DS) [22]:

$$DS = \frac{M_s - M_d}{M_d} \times 100 \quad (3-1)$$

where M_s and M_d are the weight of the swollen and dry membranes, respectively.

3.4.5 Determination of membrane mechanical properties

Pure PBS membrane and PBS/PVP membranes prepared at different PVP concentrations were analyzed via tensile mechanical test using a Zwick (STM-20, Korea) universal testing machine. The test was conducted at a crosshead speed of 1 mm/min on rectangular strips of membrane samples with dimensions of 70 mm × 5 mm.

3.4.6 PV experiments

PV performance of the prepared membranes was investigated through dehydration of acetone/water mixtures. Fig. 3-1 represents the experimental set-up utilized in the present study as well as its schematic illustration.

(a)



(b)

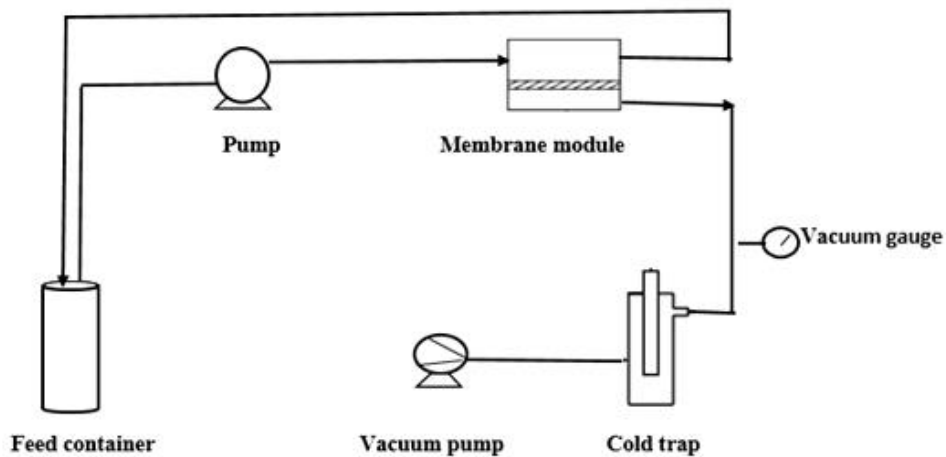


Fig. 3.1 The utilized PV set-up: a) experimental set-up, and b) schematic diagram

In order to run the PV experiments, 500 g of the solution containing acetone/water mixture at 85/15 weight ratio was poured in the feed tank and pumped into the PV cell. The membrane was a circular sample with an effective surface area of 19.6 cm² which was placed horizontally in the cell. The feed passed across the membrane top surface at 4 L/min flow rate and recirculated to the feed tank at atmospheric pressure. The permeate passed through the membrane, evaporated at the downstream at vacuum pressure of approximately 18 mmHg which was induced by a vacuum pump. The cold trap was placed in liquid nitrogen reservoir (-196 °C) and utilized for collection of permeate. The duration of the PV process was 1 h.

To calculate the weight of the collected permeate, the cold trap weight was measured using an electronic balance with an accuracy of 0.001 g prior to the experiment and also at the end of it. The concentration of acetone in the permeate samples was determined using ATAGO (Japan) refractometer.

The refractometer is an inexpensive analytic device used to measure a substance's refractive index. The refractometer measures the change in angle as a light beam passes through a transparent sample and then into a glass of known density. By measuring the change in the angle, the density of the sample can be computed from the known density of the glass. The density of sample is dependent upon its composition. Rather than doing all the necessary calculations to first compute density and then composition, it is much easier to build a calibration curve for a given refractometer. With a proper calibration curve, the measurement of the refractive index can be related to the value of the composition of the sample [23].

In the present research, the refractometer was firstly calibrated for acetone/water mixtures. To do so, several acetone/water mixtures containing 0, 10, 20, 30, 40, 50, 60, 70, 80, 90,

and 100 wt. % acetone were prepared. Then, the refractive index of each sample was determined via the refractometer and the corresponding data was plotted as shown in the calibration curve in Fig. 3.2. The obtained calibration curve was used to calculate the concentration of acetone in permeate samples.

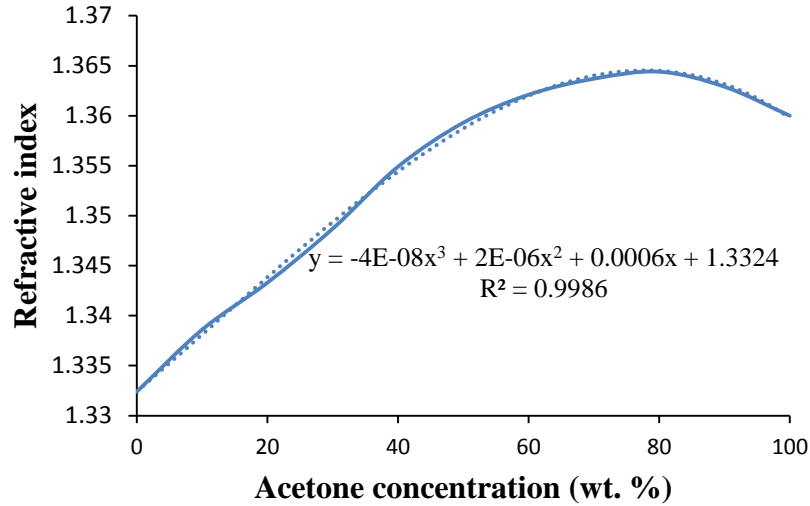


Fig. 3.2 Refractive index calibration curve for acetone/water mixtures

PV performance was studied in terms of permeation flux (J), separation factor (α), and PV separation index (PSI). These parameters were calculated via the following equations [24]:

$$J = \frac{Q}{A \cdot t} \quad (3-2)$$

$$\alpha_{i,j} = \frac{y_i/y_j}{x_i/x_j} \quad (3-3)$$

$$PSI = J(\alpha - 1) \quad (3-4)$$

where Q , A , and t are the total mass of the permeate, effective area of the membrane, and operating time, respectively. Subscripts i and j refer to water and acetone, respectively, and y and x are the weight fractions of components in the permeate and feed, respectively.

Chapter Four

Results and discussion

4.1 Introduction

To assess the influence of PVP addition to PBS membranes on the properties of the obtained PV membranes, PBS/PVP solutions with PVP concentrations of 0, 1, 2, and 3 wt. % were prepared and the corresponding membranes were fabricated according to the procedure mentioned in chapter 3. The top surface and cross sectional morphology of the resultant membranes, their chemical structure, and their relative hydrophilicity/hydrophobicity was investigated via FESEM, ATR-FTIR characterization, and water contact angle measurement, respectively. Moreover, the swelling degree of the membranes was determined followed by investigation of the PV performance of the obtained membranes through PV dehydration of acetone/water mixture. The results of the membranes characterization as well as detailed discussion on the results are provided in the following sections.

4.2 Membrane morphology

FESEM characterization was applied in order to study the morphology of the pure PBS membrane as well as the PBS/PVP membranes prepared at various PVP concentrations. Figs. 4.1 and 4.2 illustrate the FESEM images the membrane top surface and cross section, respectively. As observed in Fig. 4.1, surface of the pure PBS membrane and the PBS/PVP

blend membranes was non-porous. With respect to Fig. 4.2, a dense, non-porous structure was observed for both pure PBS membrane and blend membranes.

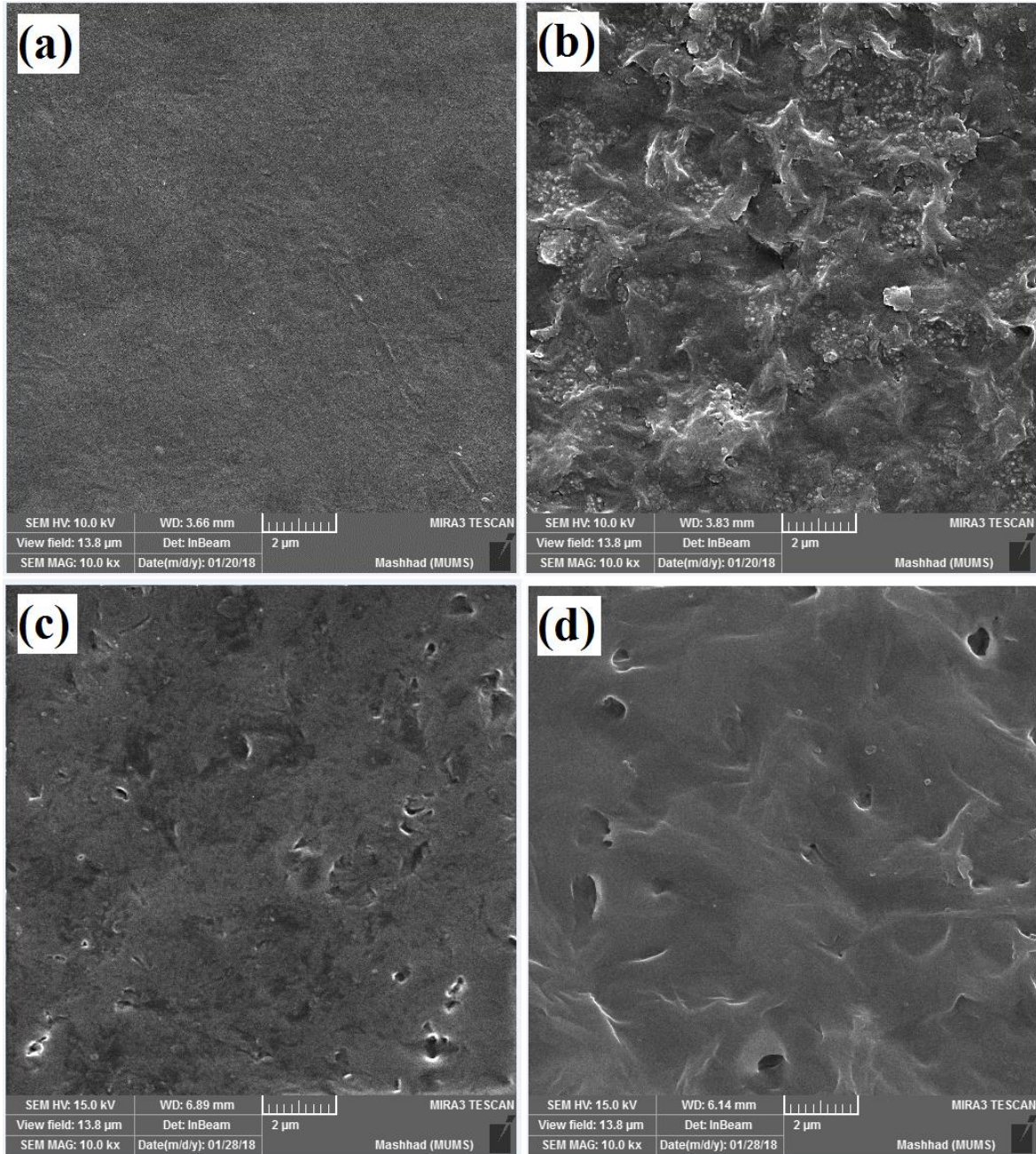


Fig. 4.1 Top surface FESEM images of the PBS/PVP membranes with respect to PVP concentration: a) 0 wt. %, b) 1 wt. %, c) 2 wt. %, and d) 3 wt. %

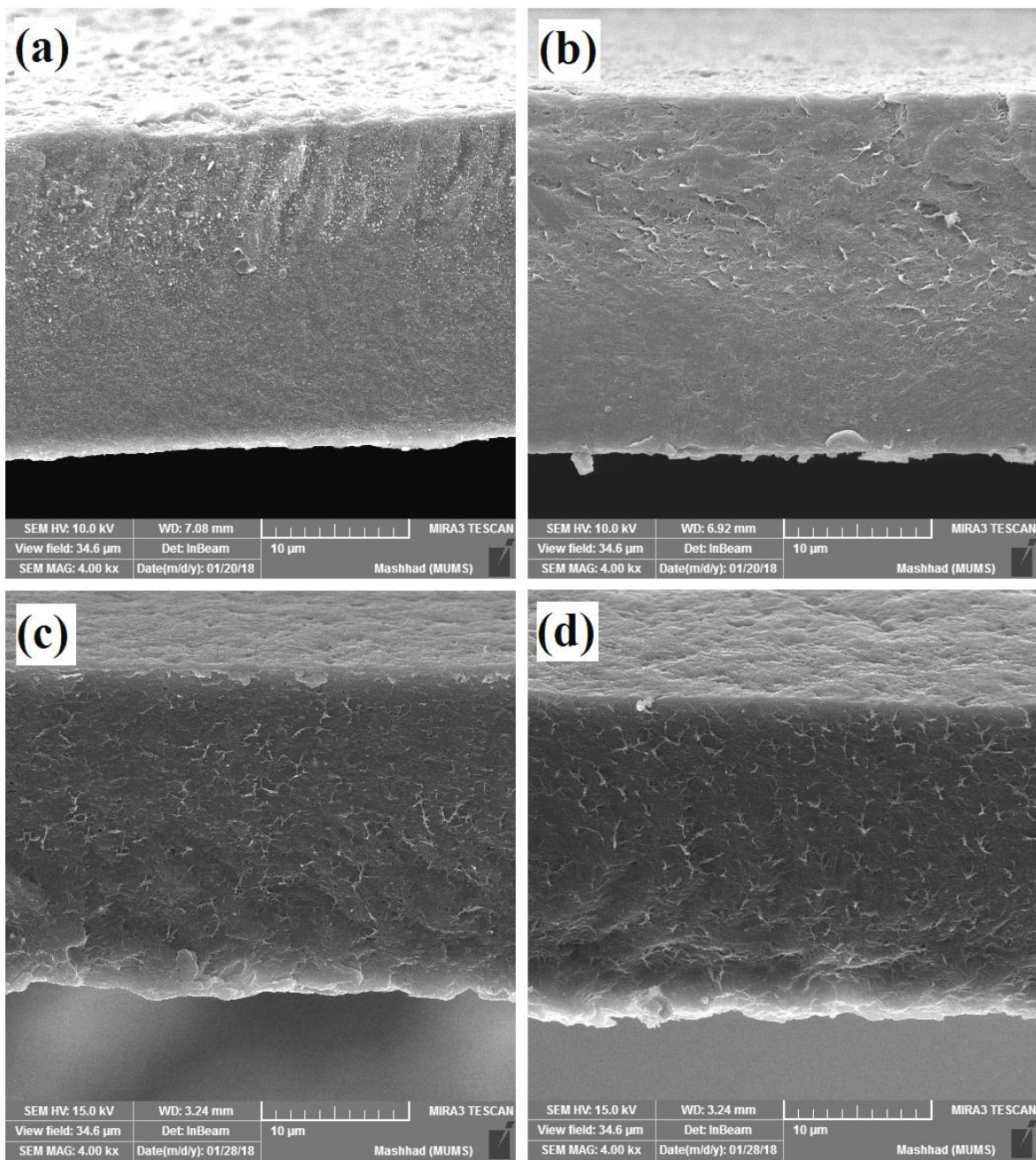


Fig. 4.2 Cross sectional FESEM images of the PBS/PVP membranes with respect to PVP concentration: a) 0 wt. %, b) 1 wt. %, c) 2 wt. %, and d) 3 wt. %

4.3 Chemical structure

ATR-FTIR spectroscopy was utilized for investigation of the chemical structure of the pure PBS membrane as well as the PBS/PVP membrane prepared at 3 wt. % PVP. The obtained

ATR-FTIR spectra are shown in Fig. 4.3. For better understanding of the explanation of the results, the chemical structures of PBS and PVP are provided in Fig. 4.4.

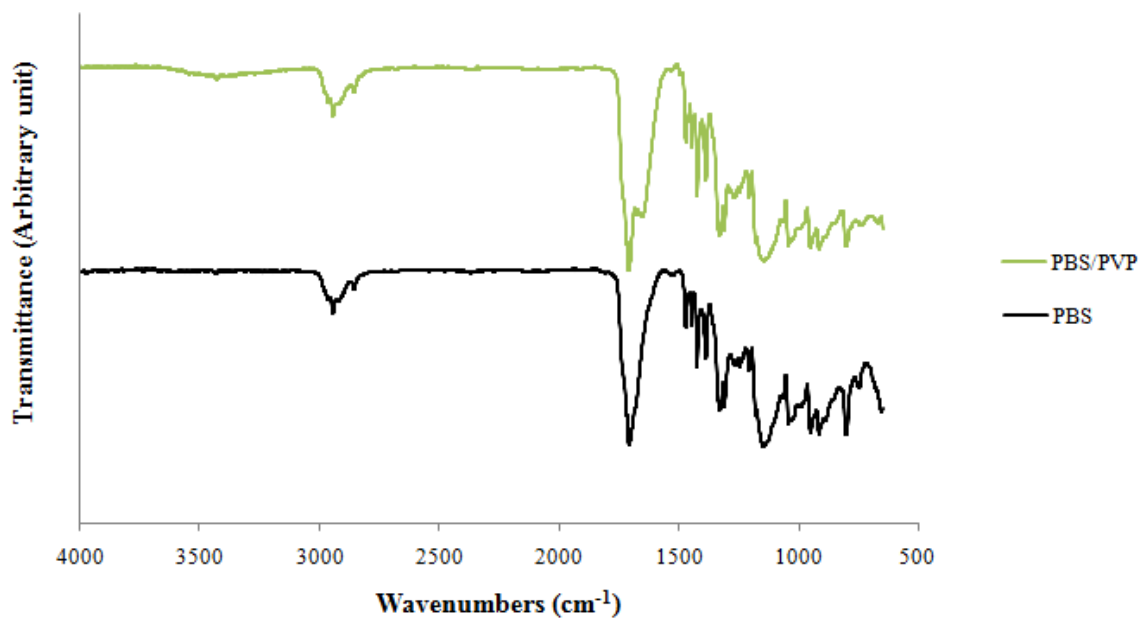


Fig. 4.3 ATR-FTIR spectra of the PBS membrane and the PBS/PVP membrane prepared at 3 wt. % PVP

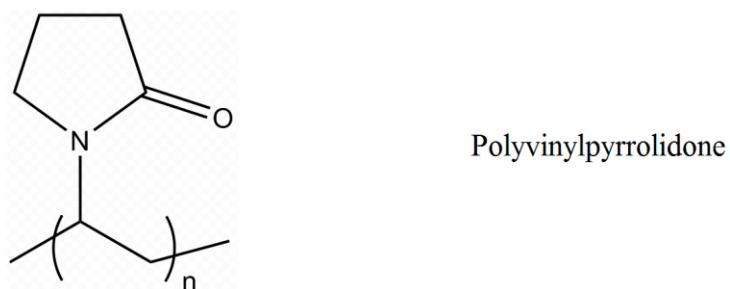
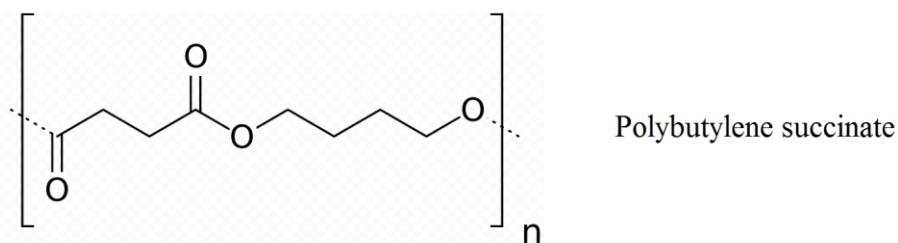


Fig. 4.4 Chemical structures of PBS and PVP

Regarding Fig. 4.3, the pure PBS membrane exhibited the characteristic peaks of PBS polymer. According to the literature [25], the band at 1707 cm^{-1} is related to stretching vibrations of the ester group in PBS, specifically in the C=O bonds of the carbonyl. Moreover, the bands at wavenumbers of 1329 and 1310 cm^{-1} are assigned to the symmetric and asymmetric deformational vibrations of CH_2 groups in the main chain of PBS, respectively. The peaks at 1147 and 1245 cm^{-1} are attributed to the -COC- stretching bonds in the ester group while the band at 914 cm^{-1} is due to vinyl groups [25].

With respect to the results, addition of PVP to PBS polymer resulted in the appearance of a peak at 1651 cm^{-1} . This peak is assigned to amide group of PVP which is a vibration absorption band formed by the combination of C=O and C-N [26]. In another study by Zereszki et al. [21], the appearance of a new absorption peak at 1655 cm^{-1} was spot as an indicative of the presence of PVP in the PLA/PVP blend membrane. The FTIR results suggest that PVP is trapped in the PBS network, providing the polymer with a more hydrophilic nature than the neat PBS.

4.4 Water contact angle

In order to compare the relative hydrophilic/hydrophobic property of the obtained membranes, water contact angle measurement was conducted on the pure PBS membrane as well as the PBS/PVP membranes prepared at different PVP concentrations. Fig. 4.5 illustrates the variations in the membrane contact angle with respect to the concentration of PVP in the casting solution. Moreover, the images of water droplets dispensed on the membrane surface are provided in Fig. 4.5, too. As observed, the highest water contact angle was obtained for the pure PBS membrane at 63.7° implying that this membrane represented the lowest hydrophilicity.

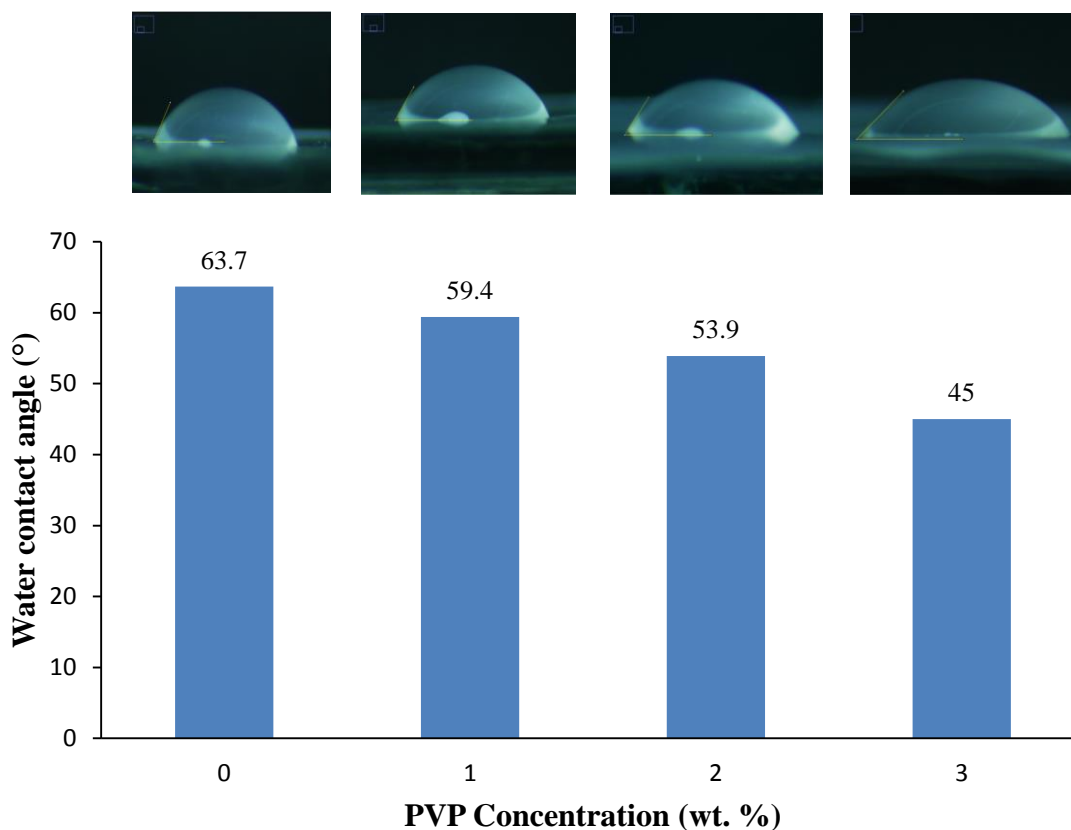


Fig. 4.5 Water contact angles of the PBS/PVP membranes and images of corresponding water droplets with respect to the PVP concentration

According to Fig. 4.5, the reduction of water contact angles was observed with either addition of PVP to the PBS membrane or increasing its concentration in the blend membranes. For example, the water contact angle of the membrane prepared at 1 wt. % PVP was 59.4° which is 4.3° smaller than that of the pure PBS membrane while blending the PBS casting solution with 3 wt. % PVP led to a decrease of almost 19° in water contact angle value compared to that of the pure PBS membrane. The observations implied the higher relative hydrophilicity of the blend membranes compared to that of the neat PBS membrane [20]. The obtained results are compatible with the results of a previous study in which the addition of PVP to the polymeric membranes resulted in the lower water contact

angle and thus higher hydrophilicity [21]. PVP is generally considered a strongly hydrophilic additive [21] and the higher hydrophilicity of the blend membranes was mainly attributed to the more polar groups of carbonyl in blend membrane which form hydrogen bonding with water molecules [20].

4.5 Swelling degree

Membrane samples were immersed in acetone/water mixture containing 15 wt.% water and their swelling degree was determined during 4 days until a constant value was obtained.

Fig. 4.6 shows the variations in the membrane swelling degree at different PVP concentrations in the casting solution.

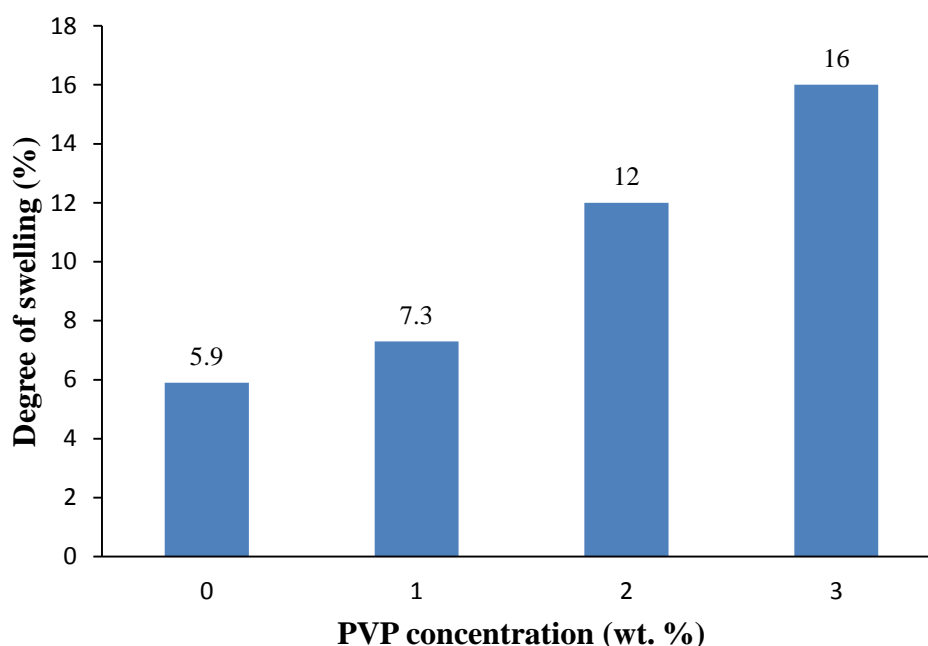


Fig. 4.6 Swelling degree of the PBS/PVP membranes with respect to PVP concentration

With respect to Fig. 4.6, it is clear that the pure PBS membrane exhibited the lowest swelling degree at 5.9%. Moreover, the blend membranes experienced greater degree of swelling compared to that of the pure PBS membrane which increased with increasing PVP

concentration. For example, the swelling degree of the membrane prepared at 1 wt. % PVP was 7.3% which reveals that blending PBS with a small amount of PVP led to a significant increase in degree of swelling. In addition, the swelling degree of the PBS/PVP membrane prepared at 3 wt. % PVP increased by 2.7 times compared to the pure PBS membrane and was determined as the highest value among that of the other samples.

The obtained results can be explained as follows: PVP is reported to be a strongly hydrophilic additive [21]. The results of determination of membrane water contact angles in section 4.3 revealed that the membrane hydrophilicity increased with PVP addition as well as increasing PVP concentration. It is also reported that a more hydrophilic membrane is more selective towards polar molecules [21]. Hydrogen bonding is formed within the free carbonyl group of PVP and water molecules and thus the membrane swells easily [20]. Consequently, higher membrane swelling degree is inevitable at increased concentrations of PVP as a hydrophilic additive.

4.6 Mechanical properties

The influence of PVP on membrane mechanical properties was assessed via tensile test. Fig. 4.7 shows the obtained stress-strain curves for the pure PBS membrane and the PBS/PVP membranes prepared at different concentrations of PVP. In addition, the corresponding mechanical properties including the tensile strength and elongation at break are tabulated in Table 4.1.

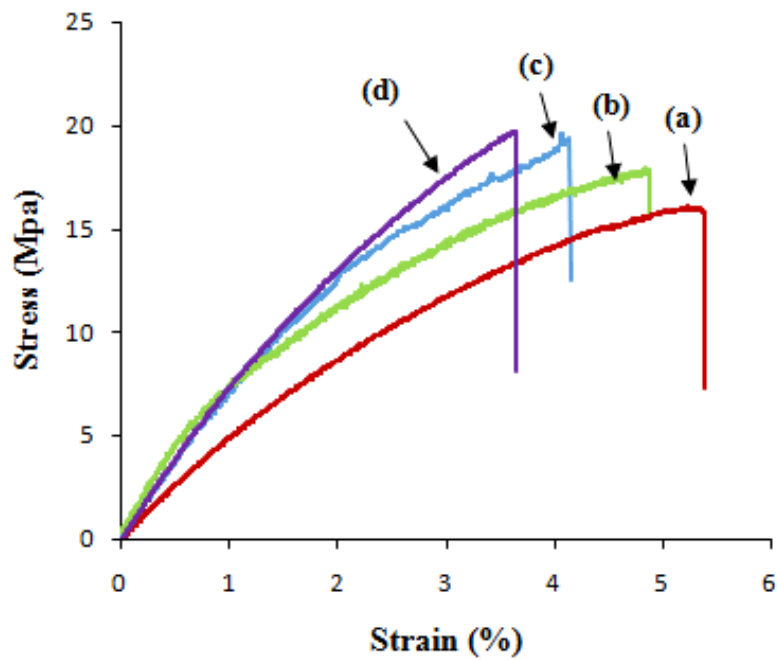


Fig. 4.7 Stress-strain curves of the PBS/PVP membranes with respect to PVP concentration: (a) 0 wt. %, (b) 1 wt. %, (c) 2 wt. %, and (d) 3 wt. %

Table 4.1 Tensile mechanical properties of the PBS and PBS/PVP membranes

Membrane	Tensile strength (MPa)	Elongation at break (%)
Pure PBS	15.47	5.4
PBS-1 wt. % PVP	17.6	4.9
PBS-2 wt. % PVP	19.3	4.1
PBS-3 wt. % PVP	19.6	3.6

It was found that the addition of PVP and increasing its concentration increased the tensile strength of the membrane. However, the elongation at break had a completely different

trend. PVP addition contributed to a decrease in the membrane elongation at break whereas increasing the concentration of PVP was accompanied by further decrease in elongation. It means that the pure PBS membrane represented the lowest tensile strength and highest elongation at break, at 15.47 MPa and 5.4%, respectively, and the membrane prepared at 3 wt. % PVP exhibited the highest tensile strength and lowest elongation at break, at 19.6 MPa and 3.6%, respectively. The interpretation of the results is only possible by taking the inherent characteristics of PBS and PVP into account.

In the first step, PBS is a biodegradable macromolecular plasticizer [27]. Its plasticizing effect on PLA/PBS blends [28] as well as poly(vinyl chloride) (PVC)/PBS blends [29] was reported elsewhere. On the other hand, PVP is known to function as an anti-plasticizer [30] to the extent that the utilization of plasticizers was proposed for decreasing its hygroscopicity or to control tack and/or brittleness [10].

It is widely known that the addition of a plasticizer facilitates the movement of polymeric chains and reduces brittleness of the prepared membrane [31]. A drop in tensile strength as well as higher elongation at break was previously observed via blending polyphenyl sulfone (PPSU) with PEG as a plasticizer [31]. Moreover, the results of previous literature on characterization of sheets prepared using PVC/PBS blends indicated that with the increasing PBS content, the tensile strength decreased while the elongation at break increased [29]. This observation was explained by the improved flexibility of PVC sheets through PBS addition [29].

According to the aforementioned explanations, it could be concluded that blending PBS as a plasticizer [27] with PVP as an anti-plasticizer [30] resulted in decreased flexibility of the resultant membrane and thus higher tensile strength in addition to lower elongation at break.

4.7 PV performance

Performance of the obtained PBS and PBS/PVP membranes was studied via PV dehydration of acetone/water mixture. In order to compare the PV performance of the prepared membranes, it is better to study the flux variation of individual components, acetone and water, at various PVP concentrations (Fig. 4.8).

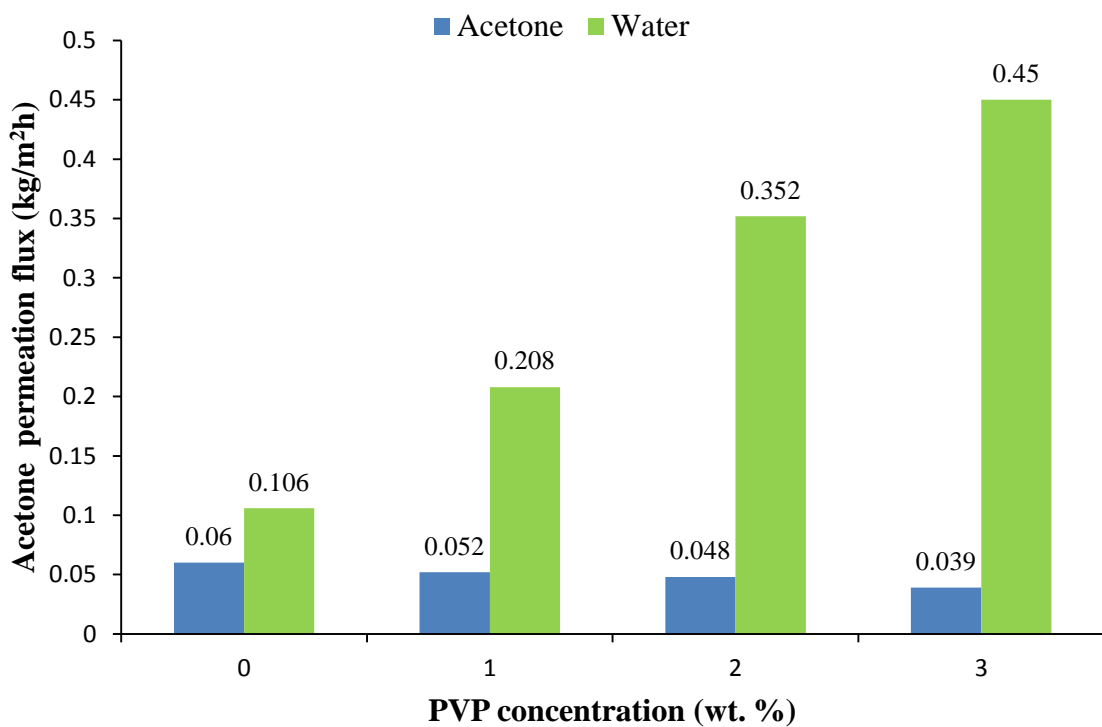


Fig. 4.8 Water and acetone permeation flux through the PBS/PVP membranes with respect to PVP concentration

With respect to Fig. 4.8, the water flux through all of the membranes was noticeably higher than that of acetone. Moreover, it was found that the introduction of PVP to the polymer matrix increased the water flux.

Sorption of acetone/water by the membrane during PV process may lead to the formation of flexible swollen membrane which in turn increases the free volume in the membrane structure through which all components of the mixture might diffuse easily [22]. It was previously indicated that the introduction of PVP to the PBS membrane and increasing its concentration resulted in higher degree of swelling (Fig. 4.6). Furthermore, the addition of PVP remarkably improved the hydrophilicity of the membranes because of the strong polarity and introduction of hydrophilic groups. Therefore, the hydrogen bonding between the membrane and water molecules was formed more easily and the affinity between water and membranes increased [17]. Increased membrane swelling and higher affinity of the blend membrane with water, which was previously proved through comparison of the measured water contact angles, brought about higher water fluxes.

However, introduction of PVP and increasing its concentration was accompanied by a constant slight reduction in acetone permeation flux. Soloukipour et al. [32] reported a relationship between the hydrophobicity of the membrane and the flux of organic component. They reported that the isopropyl alcohol flux was higher through the more hydrophobic polyether block amide (PEBA)/polyvinylidene fluoride (PVDF) membrane prepared at 95/5 weight ratio in comparison with the pure PEBA membrane [32]. Accordingly, the effect of increased membrane hydrophilicity at higher PVP loading on acetone permeation was more dominant than the influence of the degree of swelling in the present research and consequently inhibited the permeation of acetone as an organic molecule through the membrane and thus lower acetone fluxes were observed.

Fig. 4.9 indicates the total permeation flux at different PVP concentrations. Clearly, addition of PVP to the PBS membrane resulted in an increase in total permeation flux from 0.167 to 0.26 kg/m²h. It is noteworthy that increasing PVP concentration increased the

total flux further and the highest total flux (0.49 kg/m²h) was achieved at 3 wt. % PVP concentration. The significantly higher water flux at higher PVP loading was the reason for the increased total flux.

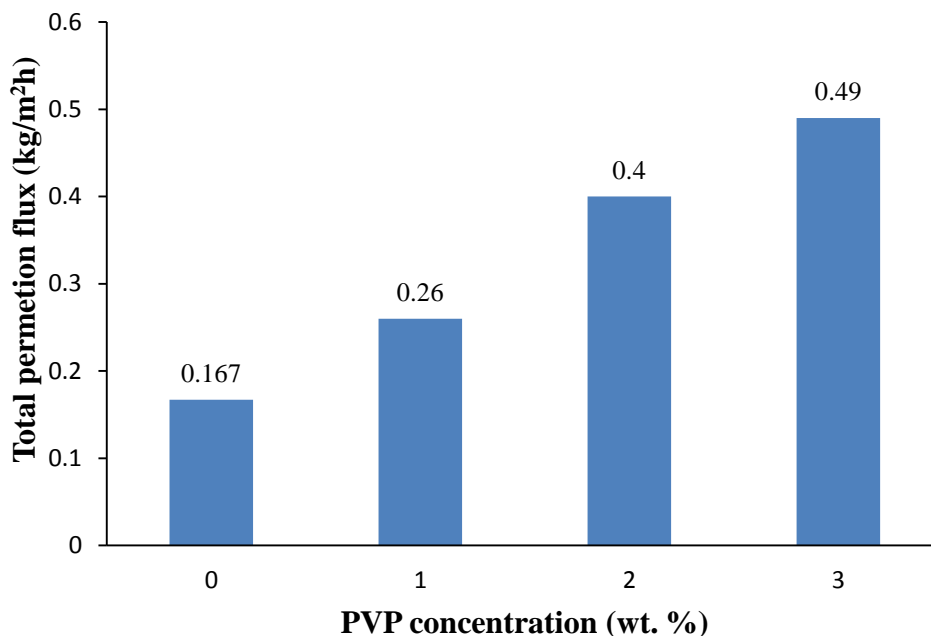


Fig. 4.9 Total permeation flux through the PBS/PVP membranes with respect to PVP concentration

In addition to the membrane flux, separation factor (α) and PV separation index (PSI) can also be utilized for investigation of the membrane PV performance. The separation factor of the prepared membranes was calculated and depicted in Fig. 4.10. Accordingly, the separation factor was significantly higher for all blend PBS/PVP membranes in comparison with those of pure PBS membrane.

With respect to Fig. 4.10, separation factor of the prepared membranes noticeably increased from 10.07 for the pure PBS membrane to 65 for the PBS/PVP blend membrane obtained at 3 wt. % PVP. The significantly higher water fluxes as well the slightly lower

acetone fluxes of the PBS/PVP blend membranes increased the numerator of Eq. (3.3) and hence increased the separation factor.

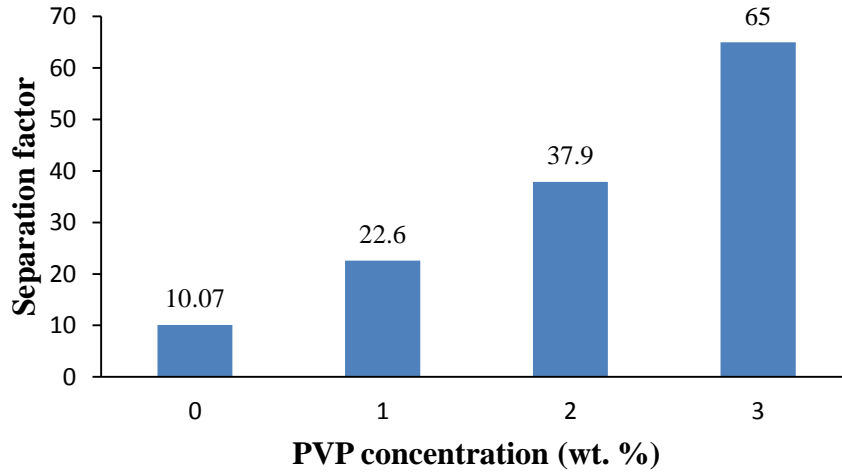


Fig. 4.10 Separation factor of the PBS/PVP membranes with respect to PVP concentration

PSI is a good parameter for determination of the overall performance of a membrane and its separation ability. The PSI values of the prepared membranes are shown in Fig. 4.11. Regarding this Figure, the blend membranes have remarkably higher PSI values in comparison with the pure PBS membrane.

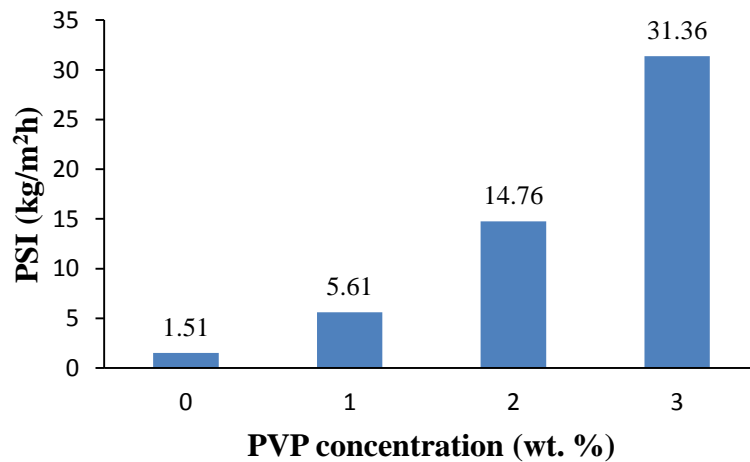


Fig. 4.11 PSI of the PBS/PVP membranes with respect to PVP concentration

As observed in Fig. 4.11, the pure PBS membrane exhibited the minimum PSI value of 1.51 kg/m²h in comparison with the other membranes. In contrast, the membrane prepared at PVP concentration of 3 wt. % represented the maximum PSI value of 31.36 kg/m²h among the others which indicates that the PSI value of this membrane is approximately 21 times as high as the pure PBS membrane. According to the results, the PBS/PVP membrane fabricated by addition of 3 wt. % PVP to the membrane casting solution revealed the best combination of separation factor and permeation flux as compared to the other membrane samples.

Chapter Five

Conclusion and suggestions

5.1 Introduction

In the present study, novel PBS/PVP membranes were prepared and investigated for PV dehydration of acetone/water mixtures. Influence of PVP additive on the membrane morphology, chemical structure, and relative hydrophilic/hydrophobic property was studied through FESEM imaging, ATR-FTIR spectroscopy, and water contact angle measurement. Moreover, the swelling degree of the membrane samples was determined and the PV dehydration performance of the membranes was compared. A summary of the research conclusion and also the suggestions for future work are mentioned in the following sections.

5.2 Conclusion

A summary of the results include:

- 1- According to the FESEM results, the surface of the pure PBS membrane and the PBS/PVP membranes was non-porous. Moreover, both pure PBS membrane and blend membranes exhibited dense cross sectional structure.
- 2- The pure PBS membrane exhibited the characteristic peaks of PBS polymer in the FTIR spectrum. However, addition of PVP to PBS polymer resulted in the

appearance a new absorption peak which confirmed the presence of PVP in the PBS/PVP network

- 3- Results of water contact angle measurement revealed the highest water contact angle for the pure PBS membrane (the lowest hydrophilicity). In addition, it was shown that the introduction of PVP to the PBS network, the water contact angle decreased and thus the hydrophilicity improved.
- 4- The swelling degree of the membrane samples immersed in water/acetone mixture was determined and it appeared that the PBS/PVP blend membranes had greater degree of swelling compared to that of the pure PBS membrane which increased with increasing PVP concentration.
- 5- According to the results of tensile test, the addition of PVP and increasing its concentration increased the tensile strength of the membrane. However, the elongation at break decreased.
- 6- Performance of the obtained PBS and PBS/PVP membranes during PV dehydration of acetone/water mixture indicated that the water flux through all of the membranes was noticeably higher than that of acetone. The addition of PVP remarkably increased the water flux while a slight reduction in acetone flux was observed. As a result of increased water flux, the total permeation flux of the PBS/PVP membrane prepared at 3 wt. % PVP was approximately 3 times higher than that of the pure PBS membrane. In addition, the separation factor and PSI increased by almost 6.4 and 21 fold, respectively, in comparison with the pure PBS membrane. With respect to the results, the PBS/PVP membrane obtained by 3 wt. % PVP to the membrane casting solution exhibited the highest separation factor and permeation flux among the other samples.

5.3 Suggestions

Suggestions for future research include:

- 1- Investigation of the influence of the molecular weight of the PVP polymer additive on the characteristics and PV performance of the PBS/PVP blend membranes; and
- 2- Investigation of the effect of operating conditions including feed temperature and composition on the PV results.
- 3- Investigation of the influence of various hydrophilic additives on the characteristics and PV dehydration performance of PBS membrane.
- 4- Application of PBS membranes in PV dehydration of other organic/water mixtures.

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