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Efficacy of Phase Inversion Technique for Polymeric Membrane Fabrication

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Abstract

An essential contribution to sustainable industrial growth is the process intensification strategy that aims to improve manufacturing by reducing energy consumption and waste production through safer and flexible equipment. Membrane technology satisfies all the process intensification requirements. Polymeric membranes are used in different separation processes at an industrial scale due to their exciting separation property, low cost, and easy manufacturing. These membranes are prepared using different methods as phase inversion, controlled stretching, melt extrusion, or electrospinning depending on the preferred membrane morphology. Phase inversion is the most used process for membrane fabrication as it permits to fabrication a wide range of membrane morphologies from dense to porous. Here we review the techniques base on the phase inversion process and their performances in fabricating polymeric membranes. The key factors that influence membrane morphology have also been discussed.

Keywords: phase change materials, chilling, thermal energy storage, oils, esters, glycerol.

Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

1.Introduction

Satisfying the current growing demand for raw materials, products, and energy within the restrictions imposed by sustainable development is particularly complex. In this perspective, one of the most challenging tasks for the industries is to increase productivity through intensification of processes. Process intensification (P.I.) consists of innovative techniques, more flexible and safe devices, and reduced energy requirements and waste production [1]. Membrane technology meets the requirements of P.I. for its low-energy consumption, mild operating conditions, good integration with conventional processes and easy scale-up. Membrane processes are applied in different sectors, from chemical to electronic technologies, including new water production, energy generation, tissue engineering and several separation processes, including nanofiltration and electrodialysis [2].

In the membrane processes utilized in wastewater treatment, the driving force is a pressure difference between the feed and the permeate side [3]. These processes are microfiltration (M.F.), ultrafiltration (U.F.), nanofiltration (N.F.) and reverse osmosis (R.O.), where the membranes present different pore sizes and so, are capable to separate different components ranging from suspended particles (M.F.) to monovalent ions (R.O.). The membrane-mediated M.F., U.F., NF and R.O. processes are schematically illustrated in Figure 1. Characteristics of the membranes used in these processes are presented in Table 1.
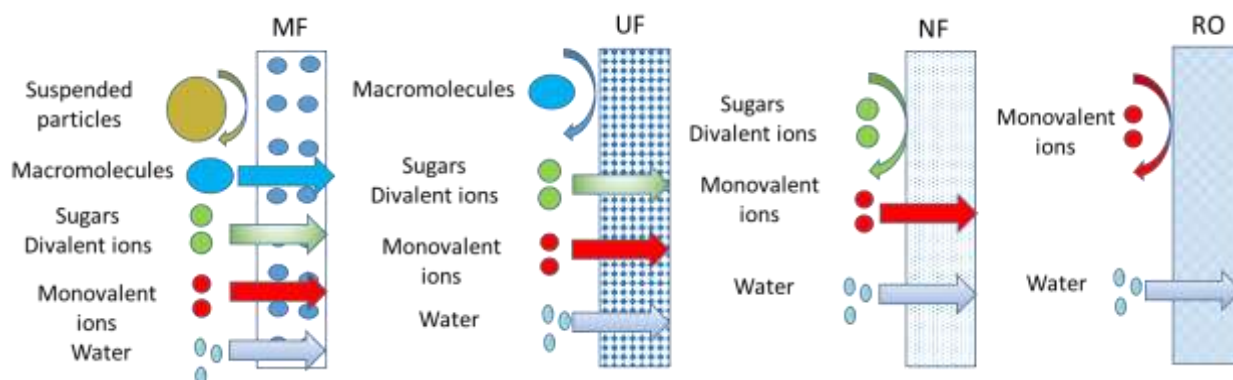

Figure 1. Schematic representation of the pressure drive membrane processes.

Table. 1. Characteristics of the membranes used in pressure-driven membrane processes. Adapted from refs [3] and [4].

	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Pore-size, (μm)	10-0.1	0.1-0.01	0.01–0.001	<1 nm
Pressure, (bar)	1-4	1-8	5-30	20-65
Separation mechanism	Sieving	Sieving	Sieving Charge Repulsion	Solution Diffusion

Membranes are categorized into two broad classes: polymeric and inorganic. The first ones are used at the industrial level in different separation processes considering their exciting properties and easy manufacturing [5, 6]. The polymers used for the preparation of M.F., U.F., NF, and reverse osmosis membranes are mainly polyethersulfone (P.E.S.), polysulfone (P.S.), cellulose acetate (C.A.), polyacrylonitrile

(P.A.N.), polyvinylidene fluoride (PVDF), and polyamides (P.A.) owing to their high chemical, thermal and mechanical resistance [7]. However, this field's critical problem is the fouling that causes a decrease in membrane performance due to the accumulation of organic and inorganic materials on the surface and in the membranes' pores [8]. Another drawback is the trade-off between permeability and selectivity. Highly permeable membranes are usually less selective and viceversa [9]. Exciting alternatives to the polymeric membranes are the inorganic ones due to their high chemical and thermal stability, even though their application at an industrial scale is restricted due to high cost [10].

Polymeric membranes have been prepared by different methods such as phase inversion, controlled stretching, interfacial polymerization, melt extrusion or electrospinning, depending on the preferred membrane morphology [11, 12]. Among these methods, phase inversion is commonly used for preparing dense and porous membranes with symmetric and asymmetric structures [7].

In this mini-review, porous polymeric membranes' preparation using techniques based on the phase inversion process has been described. In particular, three techniques are introduced: nonsolvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), and vapor-induced phase separation (V.I.P.S.). The critical factors of each technique that influence membrane morphology have been discussed.

Polymeric membranes by the phase inversion process

Polymeric membranes are widely used in different processes such as water desalination, gas separations, electrodialysis, and dialysis [13]. There are two types of polymeric membranes: rubbery and glassy. The first ones are characterized by very high mobility of the polymeric chains as their glass transition temperatures (Tg) remain below room temperature. Hence, they possess high free volume at room temperature (see Figure 2) [14, 15]. For this reason, membranes prepared by using rubbery materials present high permeability and low selectivity. Usually, rubbery polymers used in membrane preparation for gas separation processes are polydimethylsiloxane (PDMS), polyether block amide (P.E.B.A.X.; it consists of two monomers polyethylene oxide and polyamide) and polyvinyl alcohol (P.V.A.). In these materials, the permeation rate is controlled by the solubility, which is mainly determined by the ease of condensation of gas species (e.g., CO_2 is more condensable than He or H_2) [5, 16]. In comparison between PDMS and P.E.B.A.X. membranes, the last ones exhibit higher selectivities for the gas pairs CO_2/N_2 and CO_2/CH_4 due to the strong interaction of carbon dioxide the polyethylene oxide present in P.E.B.A.X. [16]. P.V.A. is also used to prepare CO_2-selective membranes and improve gas separation performance by blending the P.V.A. with amino carriers of carbon dioxide [17, 18].

Glassy polymers have very rigid structures since their Tg is above room temperature (see Figure 2) [15]. So, the polymeric chains act as obstacles to the gas molecules, and the glassy polymers have low permeability and high selectivity [19].
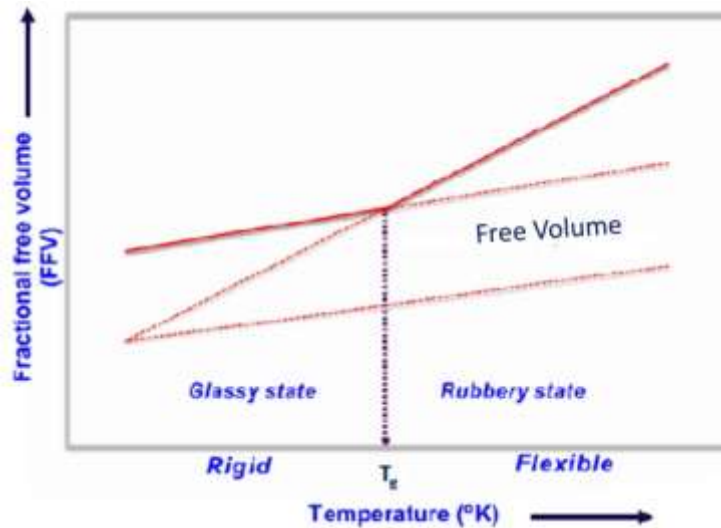
Figure 2. Free volume change for rubbery and glassy polymers. Adapted from ref. [15].

The glassy polymers essentially used to prepare commercial membranes are cellulose acetate, polysulfone, polyimide, polyamide, and poly(ether sulfone) [20]. The characteristics of some of these glassy polymers used for water treatment and gas separation processes are presented in Table 2.

Table 2. Characteristics of commercial polymeric of N.F. and R.O. membranes.

Membrane	Manufacturer	Top layer material	pH range	Rejection, %	Ref.
NANOFILTRATION					
NF70	Dow Filmtech	Aromatic crosslinked polyamide	3-9	95 %$MgSO_4$	[21]
NF90	Dow Filmtech	polyamide	3-10	85%–95% NaCl >97% $CaCl_2$	
NTR-729HF	Hydranautics	Poly(vinyl)alcohol/ polyamide	2-12	70% NaCl	
NP030	Microdyn Nadire	Polyethersulfone	1-14	80%–95% Na_2SO_4	
DK25040	Filtration Engineering	Polyamide	2.3–11	30% CaCl2	
AFC80 PCI	Membrane System	Polyamide	1.5–10.5	80% NaCl	
NP010	Microdyn Nadire	Polyethersulfone	1-14	25%–40% Na2SO4	[22]
NP030	Microdyn Nadire	Polyethersulfone	1-14	80%–95% Na2SO4	
Reverse Osmosis					
AG4040C	GE-Osmonics	-	4-11	99.0% NaCl	[21]
4040-HR	Koch	Polyamide	4-11	99.2% NaCl	
8040-SW-400-34	Koch	Polyamide	4-11	99.5% NaCl	
SW30HR-380	Dow Filmtec	-	2-11	99.7% NaCl	[23]
SC5100B	Toray	Cellulose Acetate	5.5-6.0	98.0 % NaCl	[24]
GAS SEPARATION					
Module Type	Manufacturer	Material	Separation		
Hollow fiber	Permea (Air Products)	Polysulfone	Air separation (O_2/N_2)		[25, 26]
-	Air Liquid	Polyimide Polyamide	Hydrogen purification (H_2/CO)		
-	Cynara (Natco)	Cellulose Acetate	Acid gas treating (CO_2/CH_4)		
-	Separex (U.O.P.)	Cellulose Acetate	Acid gas treating (CO_2/CH_4)		

As has been stated earlier, polymeric membranes have been prepared by a variety of methods such as phase inversion, interfacial polymerization, melt extrusion, and electrospinning [11, 12]; out of which phase inversion is the most popular one for preparing asymmetric and symmetric structures, with the possibility of controlling thickness, porosity and pore size [27]. A thermodynamically stable polymeric solution prepared through a demixing process, is transformed from liquid to solid state controlled [27, 28]. According to desolvation mechanisms, the phase inversion techniques applied for the membrane production are nonsolvent induced phase separation (NIPS), thermally induced phase separation (TIPS), and vapor induced phase separation (V.I.P.S.).

In the immersion precipitation or nonsolvent induced phase separation (NIPS) process, a stable polymeric solution is cast on a support to form a thin film. Subsequently, the support is immersed in a coagulation bath containing a nonsolvent (usually water) for inducing the polymer precipitation through solvent and nonsolvent exchange [29, 30]. The success of membrane preparation in the NIPS process depends on different factors: choice of a solvent nonsolvent system (completely miscible), the concentration of the polymer solution, coagulation bath composition, and film casting conditions [31]. The thermodynamic behavior of polymeric solution during the immersion-precipitation process is shown in Figure 3. Initially, the solution is located in a stable region (A). By immersing the solution (cast on support) in the nonsolvent, immediately starts the liquid-liquid demixing and the polymeric solution reaches the metastable region (binodal region) (see Fig. 3a) [32]. The point t indicates the composition at the top of the film. This process is speedy (instantaneous demixing), and the membrane shows a finger-like structure with a thin skin layer. When the demixing is delayed, all film positions are in regions thermodynamically stable, and the demixing starts when more nonsolvent diffuses into the film. When this happens, the line crosses the binodal curve (see Fig. 3b) [32]. In this case, the membranes show a sponge-like structure with a dense top layer.
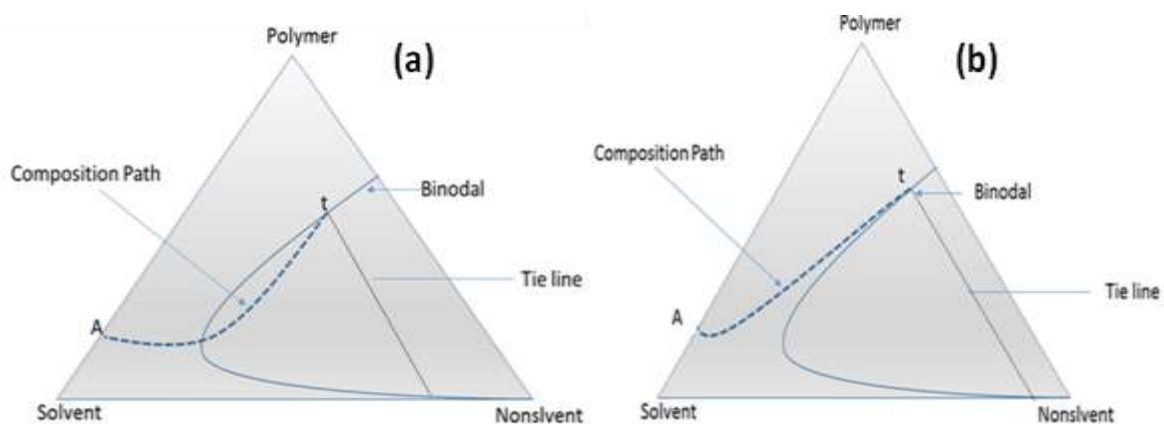

Figure 3. Composition paths of the casted film after immersion in the nonsolvent: Instantaneous demixing and (b) Delayed demixing.

The addition of a small amount of solvent in the coagulation bath permits forming a dense membrane because of a decrease in the mass exchange rate between solvent and nonsolvent, causing a delayed demixing [33]. Another essential aspect of being considered is the miscibility of the solvent and nonsolvent. High miscibility of solvent and

nonsolvent produces a highly porous membrane. A reduced affinity between the solvent and nonsolvent causes delayed demixing, so an asymmetric membrane with a dense top layer is obtained [14]. The casting solution's temperature also influences the membrane's morphology due to its influence on solution viscosity.

As a consequence, it affects the solvent nonsolvent exchange rate during phase inversion [34]. The presence of an additive in the polymeric solution also affects the membrane morphology significantly [35]. It can accelerate or suppress pore formation. Cao et al. prepared PVDF membranes by NIPS and evaluated the effects of 1,2-propylene glycol (used as additive) and polymer concentration on the membrane structure [36]. The water flux increased with the additive content in the polymeric solution. It is well known that the additives influence the morphology of the membranes, interconnectivity of the pores and membrane hydrophilicity [37].

Mixed matrix membranes were synthesized by NIPS using PVDF as polymer and lithium chloride (LiCl) as a pore-forming agent [38]. Different studies evidenced that LiCl improves membranes' water permeability by reducing their mean pore size and increasing porosity [39, 40]. In Figure 4, a comparison between the cross-sections of the pristine and mixed matrix membranes is shown. The mixed matrix membranes were symmetric and porous. The bottom side of the images displayed a spherulitic structure, and the top side a smooth layer.
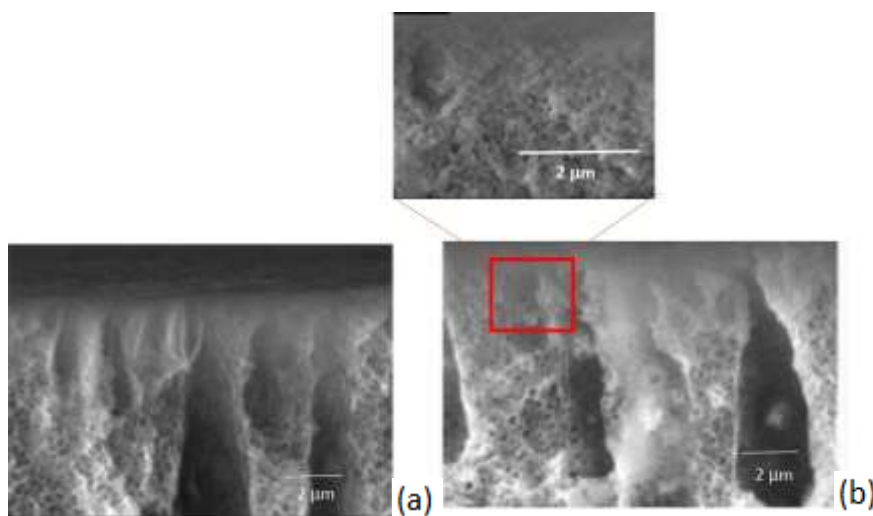

Figure 4. Membrane cross section of a) PVDF membrane, and b) MMM (22 wt.% of M.F.I. zeolite). Adapted from ref. [38].

Recently, PSf/C.A. membranes were prepared by NIPS and the effect of two additives on the membrane morphology was studied [41]. The additives used were the polyvinylpirrolidone (PVP) (a pore-forming agent) and the Pluronic F127 (PLU), a non-ionic surfactant. The membranes prepared with 3 wt. % of PVP exhibited macro-voids along the section. On the other hand, membranes prepared with 3 wt. % of PLU exhibited a finger-like structure.

When simple solvent evaporation causes the precipitation, the technique is called dry phase inversion technique [42] and the membrane presents a dense structure. When a solvent evaporation step is executed before phase inversion, the process is called dry-

wet phase inversion [43]. In this case, an initial evaporation step determines a skin layer's formation with a local increase of the polymer concentration. When the casted film is immersed in a coagulation bath, the skin layer acts as a barrier to solvent and nonsolvent diffusion, causing a delay in demixing [44]. Poly(ether ether ketone) with a cardo group (P.E.E.K.W.C.) was utilized for the preparation of membranes by dry/wet phase separation technique, using three chlorinated solvents; chloroform (T.C.M.), dichloromethane (D.C.M.) and 1,2-dichloroethane (D.C.E.) [45]. Membranes with dense skin layers were obtained using T.C.M. and D.C.M. solvents, while the membranes with a porous skin layer were obtained using D.C.E. solvent. Such a difference in the membranes' skin layer morphology resulted from distinct solvents' distinct volatility (D.C.M.> T.C.M.> D.C.E.).

In the thermally induced phase separation (TIPS) technique, membrane formation is induced by decreased temperature [46]. The polymer is first dissolved in a "latent solvent" (substance that does not act as a solvent for the polymer at room temperature) at elevated temperature (near the melting point of the polymer) [47]. The solution is casted in the desired shape and then cooled down to induce phase separation and solidification. Extraction of the latent solvent permits to obtain of membranes with porous structures [48]. This technique is used for preparing membranes with semi-crystalline polymers that cannot be easily dissolved in solvents such as polypropylene (P.P.) and polyethylene (P.E.) [49-52]. Yeon et al. fabricated P.E. membranes with large pore diameters for manufacturing prismatic batteries [53]. Using soybean oil (S.B.O.) and dioctyl phthalate (D.O.P.) as diluents they prepared several ternary and binary mixtures (PE/SBO, PE/DOP and PE/DOP/SBO). The obtained experimental results indicated that the microporous membranes' pore size can be controlled by using a diluent mixture. The membranes fabricated from the ternary blends presented larger pores than those obtained with the binary blends. Table 3 summarizes the results of the works reported on the preparation of P.E. membranes using the TIPS technique.

Table 3: Effect of the polymer-diluent mixture on the morphology of membranes prepared by TIPS technique.

Polymer	Diluent	Extractant	Membrane Morphology	Ref.
HDPE	DOP/isoparaffin	-	Pore size(PE/DOP): 0.17 µm Pore size(PEISOP): 0.07 µm Pore size(PE/DOP/ISOP):0.07-0.5 µm	[54]
PE	Liquid Paraffine	ethanol	Pore size= 3-5 µm Porosity= 50-60 %	[55]
PE	Mineral Oil	Trichloroethylene	Porosity 5.9–53%	[56]
HDPE	PP/clay platelets/SEPS	-	Pore size (PP/HDPE): 6.46 µm Pore size (PP/HDPE/SEPS): 3.82 µm Pore size (PP/HDPE/SEPS/clay): 2.02-2.96 µ	[57]
LLDPE	OPE/p-xylene	-	PE: smooth surface PE/OPE: fibrous	[58]

HDPE= = high density polyethylene; DOP= dioctyl phthalate; PP= polypropylene; SEPS= polystyrene-block-poly(ethylene-ran-propylene)-block-polystyrene,

In the vapor-induced phase separation (V.I.P.S.) process, the polymeric solution is

casted on support and put in a chamber containing a vapor of nonsolvent saturated with a solvent [59]. The membrane formation occurs due to the diffusion of the nonsolvent into the casted film. In this method, the mass transfer rate is meager, which avoids macrovoids formation [60]. This technique permits a better control of the membrane morphology. Porous membranes prepared by this technique are used in water treatment [61, 62] and the dense gas separation process [63, 64]. Peng and coworkers investigated the effect of different parameters such as exposition time, polymer content and relative humidity of air on PSf membrane structure [65]. Results obtained by them indicate a longer exposure time during the V.I.P.S. permits a dense skin layer. Furthermore, a finger-like structure was obtained with a high polymer content; while, a low polymer content was favorable for a sponge-like structure. The humidity of air mainly affects the top surface rather than the cross-section. PVDF membranes were prepared by coupling NIPS and TIPS for M.F. and U.F. applications. Besides utilizing non-toxic solvents (triethyl phosphate, T.E.P.) in conformity with green chemistry principles, Bouyer et al. [66] prepared symmetric PVDF membranes with tailored properties. It was also possible to synthesize M.F. membranes with different pore sizes by varying the exposure time between 2.5 and 2.7 min. Recently, symmetric porous polybenzimidazole membranes were synthesized by V.I.P.S. and used as proton exchange membrane fuel cells. The membranes showed high porosity (72%) and good proton conductivity (70.8 mS cm^{-2} at 180 °C) [67].

Conclusions

For its low-energy consumption, mild operating conditions, good integration with conventional processes, membrane technology is applied for fresh water production, energy generation, tissue engineering and other separation processes. Polymeric materials play an important role in developing membranes due to their low cost, excellent processability and ample abundance. A large variety of techniques such as phase inversion, interfacial polymerization, controlled stretching, melt extrusion or electrospinning are used to fabricate polymer membranes. Phase inversion is a unique technique, which is usually used for preparing dense and porous membranes with symmetric and asymmetric structures. This mini-review is an introductory description of the polymeric membrane preparation using a technique based on the phase inversion process that has been provided. In particular, the attention has been focused on three techniques: nonsolvent induced phase separation (NIPS), thermally induced phase separation (TIPS), and vapor-induced phase separation (V.I.P.S.). The influence of the critical factors of each technique on the membrane morphology has been described.

Acknowledgements

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