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Preparation and Characterization of PLA Polymeric Membrane for Pervaporation Applications

A Thesis

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بسم الله الرحمن الرحيم

قالُوا سُبْحَانَكَ لاَ عِلْمَ لَنَا إِلاَّ مَا عَلَّمْتَنَا
إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيم

صَدَقَ اللهُ العَلِيُّ الْعَظِيمُ

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Sattar

Abstract

Flat sheet membranes were prepared by phase inversion method. The polymeric dope solution was prepared from 15% of poly lactic acid (PLA) as a natural source polymer in the ethyl lactate as solvent. The non-solvent water was used as the coagulation bath.

Several characterization tests were performed as well, The morphology (SEM image), thickness, contact angle, mechanical properties and degree of swelling were investigated with different coagulation bath temperatures (CBT)(20°c, 40°c, 60°c, 80°c) and different evaporation time (ET) (0.5 min, 1 min, 3 min, 5 min, 7 min).

The membranes were changed from finger-like structure to spongy-like structure with different coagulation bath temperatures and with evaporation time, the structure changed from finger-like structure to spongy-like structure to dense-like structure. There is a small decrease in the thickness from 0.198 to 0.144mm of membrane with coagulation bath and from 0.174 to o.042 mm with evaporation time. Mechanical properties improved by increasing the coagulation bath temperature and evaporation time.

The successful use of ME5 membrane at 7 min as evaporation time in pervaporation separation of MEOH/MTBE azeotropric mixture was demonstrated. Where, The total flux was found to increase with the increase in the feed temperature from 0.0388 to 0.208 kg/m²hr for PLA membrane and selectivity reached over 75. partial flux for methanol increases from 0.03 to 0.171kg/m²hr and partial flux for MTBE increases from 0.0062 to 0.036 kg/m²hr. In addition, by increasing the permeate pressure the total flux and partial fluxes decreases. While the selectivity increases.

Composite membrane (PLA/PVA) to separation water/EtOH was demonstrated. Where, increasing the feed temperature causes increase the total flux from from 0.9 to 7.07 kg/m²hr and selectivity reached to 6.33. Partial flux for ethanol increases from 0.7 to 6.19 kg/m²hr and partial flux for water increases from 0.162 to 1.129 kg/m²hr. Also by increasing the permeate pressure the total flux and partial fluxes decreases, While the selectivity increases.

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Nomenclature

Symbols	*Definition*	*units*
C_{w1}	Concentration on feed side	(ppm)
C_{w2}	Concentration on the boundary layer	(ppm)
C_{m1}	Concentration on the membrane	(ppm)
C_{m2}	Concentration on the other side of the membrane	(ppm)
C_{g1}	Concentration on the boundary layer on the permeate side	(ppm)
C_{g2}	Concentration on permeate side	(ppm)
J	flux	Kg/m² h
J_i	Partial flux	Kg/m² h
Q	weight of permeate	kg
t	time	hr
y_i	weight fraction	(-⁻)
C_a	Concentration of component a	(ppm)
C_b	Concentration of component b	(ppm)
v	vapor	(-)
L	Liquid	(-)
E_a	activation energy	(Kj/mol)
R	universal gas constant	KJ/Kmol.K
T	absolute temperature	(C)
r_p	average pore size	(nm)
S_p	internal surface area	(m^2/g)
V_p	pore volume	(cm^3/g)
W_s	weights of the swollen	(g)

Greek letters		***Units***
ΔC	Concentration difference	(ppm)
ΔP	Pressure difference	(bar)
ΔE	electrical potential difference	(volt)
y_i	weight fraction	(-⁻)
α	selectivity	(–)
β	enrichment factor	(–)

Dedication

To the accolade of pride

My father

To the shining moon of my night

My mother

To the stars of my sky

My sister

To the supporters of my life

My brother

To all my friends and who own place in

My heart

Sattar

List of Abbreviations	
CBT	*Coagulation bath temperature*
CBV	*commercial zeolite silicalite*
CHx	*Cyclohexan*
CP	*Concentration polarization*
CS	*chitosan*
CTA	*Triacetate*
DMC	*dimethylcarbonate*
DS	*Degree of swelling*
ED	*electrodialyses*
ET	*Evaporation time*
ETBE	*ethyl tert-butyl ether*
EtOH	*ethanol*
HEMA	*2-hydroxyethyl methacrylate*
HSA	*human serum albumin*
HZSM5	*mane for membrane*
MEOH .	*methanol*
MF	*Microfiltration*
MTBE	*methyl tirt-butyl ether*
NBR	*nitrile-butadiene copolymer*
NMP	*Normal methylperoldyn*
OSW	*Office of Saline Water*
PAA	*poly(acrylic acid)*

PAMHEMA	*2-hydroxyethyl methacrylate with different copolymer*
PAN	*polyacrylonitrile*
PB	*Polybutadiene*
PDMS	*Polydimethyllsiloxane*
PDMS-PS IPN	*polydimethylsiloxane-polystyrene interpenetrating*
PEBA	*Polyether-Bolck-polymide*
PEEKWC	*Polymer*
PEG	*Poly ethelyenglycol*
PEI	*Polyetherimide*
PES	*poly ether selfon*
PIC	*polyion complexation*
PLA .	*poly lactic acid*
POMS	*ethyl-2-methyl butyrate*
POPMI	*4,4-Oxydiphenylene pyromellitimide*
PP	*Polypropylene*
PPMS	*polyphenylmethylsiloxane*
PSI	*pervaporation separation index*
PUR	*polyurethane*
PV	*pervaporation*
PVA .	*polyvinyl alcohol*
PVDF	*polyvinylidene fluoride*
PVP	*Polyvinyl propylene*
PWF	*pure water flux*
RO	*Reverse osmose*

SBS .	*styrenebutadiene- styrene*
SEM	*scanning electron microscopy*
TIPS	*Thermally induced phase separation*
TPM	*Thermoporometry*
UF	*Ultrafiltaration*
VOCs	*volatile organic components*

Chapter one

Introduction

1.1. historical of membrane

Membrane is a selective barrier through which different gases, vapors and liquids move at varying rates. The membrane facilitates the contact of two phases without direct mixing. Molecules move through membranes by the process of diffusion and are driven by a concentration (ΔC), pressure (ΔP), or electrical potential gradient (ΔE) [Ornthida and Somenath, 2010].

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In controlled drug delivery, the goal is to moderate the permeation rate of a drug from a reservoir to the body. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components [Baker, 2004].

The first recorded observation of a membrane separation was in 1748, Abbe Nollet [Baker, 2004 and Home, 1991] discovered the effect of osmotic pressure when a pig's bladder was brought into contact with on one side a water-ethanol mixture and on the other side pure water. In 1908 [Bechhold, 1908] produced membranes with pore sizes below 0.01 micron. These membranes were initially used only in laboratory applications, but later became commercially available. The first commercial membranes were used for drinking water treatment at the end of World War II [Loeb and Sourirajan, 1961]. Subsequently, large sums of research and

development funding from the US Department of the Interior's Office of Saline Water (OSW) resulted in the commercialization of RO membranes. This also later led to the commercialization of UF and MF. The first synthetic membranes were made from cellulose acetate. Today membranes are made from a wide variety of chemically and thermally stable synthetic polymers, ceramics, metals and electrically-charged materials[Abdulghader, 2009].

1.2 Membrane processes and applications

Membrane technology involves many different membrane processes. Although the overall driving force of membrane processes is the chemical potential, the difference in chemical potential between the feed and the permeate may be attained by the difference in several factors such as pressure, temperature, concentration and electrical potential. The membrane process selected for an application depends on the targeted separation objective and the compounds involved in the separation. Table (1) lists examples of membrane processes together with their determining driving force and applications [veronica, 2009].

Membrane technology may be used in several industries: water, textile, tannery food, metal plating, electronic, pulp and paper and the chemical industry [Koltuniewwicz and Drioli, 2008].

Table (1.1). Characteristics of some membrane separation processes [Mulder,1998,Heiner et al. 2006, Judd S & Jefferson, 2003, Jalil, 2004, Kisting, 1971 and Perry and Green, 1997].

Membrane process	Driving force	Application
Microfiltration	Hydrostatic pressure difference	Sterile solution, water purification, beverage filtration effluents, cell harvesting
Ultrafiltration	Hydrostatic pressure Difference	Protein concentration(enzyme),electro deposition paint recovery, oily wastewaters effluent, blood fractionation, antibiotic separation
Nanofiltration	Hydrostatic pressure Difference	Potable water, desalination of brackish water, polyvalent ions stream cleaning, whey fractionation
Reverse osmosis	Hydrostatic pressure Difference	Food concentration, water purification, desalination (monovalent ions stream), biomedical application
Pervaporation	Chemical potential or concentration difference	Dehydration of organic solvents and removal organics from aqueous solutions
Vapour permeation	Vapour pressure Difference	Prepurification of natural Gas
Dialysis	Concentration Difference	Hemodialysis (Artificial kidney)
Electrodialysis	Electrochemical potential Difference	Desalination, water purification, deacidification of citrus juice.
Membrane distillation	Temperature and vapour pressure difference	Concentration of aqueous solutions

1.3. Advantages and Disadvantages of membrane separation processes

Membrane separation processes have numerous industrial applications and provide the following advantages: They offer appreciable energy savings; they are environmentally benign; the technology is clean and easy to operate; they replace conventional processes like filtration, distillation, and ion exchange; they produce high-quality products; and they offer greater flexibility in system design [Anil et al. 2008].

A disadvantage of the membrane processes is that in many applications, especially in the chemical and petrochemical industry, their long-term reliability is not yet proven. Furthermore, membrane processes sometimes require excessive pretreatment due to their sensitivity to concentration polarization and membrane fouling due to chemical interaction with water constituents. Furthermore, membranes are mechanically not very robust and can be destroyed by a malfunction in the operating procedure. However, significant progress has been made in recent years, especially in reverse osmosis seawater desalination, in developing membranes which not only have significantly better overall performance but which also show better chemical and thermal stability and are less sensitive to operational errors [Heiner et al., 2006].

1.4. The objectives of this work:

1. Preparation of PLA (polymer) with Ethel lactate (solvent) and composite membrane (PLA/PVA) flat sheet membranes which are suitable for pervaporation processes.
2. Characterization of the membranes in terms of morphology (SEM),thickness, contact angle, mechanical properties and degree of swelling**.**
3. Studying the effect of coagulation bath temperature (CBT) and evaporation time (E.T) on the SEM, thickness, contact angle and mechanical properties.
4. Studying the separation by pervaporation process and studying the effect of the temperature and permeate pressure on the flux, partial flux and selectivity.

Chapter two

Background and Literature Survey

2.1 Background

2.1.1 Membrane technology

Membrane technology is an evolving separation technology which uses semipermeable membranes to segregate one or more constituents from a mixture [Mulder, 1998]. As a result of the driving force applied to the system the outcomes of the membrane process are the permeate, the part of a mixture that passes through the membrane, and the retentate, the fraction that the membrane retains (Figure 2.1).

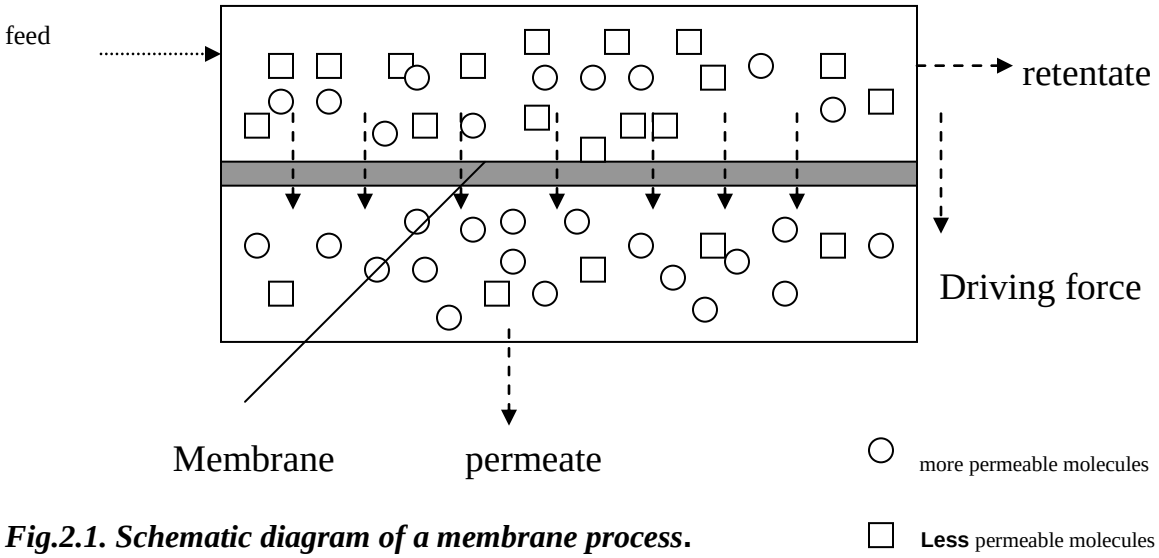

Fig.2.1. Schematic diagram of a membrane process.

The key feature of this technology is the membrane. There are different definitions of the term membrane. The definition used in this study is "membrane is a permselective material that allows one or more constituents of a mixture to pass through more readily than others" [Mulder, 1998 and Judd S & Jefferson, 2003]

Depending on the membrane process and application, different membranes are suitable. The performance of a membrane is usually given by the amount of material going through a unit of area of the membrane per unit of time (flux) and the separation effectiveness. The separation effectiveness is measured by several factors among others the selectivity and the enrichment factor. The membrane should exhibit high fluxes and separation effectiveness, and be tolerant to temperature variations and the feed stream components. It should have a low manufacturing cost and display good manufacturing reproducibility [veronica, 2009].

2.1.2. Membrane classification

Membranes are classified according to different definitions as illustrated in Figure (2.2). Membranes may be categorized according to the mechanism by which separation is achieved. Porous membranes discriminate according to size of particles or molecules, and dense or non-porous. Membranes discriminate according to chemical affinities between components and membrane materials. In porous membranes the pore can vary from micrometers to nanometers. Membranes may additionally be classified according to the nature of the functional groups comprised in the membrane, into polar or hydrophilic membranes and non-polar or hydrophobic membranes. Hydrophilic membranes preferentially permeate polar compounds, while organophilic permeate non-polar organics.

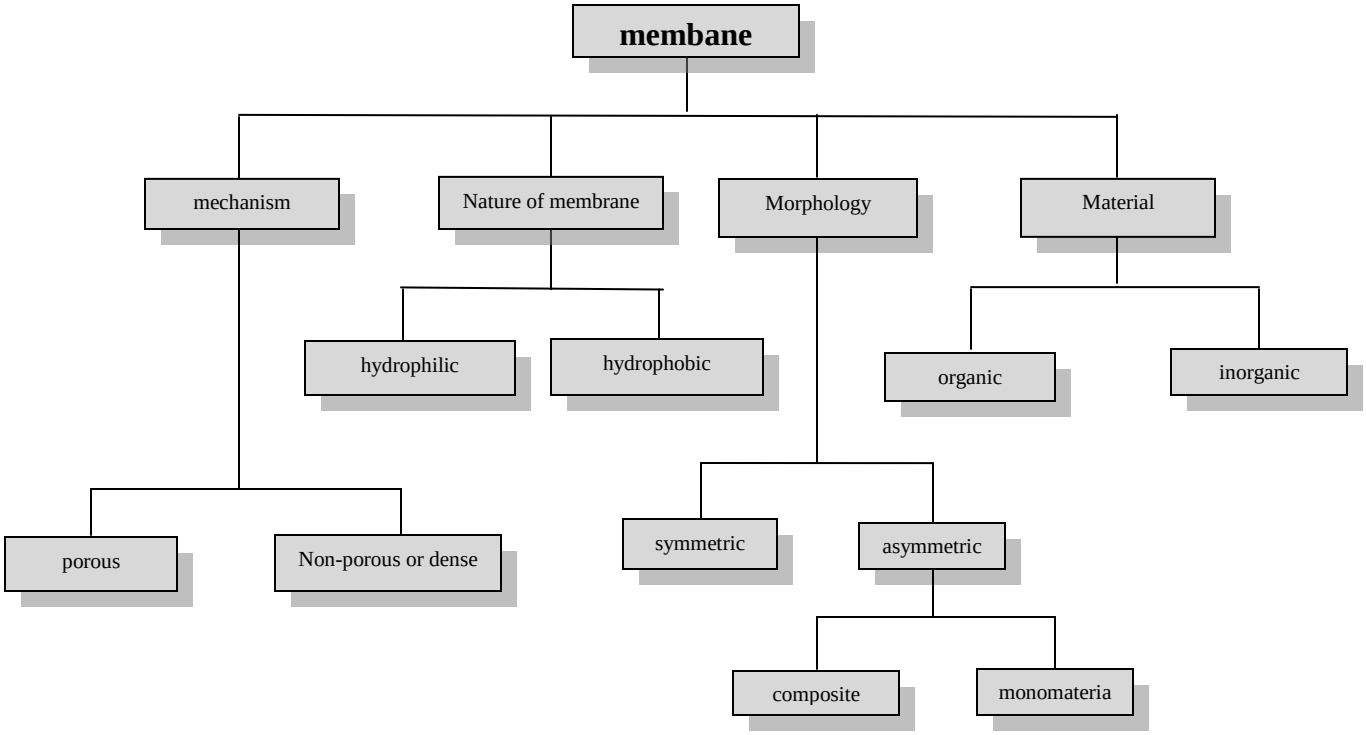

Fig.(2.2).classification of membranes according to different criteria.

Membranes may also be grouped according to their material composition, which is either organic (polymeric) or inorganic (ceramic or metallic).

Additional membrane categorization is done on the basis of their physical structure or morphology into symmetric or asymmetric. In asymmetric membranes, contrary to symmetric membranes, their pore size varies with the membrane depth. They generally have a thin, dense skin layer supported on a microporous substrate. An asymmetric membrane is formed in either an integral form or in a composite form. The main difference between the two types of asymmetric membranes is whether the skin and the substrate are made from the same polymer material (asymmetric membrane) or not (composite membrane) [Mulder, 1998].

2.1.3 The membrane transport mechanisms

The mechanism by which certain components are transported through a membrane can also be very different. In some membranes, for example, the transport is based on viscous flow of a mixture through individual pores in the membrane caused by hydrostatic pressure difference between the two phases separated by the membrane. This type of transport is referred to as *viscous flow*. The components that permeate through the membrane are transported by convective flow through micropores under a gradient pressure as driving force and the separation occurs because of size exclusion as indicated in Figure (2.3 a).Darcy's law describes this type of transport. It is dominant from of mass transport in micro- and ultrafilration but also occurs in other membrane processes.

If the transport through a membrane is based on the solution and diffusion of individual molecules in the non-porous membrane matrix due to a concentration or chemical potential gradient the transport is referred to as *diffusion*. The separation occurs because of different solubility and diffusivity into the membrane material as indicating in Figure (2.3 b). The Fick's Law describes this type of transport. The diffusion of molecules through homogeneous dense membrane occurs through the free volume elements, or empty spaces between polymer chains caused by thermal motion of the polymer molecules, which fluctuate in position and volume on the same time scale as the molecule permeates. The transition between fluctuating free volumes and individual permanent pores is controversial. In general it considered in the range of 5-10 A° in diameter.

This form of mass transport is dominant in reverse osmosis, gas separation, pervaporation or dialysis but it may occur in other processes too.

If the electrical potential gradient across the membrane is applied to achieve the desired transport of certain component through the membrane the transport referred to as *migration*. Migration occurs in electrodialysis and related processes and is limited to the transport of component carrying electrical charges such as ions [Heiner et al.2006].

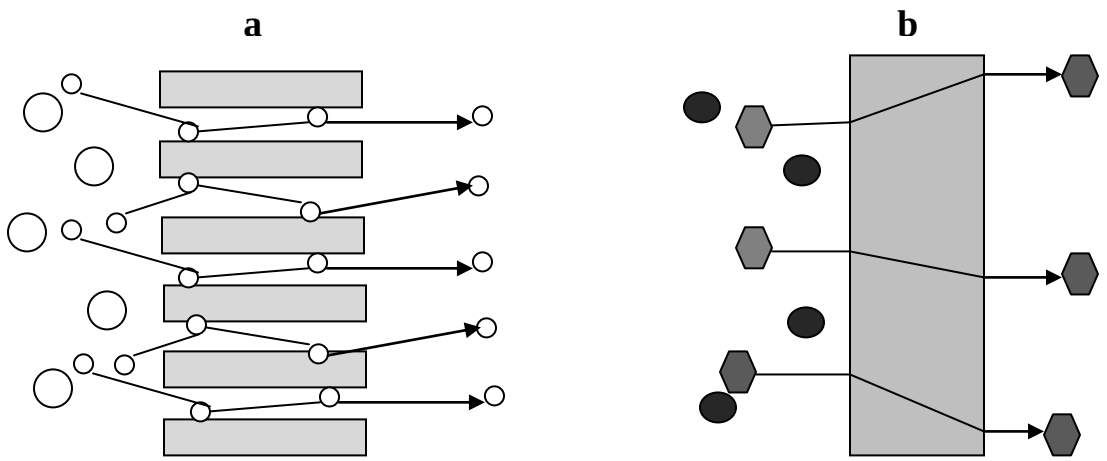

Fig.(2.3). Schematic diagram illustrating a) the sieving mechanism of a porous membrane and b) the solution diffusion mechanism in a non-porous membrane

2.1.5. Preparation and characterization

2.1.5.1. Membrane preparation

The most important part in any membrane separation process is the membrane itself. As described earlier membranes are very different as far as their structure, their function, their transport properties, their transport mechanism and the material they are made of is concerned [heiner et al., 2006]**.** Membranes can be classified, according to their morphology to symmetric and asymmetric and to their mechanism to porous and non-porous as shown in Figure. (2.2).

Dense homogeneous polymer membranes are usually prepared (i) from solution by solvent evaporation only or (ii) by extrusion of the melted polymer. However dense homogeneous membranes only have a practical meaning when made of highly permeable polymers such as silicone. Usually the permeate flow across the membrane is quite low, since a minimal thickness is required to give the membrane mechanical stability. Most of the presently available membranes are porous or consist of a dense top layer on a porous structure. The preparation of membrane structures with controlled pore size involves several techniques with relatively simple principles, but which are quite tricky[Nunes and Peinemann, 2001]. These techniques are summarized in Table (2.1).

Some of the methods are applicable to a variety of polymers, and others are material specific. Each of these methods results in different ultrastructures, porosity, and pore size distribution. For example, track-etched membranes have a narrow pore size distribution, but a low porosity. On the other hand, the phase-inversion process is a good way to form membranes with asymmetric skin structure and can result in fairly high porosity in certain cases [Van et al.,1996].

The selection of a suited base material and preparation technique depends on the application the membrane is to be used in. In some applications such as in gas separation or pervaporation the membrane material used as the barrier layer is of prime important for performance of the membrane. In other applications such as micro-or ultrafiltration the membrane material is not to quite as important as the membrane structure [heiner et al., 2006]**.**

The majority of membranes are prepared by controlled phase separation of polymer solutions into two phases: one with a high polymer concentration and one with a low polymer concentration. The concentrated phase solidifies shortly after phase separation, and forms the membrane [Van et al.,1996].

Table (2.1) Manufacturing processes of synthetic membranes

Process	Materials
Phase inversion by	Polymers:
-Thermal precipitation	Cellulose acetate, polyamide
-Precipitation from the vapor phase	Polypropylene, polyamide
-Immersion precipitation	Polysulfone, nitrocellulose
Stretching sheets of partially	Polymer:
-crystalline polymers	PTFE
Irradiation and etching	Polymers:
	polycarbonate, polyester
Molding and sintering of	Polymers: Ceramics,
fine-grain powders	metaloxides, PTFE, polyethylene

Thermally induced phase separation (TIPS) or melt casting is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying [Van et al.,1996 and Zeman & Zydney, 1996]

Precipitation from the vapor phase, during this process, phase separation of the polymer solution is induced by penetration of non-solvent vapor in the solution [Van et al.,1996].

Immersion casting (or precipitation) is probably the most widespread technology for manufacturing both MF and UF membranes. Desolvation proceeds by diffusional interchange (mass transfer) of the immersion-bath non-solvent and the lacquer-contained solvent [Zeman & Zydney, 1996]

The differences between the four techniques are originated from differences in desolvation mechanisms [Van et al.,1996].

2.1.5.2. Membrane characterization

Membrane characterization is a very important part of membrane research and development because the design of membrane processes and systems depends on reliable data relating to membrane properties. To select a membrane to be used in a particular separation process its properties must be known. Since membranes are very different in their properties and applications a large number of different techniques are required for their characterization. Some of the most important membrane characterization procedures described in the literature or recommended by membrane manufacturers are briefly reviewed here [heiner et al., 2006].

1. Characterization of porous membranes.
2. The pure water flux of micro- and ultrafiltration membranes.
3. Microscopic techniques.
4. The mechanical properties of the membranes.
5. Membrane separation properties determined by filtration test.
6. Retention and molecular weight cut-off.
7. Membrane properties determined by membrane pore size measurement.

2.1.6 Pervaporation process

Pervaporation is a separation process in which a liquid feed containing two or more components come into contact with one side of a membrane while vacuum (or purge gas) is applied on the other side to produce a permeate vapor [Fleming, 1992]. It is a promising alternative to conventional energy intensive processes such as distillation and evaporation. It is often referred to as (clean technology), especially for the treatment of volatile organic compound. The separation is not based on relative volatilities as in the case of thermal processes, but rather on the relative rates of permeation through a membrane [Ornthida and somenath, 2010]. In general, pervaporation (PV) can still be labelled as a new technology. Depending on the permeating component two main areas of pervaporation can be identified: (1) hydrophillic PV, and (2) organophilic PV. Figure (2.8) gives an overview of the areas of PV, membranes applied and application [Frank et al., 1999].

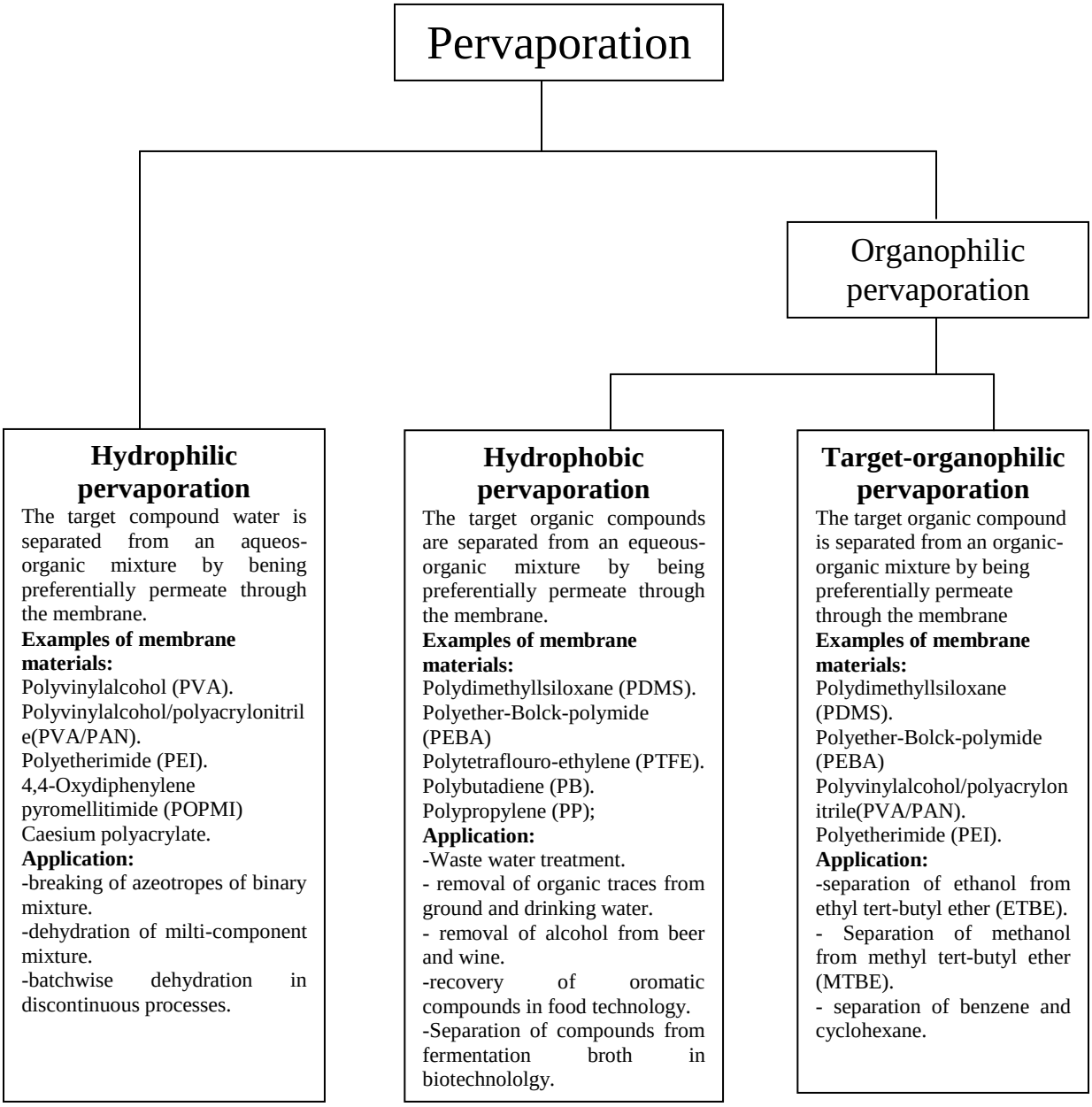

Diagram. (2.1). Areas of pervaporation: membranes and applications[Frank et al., 1999**].**

2.1.6.1. Pervaporation membranes

An ideal pervaporation membrane should consist of an ultra thin defect free skin layer (dense layer) supported by a porous support as shown in Fig.(2.9). The skin layer is perm-selective and hence responsible for the

selectivity of the membrane. However, the porous support also plays an important role in overall performance of the membrane. Ideal pervaporation membrane should posses the following characteristics[Anil et al., 2008].

1. The top layer/skin should be as thin as possible and without any defects.
2. It should exhibit high sorption and diffusion selectivities for the desired solute when contacted with a mixture containing it.
3. It should not swell excessively to maintain the selectivity and structural stability.
4. It should possess good mechanical strength, chemical and heat stability.
5. It should offer high fluxes without compromising selectivity.

The thin dense layer of composite pervaporation membranes is coated on a substructure consisting of a porous support membrane with an asymmetric pore structure and a carrier layer of woven or non-woven textile fabric. The thin dense layer or separating layer defines the type of composite membrane and thus the nature of the separation. The separating layer may be hydrophobic or hydrophilic according to the functional groups of the membrane material [veronica, 2009].

The porous support under the organic separating layer is made of structural polymers such as polyacrylonitrile, polyetherimide, polysulfone, polyethersulfone, and polyvinyldenfluoride [Bruschke, 2001]. Ideally, the porous substrate presents negligible resistance to mass transport [Koops et al., 1993]. Otherwise, the substrate resistance leads to decreased membrane productivity and selectivity [Pinnau & Koros, 1991].

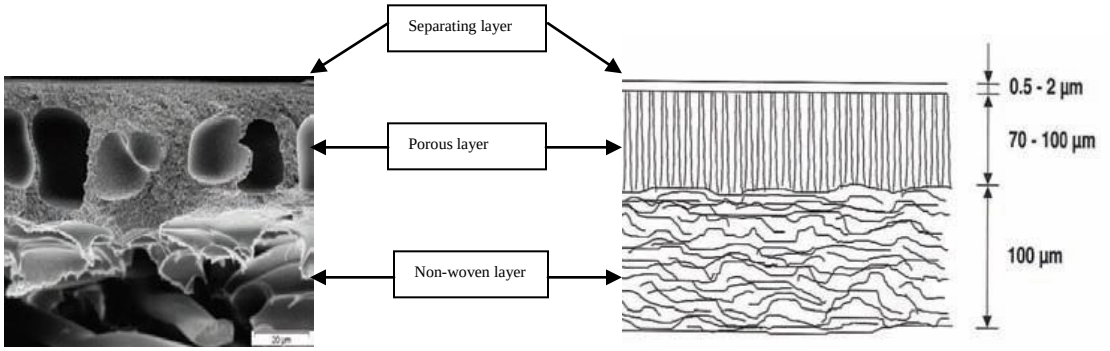

Fig.(2.9). Cross-section of a composite membrane [veronica, 2009, Koltuniewwicz & Drioli, 2008].

Pervaporation membranes may also consist of dense homogeneous polymer films. Such membranes show high selectivities in the separation of liquid mixtures. However, they exhibit low fluxes due to their high thickness (50– 250 µm) figure (2.10) [Dotremont, 1994 and Zereshki et al., 2010]

Fig.(2.10).cross section of homogenous dense membrane [Zereshki et al., 2010]

2.1.6.2. Mechanism of pervaporation transport

In a pervaporation process, a liquid feed is in contact with a membrane, and a permeate is evolved in the vapor state from the opposite side of the membrane, which is kept under low pressure (vacuum pervaporation), or swept by a stream of gas (sweeping gas pervaporation) or

(by temperature difference between the liquid feed and the vapor [heiner et al., 2006]). Eventually, the permeate is collected in a liquid state by condensation in a cooled container [Huang, 1991]. Solution-diffusion is generally the accepted mechanism for mass transport through non-porous membranes [Shao and Huang, 2007]. Permeation through the membrane consists of the following steps [Peng, et al., 2003], as also shown in Fig.(2.11):

1. Diffusion through the liquid boundary-layer on the feed side of the membrane (C_{w1} to C_{w2}).
2. Selective partitioning of molecules in to the membrane (C_{w2} to C_{m1}).
3. Diffusion across the membrane under a concentration gradient (C_{m1} to C_{m2}).
4. Diffusion away from the membrane through the boundary layer on the permeate side of the membrane (C_{g1} to C_{g2}).

These mechanisms govern the mass transport across pervaporation membranes. Separation takes place duo to the differences in the partitioning coefficient, diffusivity, and vaporization of the feed side components. The flux (J) and partial flux (J_i $and J_r$) through a pervaporation membrane were calculated from the following expressions:

$$J = \frac{Q}{At} \qquad (2.1)$$

$$J = y * J \qquad (2.2)$$

$$J = y * J \qquad (2.3)$$

Where, Q is the weight of permeate obtained at time *t*, A is the effective membrane area and (y_i *and* y_r) weight fraction of component in the permeate side [Ghosh et al., 2010].

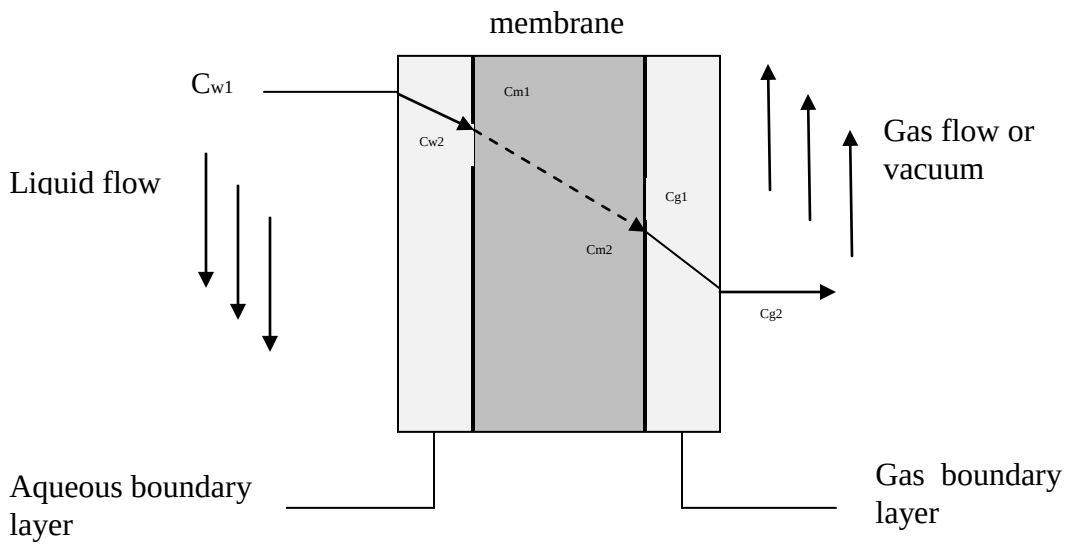

Fig.(2.11). Concentration profile in a pervaporation process, where cw, cm, and cg refer to analyte concentration in aqueous, membrane and gas phase, respectively.

The other important parameter is selectivity which is represented by terms such as separation factor (selectivity) (α) and enrichment factor (β). The separation factor of a membrane for species a and b can be defined as :

$$\alpha = \frac{\left(\frac{C}{C_b}\right)}{\left(\frac{C}{C_b}\right)} \qquad (2.4)$$

The enrichment factor is used as an indicator of the separation selectivity for component a:

$$\beta = \frac{(C)}{(C)} \qquad (2.5)$$

Where C_a and C_b are the concentration of a and b in vapor (v) and liquid (L) phase, respectively.

The operational variables are critical for controlling the pervaporation process [Smitha et al., 2004]. For example, a change in the feed concentration directly affects the sorption phenomena at the liquid-membrane interface and also the permeation characteristics dictated by the solution-diffusion principle. Pressure at the feed and permeate side is also important. Pervaporation operation is carried out by applying vacuum or sweep gas to the permeate side of the membrane, which creates a chemical potential difference. This can be explained by the increase in driving force in the hand term of equation (2.1). Temperature affects all of the steps in the analyte transport process mentioned above, and also alters the driving force for mass transfer. Arrhenius-type relationships have been used to describe the effect of the temperature on the flux as follows [Peng et al.,2003, Huang & Lin, 1968 and I. Cabasso et al., 1974].

$$J = J \exp\left(\frac{E}{RT}\right) \qquad (2.6)$$

Where J_o is constant, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature.

2.1.6.3 Concentration polarization

Concentration polarization (CP) of the permeants (components in feed mixture) and its resistance to permeation through the membrane is encountered in most membrane processes. In an ideal case, in the absence of any CP, the concentration of the permeants should not change from bulk-feed to membrane-feed interfaces. However, due to fluid viscosity (shearing action between two successive liquid layers opposing their relative velocity) there is a decrease in velocity of the permeants from bulk-feed to the stationary membrane surface where the velocity of the fluid is zero. Thus, the concentration of the permeant at the membrane interface becomes lower than that in bulk-feed. In the case of UF, MF, or RO, the retained solute on the membrane surface may cake out (when its concentration exceeds its solubility product) and thus choke the membrane pores and as it accumulates more and more, a diffusive back flow from membrane phase to bulk liquid is developed. These are accompanied by a decreased flux with time. In the case of pervaporation, CP is not so important due to relatively low permeation rates experienced in these dense membranes. Further, unlike UF, RO, or MF, none of the permeants is retained on the membrane surface. In PV all of the permeants pass through the membrane by a solution–diffusion mechanism. However, in these membrane processes CP becomes significant, when the membrane is very thin and highly selective to one of the permeants present in very low concentration (e.g., removal of traces of volatile organic compound from its aqueous feed). In this case, the rate of permeation of this permeant through the membrane becomes much faster than its rate of supply from bulk-feed to the feed-membrane interfaces resulting in CP for this permeant. However, in the case of PV, on the downstream side no such CP

occurs due to very large values of the gas phase diffusion coefficient [Anil et al. 2009].

2.1.6.4 Temperature polarization

Temperature polarisation occurs as a result of the energy required for evaporation of the compound removed. As the heat of vaporisation goes through the membrane a temperature drop occurs in the boundary layer. The temperature at the surface of the membrane is lower than in the bulk of the liquid. Consequently the membrane is operating at a lower temperature than is indicated from measurements in the bulk of the feed. As fluxes of the components through membranes increase with temperature, a reduction in temperature creates a reduction in flux [Bruschke 2001].

2.1.6.5 Pervaporation application

Pervaporation has applications in all types of the separation involving aqueous/organic phases [Anil et al. 2009]. These are:

1. Dehydration of organics.
2. Organic-organic separation
3. Removal of organics from aqueous phase

Among these three categories, the first two are conducted in this thesis: the removal of methanol (MEOH) from methyl *tert*-Butyl ether (MTBE) and removal of water from ethanol (EtOH).

A- Dehydration of organics

Several hundred plants have been installed for the dehydration of ethanol by pervaporation. This is a particularly favorable application for

pervaporation because ethanol forms an azeotrope with water at 95% and a 99.5% pure product is needed. Because the azeotrope forms at 95% ethanol, simple distillation does not work [Baker 2004]. Therefore, In azeotropic systems the use of pervaporation has significant advantages over traditional distillation. Traditional distillation is only able to recover pure solvents with the use of entrainers, which then must be removed using an additional separation step [Chapman *et al.* 2008]. The removal of water from ethanol azeotropic mixtures is the most successful application of pervaporation on an industrial scale [Afonso & Crespo, 2005]. Other solvents commonly dehydrated by pervaporation are isopropanol, ethylacetate, butylacetate, acetone, acetonitrile, pyridine, methylethyl ketone, n-butanol and n-propanol [Sulzer Chemtech Ltd 2009].

The dehydration of organic solvents by pervaporation is conducted using hydrophilic membranes. It is the best developed of the three categories of applications [Zhao *et al.* 2008, Koltuniewicz & Drioli 2008]. Hydrophilic membranes incorporate attractive interactions between water and the membrane material so that water is preferentially permeated through the membrane. Attractive interactions include dipole-dipole interactions, hydrogen bonding and ion-dipole interactions [Semenova *et al.* 1997]. For membranes used in dehydration, a crucial issue is to control their swelling degree in aqueous feed under pervaporation conditions [Xiao *et al.* 2006]. The hydrophilic membranes may exhibit fluxes and selectivity depending upon the chemical structure of the active layer and the mode of cross-linking. Polymeric membranes for dewatering organic solvents are made of different materials such as PVA [Peters *et al.* 2008], natural polymers such as chitosan (CS) [Shao & Kumar 2009], alginate [Dong *et al.* 2006], polysulfone [Hung *et al.* 2003], and polyimides [Qiao & Chung 2006].

***B*- Organic-organic separation**

The separation of organic-organic mixtures is of major interest in the petrochemical industries [Ravanchi *et al.* 2009]. Molecular separation processes are responsible for approximately 40% of the total energy consumption worldwide in petrochemical industry [Kreiter *et al.* 2008]. Consequently, this chemical sector is searching for more energy-efficient separation processes to reduce energy consumption. In the separation of anhydrous organic mixtures, pervaporation competes with distillation in cases where the organic compounds form azeotropes with each other or have close boiling points [Baker 2004].

The degree of separation of a binary mixture is a function of the relative volatility of the components, the membrane selectivity, and the operating conditions. For azeotropic or close-boiling mixtures, the relative volatility is close to 1, so separation by simple distillation is not viable. However, if the membrane permeation selectivity is much greater than 1, a significant separation is possible using pervaporation. An example of such a separation is given in Figure (2.12), which shows a plot of the pervaporation separation of benzene/cyclohexane mixtures using a 20-μm-thick crosslinked cellulose acetate-poly(styrene phosphate) blend membrane [Cabasso, 1983]. The vapor–liquid equilibrium for the mixture is also shown; the benzene/cyclohexane mixture forms an azeotrope at approximately 50% benzene. A typical distillation stage could not separate a feed stream of this composition. However, pervaporation treatment of this mixture produces a vapor permeate containing more than 95% benzene. This example illustrates the advantages of pervaporation over simple distillation for separating azeotropes and close boiling mixtures [Baker, 2004].

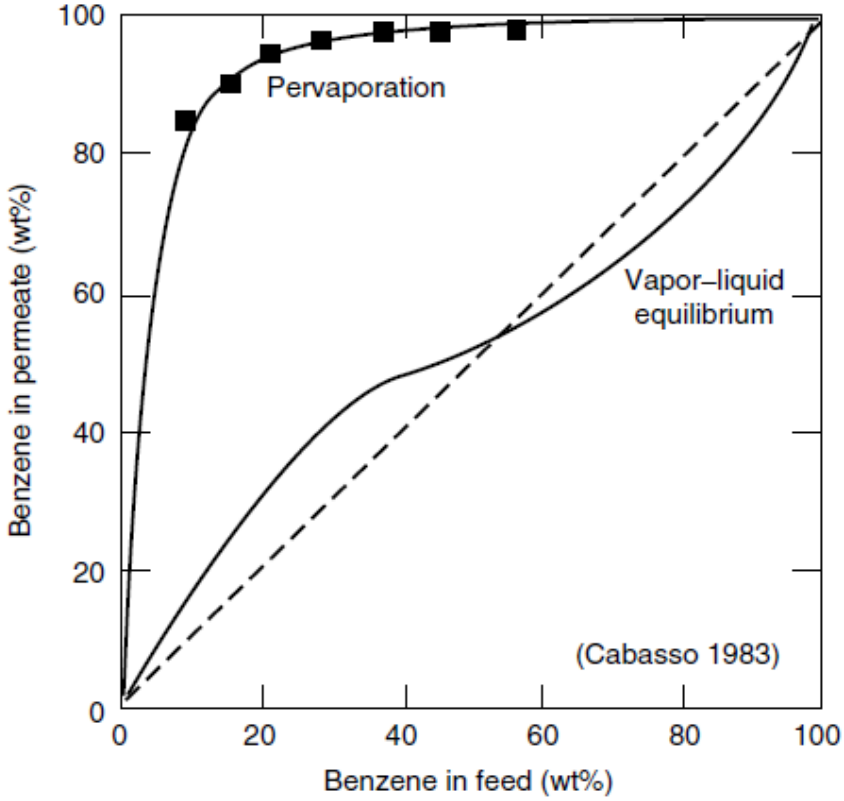

Fig.(2.12) Fraction of benzene in permeate as a function of feed mixture composition for pervaporation at the reflux temperature of a binary benzene/cyclohexane mixture[Cabasso, 1983].

Most of the work published on the pervaporation of organic-organic mixtures refers to the following systems: methanol/MTBE, benzene/cyclohexane, dimethylcarbonate (DMC)/methanol and tiophene/n-octane [Veronica, 2009].

The separation of methanol–MTBE mixtures is needed in the manufacturing process of the octane enhancer MTBE. The formation of an azeotrope of the unreacted methanol and MTBE (14.3 wt% methanol) makes it difficult or even impossible to separate this mixture around the azeotropic

point by conventional distillation alone. Hydrophilic membranes are utilised for removing methanol from the system. Most of the membranes referred to in the literature contain polymeric materials such as cellulose acetate. Some of the membranes are blended [Wu *et al*. 2008] or contain inorganic compounds (hybrid membranes) such as metal oxide particles [Wang *et al.* 2009b] to improve the pervaporation performance. Cross-linking of polymers is also used to enhance the mechanical strength of the membrane [Ray & Ray 2006b].

C- ***Removal of organics from aqueous phase***

These classes of application deal with removal of trace organics from a predominantly aqueous body. Several organic chemicals have solubilities in water sufficient to reckon both in terms of the potential economic loss and pollution. The solubilities are too low to be dealt with by distillation since distillation is expensive. PV is an ideal alternative in this case. In stark contrast to distillation wherein the selectivities are in single digits, PV can yield several orders of magnitude higher selectivities [Netke et al. 1995, Samdani et al. 2003, Kanani et al. 2003] resulting in very high recovery of the dissolved organics at much lower cost. The selectivities can be further improved albeit at a loss of flux by incorporating hydrophobic fillers in a hydrophobic membrane [Anil et al. 2009].

The separation of organic compounds from aqueous systems is preferentially conducted using pervaporation hydrophobic rubbery polymer membranes because they are more permeable to VOCs [Yeom et al. 1999]. The problem of using organophilic rubber membranes is that they give high flux at the cost of selectivity [Ray & Ray 2006a].

Among the several pervaporation membrane materials used for VOCs removal are polydimethyl siloxane (PDMS), polyphenylmethylsiloxane (PPMS), nitrile-butadiene copolymer (NBR), polyvinylidene fluoride (PVDF), styrenebutadiene- styrene (SBS), polyether-block-polyamides (PEBA), polyoctylmethyl siloxane (POMS) and polyurethane (PUR) [Shao & Kumar 2009, Luo *et al.* 2008, Brun *et al.* 1985, Srinivasan *et al.* 2007, Liu *et al.* 2005a, Panek & Konieczny 2007, Konieczny *et al.* 2008, Das *et al.* 2006].

Some interesting pervaporation applications in the removal of organics from aqueous solutions are:

– the aroma recovery [Pereira *et al.* 2006],

– removal of products from reaction mixtures to shift the equilibrium to the side of the wanted product [Liu *et al.* 2005b],

– in analytical applications to enrich a given component for quantitative detection [Brown *et al.* 2007].

– the separation of product/inhibitors from fermentation broths [Shao & Kumar 2009, Liu *et al.* 2005a], and

– the separation of VOCs from wastewaters [Peng *et al.* 2003, Konieczny *et l.* 2008].

Pervaporation is used for separating many different types of VOCs from aqueous solutions with different polymeric membranes such as alcohols, esters, halogenated hydrocarbons and aromatics. Examples are methyl acetate, ethyl acetate, propyl acetate, butyl acetate, pentyl acetate, *i*-pentyl acetate, hexyl acetate, ethyl butyrate and ethyl-2-methyl butyrate with POMS- polyetherimide (PEI) membranes [Trifunovic & Tragardh 2005]; 1,1,2,2-tetrachloroethane, chloroform, carbon tetrachloride and trichloroethylene with PUR–poly (methyl methacrylate) membranes [Das *et*

al. 2006]; toluene with PDMS composite membranes, and PDMS and PEBA membranes filled with carbon black [Panek & Konieczny 2007].

2.1.6.7 Advantages and Disadvantages of pervaporation

Pervaporation has the following advantages [Anil et al., 2008]:

1. Very low capital and operating cost: The separation could be made more economical by using a hybrid membrane process, i.e., a combination of distillation and pervaporation processes. Thus, a part of the total separation employs distillation where it is economical. PV replaces the subsequent separation where distillation becomes expensive. The overall operating cost of such a hybrid process is much lower than that of distillation alone.
2. Azeotropes can be readily broken by using an appropriate membrane.
3. No additive is needed for the final separation.
4. Easy operation and space saving.
5. Reduced energy demand, low-grade heat, and a vacuum pump are required.
6. Freedom from environmental pollution caused by the entrainers.
7. Possibility of multipurpose application and easy scale-up.
8. Membrane properties can be varied and adjusted to suit different applications.
9. Closed loop operations with only a small volume of recycled permeate.

The disadvantages of the pervaporation process are summarized below [Frank et al., 1999 and Feng & Huang, 1997]:

1. Low fluxes
2. Concentration polarization.
3. Temperature polarization.
4. Requirement of more or less tailor-made membrane.
5. Membrane swelling

2.2. Literature survey

2.2.1. Membrane preparation

Amirilargani et al.(2010) investigated the effects of different CBT and PVP concentration as a pore former hydrophilic additive in the PES/ethanol/ NMP casting solution on the membrane morphology and performance. It was found out that the membrane morphology and performance significantly depend on CBT and PVP concentration in the casting solution. They also observed that all the prepared membranes have asymmetric structure. Increasing CBT from 0°C to 25°C and 50°C results in the formation of big macrovoids in the sublayer of the membranes and enhances permeation through the membranes, while reducing the protein rejection. Contact angle measurements of the prepared membranes showed that the surface hydrophilicity of membranes improves by increasing PVP concentration in the casting solution. The bottom surfaces of the prepared membranes are more hydrophilic in comparison of their top surfaces. Mechanical properties measurements indicated that little addition of PVP (1wt%) enhances tensile strength and elongation of the membranes. Pure water flux was observed to enhance significantly by increasing PVP

concentration from 0 to 6 wt%. It was observed that protein (BSA) solution flux increases and protein rejection decreases by addition of PVP (0–6 wt%) to the casting solution. However, protein solution flux decreases and protein rejection increases at higher concentrations of PVP (6–9 wt%).

***Ehsan et al. (2010*)** prepared various membranes with different PEG concentrations and CBTs, and determined their morphology, thickness, pure water flux (PWF), human serum albumin (HSA) rejection, and thermal/chemical stabilities. It was found that:

1. Increasing PEG concentration in the cast film results in the facilitation of macrovoid formation in the membrane sublayer, which increases PWF and decreases HSA rejection.

2. Increasing PEG concentration, which contrary to NMP (solvent) has a relatively low affinity to cellulose acetate (CA) (polymer), in the cast film results in the aggregation and contraction of the polymer chains during membrane formation in the coagulation bath. This result in a restriction in the rotation of CA segments around the main chain bonds and, thus, higher Tg values, which translates into higher thermal/chemical stabilities of the membranes.

3. The reduction of CBT results in the following:

a. Suppression of macrovoid formation in the membrane sublayer and the formation of a denser structure.

b. Reduction of the PWF.

c. An increase in the HSA rejection and thermal/chemical stabilities.

Jinming et al.(2010) studied the influence of CBT on PES membranes fabricated using PEG and Pluronic F127 as additives. At higher CBT, the pore size of skin layer is slightly increased for PES/PEG membranes and is significantly enlarged for PES/Pluronic F127 membranes.

Meanwhile, at higher CBT, the water permeation of two types of PES membranes is enhanced but the antifouling property is decreased. The lower surface coverage of Pluronic F127 molecules at higher CBT is the main reason for the decreased antifouling property of PES/Pluronic F127 membrane.

Payman et al. (2011) prepared polyacrylonitrile (PAN) fibers at two coagulation bath temperatures of 5°C and 60°C and investigated the morphology of nascent fibers by scanning electron microscopy and calorimetric porosimetry method of thermo porometry. SEM images showed that by increasing the coagulation bath temperature, the shape of the fiber cross-section changes from bean to circular with larger pore size. These observations were explained by the counter-diffusion of non-solvent/solvent and by the phase behavior of water/PAN/DMSO system. Meso-porosity of PAN fibers was investigated through thermoporometry TPM and porosity parameters including average pore size (rp), pore volume (Vp) and internal surface area (Sp) were calculated. Results showed that rp and Vp increase with coagulation bath temperature. Wet-spun fibers at low coagulation temperature have higher surface area Sp than wet-spun fibers at high coagulation temperature. This study also showed that TPM method can be employed to characterize meso-porosity of wet-spun PAN fibers which affects the properties of final carbon fibers. The main feature of the method is its ability to detect closed pores, inaccessible by other standard porosimetry methods.

Madaeni et al (2011) investigated the influence of the coagulation bath temperature and evaporation time on membrane morphology, is extremely dependent on the temperature difference between the coagulation bath and the casting solution. For similar temperatures of casting solution

and coagulation bath, the higher flux was obtained for shorter evaporation time. However, for dissimilar temperature, higher flux was achieved for longer evaporation time.

2.2.2. Pervaporation process

The term of pervaporation is a combination of two words, permselective and evaporation. It was first reported in 1917 by Kober, who studied several experimental techniques for removing water from albumin/toluene solution. Although the economic potential of pervaporation was shown by [Binning et al., 1961]. Commercial applications were delayed until the mid-1970, where adequate membrane material first became available.

Liang and Ruckenstein (1995) showed that the pervaporation of ethanol-water mixtures, the permeation rate of polydimethylsiloxane-polystyrene interpenetrating polymer network (PDMS-PS IPN) supported membrane decreases and the separation factor increases with increasing crosslinked PS content. Both the permeation rate and the separation factor increase with increasing feed temperature. The composite membrane is either selective to ethanol or water, depending on the concentration of ethanol in the feed. At low concentrations, it is selective for ethanol. An explanation is suggested for this inversion. The permeation rate and separation factor are at 60°C in the range 160-250 g/m 2 h and 5.5-2.9 for an ethanol-water mixture containing 10 wt% EtOH, respectively, depending upon the content of cross-linked PS in the IPN membrane.

Jae et al.*(1997)* compared the pervaporation of methanol-MTBE mixtures through triacetate (CTA) with that through cellulose acetate (CA) membrane. They showed that both methanol and MTBE have a higher flux with CTA than with CA, whereas the selectivity with CTA was lower than with CA. This is probably due to a looser structure of CTA, which has bulkier side groups and a relatively weak dipole-dipole interaction without hydrogen bonding as compared with CA. It was also possible to predict properly the flux of methanol and MTBE for both CTA and CA by using the solution-diffusion model, in which the diffusion coefficients of methanol and MTBE were assumed to be concentration dependent, i.e. for CA the diffusion coefficients depend on the concentration of methanol, while for CTA they depend on the concentrations of both methanol and MTBE.

Sang-Gyun et al. (2000) prepared the PIC membranes by using ionic groups of sodium alginate and chitosan. The polyion complexation, i.e. ionic crosslinking density, membrane thickness, and the affinity for polar component, was changed with changing the polymer content of solutions, relatively. They showed that the overall polyion complex membranes have very high permselectivity and permeability because of the excellent polarity and the relatively high free volume. Also the permeation rate decreased with increasing polyion complexation but the separation factor increased highly. Especially, with the increase of temperature, the permeation rate and the separation factor increased simultaneously. For the reason of the increase of the separation factor, it was considered that the positive motion of polymer chains in membranes play a dominant role in excluding the diffusion of MTBE. They also observed that in spite of the increase of the polyion complexation, the activation energy of permeation decreased. From these results, it was considered that the permeation behavior through the polyion

complex membranes is determined by the change of effective free volume in membranes.

Masakazu et al.(2000) prepared the membranes from agarose permeated MeOH from MeOH/MTBE mixtures by pervaporation. Shows that the permselectivity toward MeOH reached over $9*10^5$. It was made clear that agarose can be used as one of promising materials for the separation of MeOH from MTBE production. From pervaporation and sorption data, the permselectivity is due to both solubility selectivity and diffusivity selectivity.

Mbaye and Guangsheng (2001) investigated the effect of feed concentration in the sorption and permeation of methyl *tert*-butyl ether and methanol mixtures through a triacetate cellulose membrane. With the increase of the feed MeOH concentration the total permeation flux increases strongly, whereas the selectivity decreases until a minimum value. The tendency displayed by the selectivity is related to the behavior of the MTBE permeation flux and that of the swelling ratio. The mutual interactions between penetrant molecules play an important role in this behavior, especially near the azeotropic concentration. However, the thermodynamic equilibrium of MeOH/MTBE binary mixtures, which favors a spontaneous aggregation of molecules of the same nature (as in minimum boiling azeotrope mixtures), is not sufficient to explain the high selectivity of the polymer. Thus, a further study of the interactions in the MeOH/ MTBE/triacetate cellulose ternary mixture around the binary azeotropic concentration could be interesting. They also studied the effect of the feed temperature. With the increase of the temperature the selectivity decreases, but the total permeation flux is greatly enhanced. An Arrhenius law may describe the total permeation flux variation for high feed concentrations. The

temperature effect is relatively more intensive at low feed MeOH concentrations, and the activation energy becomes dependent on the feed concentration. Finally the cellulose triacetate membrane exhibits high potentials for the pervaporation separation of the MeOH/MTBE mixtures because its permselective performance is among the highest in comparison with those polymeric membranes previously used in separating MeOH/MTBE mixtures.

Nilufer and Sema (2004) showed that the pervaporation characteristics can be controlled with adjusting PVA/PAA ratio in the membranes. Sorption may increase with higher MeOH concentration and this causes higher permeability, but because of the decline of the selective sorption, pervaporation selectivity decreases also. As the cross-linking agent in the membrane increases, cross-linking degree also increases, therefore, swelling decreases. Because the membrane acts as a perm-selective medium, preferential sorption increases. Since polymer segment mobility decreases with cross-linking, the diffusion of penetrants through the membranes also decreases. Lower diffusion and lower sorption cause lower flux and higher selectivity.

Pervaporation has been considered as an alternative separation technique. It may not be practical to separate completely any entire reactor effluents or it may not replace distillation columns in the petrochemical industry. Pervaporation should be used in combination with a conventional separation technique such as a hybrid distillation-pervaporation system to break the azeotropy economically.

Ray and Ray (2006) studied three types of membranes and used these membranes for selective separation of methanol from its mixtures with MTBE by pervaporation. These membranes were found to give high degree

of permeation and selectivities for methanol. The copolymer membranes were found to show both sorption and diffusion selectivity for methanol. The degree of cross-linking of the membranes was found to increase with increase in % of HEMA in the membrane from copolymer-1 to -3. Methanol selectivity of the membranes was found to increase with increasing % of HEMA or cross-linking in the copolymers with lowering of flux. MTBE was also found to have a negative coupling effect on methanol flux. The membranes were found to show selectivity for methanol in both sorption and diffusion stage. Fickian diffusion selectivity of methanol was also found to increase with increasing degree of cross-linking from PAMHEMA-1 to -3 membranes while it decreased with temperature.

***Mehranaz et al (2008*)** studied the separation of methanol from MTBE by PV using the PVA membrane, they investigated the effects of feed temperature, feed concentration, feed flow rate and permeate pressure on flux and separation factor in two modes of continuous and batch (the effects of temperature and feed flow rate in batch and continuous mode, respectively). Results of the experiments in the two modes were similar. Effects of temperature (in batch mode) and feed concentration (in both modes) on the membrane performance were found to be almost similar. Increasing temperature and feed concentration increases both permeation fluxes (methanol and MTBE) but reduces methanol separation factor. The membrane shows less selectivity at feed concentration of 30 wt.% compared to lower concentrations, so it can be concluded that this membrane has better performance at lower feed concentrations. Increasing feed flow rate (in continuous mode) can effectively diminish concentration and temperature polarization effects, this results in increasing both total permeation flux and separation factor. Contrary to the effects of temperature

and concentration, both permeate flux and selectivity increase with decreasing permeate vacuum pressure (in both modes) and this has a positive influence on PV performance. A PSI of up to 110 kg/m2 h was obtained in this study. It was found that feed temperature and feed concentration have negative, while permeate pressure has positive influence on PSI. As a result, it can be said that for separation of this organic mixture, relatively high vacuum (low permeate pressure) and low temperature is preferential. However, high vacuum systems are costly and an optimum permeate pressure can be designed based on the balance of PSI and operating cost.

Xiaocong et al.(2008) prepared HZSM5-filled CA membranes by incorporating HZSM5 into the CA solution. They studied the pervaporation performance for separation of methanol/MTBE mixtures in terms of the permeation flux and separation factor with respect to the HZSM5 content, methanol concentration in the feed, operating temperature and feed flow rate. With the increase of HZSM5 content in the membrane, the separation factor first increased and then decreased while permeation flux increased. The diffusion coefficients of methanol were much larger than those of MTBE for the HZSM5-filled CA membranes, indicating that the membranes were highly selective towards methanol.

Zereshki et al.(2009) studied the feasibility of using PLA membranes in pervaporation for methanol/MTBE separation and quantified by means of separation factor, total flux, pervaporation separation index and enrichment factor. PLA membranes were able to selectively separate low concentrations of methanol from MTBE having a selectivity of more than 30 (35.5 for 1 wt%). Separation factors dropped drastically and became almost constant (around 5) for MeOH concentration higher than around 10 wt%. The

enrichment factors and permeation separation indices had similar behavior. However, because of the high permeation flux, PSI values were high (15000 g/m² .h for 1 wt%). Also they investigated the effects of other operational conditions such as feed temperature (30-50 °C) and flow rate (5-50 l/h). It was observed that increasing the feed temperature lead to a higher total flux but lower selectivity due to the increasing of free volume inside polymer and also mass transfer. However, this effect is not significant at higher temperatures. Increasing the feed flow rate enhanced both flux and selectivity avoiding the temperature and concentration polarizations on the membrane surface.

Dobrak et al. (2010) showed that the increase of the temperature caused higher increase of ethanol flux in comparison to water flux, which was explained by a temperature related decrease of the hydrogen bonding between water and alcohol molecules. The membrane selectivity was strongly dependent on the feed concentration. A significant increase of the selectivity was observed for polydimethylosiloxane (PDMS) membrane filled with commercial zeolite silicalite (CBV 3002) fillers, due to high ethanol flux and lower water flux obtained in comparison to nano-sized colloidal silicalite-1 filled membrane. Novel porous styrene–butadiene–styrene (SBS) membranes gave the highest ethanol fluxes, but membrane selectivity was rather low, in comparison to other membranes examined. On the other hand, the membrane performance of SBS membranes characterized by a dense structure was similar to the performance of filled PDMS membranes.

Zereshki et al. (2011) studied the pervaporation characteristics of MeOH/MTBE mixtures through PEEKWC membranes at different operating conditions. The prepared membranes were found to be MeOH selective.

Transmembrane flux and selectivity are strongly affected by MeOH concentration in feed. The separation factor sharply decreased from the initial high value (254) at low MeOH content, to 6.6 at 22 wt% MeOH, and then, to 3.2 at 54 wt% MeOH. It was around 14 at the azeotropic concentration. The total flux gradually increased in the range of 0.015–0.113 kg/m2 h for 1–87 wt% MeOH. It was found that increasing the feed flow rate in the range of 5–45 l/h has a positive effect on both the separation factor and the flux. However, it was not significant particularly at higher MeOH concentrations. The temperature influence on pervaporation performance was studied from 30 to 50 ◦C for various feed concentrations. It was observed that the selectivity decreased and the flux increased at higher temperatures. The effect on the separation factor was more intensive at low MeOH content feed and becomes nearly negligible at high concentrations. The observed results were explained taking into account the higher degrees of swelling at higher MeOH contents, lower concentration and temperature polarization at higher flow rates, and higher molecular and chain motions at higher temperatures providing more free volume in membrane structure.

Table (2.2) summary of separation performance of various membranes for the separation of MeOH/MTBE mixture.

In this study, flat sheet membranes were manufactured from a binary solution of PLA and Ethel Lactate by phase inversion technique with two parameters: the first is with different CBTs and effect of this parameter on the thickness, contact angle, morphological and mechanical properties. Where, all of these membranes with this parameter have pores; therefore, they are coated with PVA skin layer (composite membrane) to become suitable for pervaporation process. the other parameter is with different evaporation times and the effect of this parameter on the thickness, contact

angle, morphological and mechanical properties. It is found that the membrane at 7 min (ME5) is a totally dense layer and suitable for pervaporation process. Therefore, pervaporation process is applied to the composite and ME5 membranes with two parameters: feed temperature and permeate pressure. Although the effect of CBTs and evaporation time on morphology and other properties of many polymeric membranes has been investigated but not with PLA. the Ethel lactate is never used before as a solvent with PLA polymer. In addition, the composite PLA with PVA has not been reported ever before. This is one of the objectives of the present research.

Table (2.2) summary of separation performance of various membranes for the separation of MeOH/MTBE mixture.

Membrane type	Solvent	Temperature(°C)	Permration flux(kg/m²hr)	Selectivity	Reference
Triacetate cellulose	Dioxane	50	3.2	65	Mbaye and Guangsheng(2001)
PVA/PAA	Water	25	0.09	30	Nilufer and Sema (2004)
PAMHEMA	Water	50	0.14	320	Ray and Ray (2006)
Cellulose acetate	Acetone	50	0.54	140	Xiaocong et al (2008)
PLA	Chloroform	30	1.05	35	Zereshki et al (2009)
PEEKWC	Chloroform	30	0.1	254	Zereshki et al (2011)
PLA	Ethel lactate	35	0.088	75.28	This work

Chapter three

Experimental Work

3.1. Introduction

The experimental work was carried out in three stages. The first stage the preparation of flat sheet membranes by phase inversion method with two parameter:

1- Different coagulation bath temperatures (CBT)(20°C, 40°C, 60°C, 80°C).

2- Different evaporation time (ET) (0.5 min, 1 min, 3 min, 5 min, 7 min).

The second stage is the characterization of the membrane prepared by several measurements, such as, thickness, contact angle, scanning electron micrographs (SEM), mechanical properties and degree of swelling.

The third stage, is determination of the best membranessuited forpervaporationapplications . In this study, two membranes were chosen as suitable for this process. The first one is at evaporation time (7 min ME5),this membranehasgood mechanicalproperties, totally dense layer and has good degree of swelling for methanol and MTBE. The second was chosen atthe best conditionsfrom CBT at (20°C)and they membrane was preparedbyspecialmachine to produce flat sheet membrane and isthencovered bya denselayerof(PVA)to be suitable for pervaporation, for use to separate water-ethanol. All experimental work were done in the Institute of Membrane Technology (ITM-CNR) at Calabria University, Italia.

3.2 Materials

PLA polymer with the trade name of Nature Green 2100D (Poly (L-lactic acid), PLLA; D% comonomer of up to 1.47±0.2%; high crystalline) was supplied by Cargill-Dow Inc. (USA). Ethyl lactate as the solvent with minimum assay 99.5% .also PVA polymer with a degree of polymerization 1799 in the form of 99% hydrolyzed powder was supplied by Tianjin Chemical, and distilled water as solvent with PVA and non-solvent with PLA. The feed component methanol 99.8% was purchased from merck, tert-butyl methyl ether 99.7% was obtained from sigma-aldrich, ethanol 99.5% and distilled water. All the chemicals as well as the polymer itself were used as received without further purification.

3.3Membrane preparation

The preparation of membraneswerecarried out in twoparts:

1- PLA was dissolved in ethyl lactate by stirring for at least 5h at 100°C temperature. A homogeneous solution of 15wt% by polymer weight in solvent was obtained. In this part, four different membranes were named as (MC1, MC2, MC3, MC4). The solution remained untouched for 1h for degassing. The solutions are casted on glass plates with a steel knife at 100°C with the gap set at 450μm, and then immediately immersed into the coagulation bath of water to washed residual solvent Fig.(3.1). The coagulation baths were kept at 20,40,60 and 80°C by a controlled-temperature water bath. The resulting asymmetric membrane was the top dense layer but with some pores. Therefore, the best conditions were chosen at 20°C and the casting was done by special machine for preparation photo.(3.1) after that a dope solution from PVA (polymer) and water (solvent) was prepared by stirring for 24h at 40°C temperature, and

remained untouched for 2h for degassing. Then casting the PVA solution on the PLA membrane with gap set of 250μm and it was left to dry for 24h.Thus the resulting composite membrane was suitable for prevaporation process.

2- PLA was dissolved in ethyl lactate by stirring for at least 5h at 100°C temperature. A homogeneous solution of 15 wt% by polymer weight in solvent was obtained. In this part, five different membrane named as (ME1, ME2, ME3, ME4, ME5)were prepared. The solution remained untouched for 1h for degassing. The solution was casted on glass plates with a steel knife at 100°C inside the oven at 100°C with gap set at 450μm. Membranes were formed by solvent evaporation at different evaporation time (0.5 min, 1 min, 3 min, 5 min and 7 min). However, the membrane with high evaporation time (7 min) was totally dense layer and suitable for pervaporation process.

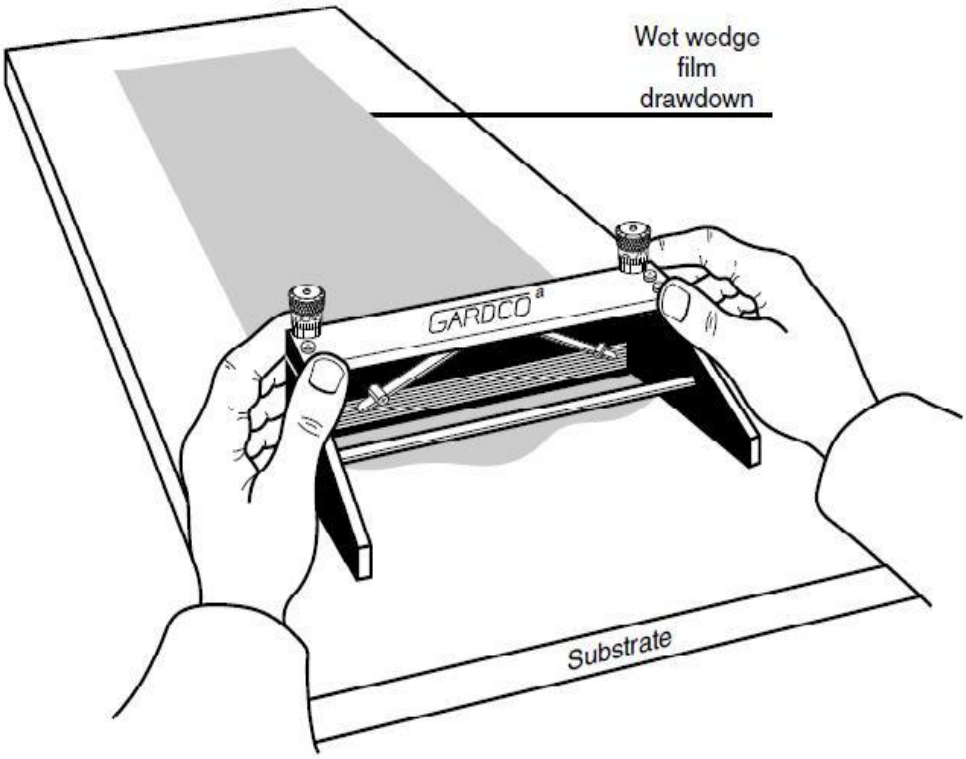

Fig.(3.1). A typical hand-casting knife. (courtesy of paul N. Gardner Company, Inc.,Pompano Beach, FL)[Baker, 2004].

photo.(3.1).Machine for producing flat sheet membrane.

3.4 Membrane characterization

3.4.1 Thickness measurements

The measurement of thickness was performed using a digital micrometer (mahr, 40E, Germany) with accuracy of ±4μm Fig.(3.2). At least 5 spot for each membrane were used and the average was taken.

Fig.(3.2).Digital micrometer

3.4.2 Contact angle measurements

The contact angle measurements were carried out using an optical instrument (Nordtestsrl, G-I, Italy) photo.(3.2) to check the hydrophilicityof the membranes. Distilled water was dropped on the surface of the membrane samples, and the average contact angle was obtained by measuring the same sample at 10 different sites.

photo.(3.2). Optical instrument (Nordtestsrl, G-I, Italy)

3.4.3 ***Mechanical properties***

Mechanical tests were performed using a Zwick/Roell universal testing machine, single column model Z2.5, equipped witha 50N maximum load cell (BTC-FR2.5TN-D09, Germany) photo.(3.3). For each test, three samples were used (1 cm)* (5 cm). The average values were reported for Young's modulus, max stress and Elongation at break.

Photo.(3.3). mechanical tests (BTC-FR2.5TN-D09, Germany).

3.4.4. *Scanning electron microscopy (SEM) analysis*

SEM was used to study the surface morphology and to probe thecross-sectional views of the membranes [Wei et al., 2010]. The membrane sampleswere fractured in liquid nitrogen, and then coated with a thin layerof gold prior to SEM measurement. The SEM measurements wereconducted using SEM micrographs (Cambridge Stereoscan 360, Cambridge Instruments, UK) photo. (3.4).

Photo.(3.4). SEM micrographs (Cambridge Stereoscan 360, Cambridge Instruments, UK).

3.4.5 *Swelling experiment*

Small strips of themembranes (1 cm×3 cm) were weighed andimmersed in MEOH, MTBE, EtOH and water. At least three samples of eachmembranewere used for each solution. Swelling samples remainedat room temperature for 72 h to reach swelling equilibrium, and then they weretaken out and quickly wiped using tissue papers to remove the liquid drops on their surface. A digital balance (Gibertini, Crystal 500,Italy) with the accuracy of 0.001 g was used to weigh the

swollenmembranes. The degree of swelling (DS) for each membrane wascalculated as below (Eq. (3.1)):

$$DS(\%) = \left(\frac{Ws - Wd}{Wd}\right) * 100 \qquad (3.1)$$

whereWs and Wd are the weights of the swollen and dry membranes, respectively.

3.5Pervaporation experiments

3.5.1 Equipment and apparatus

Fig (3.3) and photo (3.5) show a schematic diagram and a photographic picture of pervaporation experimentalrespectivly. The equipment and apparatus consist of the following parts:

1. Double-jacket reservoir.
2. Feed pump.
3. Membrane cell.
4. Three way sampling valve.
5. Digital vacuum meter.
6. Liquid nitrogen condenser.
7. Vacuum purge valve.
8. Cold trap.
9. Two stage vacuum pump.

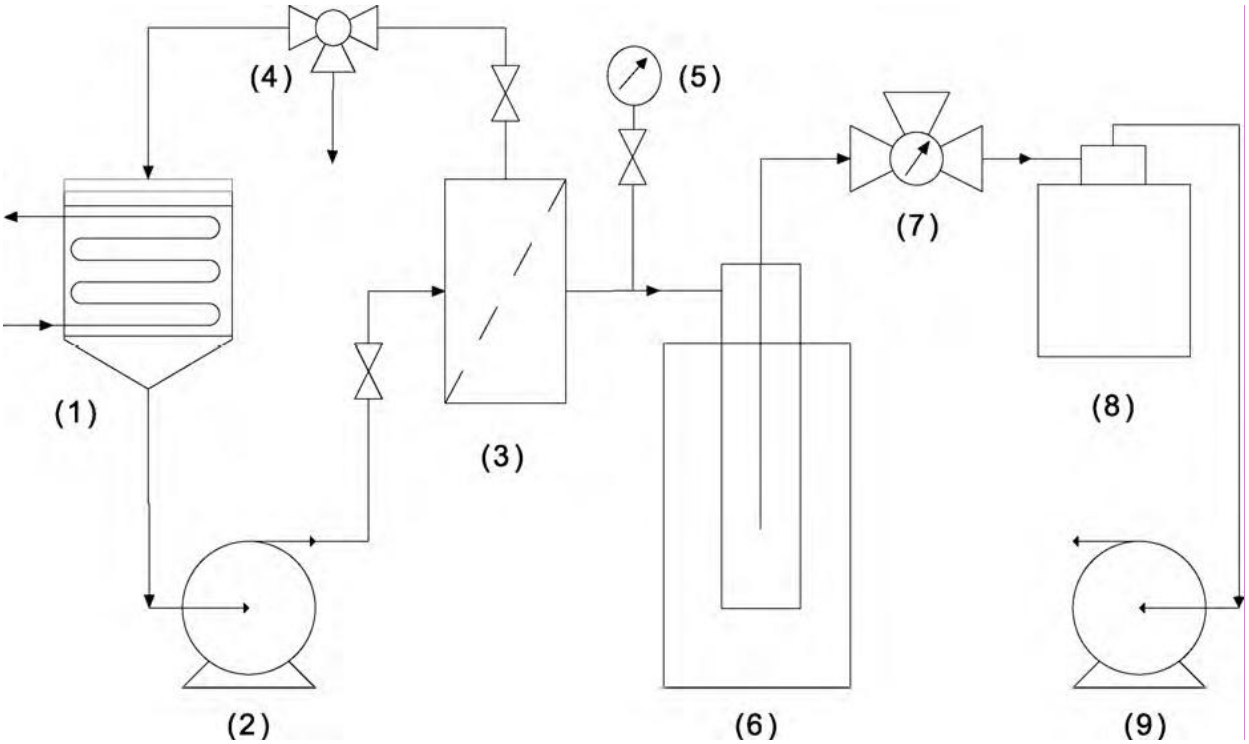

Fig.(3.3). Pervaporation apparatus.

photo.(3.5). photographic picture for pervaporation system

3.5.2. Experimental procedure of prevaporation

Pervaporation tests were carried out using a lab scale apparatus which is schematically shown in Fig.(3.3).MEOH/MTBE mixture atthe azeotropic point was poured into the double-jacket reservoir with a capacity of around 300 ml. A thermo digital circulating bath (Neslab RTE-201, USA) was used to keep the temperature of feed solution constant (20°c). Feed was pumped through a gear pump(2035 Manual, Verder, Germany) at the flow rate of 50 l/hto the membrane cell (Sem- pas, Membrantechnik GmbH, Germany) that is assembled from two cylindrical half-cell made of stainless steel fastened together by nuts and bolts. The membrane was supported on a sintered (perforated) stainless steel plate placed at the join of two half-cell. A round membrane with an effective area of 56.7 cm^2 was used. A glass condenser was used to collect the permeated vapor under a vacuum of 4±1mbar using liquid nitrogen. The applied vacuum is provided by a two-stage vacuum pump (RV5, Edwards, UK) which was protected with a cold trap. This vacuum was measured using an Active Pirani Gauge (APG-M-NW16 AL, Edwards, UK) and the value was read on a 5 Padigital vacuum meter (APG-A921, Italy). Retentate stream was recycled back to the feed tank. Collected permeate was weighed using a milligram balance (Gibertini, Crystal 500, Italy) immediately after the test.

Pervaporation experiments were carried out and repeated by increasing the permeate pressure (27 and 50 mbar). After that increasing the feed temperature (30 and 35°C) and for each degree of temperature increasing the permeate pressure from (6 mbar to 27 and 50 mbar). After reaching the steady state, permeate were collected for at least 3h and the permeation flux was calculated by equation (2.1) and the partial flux was calculated by equations (2.2 and2.3).Thepervaporation permeate and the feed were analyzed using an Abby 60 type direct reading

refractometer(60/DR, Bellingham+stanly Ltd., UK) at 25°C temperature for each test. Having the concentration of the permeated components and the total flux, the partial flux of each component could be easily obtained. The permeation selectivity (separation factor) of MEOH was calculated from Eq. (2.4).

Chapter three

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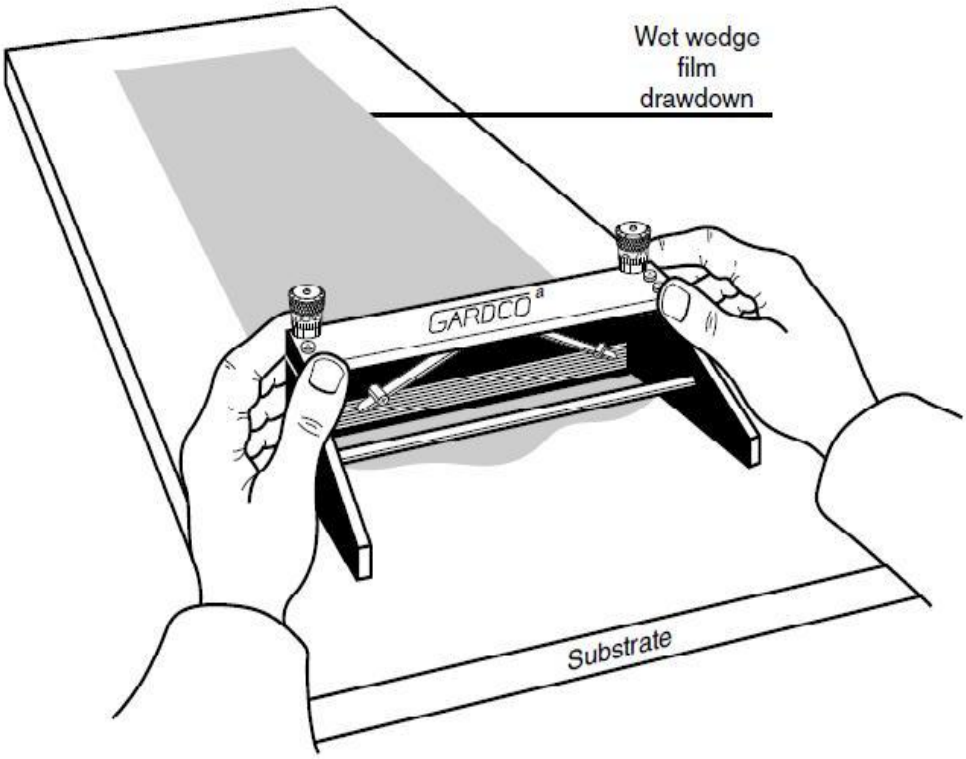

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swollen membranes. The degree of swelling (DS) for each membrane was calculated as below (Eq. (6)):

$$DS(\%) = \left(\frac{Ws - Wd}{Wd}\right) * 100 \qquad 6$$

where Ws and Wd are the weights of the swollen and dry membranes, respectively.

3.5 Pervaporation experiments

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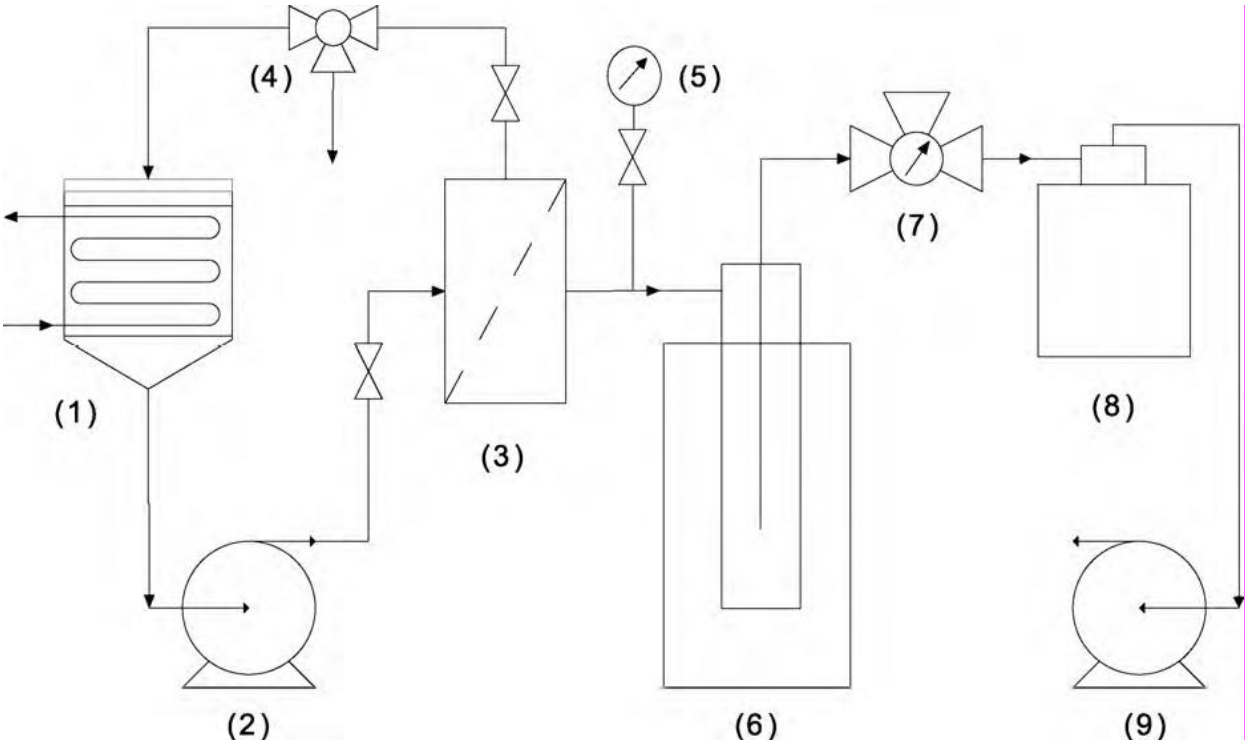

Fig. (3.7). Pervaporation apparatus.

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3.5.2. Experimental procedure of pervaporation

Pervaporation tests were carried out using a lab scale apparatus which is schematically shown in Fig.(3.6). MEOH/MTBE mixture at the azeotropic point was poured into the double-jacket reservoir with a capacity of around 300 ml. A thermo digital circulating bath (Neslab RTE-201, USA) was used to keep the temperature of feed solution constant (20°c). Feed was pumped through a gear pump (2035 Manual, Verder, Germany) at the flow rate of 50 l/h to the membrane cell (Sem- pas, Membrantechnik GmbH, Germany) that is assembled from two cylindrical half-cell made of stainless steel fastened together by nuts and bolts. The membrane was supported on a sintered (perforated) stainless steel plate placed at the join of two half-cell. A round membrane with an effective area of 56.7 cm^2 was used. A glass condenser was used to collect the permeated vapor under a vacuum of 4±1mbar using liquid nitrogen. The applied vacuum is provided by a two-stage vacuum pump (RV5, Edwards, UK) which was protected with a cold trap. This vacuum was measured using an Active Pirani Gauge (APG-M-NW16 AL, Edwards, UK) and the value was read on a 5 Pa digital vacuum meter (APG-A921, Italy). Retentate stream was recycled back to the feed tank. Collected permeate was weighed using a milligram balance (Gibertini, Crystal 500, Italy) immediately after the test.

Pervaporation experiments were carried out and repeated by increasing the permeate pressure (27 and 50 mbar). After that increasing the feed temperature (30 and 35°C) and for each degree of temperature increasing the permeate pressure from (6 mbar to 27 and 50 mbar). After reaching the steady state, permeate were collected for at least 3h and the permeation flux was calculated by equation (1) and the partial flux was calculated by equations (2 and 3). The pervaporation permeate and the feed were analyzed using an Abby 60 type direct reading refractometer

(60/DR, Bellingham+stanly Ltd., UK) at 25°C temperature for each test. Having the concentration of the permeated components and the total flux, the partial flux of each component could be easily obtained. The permeation selectivity (separation factor) of MEOH was calculated from Eq. (4).

Chapter four

Results and Discussions

4.1. SEM images of the prepared membranes

Microscopic study using SEM images was carried out to find out qualitative information regarding cross sectional and surfaces morphology of the prepared membranes. SEM images of the prepared membranes are illustrated in Figures (4.1) and (4.2). These images illustrate the effects of the coagulation bath temperature and the evaporation time on morphology of PLA membranes.

4.1.1 Effect of the coagulation bath temperature on morphology of the PLA membranes

Figure (4.1) shows the effects of four different levels of CBT (20°C to 80°C) on the membrane morphology. Figure (4.1 a) shows the structure of cross-section scanning electron microscopy pictures of flat sheet PLA membrane. The membrane prepared at a CBT of (20°C MC1), is different from those prepared with increasing CBT. It can be observed that the membrane has three layers of small spongy-like structure, large tear-like structure and finger-like structure.

An explanation for these observations requires an understanding of the membrane formation mechanism. When the cast film is immersed into the distilled water bath, precipitation starts because of the low miscibility between the polymer (PLA) and nonsolvent (water). Simultaneously, the miscibility between the solvent (Ethyl lactate) and the nonsolvent (water) causes diffusional flow of the solvent and the nonsolvent (exchange of the solvent and nonsolvent) at several points of the film's top layer and the sublayer, which subsequently leads to the formation of nuclei of a polymer-poor phase [Saljoughi et al., 2010].

The rate of the demixing process affects the morphology of the membranes. Instantaneous demixing often leads to the formation of macrovoids in the membrane structure, whereas slow demixing results in a denser structure [Mohammadi & Saljoughi,2009]. Thus, the macrovoids in MC1 (20°C CBT) because the instantaneous demixing is dominant.

For the MC2 at 40°C as CBT the finger-like structure disappeared from the cross-section and the spongy-like layer increased with some tear-like structure, which means that the exchange between the solvent and the non-solvent decrease. And this is clear for MC3 at 60°C where the polymer concentration increases and the membrane changed to spongy-like structure because of slow demixing. In the case of slow demixing, nucleation occurs after a certain period of time, and the polymer concentration increases in the top layer. Then, nucleation starts in the inferior layer at short time intervals successively. Hence, the size and composition of the nuclei in the former layer are such that new nuclei are gradually formed in their neighborhood. In other words, in slow demixing, free growth of limited nuclei (on the top layer) is prevented, and a large number of small nuclei are created and distributed throughout the polymer film. Consequently, contrary to instantaneous demixing, the formation of macrovoids is suppressed, and denser membranes are synthesized [Saljoughi et al.,2009a, Saljoughi et al.,2009b, Mohammadi & Saljoughi,2009].

Fig (4.1 b) shows the structure of the top layer SEM pictures. It can be noticed that the top layer for MC1, MC2 and MC3 is totally dense layer because it is more solvent evaporated before immersion in bath, and polymer concentration increases in top layer.

Fig (4.1 c) shows the structure of the bottom layer pictures. MC1 has more pores on the surface. These pores began to be less and big by increasing the CBT as shown on the bottom surface of the MC2 and MC3. The top layer hinders the

exchange rate of the solvent and non-solvent through the membrane surface during immersion process [Gao et al.2009]. Therefore, more solvent is exchanged with non-solvent from the bottom layer, this causes more pores at the bottom layer. Increasing the CBT to 80°C damages the membrane as shown in MC4.

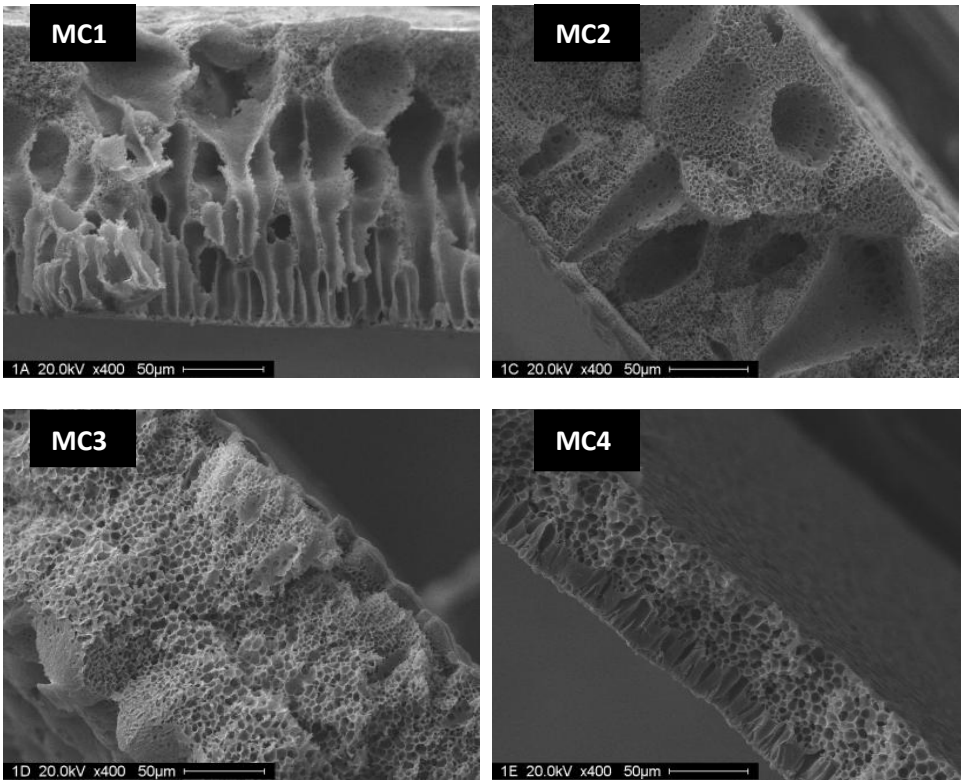

Fig.(4.1 a). Cross-sectional SEM morphology of PLA membranes at different CBT. MC1 at 20°c, MC2 at 40°c, MC3 at 60°c,MC4 at 80°c.

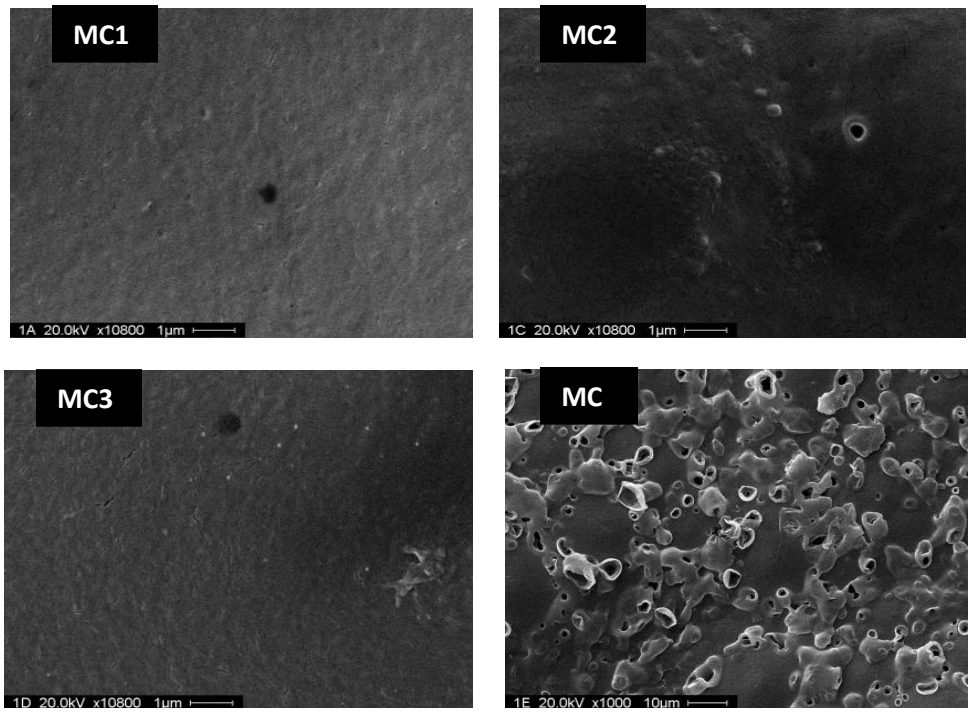

Fig.(4.1 b). Top layer SEM morphology of PLA membranes at different CBT. MC1 at 20°c, MC2 at 40°c, MC3 at 60°c,MC4 at 80°c.

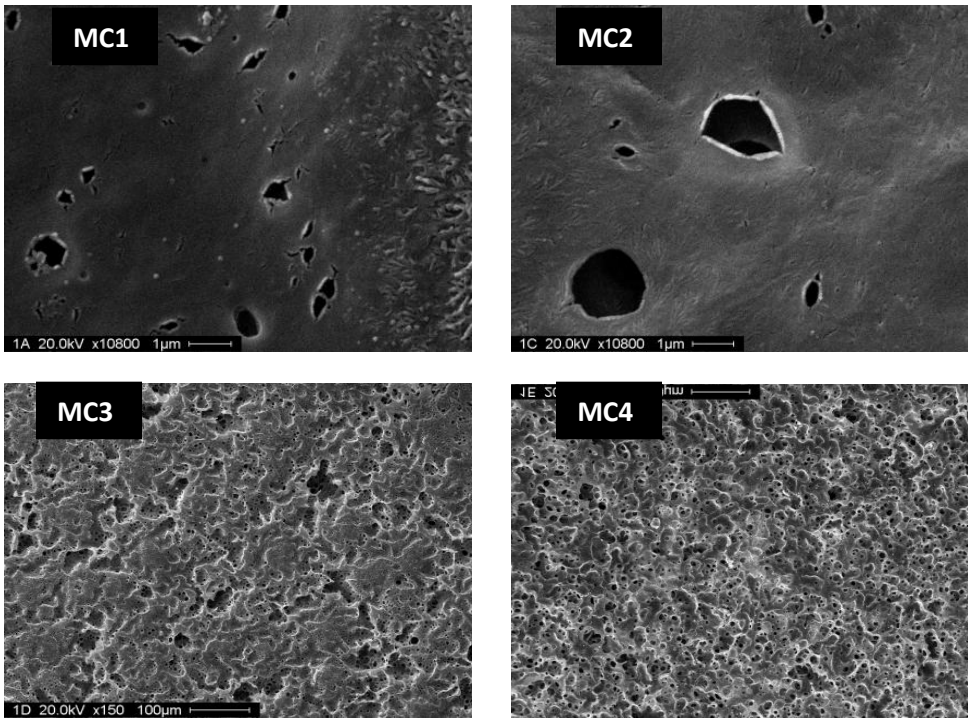

Fig.(4.1 c). Bottom layer SEM morphology of PLA membranes at different CBT. MC1 at 20°c, MC2 at 40°c, MC3 at 60°c,MC4 at 80°c.

4.1.2 Effect of evaporation time on morphology of the PLA membranes

Figure(4.2) shows the effect of the evaporation time (0.5 min, 1 min, 3 min, 5 min and 7 min) on the morphology of the PLA membrane at CBT (20°C). Figure (4.2 a) shows the structure of cross-section scanning electron microscopy SEM pictures. The membrane prepared at evaporation time E.T. of (0.5 min ME1), is different from these prepared with increasing the E.T. It can be seen that very small macrovoids are present at cross section of the membrane due to some solvent evaporation through the short period (0.5 min) and after that immersion in water. Thus, the instantaneous demixing occured therefore the microvoids formed. For (ME2 at 1 min) it can be noticed that an asymmetric structure with spongy-like structure in the top layer and macrovoids formed in the supported layer. Gradually, this spongy layer increases with increasing the evaporation time to 3 min (ME3). That means with increasing the evaporation time, more of the solvent evaporated and a little of it demixed with the water in comparison with ME1 and ME2. Therefore, the polymer concentration increases form this spongy-like structure . For 5 and 7 min (ME4 and ME5), it can be seen that the cross-section is fully dense structure because all of the solvent was evaporated and there is no solvent demixed with water. Therefore, a rigid dense skin layer is formed. These observations are in agreement with the literature [Madaeni et al., 2011].

Fig.(4.2 b) shows the structure of the top layer SEM pictures. It can be noticed that the surface of ME1 membrane has more pores because the instantaneous demixing between the solvent and non-solvent. In addition, those pores may be due to the adsorption of vapor from the surrounding area during solvent evaporation of the casting solution. The absorption of air and water would reduce the thermodynamics stability of the casting solution, leading to a quick phase inversion before immersion in the coagulation bath. Consequently, larger

pores and macrovoids are formed in the membrane [Gao et al. 2009]. For ME2 these pores began to be less than ME1, and gradually disappeared from the top layer as shown in ME3, ME4 and ME5, due to more solvent evaporation and the increase of polymer concentration on the top layer.

Fig.(4.2 c) shows the structure of the bottom layer SEM pictures. It can be noticed that there are more pores on the bottom surface of ME1 membrane. This is also because of the instantaneous demixing. These pores disappear with the increase in the evaporation time because the polymer concentration increase on the bottom layer. There is no bottom layer picture for ME4 and ME5 because these membranes are dense layers. Therefore, the picture is the same for top and bottom.

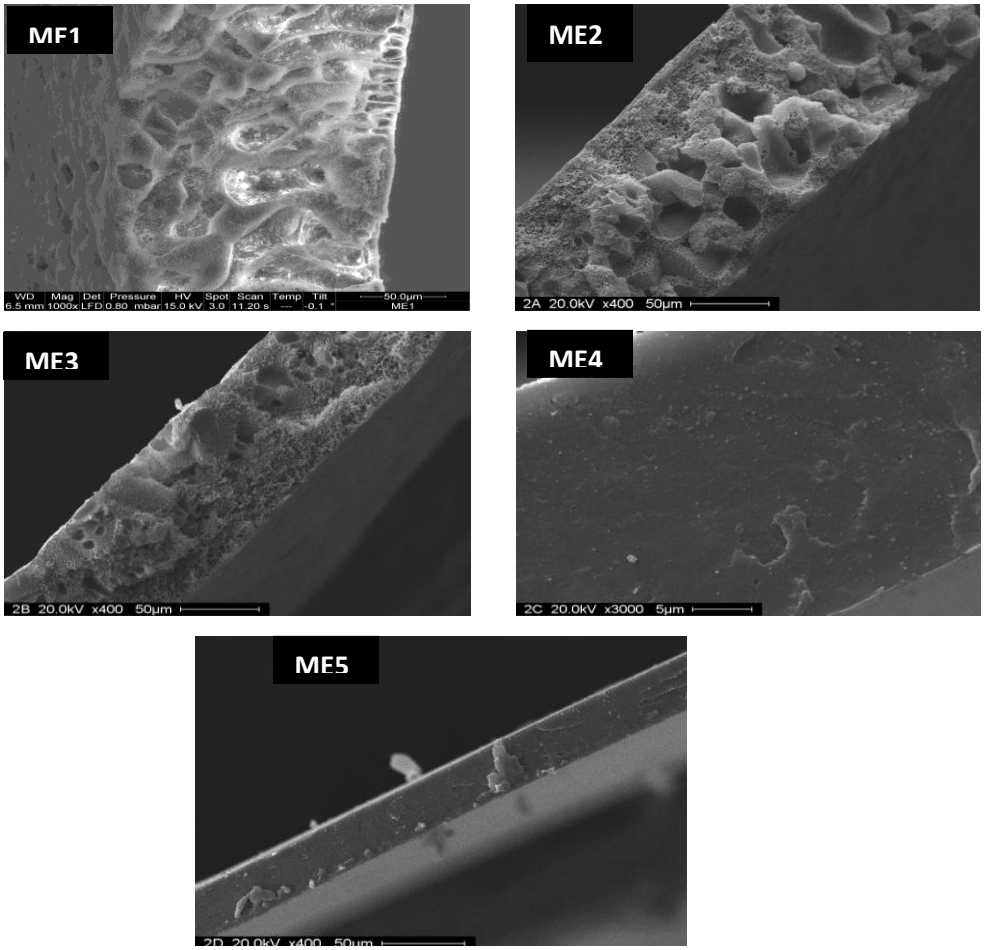

Fig.(4.2 a). Cross-sectional SEM morphology of PLA membranes at different evaporation time. ME1 at 0.5 min, ME2 at 1 min, ME3 at 3 min,ME4 at 5 min, ME5 at 7 min.

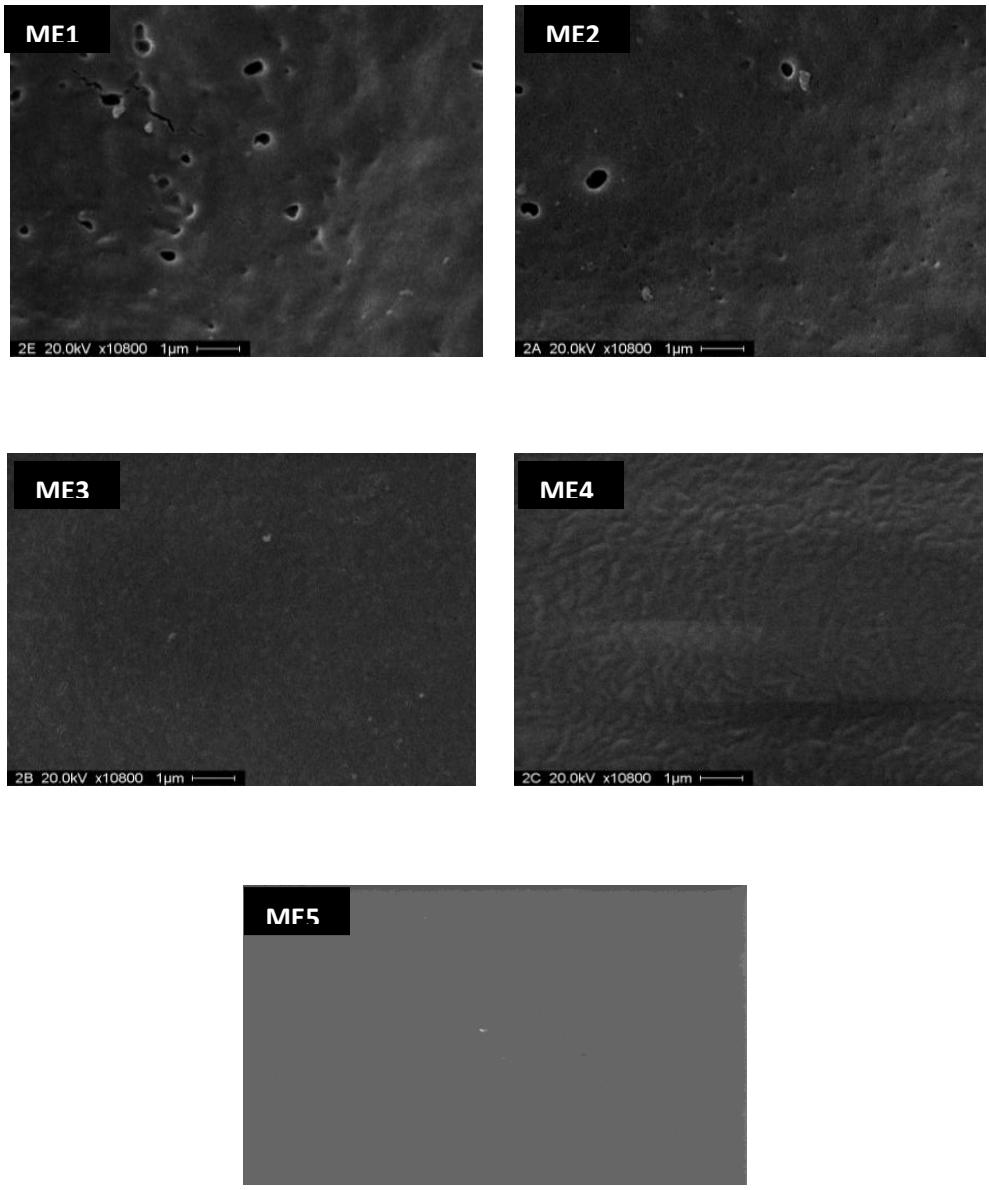

Fig.(4.2 b). Top layer SEM morphology of PLA membranes at different evaporation time. ME1 at 0.5 min, ME2 at 1 min, ME3 at 3 min,ME4 at 5 min, ME5 at 7 min.

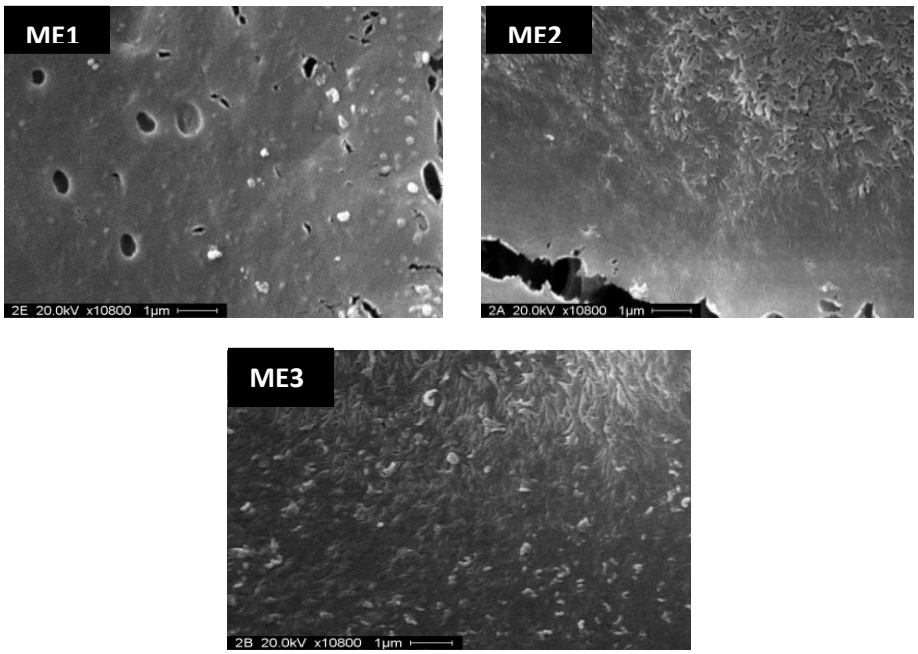

Fig.(4.2 c) Bottom SEM morphology of PLA membranes at different evaporation time. ME1 at 0.5 min, ME2 at 1 min, ME3 at 3 min,ME4 at 5 min, ME5 at 7 min.

4.2 Effect of the coagulation temperature and evaporation time on the thickness of the membrane

Fig.(4.3 a) shows the effect of the coagulation bath temperature on the thickness of the membrane. It can be noticed that the thickness decreases (0.198, 0.189, 0.183 and 0.144mm) by increasing the coagulation bath temperatures to (20, 40,60 and 80°C) respectively. At low CBT (20°C) fast precipitation process occurs. Therefore, the cast film rapidly solidified and by increasing the CBT from (40 to 80°C), stopping of the precipitation process takes place longer and this results in formation of the thinner membranes..

Fig.(4.3 b) represents the effect of the evaporation time on the thickness of the membrane. From this figure it can be seen that the thickness of the membrane decreases with increasing the evaporation time (0.5 min and 7 min) (ME1-ME5). At low evaporation time (0.5,1 and 3 min) some of the solvent evaporated and the

other demixed in water. At high evaporation time (5 and 7 min) more solvent is evaporated from the surface of the wet film and a rigid dense layer is formed. Therefore, the thickness of the membrane decreases with the amount of evaporated solvent.

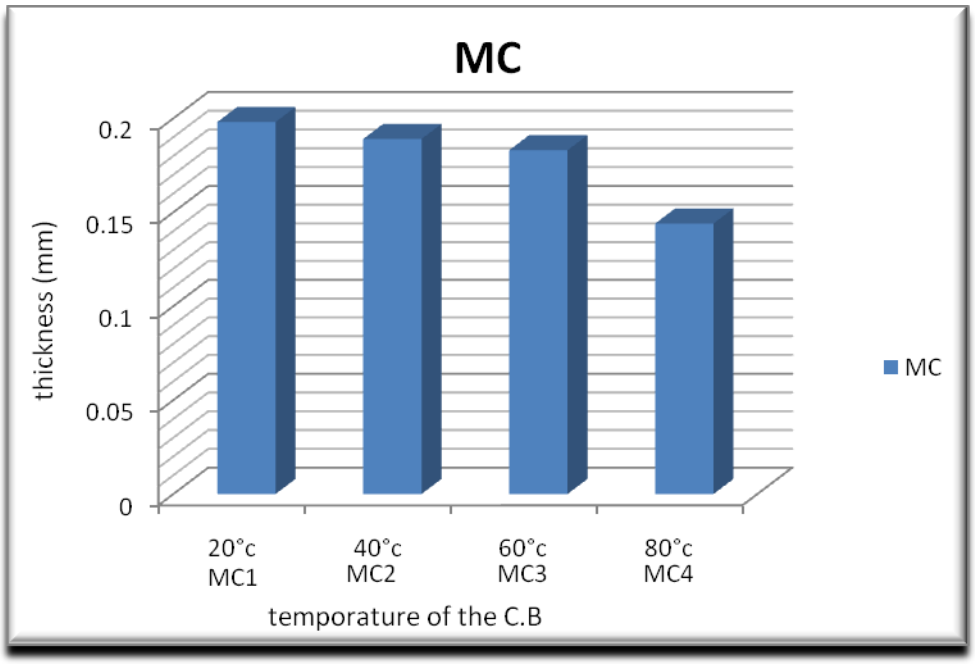

Fig.(4.3 a). Thickness of the membrane with temperature of the coagulation bath

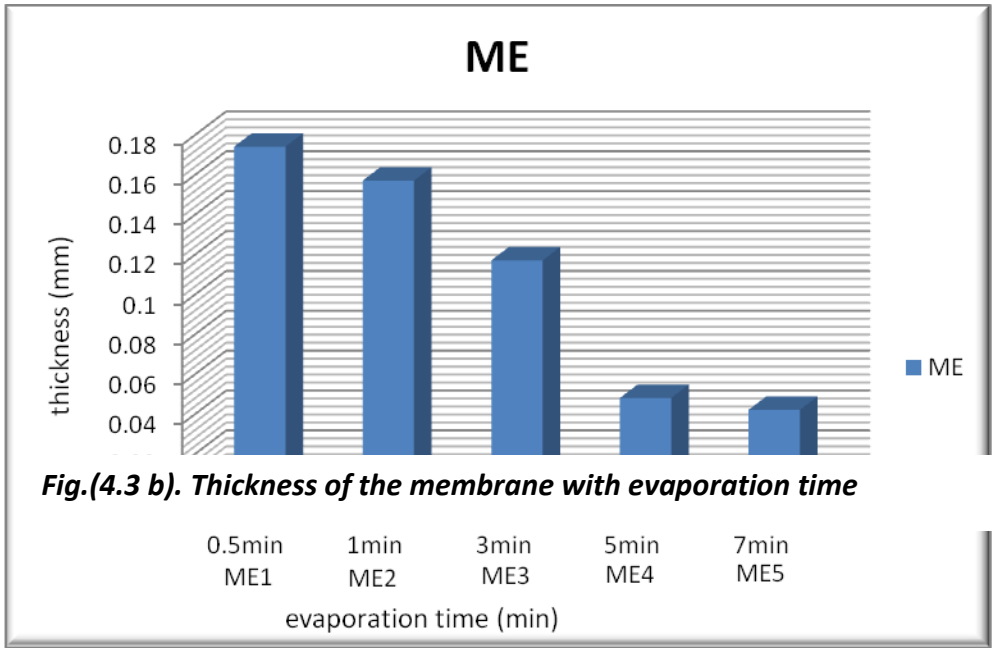

Fig.(4.3 b). Thickness of the membrane with evaporation time

4-3 Effect of the coagulation bath temperature and evaporation time on the contact angle of the membrane

Hydrophilicity is one of the important properties of membranes, which greatly affects their flux and antifouling ability [Amirilagani 2010]. Contact angles were measured to evaluate the effect of CBTs and evaporation time on hydrophilicity.

Figure (4.4 a) shows the effect of the CBTs on the contact angle for the PLA membrane. When increasing the CBT, contact angle of the membrane increases (except MC4 at 80°C, the contact angle decrease because the water drop distributed quickly after contacts with the surface because there are many big pores on the surface). This indicates that hydrophilicity of the membrane decreases by increasing the CBT.

Fig.(4.4 b) shows the effect of the evaporation time on the contact angle. It can be seen that at low evaporation time (0.5, 1 and 3 min) the contact angle increases. This may be attributed to the differences in the morphologies of the top

layer. Where as, on the top layer of the ME1 membrane more pores were found and these pores began to be reduced on the suface of the ME2 and ME3 as showen in Figure (4.2 b). These pores are the main causes for the dicrease in the contact angle. By increasing the evaporation time to the prepared membrane (ME4 and ME5) (5 and 7 min) respectivly, the contact angle decreases. Therefore, all the membranes are concidered more hydrophilic, having an affinity for water and usually other polar molecules incloding alcohols [Zereshki et al. 2009 (1)].

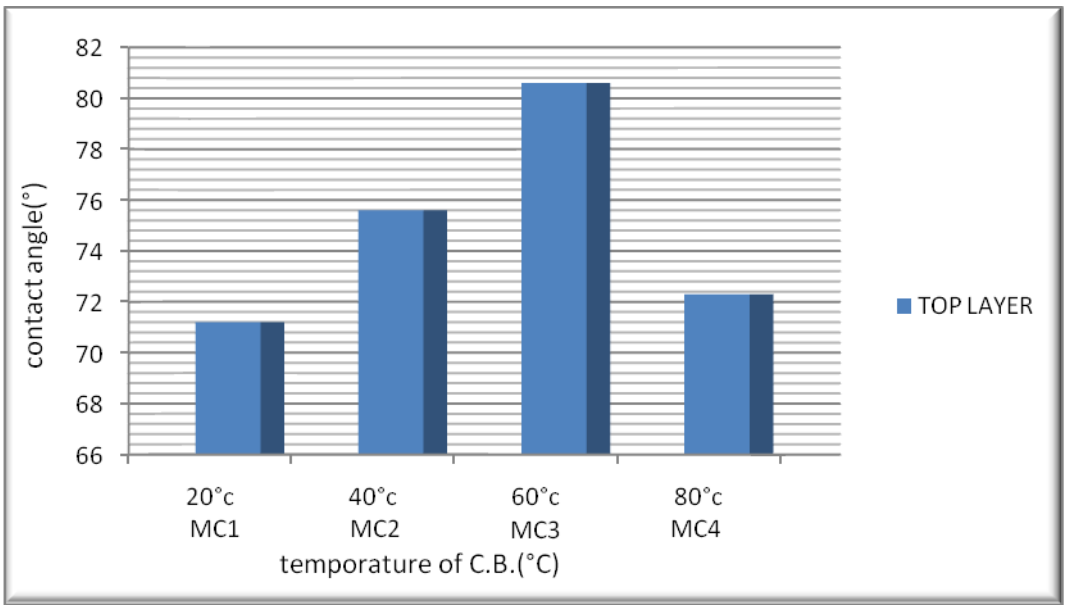

Fig.(4.4 a) Contact angles with different CBT.

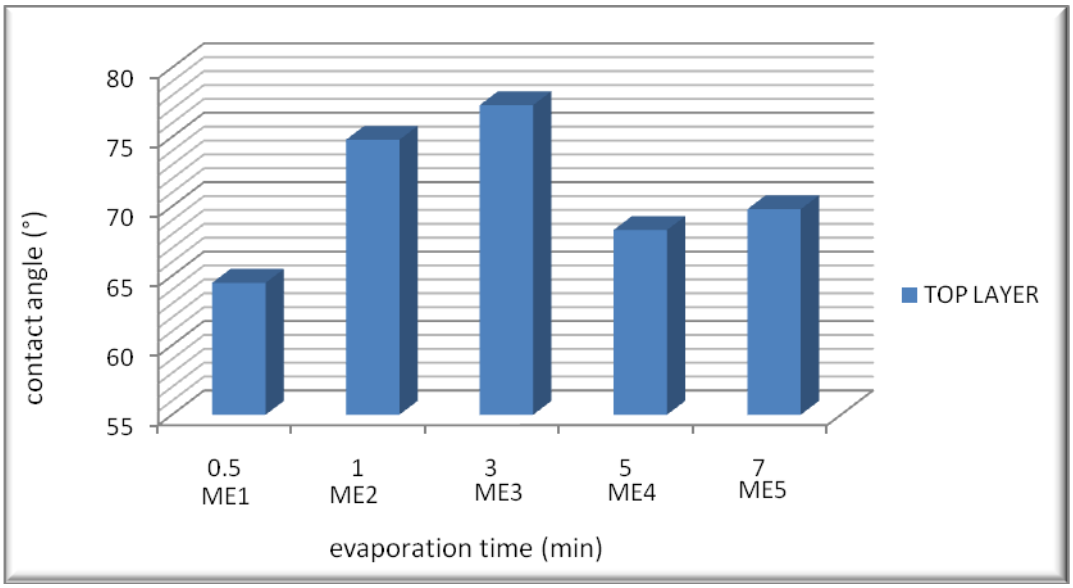

Fig.(4.4 b). Contact angle with evaporation time

4. 4.Effect of the coagulation bath temperature and evaporation time on the mechanical properties of the PLA membranes

In the industrial applications of membranes, the mechanical properties are very important in the membrane performance. Therefore, the Young's modulus, maximum stress and elongation at break were measured and are shown in. Fig.(4.5 a, b and c). This figure shows the mechanical properties of the PLA membrane prepared with different CBT. From Figure (4.5 a and b) it can be seen that the Young's modulus increases from 144.98 N/mm² to 296.56 N/mm² and maximum stress increases from 3.5 N/mm² to 8.78 N/mm² by increasing the CBT. The mechanical properties of the prepared flat sheet membranes depend on membrane morphology which is affected by different CBT. It has been observed that increase of the CBT the structure layers of the membrane prepared change gradually from finger-like structure to sponge-like structure as shown in Figure (4.2). This change in morphology of the membrane improves the mechanical properties, while the

elongation at break is decreasing Fig.(4.5 c) due to the macrovoids in the cross-section of the membrane and this macrovoids disappeared by increasing the CBT.

Generally, macrovoids in membranes are undesirable because they represent mechanical weak points, which may lead to membrane failure when the membranes are operating under high pressures [Xu & Xu, 2002, Xu & Alsalhy 2004].

Fig.(4.6 a, b and c) shows the effect of evaporation time on the mechanical properties. It can be seen that the mechanical properties increase by increasing the evaporation time. Young's modulus increases from 133.87 N/mm² at 0.5 min to 910 N/mm² at 7 min, Max stress also increases from 2.94 N/mm² at 0.5 min to 34.46 N/mm² at 7 min and the elongation at break increases from 2.44% at 0.5 min to 11.1% at 7 min as shown In Fig.(4.6). Therefore, the PLA membrane with (7 min ME5) evaporation time has the best mechanical properties. The enhancement of the mechanical properties for these membranes due to the developed spongy-like structure at (ME1, ME2 and ME3) reaching a rigid dense skin layer at (ME4 and ME5).

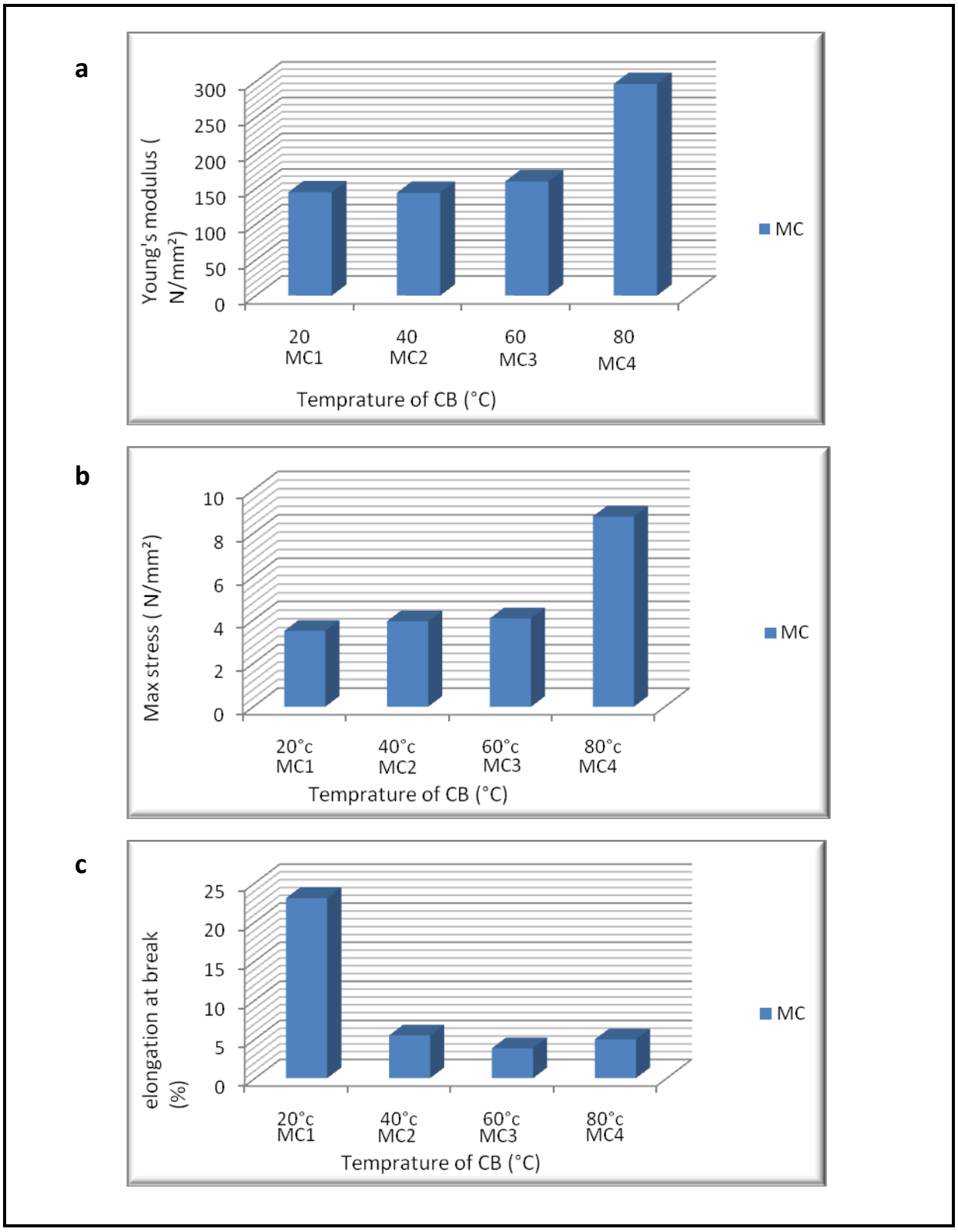

Fig.(4.5) Mechanical properties (a)Young's modulus, (b) Max. stress, and (c)elongation at break as a function of the CBT

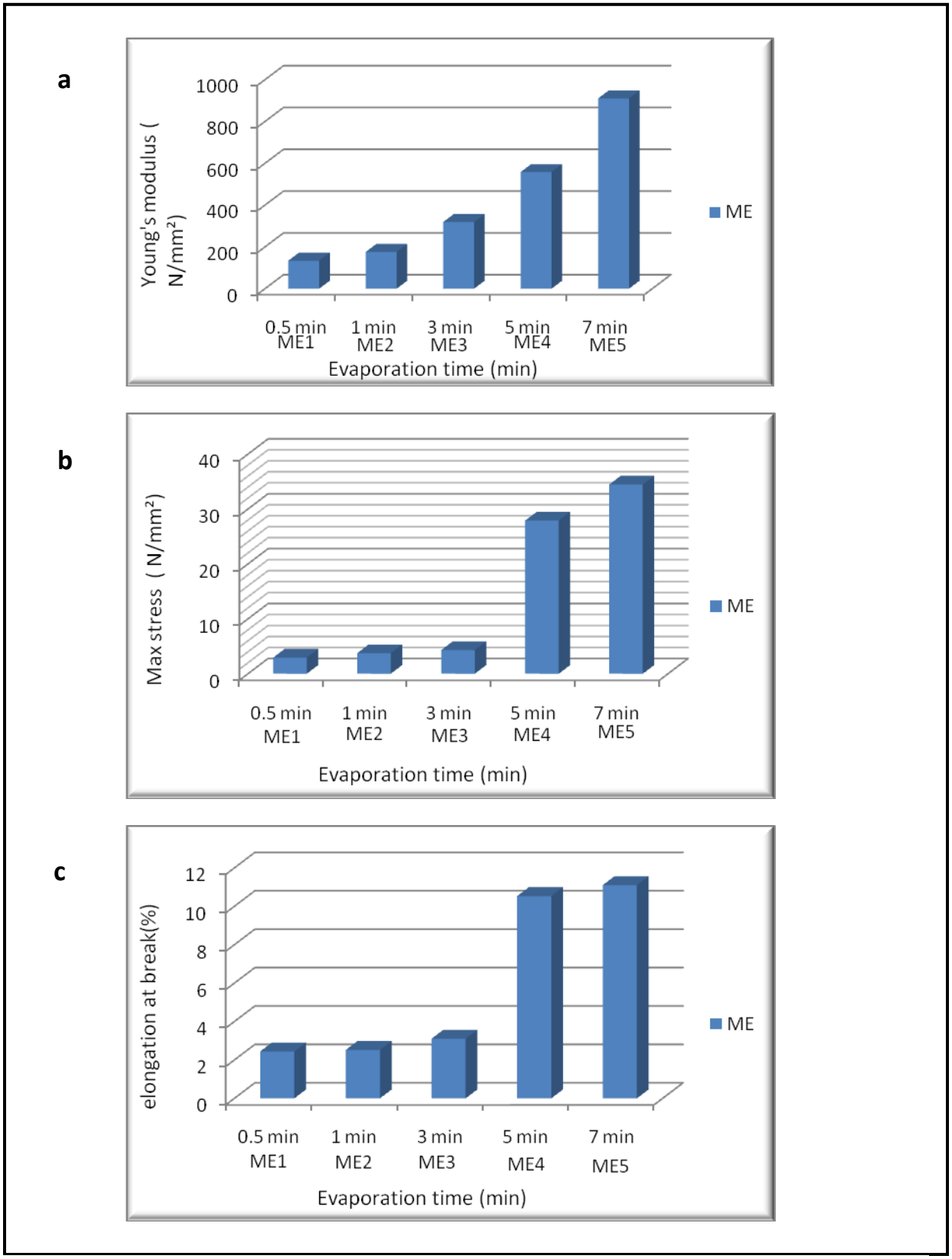

Fig.(4.6) Mechanical properties (a)Young's modulus, (b) Max. stress, and (c)elongation at break as a function of the evaporation time

*4. 5. **Swelling of PLA membrane***

In this work, it was tried to determine the degree of swelling for ME5 membrane in pure MEOH and pure MTBE. Result of the swelling measurements in pure methanol and pure MTBE are presented in Figure (4.7 a). The amount of the methanol absorbed is more than the MTBE. Therefore, more methanol permeate through the membrane when treating methanol/MTBE mixture in pervaporation process. Also the degree of swelling for MC1membrane that was used as a support layer for the composite membrane with PVA to separate ethanol and water. The results of the swelling measurements in pure water and pure ethanol are presented in Fig.(4.7 b). The amount of ethanol absorbed is more than water. Thus, the swelling degree may be used to predict the pervaporation ability qualitatively [Lin et al. 2002]

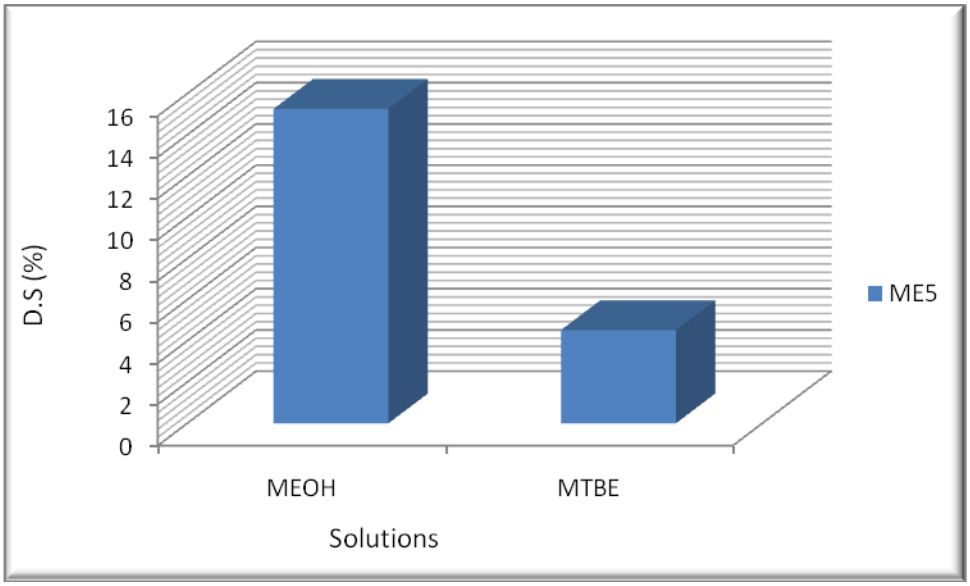

Fig.(4.7 a) Degree of swelling for ME5 membrane with MEOH and MTBE.

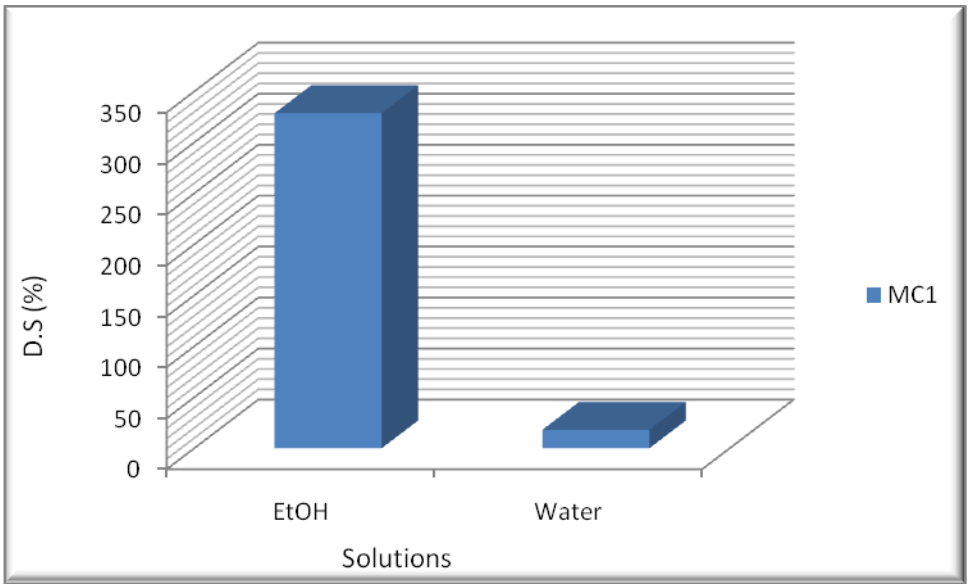

Fig.(4.7 b).Degree of swelling for MC1 membrane with EtOH and water.

4.6 Composite membrane

The morphology for composite membranes is shown in Figure (4.8). Where, the sublayer is MC1 as shown in Fig (4.1 a), and the top layer is PVA dense layer. This membrane has good mechanical properties (Young's modulus is 270 N/mm², Max stress is 8.4 N/mm² and elongate at break 18.66 %). The degree of swelling for PLA support layer shown in Fig.(4.7 b). The contact angle for this membrane is (60°).

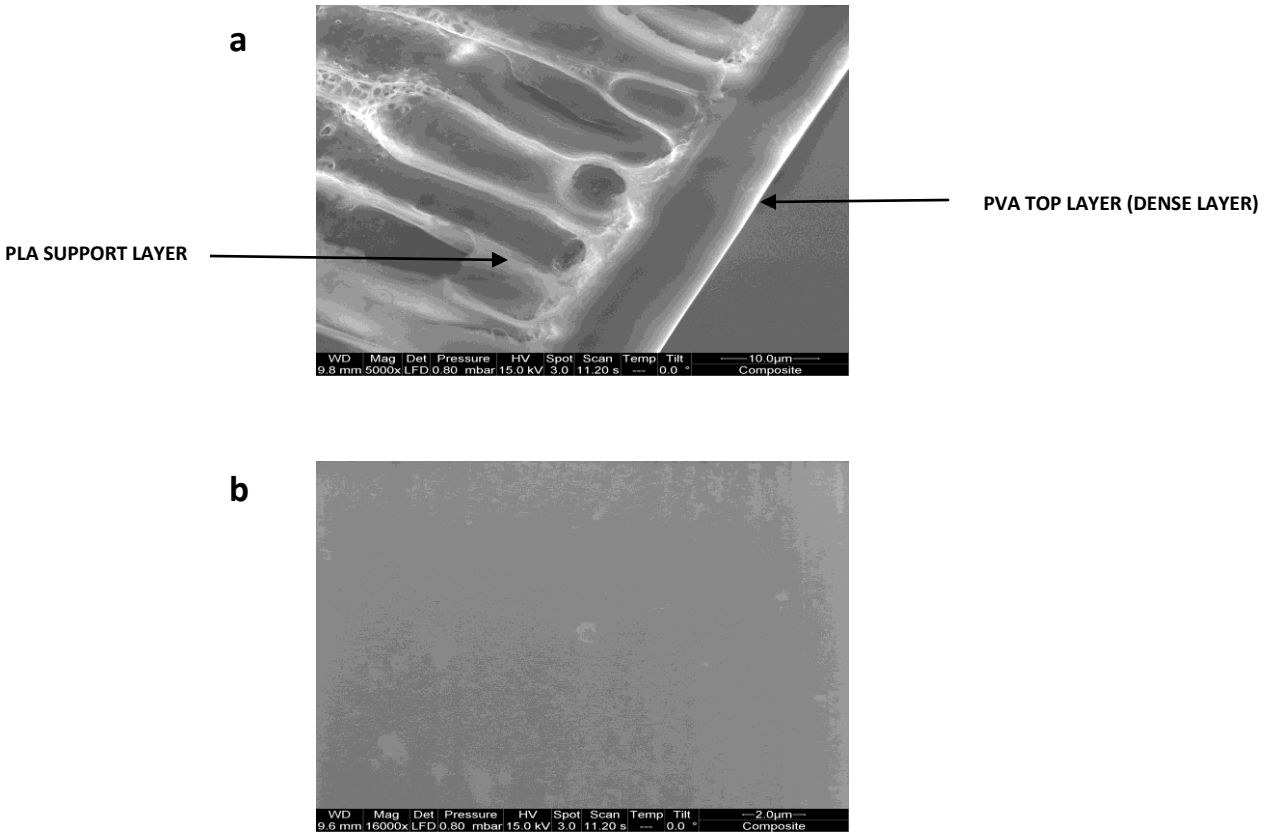

Fig.(4.8). Composite membrane SEM a) cross-section, b) top layer

4.7. Pervaporation process

In PV process, the membranes were selected from the membranes prepared for pervaporation process test. ME5 is a perfect membrane for this process. It has totally suitable properties for PV process such as dense layer, good mechanical properties and good swelling behavior for organic-organic mixtures.

In addition, composite membranes (PLA/PVA) are used to separate water/ethanol. These membranes are prepared by coating the MC1 by PVA dense layer to make they suitable for pervaporation.

4.7.1. Pervaporation to separate MEOH/MTBE mixture by using PLA flat sheet membrane (ME5).

Fig.(4.9 a, b, c and d) shows the effect of feed temperature such as 20,30 and 35°C on the total flux, partial flux of MEOH and MTBE and selectivity. The methanol concentration in feed at asentropic point is (14.3 wt%). It was found that the permeation flux increases with increasing the feed temperature Fig. (4.9 a). At 6 mbar permeate pressure, the permeation fluxes were 0.063 kg/m²h at 20°C, 0.119 kg/m²h at 30°C and improved to 0.208 kg/m²h at 35°C. At 27 mbar also the permeation flux increases with temperature but the difference of result at 30 and 35°C is not very large. The same thing applies for 50 mbar. These observations, are due to the driving force in pervaporation process being chemical potential which is based on the partial vapor pressure differences of permeating component in feed and permeate sides. The vapor pressure of the feed side increases by increasing temperature, while the vapor pressure of the permeate side does not change significantly. Therefore, the driving force of mass transfer enhances [peivasti et.al.2008].

Enhancement of the diffusion coefficients of the components at higher temperatures could also increase the mass transfer [Peivasti et al. 2008 and Zereshki et al. 2010].In addition, the mobility of the polymer molecules increases by increasing the temperature in the membrane and the free volume inside membrane enlargement. Therefore, permeation rate of the constituents increases.

The molecular kinetic diameter of MEOH is much smaller in comparison with MTBE (0.4 and 0,62) respectively [Zereshki et al. 2010]. Therefore, more of the methanol pass through the membrane as shown in Fig (4.9, b) in comparison with MTBE as shown in Fig.(4.9 c).

From the data presented in Fig.(4.9 d) there is a tendency to separate MEOH from feed solution, where, the selectivity increases by increasing temperature. The highest increase in selectivity is at high temperature.

This phenomenon is considered due to the chemical and structural properties of the PLA membrane. Thus, by increasing the temperature, the mobility of the polymer chains increases but the frozen free volume formed at the preparation step decreases because of the relatively very rigid bulky specific properties of the PLA membrane Similar results were reported by other researchers [Sang-Gyun, 2000 and Sang-Gyun, 1997] . In addition, in this study, the swelling is dominant, and the pervaporation ability changes with swelling degree in the same direction. Thus, the swelling degree may be used to predict the pervaporation ability qualitatively [lin Zhang 2002]. Therefore, PLA membrane swelled more MEOH in comparison with MTBE as shown in Fig.(4.7 a). Therefore more MEOH permeated through the membrane.

In the above Figures (4.9 a,b and c) it is clear that the total flux and partial flux decrease by increasing the permeate pressure from 6 mbar to 50 mbar. Whereas, the selectivity increases as shown in Figure (4.9 d). for Fig.(28 a, b and c) at 20 and 30°C the difference of results between 6, 27 and 50 mbar is not very large. Whereas, at 35°C a large difference in the results can be seen. This is because the reduction of the driving force for transporting components. Similar results were reported by other researchers [Lin et al. 2006, N.Rajagphalan, M . cheryan 1995].

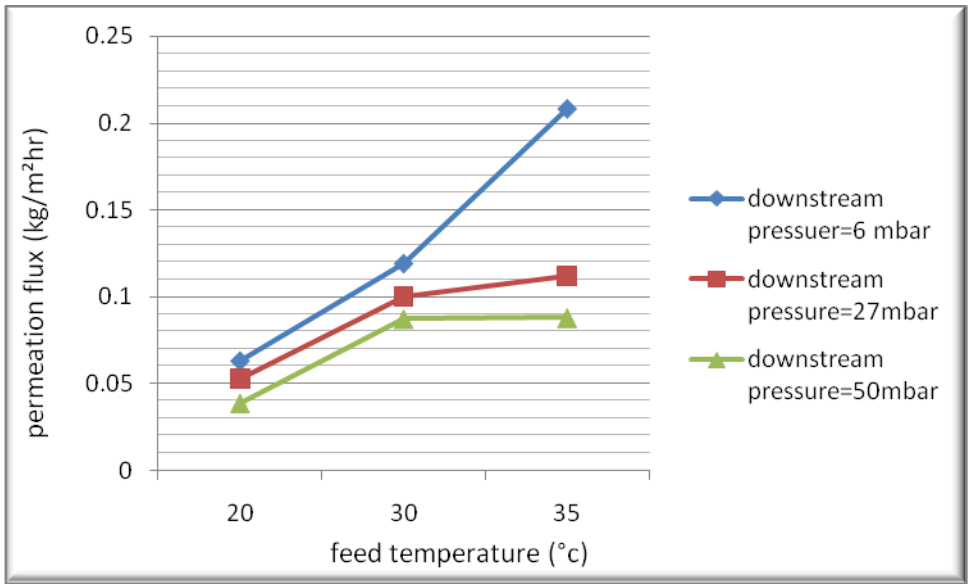

Fig.(4.9 a): Effect of feed temperature on the permeate flux as a function of the permeater pressure.

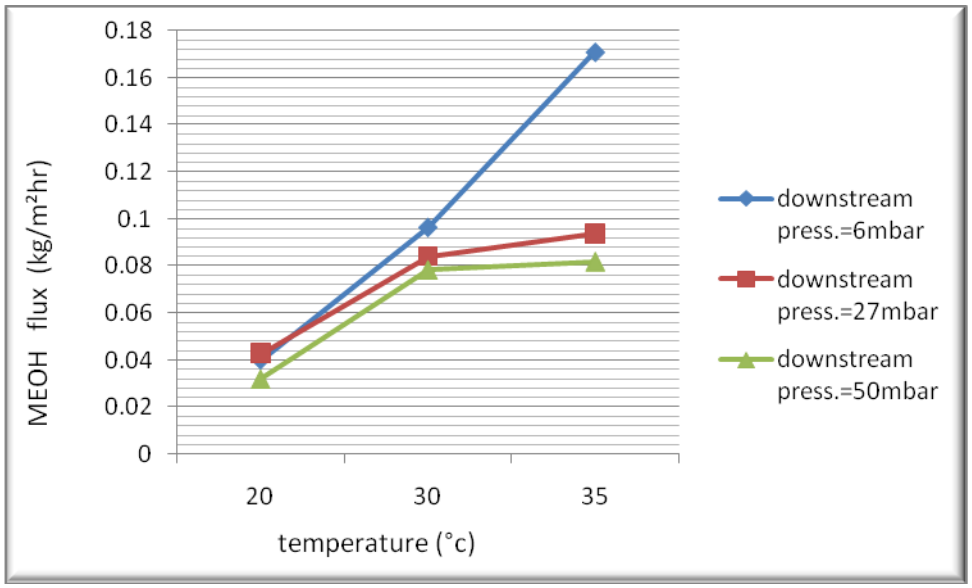

Fig. (4.9 b): Effect of feed temperature on MEOH flux as a function of the permeater pressure.

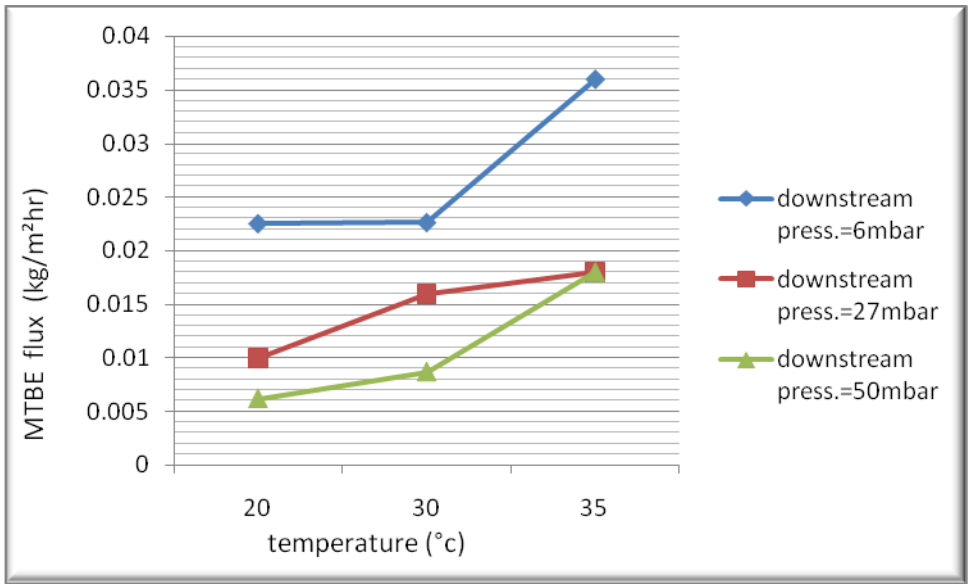

Fig.(4.9 c): Effect of feed temperature on the MTBE flux as a function of the permeater pressure.

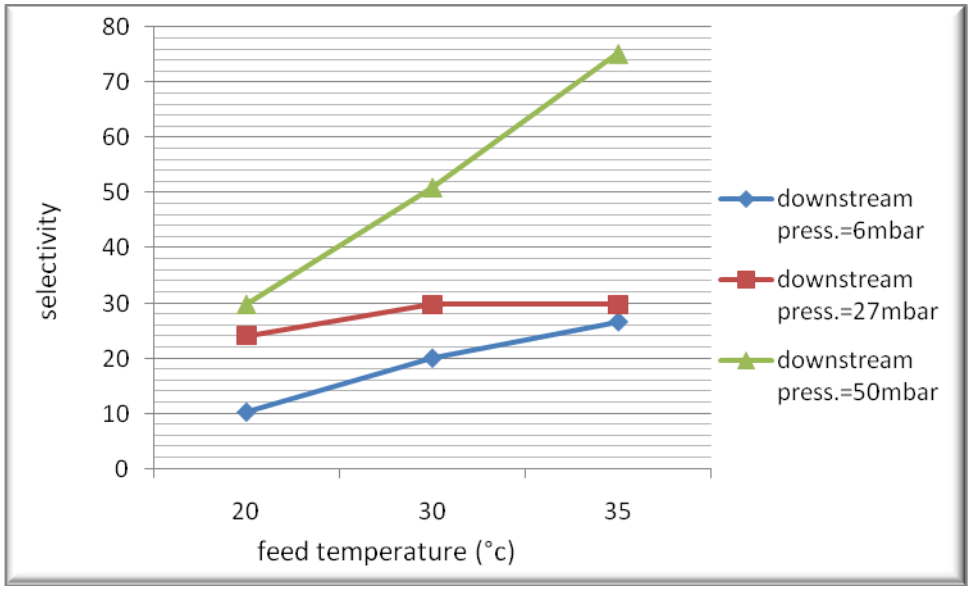

Fig.(4.9 d): Effect of feed temperature on the selectivity as a function of the permeater pressure.

4.7.2. *Pervaporation to separate water/ethanol by using (PLA/PVA) composite membrane*

Fig.(4.10 a, b, c and d) shows the effect of feed temperature such as 30, 40 and 50°C on the total flux, partial flux of water and ethanol EtOH and selectivity. The water concentration in feed is at asentropic point (5 wt%). It was noticed that increasing the temperature caused a significant increase in the total permeation flux as shown in Fig.(4.10 a). At 1.8 mbar permeate pressure, by increasing the feed temperature from 30°C to 50°C the permeation fluxes increase from 4.717 kg/m²h, to 7.076 kg/m². At 25 mbar also the permeation flux increases from 3.538 kg/m²h to 5.748kg/m²h by increasing the temperature from 30 to 50°C. A similar effect was observed by Dobrak et al. 2010, Mohammadi et al.2005 and Sampranpiboon et al. 2000. The authors stated that during pervaporation permeating molecules diffuse through free volumes of the membrane. Thermal motions of polymer chains in amorphous regions randomly produce free volumes. As temperature increases, the frequency and amplitude of polymer jumping chains are increasing. Thus, at higher temperatures, the diffusion rate of individual permeating molecules increases leading to high permeation fluxes. The same reason could also explain why the partial flux for ethanol and water increased by increasing feed temperature. as shown in Fig.(4.10 b and c). From this Figure it can be seen that at 1.8 mbar the flux of ethanol increases from 4.047 to 6.192 kg/m²h by increasing feed temperature from 30 to 50°C and the water flux increases from 0.669 to 0.884 kg/m²h at the same condition. and at 25 mbar the flux of ethanol increases from 2.972 to 4.619kg/m²h and the water flux increases from 0.566to 1.129kg/m²h. The difference between the results of ethanol and water flux is very large. This may be because of the swelling behavior, where the support layer is more swollen to ethanol in comparison to water. Therefore, more ethanol permeate through the membrane.

From the data presented in Fig. (4.10 d), an increase in selectivity with increasing temperature was observed. Dobrak and Liang [Dobrak et al. 2010 and Liang et al. 1996] also observed this effect.

Liang et al.(1996) explained it by temperature dependent decrease of the hydrogen bonding between water and alcohol molecules. When that happens, then less water is stimulated to permeate through the membrane, which is more selectively swollen by ethanol.

In the above Figure (4.10 a,b and c) the total flux and partial flux decrease with the increase in permeate pressure from 1.8 mbar to 40 mbar. Whereas, the selectivity increased as shown in Figure (4.10 d). This is due to the reduction of the driving force for transport of components. Similar results were reported by other researchers [L.G.Lin et al. 2006, N.Rajagphalan, M . cheryan 1995].

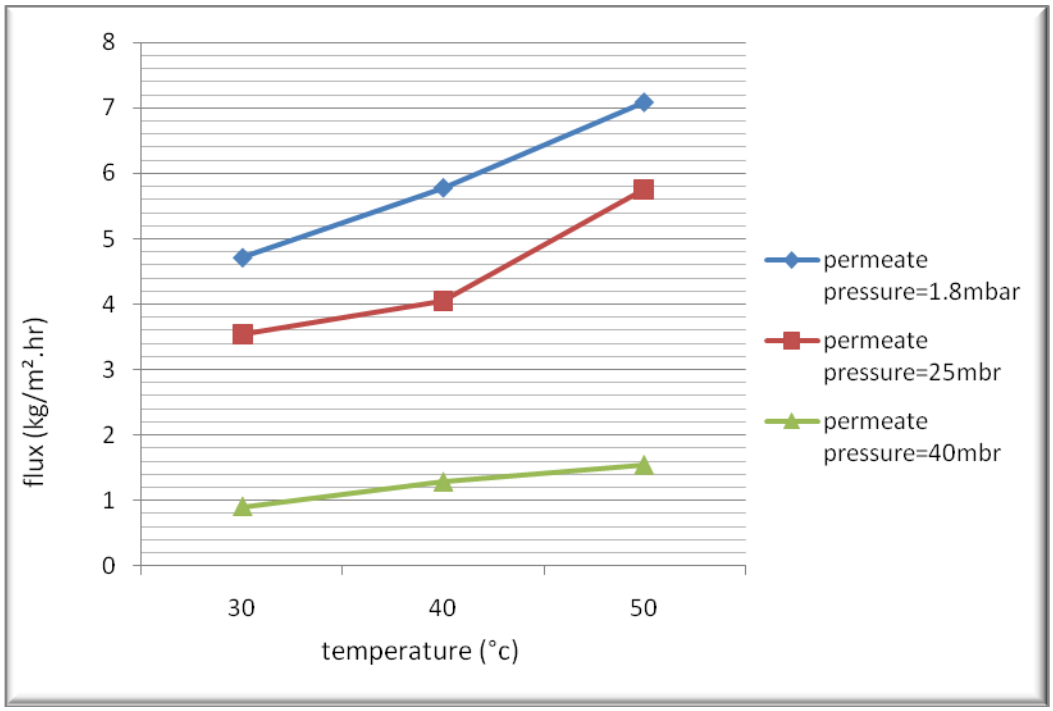

Fig.(4.10 a): Effect of feed temperature on the permeate flux as a function of the permeater pressure.

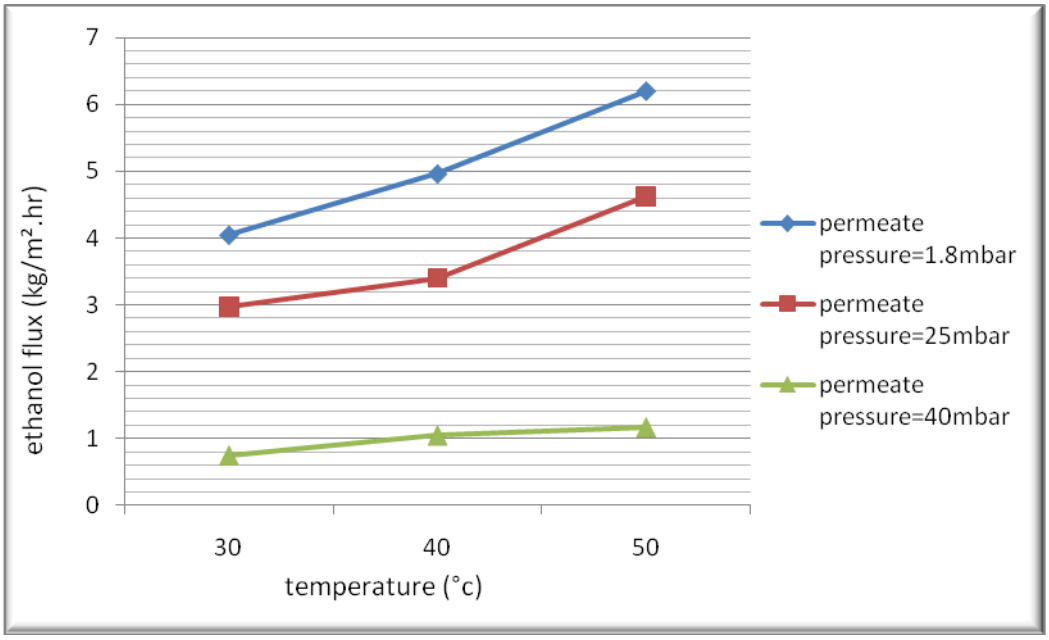

Fig.(4.10 b): Effect of feed temperature on the ethanol flux as a function of the permeater pressure.

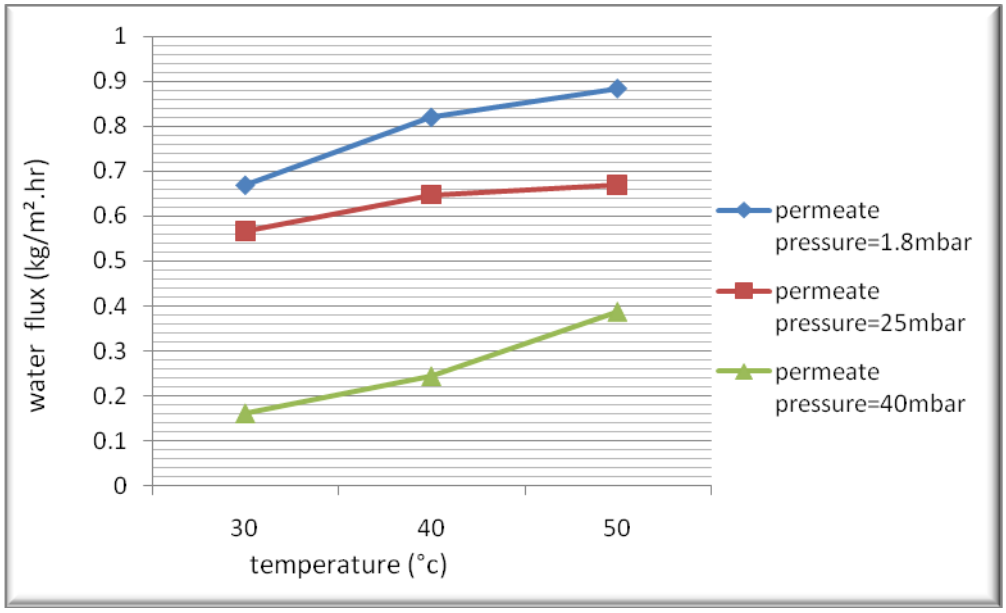

Fig.(4.10 c): Effect of feed temperature on the water flux as a function of the permeater pressure.

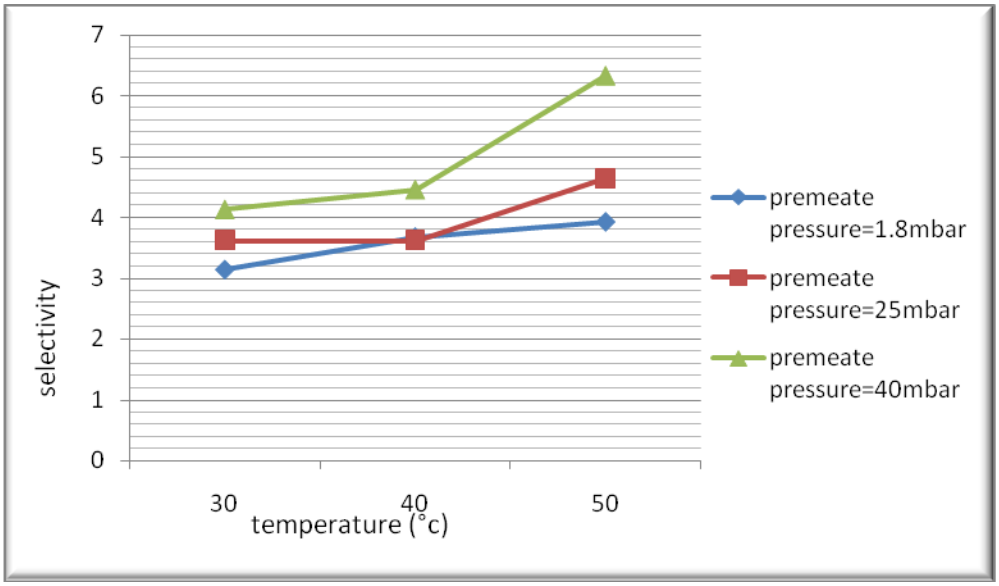

Fig.(4.10 c): Effect of feed temperature on the selectivity as a function of the permeater pressure.

Chapter five

Conclusions and Recommendations

5.1 Conclusions

The following conclusions are drawn from this work:

1- By increasing CBTs, it can be seen that:

a. The morphology of the membrane changed from finger-like structure to spongy-like structure.

b. The thickness of the membranes decreased by increasing the CBTs.

c. The hydrophilicity of the membrane decreased because contact angles increased with the increasing of the CBTs.

d. The mechanical properties were enhanced by increasing the CBTs.

All of these membranes include some pores on the dense layer (top layer). Therefore, these membranes were coated with PVA dense skin layer to become composite membrane and suitable for pervaporation processes.

2- By increasing evaporation times, it can be seen that:

a. The morphology changed from finger-like structure to spongy-like structure to dense layer at high evaporation time, and gradually, the pores disappeared from the top and bottom layers.

b. The thickness decreased by increasing the evaporation times.

c. The hydrophilicity of these membrane decreased when the membrane changed from finger-like to spongy-like structure, and increased at a dense layer.

d. The mechanical properties were enhanced by increasing the evaporation times.

At this parameter, ME5 membrane at 7 min evaporation time is totally dense layer and has good mechanical properties. Therefore, it is well suited for pervaporation process.

3- The successful use of ME5 membrane at 7 min as evaporation time in pervaporation separation of MEOH/MTBE azeotropric mixture was demonstrated, by increasing the feed temperature which caused increasing in the total flux and partial fluxes, which was explained by enhancement of the driving force and diffusion coefficient of component at higher temperature, Also the selectivity increased due to the frozen free volume formed as the preparation step decreased because of the relatively very rigid bulky specific properties of the PLA membrane. By increasing the permeate pressure the total flux and partial flux decrease and the selectivity increases.

4- Composite membrane (PLA/PVA) which is used to separate water/EtOH was demonstrated, by increasing the feed temperature which caused increasing the total flux and partial fluxes, which was explained by enhancement of the driving force and diffusion coefficient of component at higher temperature, and the selectivity also increased because the temperature decreased the hydrogen bonding between water and alcohol molecules. the total flux and partial flux decrease with the increase in permeate pressure and the selectivity increased.

5.2 Recommendations

The following recommendations are presented for future work:

1- Measuring other membrane properties such as porosity and pore size distributions for (MC1, MC2, MC3, ME1,ME2,ME3) which can be applied in other processes.
2- Studying other parameter for casting like increasing the polymer concentration or using additive to enhance the structure of the membranes as well as to see the effect of these parameters on the permeation and separation performance.
3- Using ME5 and the composite membrane in gas separation process.
4- Using ME5 and the composite membrane to separate other solutions like methanol/ETBE and EtOH/ CHx by pervaporation process.

[A]

-Abdulghader Elarbi, “Flux enhancement in a spiral wrap ultrafiltration element by using backpulsing” M.Sc. Thesis, University of Stellenbosch, (2009).

- Anil K. Pabby, Syed S. H. Rizvi andAna Maria Sastre, ”Handbook of Membrane Separations” CRC Press Taylor & Francis Group, (2008).

- Afonso CMA & Crespo J,” Green separation processes, fundamentals and

Applications”, Weinheim, Wiley–vch Verlag GmbH & Co. KGaA., (2005).

- Amirilargani M., E. Saljoughi, T. Mohammadi, and M.R. Moghbeli,” Effects of Coagulation Bath Temperature and Polyvinylpyrrolidone Content on Flat Sheet Asymmetric Polyethersulfone Membranes” Wiley InterScience, 2010.

[B]

- Baker R. W. “Membrane Technology and Applications”, 2nd Edition, John Wiley & Sons Ltd, West Sussex, 2004.

-Baker, R.W., Cussler, E.L., Eykamp, W., Koros, W.J., Riley, R.L. and Strathmann, H., “Membrane separation systems-recent developments and future directions”, , New Jersey: William Andrew Inc., (1991)

- Bechhold, H., “Durchlassigkeit von ultrafiltration”, Z. Phy. Che., 1908. 64: 328-342.

- Bruschke HEA,” State–of–Art of Pervaporation Processes in the chemical industry”, In: Nunes SP & Peinemann KV (eds) Membrane technology in the chemical industry. Weinheim, Wiley–vch Verlag GmbH: 127–172(2001).

-Brun JP, Larchet C, Bulvestre G & Auclair B," Sorption and pervaporation of dilute aqueous solutions of organic compounds through polymer membranes", J Membr Sci25: 55–100. (1985).

- Brown MA, Miller S & Emmert GL," On–line purge and trap gas chromatography for monitoring of trihalomethanes in drinking water distribution systems". Anal Chim Acta 592: 154–161(2007).

- Binning R.C., R.J. Lee, J.F. Jennings, E.C. Martin, "Separation of liquid mixtures by permeation", Ind. Eng. Chem. 53 (1961) 45–50.

[C]

- Coulson J. M. and Richardson J. F., "Chemical Engineering", Vol. 2, 5th Edition, Pergamon Press, Oxford, 2002.

- Chapman PD, Oliveira T, Livingston AG & Li K, "Membranes for the dehydration of solvents by Pervaporation", J Membr Sci 318: 5–37, (2008).

- Cabasso I., J. Jagur-Grodzinski, D. Vofsi, "Polymeric alloys of polyphosphonates and acetyl cellulose. I. Sorption and diffusion of benzene and cyclohexane", J. Appl. Polym. Sci. 18 (1974) 2117–2136.

- Cabasso I.," Organic Liquid Mixtures Separation by Selective Polymer Membranes", Ind. Eng. Chem. Prod. Res. Dev. 22, 313 (1983).

[D]

- Dotremont C," Pervaporation for the removal of chlorinated hydrocarbons from industrial waste water", PhD Thesis. Katholieke Universiteit Leuven. Faculteit Landbouwkundige en Toegepaste Biologische wetenschappen(1994).

- Dong YQ, Zhang L, Shen JN, Song MY & Chen HL," Preparation of poly(vinyl alcohol)–sodium alginate hollow–fiber composite membranes and pervaporation dehydration characterization of aqueous alcohol mixtures", Desal 193: 202–210. (2006).
- Das S, Banthia AK & Adhikari B," Removal of chlorinated volatile organic contaminants from water by pervaporation using a novel polyurethane urea–poly (methyl methacrylate) interpenetrating network membrane", Chem Eng Sci 61: 6454–6467. (2006).
- Dobrak A., A. Figoli , S. Chovau , F. Galiano , S. Simone , I.F.J. Vankelecom , E. Drioli , B. Van der Bruggen," Performance of PDMS membranes in pervaporation: Effect of silicalite filler sand comparison with SBS membranes", Journal of Colloid and Interface Science 346 (2010) 254–264.

[E]

- Ehsan Saljoughi, Mohammad Amirilargani and Toraj Mohammadi, "Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes", Desalination, 262(2010)72-78

[F]

- Fleming H.L., C.S. Slater, Pervaporation, in: W.S. Ho, K.K. Sirkar (Eds.),Membrane Handbook, Kluwer Academic Publishers, New York, 1992, p. 103.
- Frank L, Stephan H, Po-Kiong Ten, Robert W.Field and Gunther L.,"Organophilic pervaporation: prospects and performance", Chemical Engineering journal 73(1999) 113-129.

- Feng X & Huang RYM," Liquid separation by membrane pervaporation". A review. Ind Eng Chem Res 36: 1048–1066 (1997).

[G]

- Ghosh U.K., Narayan C. Pradhan and Basudam Adhikari," pervaporation separation of furfural from aqueous solution using modified polyurethaneurea membrane", J. Desalination, 252(2010)1-7.
- Gao, L.; Beibei, T.; Peiyi, W. J Membr Sci 2009, 326, 168.

[H]

- Home, R.W., A physicist in the age of enlightenment-the Abbey Nollet, 1770-French-Torlais. J. Isis. , 1991. 82: 146-147.

- Heiner S., Lidietta G. and Enrico D, " An introduction to membrane science and technology", CNR-ITM, University of Calabria,(2006).

- Huang, R.Y.M.," Pervaporation membrane separation processes", Elsevier Science Publishing Company, Inc. New York. 1991, 1-46.
- Huang R.Y.M, V.J.C. Lin, Separation of mixtures by using polymer membranes. I. Permeation of binary organic liquid mixtures through polyethylene, J. Appl. Polym. Sci. 12 (1968) 2615–2631.
-Hung MY, Chen SH, Liou RM, Hsu CS & Lai J" Pervaporation separation of a water/ethanol mixture by a sodium sulfonate polysulfone membrane", J Appl Polym Sci 90: 3374–3383. (2003).

[J]

-Judd S & Jefferson B, “Membranes for industrial wastewater recovery and re–use”, Oxford, Elsevier, (2003).

- Jorgen Waner, “membrane filtration handbook”,2nd edition,osmonics, (2001).

- Jalil, S.B., " Development of Nanofiltration polyethersulfone hollow fiber membrane for cycloDextrin Glycosyltransferase (GGTase) separation". University technologi Malaysia, Johor: MEng. Thesis, (2004).

- Jinming Peng, Yanlei Su, Wenjuan Chen, Qing Shi, and Zhongyi Jiang,” Effects of Coagulation Bath Temperature on the Separation Performance and Antifouling Property of Poly(ether sulfone) Ultrafiltration Membranes” Ind. Eng. Chem. Res. 2010, 49, 4858–4864.

- Jae Shick Yang, Hyo Jin Kim, Won Ho Jo and Yong Soo Kang” Analysis of pervaporation of methanoI-MTBE mixtures through cellulose acetate and cellulose triacetate membranes”, Elsevier Science Ltd,1997

[K]

- Kisting, R.E., "Synthetic polymeric membranes".USA: McGrew-Hill, Inc., (1971).

- Koops GH, Nolten JAM, Mulder MHV & Smolders CA, “Poly(vinyl chloride) polyacrylonirile composite membranes for the dehydration of acetic acid”, J Membr Sci 81: 57–70, (1993).

- Koltuniewwicz AB & Drioli E.,” Membranes in Clean Technologies”, Weinheim, Wiley–Verlag GmbH & Co. KGaA,(2008).

- Kreiter R, Wolfs DP, Engelen CWR, van Veen HM & Vente JF," High–temperature pervaporation performance of ceramic–supported polyimide membranes in the dehydration of alcohols", J Membr Sci 319: 126–132. (2008).
- Konieczny K, Bodzek M & Panek D," Removal of volatile compounds from the wastewaters by use of pervaporation". Desalination 223: 344–348. (2008).
-Kanani DM, Nikhade BP, Balakrishnan P, Singh G, and Pangarkar VG., "Recovery of valuable tea aroma components from steam distillation condensate by pervaporation", Ind. Eng. Chem. Res. 2003;42(26):6924–6932.
- Kober P.A.," Pervaporation, perstillation and percrystallization", J. Am. Chem. Soc. 39 (1917) 944–948.

[L]

- Loeb, S. and Sourirajan, S.," Sea water demineralization by means of a semipermeable membranes", University of California, Report no 6060, 1961.

- Luo Y, Tan S, Wang H, Wu F, Liu X, Li L & Zhang Z, "PPMS composite membranes for the concentration of organics from aqueous solutions by pervaporation", Chem Eng J 137: 496–502. (2008).
- Liu F, Liu L & Feng X," Separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation", Sep Purif Technol 42: 273–282. (2005a)
- Liu F, Tong Z, Liu L & Feng X," Separation of organic compounds from water by pervaporation in the production of n-butyl acetate via esterification by reactive distillation", J Membr Sci 256: 193–201(2005b).
- Liang L., E. Ruckenstein," Pervaporation of ethanol-water mixtures throughpolydimethylsiloxane-polystyrene interpenetrating polymernetwork supported membranes", Journal of Membrane Science 114 (1996) 227-23.

- Lin Zhang, Huan-Lin Chen, Zu-Ren Pan," Study on Swelling Behavior and Pervaporation Properties of AA–MMA–BA Copolymers for Separation of Methanol/MTBE/C5 Mixtures", Journal of Applied Polymer Science, Vol. 87, 2267–2271 (2003).

- Lin L.G, Wang, H.M. Qu, J.R. Yang,Y.F. Wang, D.Q.Shi, Y.Kong, "pervaporation performance of crosslinked polyethylene glycol membrane for deep desulfurization of FCC gasoline, J. Membr.sci. 280(2006)615-658.

[M]

-Mulder MHV" Basic Principles of membrane technology", 2nd ed. Dordrecht, Kluwer Academics, (1998).

- Masakazu Yoshikawa, Takahiro Yoshioka, Junko Fujime and Akira Murakami, "Pervaporation separation of MeOH/MTBE through agarose membranes" Journal of Membrane Science 178 (2000) 75–78.

- Mbaye Niang and Guangsheng Luo," A triacetate cellulose membrane for the separation of methyl tert-butyl ether/methanol mixtures by pervaporation", Separation and Purification Technology 24 (2001) 427–435.

- Mehrnaz Peivasti, Ali Madandar, Toraj Mohammadi," Effect of operating conditions on pervaporation of methanol/methyl tert-butyl ether mixtures", Chemical Engineering and Processing 47 (2008) 1069–1074.

- Mohammadi T., E. Saljoughi, Effect of production conditions on morphology and permeability of asymmetric cellulose acetate membranes, Desalination 243 (2009) 1–7.

-- MADAENI S. S., R. POURGHORBANI and V. VATANPOUR, "Investigation of Parameters Affecting the Flux of Microfiltration Poly(vinylidenefluoride) Membranes for Particulate Removal", Vol. 00, No. 0, 1–12 (2011).- Mohammadi T., A. Aroujalian, A. Bakhshi, Chem. Eng. Sci. 60 (2005) 1875 -1880.

[N]

- Netke SA, Sawant SB, Joshi JB, and Pangarkar VG.," Comparative study of membranes for pervaporation of trace organics from aqueous solutions", In: Bowen WR, Field RW, and Howell JA, eds., Proceedings of the Euro-Membrane-95 Conference. Bath, UK, September 18–20, 1995; Europ. Soc. Memb. Sci. Technol. 1995;2:116–121.
- Nilufer Durmaz Hilmioglu and Sema Tulbentci," Pervaporation of MTBE/methanol mixtures through PVA membranes", Desalination 160 (2004) 263-270.
- Nunes S. P. and K.-V. Peinemann, "MembraneTechnologyin the Chemical Industry", Wiley-VCH Verlag GmbH,(2001)

[O]

- Ornthida sae-khow and somenath mitra. "pervaporation in chemical analysis", journal of chromatography A, 1217 (2010)2736-2746.

[P]

- Perry, R.H. and Green, D.W., "Perry's Chemical Engineering's Handbook". 7th edition. McGraw-hill. (1997).

- Pinnau I & Koros WJ (1991) Relationship between substructure resistance and gas separation properties of the defect–free integrally skinned asymmetric membranes. Ind Eng Chem Res 30: 1837–1840.

-Peters TA, Benes NE & Keurentje JTF," Hybrid ceramic–supported thin PVA pervaporation membranes: Long–term performance and thermal stability in the dehydration of alcohols", J Membr Sci 311: 7–11(2008).

- Panek D & Konieczny K," Preparation and applying the membranes with carbon black to pervaporation of toluene from the diluted aqueous solutions", Sep Purif Technol 57: 507–512. (2007).

-Pereira CC, Ribeiro Jr CP, Nobrega R & Borges CP," Pervaporative recovery of volatile aroma compounds from fruit juices", J Membr Sci 274: 1–23(2006).

- Peng M, Vane LM & Liu SX," Recent advances in VOCs removal from water by Pervaporation", J Hazard mater B98: 69–90(2003).

- Panek D & Konieczny K," Preparation and applying the membranes with carbon black to pervaporation of toluene from the diluted aqueous solutions", Sep Purif Technol 57: 507–512(2007).

- Payman Sobhanipour, Reza Cheraghi and Alex A. Volinsky" Thermoporometry study of coagulation bath temperature effect on polyacrylonitrile fibers morphology" Thermochimica Acta 518 (2011) 101–106.

- Peivasti, M.; Madandar, A.; Mohammadi, T., Chem. Eng. Process. Process. Intensif. 47, 1069 2008.

[Q]

-Qiao XY & Chung TS," Diamine modification of P84 polyimide membranes for pervaporation dehydration of isopropanol", AIChE J 52: 3462–3472. (2006)

[R]

-Ravanchi MT, Kaghazchi T & Kargari A)," Application of membrane separation processes in petrochemical industry: a review", Desalination 235: 199–244. (2009).

- Ray S & Ray SK," Separation of organic mixtures by pervaporation using crosslinked rubber membranes", J Membr Sci 270: 132–145. (2006a)
- Ray S & Ray SK," Synthesis of highly methanol selective membranes for separation of methyl tertiary butyl ether (MTBE)–methanol mixtures by pervaporation", J Membr Sci 278: 279–289. (2006b).
- Rajagopalan N., M. Cheryan, " pervaporation of grape juice aroma", J. Membr.sci. 104 (1995) 243-250.

[S]

- Somasundaran, P., "Ultrafiltration and nanofiltration, in Encyclopedia of surface and colliod science", Miami: CRC Press. pp. 6398-6401(2006).

- Sulzer Chemtech Ltd internet webpage www.sulzerchemtech.com (26.05.2009).

- Semenova SI, Ohya H & Soontarapa K," Hydrophilic membranes for pervaporation: an analytical review", Desalination 110: 251–288(1997).
- Shao P & Kumar A ,"Recovery of 2,3–butanediol from water by a solvent extraction and pervaporation separation scheme", J Membr Sci 329: 160–168. (2009).
-Srinivasan K, Palanivelu K & Gopalakrishnan AN," Recovery of 1–butanol from a model pharmaceutical aqueous waste by pervaporation", Chem Eng Sci 62 2905–2914. (2007).
- Samdani AR, Mandal S, and Pangarkar VG., "Role of and criterion for sorption selectivity in pervaporative removal of trace organics from aqueous solutions", Sep. Sci. Tech. 2003;38(5):1069–1092.
- Sang-Gyun Kim, Gyun-Taek Lim, Jonggeon Jegal and Kew-Ho Lee, "Pervaporation separation of MTBE (methyl tert-butyl ether) and methanol

mixtures through polyion complex composite membranes consisting of sodium alginate/chitosan", Journal of Membrane Science 174 (2000) 1–15.
- Saljoughi, E.; Amirilargani, M.;Mohammadi," Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes" ,T. Desalination 2010, 262, 72.
- Saljoughi E., M. Sadrzadeh, T. Mohammadi, "Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes", J. Mem. Sci. 326 (2009 a) 627–634.
- Saljoughi E., M. Amirilargani, T. Mohammadi, Effect of poly(vinyl pyrrolidone) concentration and coagulation bath temperature on the morphology, permeability and thermal stability of asymmetric cellulose acetate membranes, J. Appl. Polym. Sci. 111 (2009 b) 2537–2544.
- Sampranpiboon P., R. Jiraratananon, D. Uttapap, X. Feng, R.Y.M. Huang, J. Membr. Sci. 174 (2000) 55–65.
- Smitha B., D. Suhanya, S.Sridhar, M. Ramakrishna, J.Membr.sci. 241 92004)1.
- Shao P., R.Y.M. Huang, J. Membr. Sci. 287 (2007)162.

[T]

-Trifunovic O & Tragardh G," The influence of support layer on mass transport of homologous series of alcohols and esters through composite pervaporation membranes", J Membr Sci 259: 122–134(2005).

[V]

- veronica Garcia, “reclamation of vocs, n-butanol and dichloromethane, from sodium chloride containing mixtures by pervaporation”, Academic dissertation, University of Oulu,2009.
- Van de Witte, P., Dijkstra, P.J., Van de Berg, J.W.A. and Feijen, J. "Phase separation processes in polymer solutions in relation to membrane formation". J. Membr. Sci. 117: 1-31.(1996).

[W]

- Wu H, Fang X, Zhang X, Jiang Z, Li B & Ma X,” Cellulose acetate–poly(N–vinyl–2–pyrrolidone) blend membrane for pervaporation separation of methanol/MTBE mixtures”, Sep Purif Technol 64: 183–191. (2008).
- Wang Y, Yang L, Luo G & Dai Y,” Preparation of cellulose acetate membrane filled with metal oxide particles for the pervaporation separation of methanol/methyl tert–butyl ether mixtures”, Chem Eng J 146: 6–10. (2009b).
- Wei Zhang, Zhejun Yu, Qiufang Qian, Zhennan Zhang, Xinping Wang,” Improving the pervaporation performance of the glutaraldehyde crosslinked chitosan membrane by simultaneously changing its surface and bulk structure”, Journal of Membrane Science 348 (2010) 213–223

[X]

- Xiao S, Huang RYM & Feng X,” Preparation and properties of trimesoyl chloride crosslinked poly(vinyl alcohol) membranes for pervaporation dehydration of isopropanol”, J Membr Sci 286: 245–254. (2006).

-Xu, J.; Xu, Z.L., “Poly (vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC-additives-solvent”, J. Membr. Sci., 208: 203(2002).

- Xu, Z.L.; Qusay, Alsalhy,” Effect of polyethylene glycol (PEG) molecular weights and concentrations on polyethersulfone (PES) hollow fiber ultrafiltration membranes”, J. Appl. Polym. Sci., 91: 3398(2004).

- Xiaocong Ma, Changlai Hu, Ruili Guo, Xin Fang, Hong Wu, Zhongyi Jiang,” HZSM5-filled cellulose acetate membranes for pervaporation separation of methanol/MTBE mixtures”, Separation and Purification Technology 59 (2008) 34–42.

[y]

-Yeom CK, Kim HK & Rhim JW,” Removal of trace VOCs from water through PDMS membranes and analysis of their permeation behaviors”, J Appl Polym Sci 73: 601–611. (1999)

[Z]

- Zeman, L.J. and Zydney, A.L., "Microfiltration and ultrafiltration: Principles and Applications". New York: Marcel Dekker, INC. (1996).

- Zhao Q, Qian JW, An QF, Yang Q & Zhang P,” From A facile route for fabricating novel polyelectrolyte complex membrane with high pervaporation performance in isopropanol dehydration”, J Membr Sci 320: 8–12(2008).

- Zereshki S., A. Figoli, S. S. Madaeni , S. Simone , E.Drioli,” Pervaporation separation of MeOH/MTBE using poly(lactic acid) membranes”, Journal of Applied Polymer Science, APP-2009-11-3358.

- Zereshki S., A. Figoli, S.S.Madaeni, J.C.Jansen, M.Esmaailinezhad and E. Drioli,” poly(lactic acid)/ poly(vinyl pyrrolidone) blend membrane: effect of

membrane composition on pervaporation separation of ethanol/cyclohexane mixture", J.of mem. Sci.2010.

- Zereshkia S.,b, A. Figoli c, S.S. Madaenib, S. Simonec, M. Esmailinezhadb, E. Drioli c,d," Pervaporation separation of MeOH/MTBE mixtures with modified PEEK membrane: Effect of operating conditions", Journal of Membrane Science 371 (2011) 1–9.

[A]

- Abdulghader Elarbi, "Flux enhancement in a spiral wrap ultrafiltration element by using backpulsing" M.Sc. Thesis, University of Stellenbosch, (2009).
- Anil K. Pabby, Syed S. H. Rizvi andAna Maria Sastre, "Handbook of Membrane Separations" CRC Press Taylor & Francis Group, (2008).
- Afonso CMA & Crespo J," Green separation processes, fundamentals and Applications", Weinheim, Wiley–vch Verlag GmbH & Co. KGaA., (2005).
- Amirilargani M., E. Saljoughi, T. Mohammadi, and M.R. Moghbeli," Effects of Coagulation Bath Temperature and Polyvinylpyrrolidone Content on Flat Sheet Asymmetric Polyethersulfone Membranes" Wiley InterScience, 2010.

[B]

- Baker R. W. "Membrane Technology and Applications", 2nd Edition, John Wiley & Sons Ltd, West Sussex, 2004.
- Baker, R.W., Cussler, E.L., Eykamp, W., Koros, W.J., Riley, R.L. and Strathmann, H., "Membrane separation systems-recent developments and future directions", , New Jersey: William Andrew Inc., (1991)
- Bechhold, H., "Durchlassigkeit von ultrafiltration", Z. Phy. Che., 64: 328-342. 1908.
- Bruschke HEA," State–of–Art of Pervaporation Processes in the chemical industry", In: Nunes SP & Peinemann KV (eds) Membrane technology in the chemical industry. Weinheim, Wiley–vch Verlag GmbH: 127–172(2001).
- Brun JP, Larchet C, Bulvestre G & Auclair B," Sorption and pervaporation of dilute aqueous solutions of organic compounds through polymer membranes", J Membr Sci25: 55–100. (1985).

- Brown MA, Miller S & Emmert GL," On–line purge and trap gas chromatography for monitoring of trihalomethanes in drinking water distribution systems". Anal Chim Acta 592: 154–161(2007).
- Binning R.C., R.J. Lee, J.F. Jennings, E.C. Martin, "Separation of liquid mixtures by permeation", Ind. Eng. Chem. 53 45–50(1961).

[C]

- Coulson J. M. and Richardson J. F., "Chemical Engineering", Vol. 2, 5th Edition, Pergamon Press, Oxford, 2002.
- Chapman PD, Oliveira T, Livingston AG & Li K, "Membranes for the dehydration of solvents by Pervaporation", J Membr Sci 318: 5–37, (2008).
- Cabasso I., J. Jagur-Grodzinski, D. Vofsi, "Polymeric alloys of polyphosphonates and acetyl cellulose. I. Sorption and diffusion of benzene and cyclohexane", J. Appl. Polym. Sci. 18 2117–2136(1974).
- Cabasso I.," Organic Liquid Mixtures Separation by Selective Polymer Membranes", Ind. Eng. Chem. Prod. Res. Dev. 22, 313 (1983).

[D]

- Dotremont C," Pervaporation for the removal of chlorinated hydrocarbons from industrial waste water", PhD Thesis. Katholieke Universiteit Leuven. Faculteit Landbouwkundige en Toegepaste Biologische wetenschappen(1994).
- Dong YQ, Zhang L, Shen JN, Song MY & Chen HL," Preparation of poly(vinyl alcohol)–sodium alginate hollow–fiber composite membranes and pervaporation dehydration characterization of aqueous alcohol mixtures", Desal 193: 202–210. (2006).

- Das S, Banthia AK & Adhikari B," Removal of chlorinated volatile organic contaminants from water by pervaporation using a novel polyurethane urea–poly (methyl methacrylate) interpenetrating network membrane", Chem Eng Sci 61: 6454–6467. (2006).
- Dobrak A., A. Figoli , S. Chovau , F. Galiano , S. Simone , I.F.J. Vankelecom , E. Drioli , B. Van der Bruggen," Performance of PDMS membranes in pervaporation: Effect of silicalite filler sand comparison with SBS membranes", Journal of Colloid and Interface Science 346, 254–264(2010).

[E]

- Ehsan Saljoughi, Mohammad Amirilargani and Toraj Mohammadi, "Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes", Desalination, 26272-78(2010).

[F]

- Fleming H.L., C.S. Slater, Pervaporation, in: W.S. Ho, K.K. Sirkar (Eds.),Membrane Handbook, Kluwer Academic Publishers, New York, p. 103. 1992.
- Frank L, Stephan H, Po-Kiong Ten, Robert W.Field and Gunther L.,"Organophilic pervaporation: prospects and performance", Chemical Engineering journal 73113-129(1999).
- Feng X & Huang RYM," Liquid separation by membrane pervaporation". A review. Ind Eng Chem Res 36: 1048–1066 (1997).

[G]

- Gao, L.; Beibei, T.; Peiyi, W. J Membr Sci, 326, 1682009.
- Ghosh U.K., Narayan C. Pradhan and Basudam Adhikari," pervaporation separation of furfural from aqueous solution using modified polyurethaneurea membrane", J. Desalination, 252,1-7(2010).

[H]

- Huang, R.Y.M.," Pervaporation membrane separation processes", Elsevier Science Publishing Company, Inc. New York., 1-461991.
- Heiner S., Lidietta G. and Enrico D, " An introduction to membrane science and technology", CNR-ITM, University of Calabria,(2006).
- Home, R.W., A physicist in the age of enlightenment-the Abbey Nollet, 1770-French-Torlais. J. Isis. , 82: 146-147(1991).
- Hung MY, Chen SH, Liou RM, Hsu CS & Lai J" Pervaporation separation of a water/ethanol mixture by a sodium sulfonate polysulfone membrane", J Appl Polym Sci 90: 3374–3383. (2003).
- Huang R.Y.M., V.J.C. Lin, Separation of mixtures by using polymer membranes.I. Permeation of binary organic liquid mixtures through polyethylene, J. Appl. Polym. Sci. 12, 2615–2631(1968).

[J]

- Jae Shick Yang, Hyo Jin Kim, Won Ho Jo and Yong Soo Kang" Analysis of pervaporation of methanoI-MTBE mixtures through cellulose acetate and cellulose triacetate membranes", Elsevier Science Ltd,1997

- Jalil, S.B., " Development of Nanofiltration polyethersulfone hollow fiber membrane for cycloDextrin Glycosyltransferase (GGTase) separation". University technologi Malaysia, Johor: MEng. Thesis, (2004).
- Jinming Peng, Yanlei Su, Wenjuan Chen, Qing Shi, and Zhongyi Jiang," Effects of Coagulation Bath Temperature on the Separation Performance and Antifouling Property of Poly(ether sulfone) Ultrafiltration Membranes" Ind. Eng. Chem. Res., 49, 4858–4864,2010.
- Jorgen Waner, "membrane filtration handbook",2nd edition,osmonics, (2001).
- Judd S & Jefferson B, "Membranes for industrial wastewater recovery and re–use", Oxford, Elsevier, (2003).

[K]

- Kisting, R.E., "Synthetic polymeric membranes".USA: McGrew-Hill, Inc., (1971).
- Koops GH, Nolten JAM, Mulder MHV & Smolders CA, "Poly(vinyl chloride) polyacrylonirile composite membranes for the dehydration of acetic acid", J Membr Sci 81: 57–70, (1993).
- Koltuniewwicz AB & Drioli E.," Membranes in Clean Technologies", Weinheim, Wiley–Verlag GmbH & Co. KGaA,(2008).
- Kreiter R, Wolfs DP, Engelen CWR, van Veen HM & Vente JF," High–temperature pervaporation performance of ceramic–supported polyimide membranes in the dehydration of alcohols", J Membr Sci 319: 126–132. (2008).
- Konieczny K, Bodzek M & Panek D," Removal of volatile compounds from the wastewaters by use of pervaporation". Desalination 223: 344–348. (2008).

- Kanani DM, Nikhade BP, Balakrishnan P, Singh G, and Pangarkar VG., "Recovery of valuable tea aroma components from steam distillation condensate by pervaporation", Ind. Eng. Chem. Res.;42(26):6924–6932,2003.
- Kober P.A.," Pervaporation, perstillation and percrystallization", J. Am. Chem. Soc. 39, 944–948(1917).

[L]

- Loeb, S. and Sourirajan, S.," Sea water demineralization by means of a semipermeable membranes", University of California, Report no 6060, 1961.
- Luo Y, Tan S, Wang H, Wu F, Liu X, Li L & Zhang Z, "PPMS composite membranes for the concentration of organics from aqueous solutions by pervaporation", Chem Eng J 137: 496–502. (2008).
- Liu F, Liu L & Feng X," Separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation", Sep Purif Technol 42: 273–282. (2005a)
- Liu F, Tong Z, Liu L & Feng X," Separation of organic compounds from water by pervaporation in the production of n-butyl acetate via esterification by reactive distillation", J Membr Sci 256: 193–201(2005b).
- Liang L., E. Ruckenstein," Pervaporation of ethanol-water mixtures throughpolydimethylsiloxane-polystyrene interpenetrating polymernetwork supported membranes", Journal of Membrane Science 114, 227-23(1996).
- Lin Zhang, Huan-Lin Chen, Zu-Ren Pan," Study on Swelling Behavior and Pervaporation Properties of AA–MMA–BA Copolymers for Separation of Methanol/MTBE/C5 Mixtures", Journal of Applied Polymer Science, Vol. 87, 2267–2271 (2003).

- Lin L.G, Wang, H.M. Qu, J.R. Yang,Y.F. Wang, D.Q.Shi, Y.Kong, ”pervaporation performance of crosslinked polyethylene glycol membrane for deep desulfurization of FCC gasoline, J. Membr.sci. 280615-658. (2006).

[M]

- Masakazu Yoshikawa, Takahiro Yoshioka, Junko Fujime and Akira Murakami, ”Pervaporation separation of MeOH/MTBE through agarose membranes” Journal of Membrane Science 178 75–78(2000).
- Madaeni S. S., R. POURGHORBANI and V. VATANPOUR, “Investigation of Parameters Affecting the Flux of Microfiltration Poly(vinylidenefluoride) Membranes for Particulate Removal”, Vol. 00, No. 0, 1–12 (2011).
- Mbaye Niang and Guangsheng Luo,” A triacetate cellulose membrane for the separation of methyl tert-butyl ether/methanol mixtures by pervaporation”, Separation and Purification Technology 24 (2001) 427–435.
- Mehrnaz Peivasti, Ali Madandar, Toraj Mohammadi,” Effect of operating conditions on pervaporation of methanol/methyl tert-butyl ether mixtures”, Chemical Engineering and Processing 47, 1069–1074(2008).
- Mohammadi T., E. Saljoughi, Effect of production conditions on morphology and permeability of asymmetric cellulose acetate membranes, Desalination 243, 1–7(2009).
- Mulder MHV” Basic Principles of membrane technology”, 2nd ed. Dordrecht, Kluwer Academics, (1998).
- M.Peng, L.M Vane, S.X. Liu, J. Hazard. Mater. 98-69(2003).
- Mohammadi T., A. Aroujalian, A. Bakhshi, Chem. Eng. Sci. 60, 1875 - 1880(2005).

[N]

- Netke SA, Sawant SB, Joshi JB, and Pangarkar VG.," Comparative study of membranes for pervaporation of trace organics from aqueous solutions", In: Bowen WR, Field RW, and Howell JA, eds., Proceedings of the Euro-Membrane-95 Conference. Bath, UK, September 18–20, 1995; Europ. Soc. Memb. Sci. Technol. 1995;2:116–121.
- Nilufer Durmaz Hilmioglu and Sema Tulbentci," Pervaporation of MTBE/methanol mixtures through PVA membranes", Desalination 160 (2004) 263-270.
- Nunes S. P. and K.-V. Peinemann, "MembraneTechnologyin the Chemical Industry", Wiley-VCH Verlag GmbH,(2001)

[O]

- Ornthida sae-khow and somenath mitra. "pervaporation in chemical analysis", journal of chromatography A, 1217, 2736-2746(2010).

[P]

- Panek D & Konieczny K," Preparation and applying the membranes with carbon black to pervaporation of toluene from the diluted aqueous solutions", Sep Purif Technol 57: 507–512. (2007).
- Payman Sobhanipour, Reza Cheraghi and Alex A. Volinsky" Thermoporometry study of coagulation bath temperature effect on polyacrylonitrile fibers morphology" Thermochimica Acta 518, 101–106(2011).
- Perry, R.H. and Green, D.W., "Perry's Chemical Engineering's Handbook". 7th edition. McGraw-hill. (1997).

- Peters TA, Benes NE & Keurentje JTF," Hybrid ceramic–supported thin PVA pervaporation membranes: Long–term performance and thermal stability in the dehydration of alcohols", J Membr Sci 311: 7–11(2008).
- Pinnau I & Koros WJ Relationship between substructure resistance and gas separation properties of the defect–free integrally skinned asymmetric membranes. Ind Eng Chem Res 30: 1837–1840(1991).
- Pereira CC, Ribeiro Jr CP, Nobrega R & Borges CP," Pervaporative recovery of volatile aroma compounds from fruit juices", J Membr Sci 274: 1–23(2006).
- Peng M, Vane LM & Liu SX," Recent advances in VOCs removal from water by Pervaporation", J Hazard mater B98: 69–90(2003).
- Peivasti, M.; Madandar, A.; Mohammadi, T., Chem. Eng. Process. Process. Intensif. 47, 1069 2008.
- Peng M, Vane LM & Liu SX," Recent advances in VOCs removal from water by Pervaporation", J Hazard mater B98: 69–90(2003).

[Q]

- Qiao XY & Chung TS," Diamine modification of P84 polyimide membranes for pervaporation dehydration of isopropanol", AIChE J 52: 3462–3472. (2006).

[R]

- Ravanchi MT, Kaghazchi T & Kargari A)," Application of membrane separation processes in petrochemical industry: a review", Desalination 235: 199–244. (2009).
- Ray S & Ray SK," Separation of organic mixtures by pervaporation using crosslinked rubber membranes", J Membr Sci 270: 132–145. (2006a)

- Ray S & Ray SK," Synthesis of highly methanol selective membranes for separation of methyl tertiary butyl ether (MTBE)–methanol mixtures by pervaporation", J Membr Sci 278: 279–289. (2006b).
- Rajagopalan N., M. Cheryan, " pervaporation of grape juice aroma", J. Membr.sci. 104 (1995) 243-250.

[S]

- Sang-Gyun Kim, Gyun-Taek Lim, Jonggeon Jegal and Kew-Ho Lee, "Pervaporation separation of MTBE (methyl tert-butyl ether) and methanol mixtures through polyion complex composite membranes consisting of sodium alginate/chitosan", Journal of Membrane Science 174 (2000) 1–15.
- Somasundaran, P., "Ultrafiltration and nanofiltration, in Encyclopedia of surface and colliod science", Miami: CRC Press. pp. 6398-6401(2006).
- Sulzer Chemtech Ltd internet webpage www.sulzerchemtech.com (26.05.2009).
- Semenova SI, Ohya H & Soontarapa K," Hydrophilic membranes for pervaporation: an analytical review", Desalination 110: 251–288(1997).
- Shao P & Kumar A ,"Recovery of 2,3–butanediol from water by a solvent extraction and pervaporation separation scheme", J Membr Sci 329: 160–168. (2009).
- Srinivasan K, Palanivelu K & Gopalakrishnan AN," Recovery of 1–butanol from a model pharmaceutical aqueous waste by pervaporation", Chem Eng Sci 62 2905–2914. (2007).
- Samdani AR, Mandal S, and Pangarkar VG., "Role of and criterion for sorption selectivity in pervaporative removal of trace organics from aqueous solutions", Sep. Sci. Tech. 2003;38(5):1069–1092.

- Saljoughi, E.; Amirilargani, M.;Mohammadi," Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes" ,T. Desalination 2010, 262, 72.
- Saljoughi E., M. Sadrzadeh, T. Mohammadi, "Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes", J. Mem. Sci. 326 (2009 a) 627–634.
- Saljoughi E., M. Amirilargani, T. Mohammadi, Effect of poly(vinyl pyrrolidone) concentration and coagulation bath temperature on the morphology, permeability and thermal stability of asymmetric cellulose acetate membranes, J. Appl. Polym. Sci. 111 (2009 b) 2537–2544.
- Sampranpiboon P., R. Jiraratananon, D. Uttapap, X. Feng, R.Y.M. Huang, J.Membr. Sci. 174 (2000) 55–65.
- Smitha B., D. Suhanya, S.Sridhar, M. Ramakrishna, J.Membr.sci. 241 92004)1.
- Shao P., R.Y.M. Huang, J. Membr. Sci. 287 (2007)162.

[T]

- Trifunovic O & Tragardh G," The influence of support layer on mass transport of homologous series of alcohols and esters through composite pervaporation membranes", J Membr Sci 259: 122–134(2005).

[V]

- Van de Witte, P., Dijkstra, P.J., Van de Berg, J.W.A. and Feijen, J. "Phase separation processes in polymer solutions in relation to membrane formation". J. Membr. Sci. 117: 1-31.(1996).
- Veronica Garcia, “reclamation of vocs, n-butanol and dichloromethane, from sodium chloride containing mixtures by pervaporation”, Academic dissertation, University of Oulu,2009.

[X]

- Xiao S, Huang RYM & Feng X,” Preparation and properties of trimesoyl chloride crosslinked poly(vinyl alcohol) membranes for pervaporation dehydration of isopropanol”, J Membr Sci 286: 245–254. (2006).
- Xu, J.; Xu, Z.L., “Poly (vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC-additives-solvent”, J. Membr. Sci., 208: 203(2002).
- Xu, Z.L.; Qusay, Alsalhy,” Effect of polyethylene glycol (PEG) molecular weights and concentrations on polyethersulfone (PES) hollow fiber ultrafiltration membranes”, J. Appl. Polym. Sci., 91: 3398(2004).
- Xiaocong Ma, Changlai Hu, Ruili Guo, Xin Fang, Hong Wu, Zhongyi Jiang,” HZSM5-filled cellulose acetate membranes for pervaporation separation of methanol/MTBE mixtures”, Separation and Purification Technology 59 (2008) 34–42.

[W]

- Wang Y, Yang L, Luo G & Dai Y,” Preparation of cellulose acetate membrane filled with metal oxide particles for the pervaporation separation of methanol/methyl tert–butyl ether mixtures”, Chem Eng J 146: 6–10. (2009b).

- Wei Zhang, Zhejun Yu, Qiufang Qian, Zhennan Zhang, Xinping Wang," Improving the pervaporation performance of the glutaraldehyde crosslinked chitosan membrane by simultaneously changing its surface and bulk structure", Journal of Membrane Science 348 (2010) 213–223
- Wu H, Fang X, Zhang X, Jiang Z, Li B & Ma X," Cellulose acetate–poly(N–vinyl–2–pyrrolidone) blend membrane for pervaporation separation of methanol/MTBE mixtures", Sep Purif Technol 64: 183–191. (2008).

[y]

- Yeom CK, Kim HK & Rhim JW," Removal of trace VOCs from water through PDMS membranes and analysis of their permeation behaviors", J Appl Polym Sci 73: 601–611. (1999).

[Z]

- Zeman, L.J. and Zydney, A.L., "Microfiltration and ultrafiltration: Principles and Applications". New York: Marcel Dekker, INC. (1996).
- Zhao Q, Qian JW, An QF, Yang Q & Zhang P," From A facile route for fabricating novel polyelectrolyte complex membrane with high pervaporation performance in isopropanol dehydration", J Membr Sci 320: 8–12(2008).
- Zereshki S., A. Figoli, S. S. Madaeni , S. Simone , E.Drioli," Pervaporation separation of MeOH/MTBE using poly(lactic acid) membranes", Journal of Applied Polymer Science, APP-2009-11-3358.
- Zereshki S., A. Figoli, S.S.Madaeni, J.C.Jansen, M.Esmaailinezhad and E. Drioli," poly(lactic acid)/ poly(vinyl pyrrolidone) blend membrane: effect of membrane composition on pervaporation separation of ethanol/cyclohexane mixture", J.of mem. Sci.2010.

- Zereshkia S.,b, A. Figoli c, S.S. Madaenib, S. Simonec, M. Esmailinezhadb, E. Drioli c,d," Pervaporation separation of MeOH/MTBE mixtures with modified PEEK membrane: Effect of operating conditions", Journal of Membrane Science 371 1–9(2011).

Appendix A

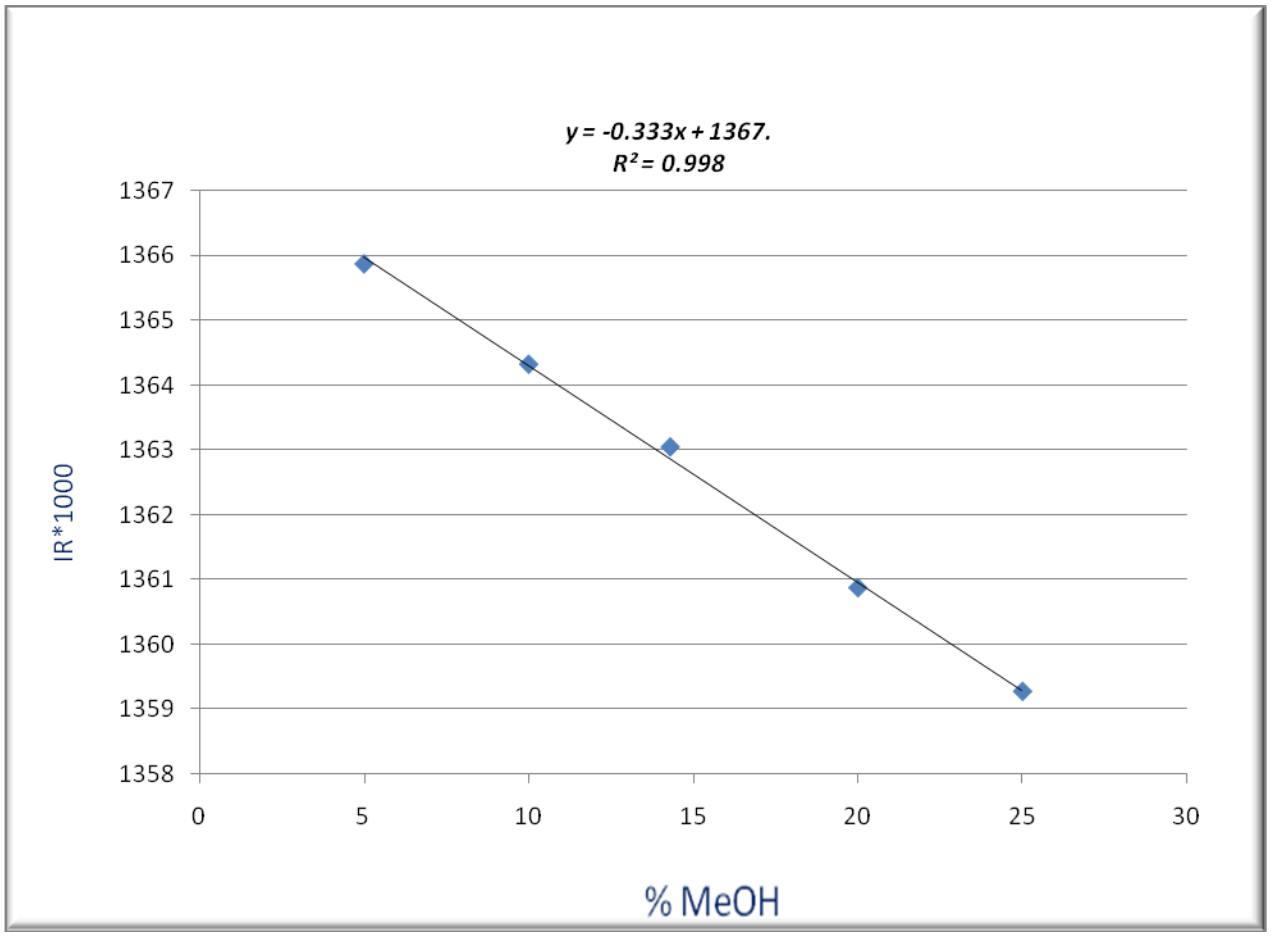

Figure (A.1) Calibration curve between MEOH concentration and refractometer index

Table (A.1) The concentration of methanol and refractometer index

% metanolo	5	10	14.3	20	25
IR* 1000	1365.875	1364.325	1363.05	1360.875	1359.275

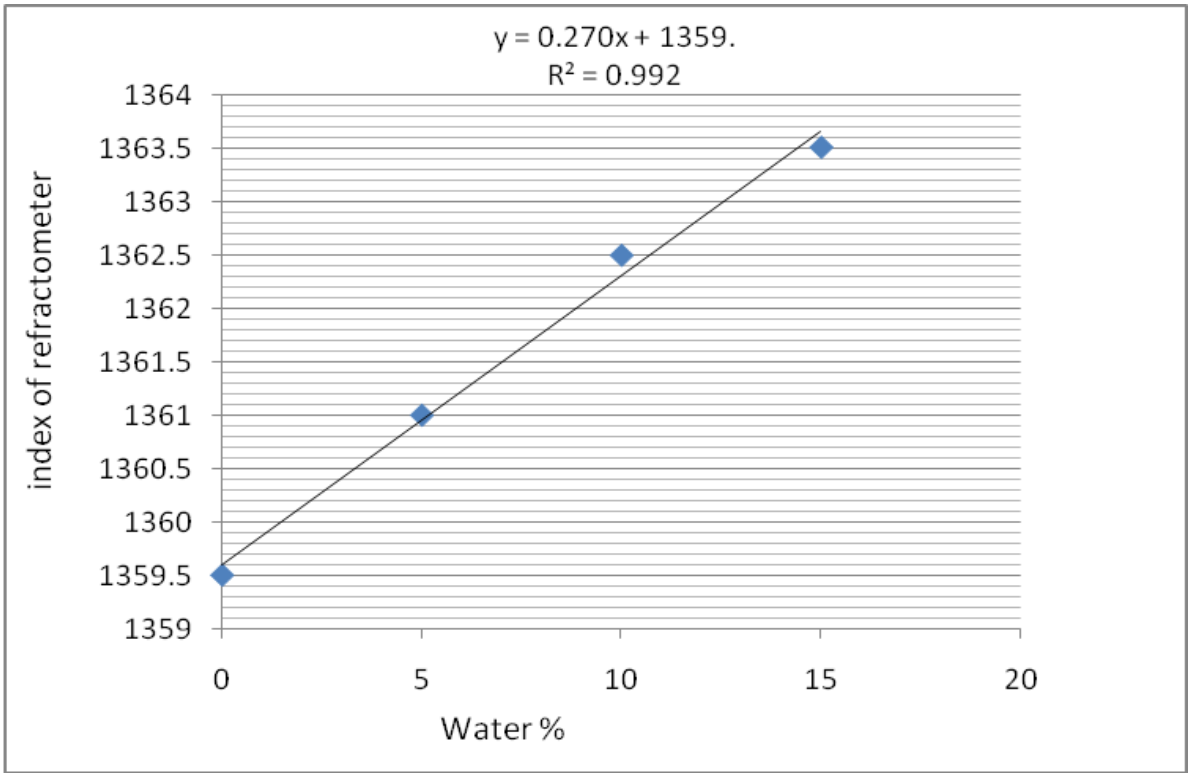

Figure (A.2) Calibration curve between water concentration and refractometer index

Table (A.2) The concentration of water and refractometer index

% watwe	0	5	10	15
IR* 1000	1359.5	1361	1362.5	1363.513

Appendix B

Table (B.1) Results of the characterization of the membrane with different of CBT.

membrane	*Temperature of CB*	*Thickness of the membrane*	*Contact angle*	*Young's modulus (N/mm²)*	*Max stress (N/mm²)*	*Elongation at Break(%)*
MC1	*20°c*	*0.198*	*71.2*	*144.89*	*3.5*	*23.05*
MC3	*40°c*	*0.189*	*75.6*	*144.07*	*3.95*	*5.47*
MC4	*60°c*	*0.183*	*80.6*	*160.07*	*4.08*	*3.83*
MC5	*80°c*	*0.144*	*72.3*	*296.56*	*8.78*	*4.97*

Table (B.2) Results of the characterization of the membrane with different of evaporation time.

membrane	Evaporation time	Thickness of the membrane	Contact angle	Young's modulus (N/mm^2)	Max stress (N/mm^2)	Elongation at Break(%)
ME1	30 sec	0.174	64.5	133.87	2.94	2.44
ME2	1 min	0.157	74.8	175.71	3.74	2.52
ME3	3 min	0.117	77.3	318.63	4.3	3.1
ME4	5 min	0.048	68.3	557.73	27.9	10.53
ME5	7 min	0.042	69.8	910	34.46	11.1

Table (B.3) Results of the pervaporation application on ME5 membrane

TEMP.(°C)	PRESS.(mbar)	FLUX(kg/m².hr)	partial flax of methanol(kg/m².hr)	partial flux of MTBE(kg/m².hr)	SELEC.
20	6	0.063	0.04	0.0225	10.29
20	27	0.0529	0.0428	0.01	24.145
20	50	0.0388	0.0325	0.0062	29.75
30	6	0.119	0.0964	0.0226	20.09
30	27	0.1	0.0844	0.016	29.75
30	50	0.0873	0.0785	0.0087	51
35	6	0.208	0.171	0.036	26.7
35	27	0.112	0.094	0.018	29.75
35	50	0.088	0.082	0.018	75.28

Table (B.4) Results of the pervaporation application on composite membrane

TEMP.(°C)	PRESS.(mbar)	FLUX(kg/m².hr)	partial flax of water(kg/m².hr)	partial flux of ethanol(kg/m².hr)	SELEC.
30	1.8	4.717908394	0.669942992	4.047965402	3.14452
30	25	3.538431295	0.566149007	2.972282288	3.61904
30	40	0.908197366	0.16211323	0.745993316	4.12892
40	1.8	5.779437783	0.820680165	4.958757617	3.674
40	25	4.049538038	0.647926086	3.401611952	3.61904
40	40	1.285630037	0.244269707	1.04136033	4.45679
50	1.8	7.076862591	0.884607824	6.192254767	3.921
50	25	5.748771378	1.129058699	4.619137802	4.64418
50	40	1.546425529	0.386606382	1.159819147	6.33333

الخلاصة

الأغشية الورقية حضرت بطريقة انعكاس الطور. المحلول البوليمري حضر من 15% من مادة البولي لكتك أسد وهو من البوليمرات الطبيعية والذي يتم إذابته بواسطة المذيب اثيل لكتيت. الغير مذيب هنا هو الماء ويستخدم كحمام مائي.

الدراسة تبين تأثير مختلف درجات الحرارة للحمام المائي (20, 40, 60 و 80 درجة مئوية) وكذلك مختلف وقت التبخير (0.5, 1, 3, 5 و 7 دقيقه) على تركيب المقطع العرضي للألياف المصنعة وسمك هذه الألياف و زراية التماس وكذلك الخواص الميكانيكية وإيجاد غشاء مناسب لعملية (pervaporation). المقطع العرضي والسطوح للأغشية المحضرة درست باستخدام الماسح الالكتروني الميكروسكوبي (SEM), والسمك درس باستخدام مقياس الأبعاد الرقمي وزاوية التماس تم قياسها بواسطة جهاز ضوئي اسمه (نورتيست) بينما الخواص الميكانيكية بواسطة آلة فحص المواد والمسماة زويك\روول.

نجحنا باستخدام الغشاء (ME5) عند 7 دقيقه كوقت لتبخر المذيب لفصل الميثانول والمثيل تترابيتويل ايثر عند نقطة الازونتروبك بواسطة عملية (pervaporation). حيث عند زيادة درجة حرارة المحلول الداخل يتسبب بزيادة كلا من التدفق الكلي والتدفق الجزئي للميثانول ومادة المثيل تترا بيتويل اثير. والذي يمكن تفسير هذه الظاهرة بواسطة تحسين قوة الدفع ومعامل الانتشار عند درجات الحرارة العالية. وكذلك الاختيارية أيضا تزداد نتيجة نقصان انجماد الحجوم الحرة ألمشكله أثناء خطوة التحضير بسبب نسبية الخواص المحدده للطبقة المتصلبة لغشاء البولي لكتك أسد . بالاظافة, بزيادة الضغط ألنفوذي يقل التدفق الكلي والجزئي بينما الانتقائية تزداد.

الغشاء المركب من المادتين (بولي لكتك أسد\وبولي فينول الكحول) درس لفصل الماء\ايثانول بواسطة ال pervaporation حيث بزيادة درجة حرارة المواد الداخلة تسبب زيادة التدفق الكلي والجزئي. ويمكن أن تفسر هذه الظاهرة بواسطة تحسين قوة الدفع ومعامل الانتشار عند درجات الحرارة العالية. والانتقائية أيضا تزداد وذلك لان درجات الحرارة تقلل الاصره الهايدروجينيه بين الماء والايثانول. بالاظافة, بزيادة ضغط النفوذي يقل التدفق الكلي والجزئي بينما الانتقائية تزداد.

وزارة التعليم العالي و البحث العلمي
الجامعة التكنولوجية
قسم الهندسة الكيمياوية

تحضير وتقيم اداء الاغشية البوليمريه (PLA) لعمليات البيرفابوريشن

رسالة مقدمة الى
قسم الهندسة الكيمياوية في الجامعة التكنولوجية كجزء من متطلبات نيل درجة الماجستير في
علوم الهندسة الكيمياوية / الوحدات الصناعية

من قبل

عبد الستار هاشم غانم

(بكالوريوس علوم في الهندسة كيمياوية 2006)

بآشراف

ا. م. د. قصي فاضل الصالحي

2012