A New Insight into Morphology of Solvent Resistant Nanofiltration (SRNF) Membranes: Image Processing Assisted Review

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Abstract

The aim of this review is to investigate the morphological properties of polyimide based SRNF membranes by mean of image processing. Effect of phase inversion parameters like polymer concentration, volatile co-solvent, pre-evaporation time, additives in coagulation bath, polymers weight ratio in composite membranes, addition of nano particles and cross-linking agents have been reviewed. The voids of membrane were targeted to survey in the aspect of void area concentration in the SEM micrograph, mean of voids area, voids orientation and circle equivalent diameters of voids. This method by mean of the developed software could make the morphological studies of membranes easy. The population of different measured parameters of the voids could also measure. In conclusion for polyimide based membranes there are specific trends for change in voids properties by changing of phase inversion parameters. It was predictable, but investigated qualitatively up to now and this review can confirm the qualitative observations and also open new discussions about, for example void orientations that are not investigated in any study up to now.

Keywords

Morphological Property;
Solvent Resistant Nanofiltration;
Nano-porous Membrane;
Phase Inversion;
Image Processing.

1. Introduction

Organic synthesis in the chemical and petroleum industry are frequently performed in organic solvents and include products with high added value that should be removed from the organic solvents. On the other hand, organic solvents, that uses as raw materials, in chemical synthesis, and as cleaning agents, must recovered or discarded at the end of the process. The costs of processing these organic solvents for separation, recovery, or disposal are expensive and have a significant impact to the expenses of chemical process. This Review considers a new technology for more efficient solvent separations, so-called solvent resistant nanofiltration (SRNF).

The first experiments on membranes started

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at around 18th, but industrial applications of synthetic membranes has been developed at the second half of the former century. Sometimes, membrane separation process is used as a modifier process to improve the separation ability of some other separation processes [1] and sometimes it uses instead of some methods (such as thermal separation methods or electro dialysis methods) [2] to achieve a cheap, simple, short and selective separation. Liquids have essential roles in some industries and necessity to purity always is a key aspect. Pressure-driven membrane filtration which uses for liquid separation has been categorized in some kinds of processes such as: reverse osmosis (RO), forward osmosis (FO), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) etc. [3]. SRNF is a type of nanofiltration process that employs membranes that have chemical resistance against organic solvents to prevent from any damage to separation agent (membrane) against chemical impacts. Distillation process is one of the other methods that widely used to separate solvents [4-6]. But in some cases this is not feasible to use this expensive process [7]. Then membrane technology opens new window to a user friendly process as SRNF for separation of organic solvents from other components [8]. Nano sized pores uses for SRNF that separates materials according to their molecular sizes [9, 10]. Actually, nanofiltration has properties between ultrafiltration and reverse osmosis and the pore size of membranes are usually about 1nm. They are able to separate inorganic salts and small organic molecules as a RO membrane. M. Mudler [11] classified membrane filtrations according to pressure that needs as driving force for membrane separation. For UF it was between 1 to 5 bar, for NF ranged from 5 to 20 bar and for RO it has upper values than 10 bar. SRNF or organic solvent nanofiltration (OSN) have begun from about 1965 [12]. Many studies have been focused on these types of membranes up to now and there are more than 70 publications per year in the field of SRNF membranes. In a recent study, P. Marchetti et.al classified SRNF processes as three groups according to their separation mechanism for membrane processing of liquids which are concentration, solvent exchange and purification [3]. To preparation of SRNF membranes there are two roads, use of chemical resistant polymers to membrane production or modification of polymeric materials to have strength against chemical agents [13-15]. Some of the most useful materials used in SRNF membrane preparation is polyacrylonitrile, polyimide, polybenzimidazole etc. Between these materials polyimide (PI) is most convenient and commercialized polymeric membrane for solvent purification applications.

In addition to chemical resistance of these membranes, they should have good separation ability. It's very dependent to morphology of membrane that completely relates to membrane preparation method [16, 17]. The morphology of membranes and totally polymers usually has observed by mean of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to detect nano scales structure elements [18, 19]. According to Khulbe et.al [20] there are two groups of membranes when classified according to their structures: homogenous (symmetric) that has a uniform structure across the membrane film layer and heterogeneous (asymmetric) that has not the same morphology pattern during the thickness of membrane film. Furthermore, the heterogeneous membranes have three branches: (I) integrally skinned asymmetric membranes; (II) integrally skinned asymmetric membranes with a porous skin layer; (III) thin film composite membranes. Asymmetric membranes and thin film composite membranes are usually use for NF and accordingly SRNF [21-23]. Figure 1 shows the asymmetric morphology in a schematic illustration. The upper part shows the dense skin layer of membrane and the down part illustrates the porous layer.

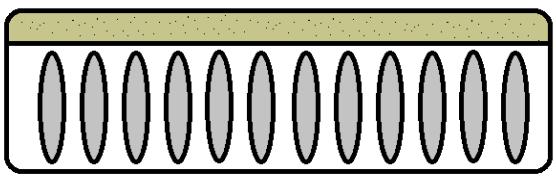


Figure 1. Asymmetric morphology of membranes.

In this review, the SRNF polyimide membranes that investigated up to now, have been studied by focus on morphology (SEM images) and the morphological properties which have been investigated by mean of image processing. Effects of measured parameters on separation process performance have discussed and also relations between morphology and membrane preparation parameters for polyimide SRNF membranes have been investigated.

2. SRNF polymeric membranes

There are two groups of SRNF membranes, polymeric and non-polymeric types. With an overall

look at membranes, non-polymeric membranes have lower variety than polymeric membranes. On the other hand they usually are so brittle and scale up process for these types of membranes is so difficult [24]. The solvent resistance of non-polymeric membranes is very high and their regeneration after process is easy [25]. But there are also many polymeric materials that have good resistance against organic solvents. One of the other advantages of polymeric membranes is their preparation process that is easy and cheap. In the present review the focus is on a type of polymeric SRNF membranes; polyimide.

2.1. Materials and methods use in SRNF polymeric membrane preparation

Polymeric materials that use in SRNF membranes preparation should have chemical resistance against organic solvents in addition to some characteristics that other membranes need to have. Some examples of these characteristics are good film forming, thermal stability, price and availability. The other important part that should be note is the mechanical properties of polymeric films that let membranes to scale up easily. Table1 shows the most common polymers or monomers have been used in preparation of SRNF polymeric membranes. There are two major kinds of preparation methods for SRNF membranes, phase inversion method for integrally skinned asymmetric membranes and preparation methods for thin film composite membranes [10].

2.1.1. Phase inversion

The most common method in the industry of polymeric membranes for phase inversion is dry-wet phase inversion technique (Loeb-Sourirajan method [26-28]) that explained below:

Dry-wet phase inversion technique

In this method at the first step a polymer solution prepares in specified conditions. The solution casts on a suitable surface by mean of casting instrument with a specified thickness and after partial vaporization of solvent, the cast film immerses in a non-solvent bath called coagulation bath. In this method a thin skin layer of polymer creates on top surface of membrane film because of partial evaporation of solvent at the first step of solid forming [29]. The porous layer creates during solvent exchange process that non-solvent diffuses in to the polymer matrix and solvent diffuses out of the matrix. This method can prepare integrally skinned asymmetric membranes. Figure 2 shows a pilot plant automatic instrument for phase inversion membrane preparation.

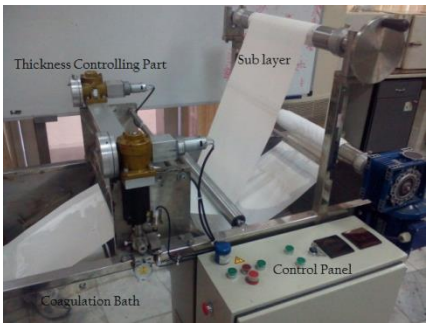


Figure 2. A pilot plant automatic instrument for phase inversion membrane preparation.

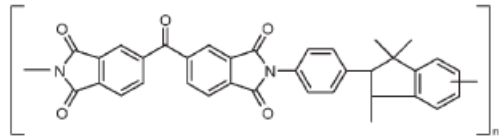
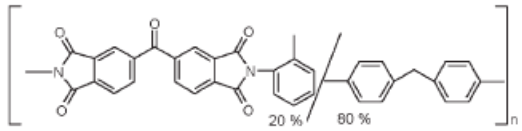
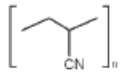
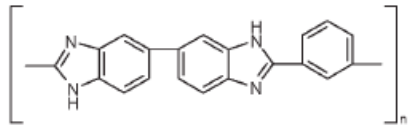
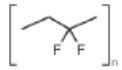
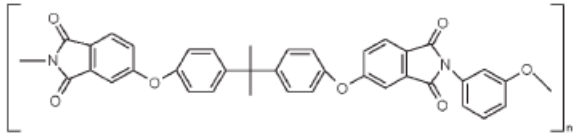
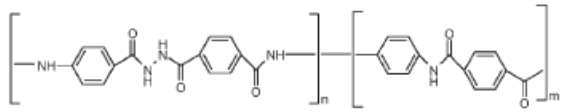
This type of phase inversion process has some important notes that directly affect the membrane main properties such as morphological properties [38, 85]. Solvent choosing, polymer concentration, addition of additives, evaporation process, non-solvent selection and post treatment are among the most important matters that should be considered [20, 86].

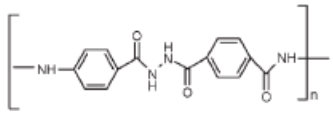
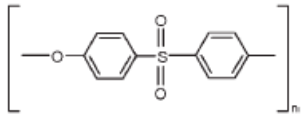
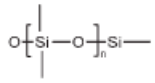
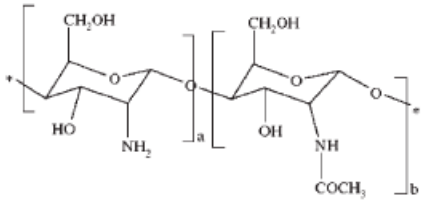
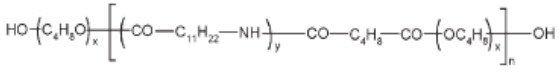
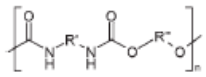
Solvent choosing: Some of most convenient solvents that have been used for preparation of casting solution in this method are N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) [14, 15, 87-97]. Two noticeable effective parameters on solvent selection are: 1) type of polymer used for membrane preparation, 2) affinity between solvent of casting solution and the non-solvent in the phase inversion bath [20].

Polymer concentration: Polymer concentration in the casting solution has a very important role in the morphology of membranes. The solution with higher concentration has smaller pores in the surface and also has thicker skin layer. By increasing polymer concentration in the phase inversion process, the exchange rate between solvent and non-solvent, because of higher resistance against counter-diffusion of solvent and non-solvent, decreases. This effect leads the membranes to have smaller pores and with more density of thin skin layer. However, the thickness of thin layer would be lower because of slowing down the pre-evaporation process.

This effect is very significant in preparation of NF membranes and accordingly in SRNF membranes to avoid from micro-pores forming. On the

Table 1. Major polymers and methods used to preparation of SRNF membranes.

Polymer/Monomer	Application	structure	Method of preparation	References
Polyimide (PI) Matrimide	NF, UF support		Phase inversion	[13, 30-35]
Polyimide (PI) P84	NF, UF support		Phase inversion	[36-38]
Polyacrylonitrile	NF, UF support		Phase inversion	[34, 39-63]
Polybenzimidazole	NF		Phase inversion	[64-66]
Poly (vinylidene fluoride)	UF support		Phase inversion	[49, 67-69]
Poly (etherimide)	NF		Phase inversion	[70-73]
Polyamide	NF		Phase inversion	[74, 75]

Polymer/Monomer	Application	structure	Method of preparation	References
Poly (amide hydrazine)	NF		Phase inversion	[76]
Poly (ethersulfone)	NF, UF support		Phase inversion	[77-80]
Polydimethylsiloxane	NF		TFC (solvent casting)	[32, 50, 53, 58-61, 81-83]
Chitosan	NF		TFC (solvent casting)	[55]
Poly (ether-b-amide)	NF		TFC (solvent casting)	[84]
Polyurethane	NF		TFC (solvent casting)	[57]
Polyphosphazene	NF		TFC (solvent casting)	[10]

other hand, permeability of membranes prepared with more concentrated solvent is lower than low concentrated cases and this case for selectivity of membranes is reversed [98].

Additive addition: Some additives such as those illustrated in Figure3, are usually used to achievement a flexible phase inversion process. It means that the phase inversion process and naturally the morphology of membrane with this act can be controlled. The most important additives for SRNF membrane formation are volatile solvent, non-solvent and pore-forming additives [64, 88, 99-104]. Some examples of materials have been used for this goal have been illustrated in Figure 3.

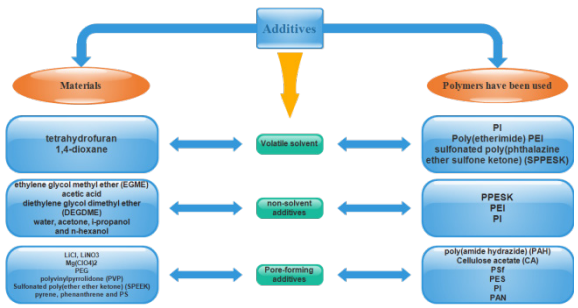


Figure 3. Additives for preparation of SRNF membranes casting solution [64, 88, 99-104].

Evaporation process: The partial evaporation of solvent that happens at the first step after the casting has some effective parameters that could change the morphology of membranes. Time, temperature and air velocity (in the forced convection evaporations) are important parameters in partial evaporation. According to literature higher time, temperature and air velocity at the partial evaporation of solvent could leads membranes to higher selectivity, lower permeability and less macro voids [20, 79, 95, 99, 105].

Non-solvent: Morphology of membranes in the phase inversion method is also sensitive to composition of non-solvent bath (coagulation bath). Some experimental research show that addition of an amounts of alcohols such as ethanol and methanol [73] to the gelation bath can slow down the rate of solvent exchange, so it has an effect as same as high polymer concentration (i.e. higher selectivity, lower permeability and less macro pores) [106, 107]. This was prepared by some other researchers through adding the solvent of casting solution to the gelation bath [108]. The bath temperature is the other parameter that can be controlled the pore sizes and dense skin layer thickness. Higher temperature of coagulation bath results higher exchange rate and higher permeability and more macro voids [68, 109]. Table 2 shows the parameters that control pore and void sizes and their effect on morphology and performance of membranes during dry-wet phase inversion technique.

Polymeric membranes exist from polymeric materials which are soluble in some solvents according to their structure. For preparation of solvent resistant nanofiltration membranes, chemical stability of the membrane is a main aspect. But the polymers are commonly unstable against some solvents. To achieve chemical stability and also thermal stability and improvement of membrane performance, some treatments are needed that often called post treatments [110]. Table 3 illustrates some of the most important post treatment methods used by researchers to modify of membranes as SRNF membrane.

Table 2. Major polymers and methods used to preparation of SRNF membranes.

Parameter	Change in value	Void concentration	Selectivity	Permeability
Polymer concentration	Increment	Decrement	Increment	Decrement
Evaporation time	Increment	Decrement	Increment	Decrement
Evaporation temperature	Increment	Decrement	Increment	Decrement
Air velocity	Increment	Decrement	Increment	Decrement
Gelation bath composition	Addition of alcohols	Decrement	Increment	Decrement
Gelation bath composition	Addition of casting solvent	Decrement	Increment	Decrement

2.1.2. Preparation methods for thin film composite membranes

Dip coating

Dip coating is a conventional membrane preparation technology and has been widely applied to fabricate ceramic membranes with macro-porous to micro-porous levels upon porous supports. During the dip-coating, a wet layer of ceramic particles is deposited upon a porous support by coating the dry support surface with a particle-dispersed suspension, or sol, followed by a controlled sintering process. However, the repeated coating-sintering procedure has many drawbacks, such as the need for additional preparation steps, the reduction of the membrane permeation properties and the extra energy consumption of the sintering process [117].

Zhu et al. suggested a modified dip-coating method to prepare pinhole-free ceramic membranes. In this method, tangential flow of suspension was used against the support dipping in order to assist the capillary-filtration effect. This modified dip coating method for preparation of pinhole-free membranes was very effective and was able to resist the presence of pinhole defects in the supports and avoid new pinhole occurrences. The modified dip-coating method had several advantages compared with the repeated coating-sintering procedure, such as not producing additional undesired membrane thicknesses, not reducing the membrane permeation properties, and requiring only a single coating-sintering procedure [117].

Table 3. Methods for post treatment o SRNF membranes.

Membrane type	Post-treatment type
Phase inversion [111]	cross-linking
Phase inversion [112]	wet annealing
Phase inversion [3]	Dry annealing
Phase inversion [113]	drying by solvent exchange
Phase inversion [110]	treatment with conditioning agents
TFC [10]	curing
TFC [114]	grafting
TFC [115]	plasma
TFC [116]	UV
TFC	chemical treatment

In the dip coating method an integrally skinned asymmetric membrane with a porous skin layer uses as the base of the membrane (it prepared by dry-wet phase inversion method) and then it immersed in a bath that contains a diluted solution of a polymer. After this step, the membrane film takes out of the bath and the solvent has let to evaporate from it. After evaporation a thin film of polymer that was in the polymer solution bath places on top of the base porous membrane [78, 118]. Figure 4 shows the dip coating process in a schematic.

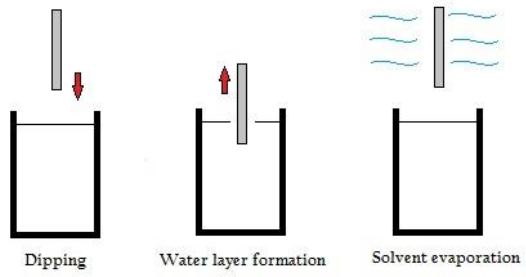


Figure 4. Dip coating method for preparation of TF on the sub-layer.

Interfacial polymerization

This is one of the methods that widely uses for preparation of reverse osmosis and nanofiltration membranes. Cadotte developed this method for the first time [119]. In this method the monomer exists in two immiscible solutions. After immersing the porous support layer of membrane in one of them, the solution places on the surface pores of the support. Then the support takes out from the first solution and floats in the second one. As there are two immiscible solvents, an interface will form on the support membrane and polymerization reaction will occur over there. At last and after evaporation of solvents, a very thin film forms on top of the porous layer. Preparation of a thin film composite (TFC) membrane occurs during the IP reaction between two monomers. Figure 5 is schematic diagrams of TFC membrane preparation using the IP technique [117]. To prepare a very thin PA active layer on top of a support membrane, first the substrate typically will be immersed into an aqueous solution consisting of an amine monomer, prior to immersion in a second organic solution containing an acryl chloride monomer. The membrane is then subjected to heat treatment to densification of the polymerization properties of the PA layer and/or enhances adhesion of the PA

thin layer to the surface of the support membrane. Due to the significant advantages of the IP technique in optimizing the properties of the skin layer and micro-porous substrate layer, a wide variety of membranes have been successfully developed by many companies, allowing for the application of membranes for various industrial separation processes [117].

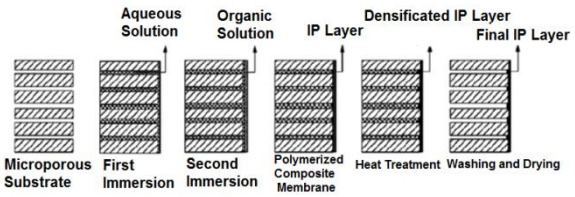


Figure 5. Schematic diagrams of the preparation process of TFC membranes by conventional IP technique [117].

3. Digital image processing

To calculate the properties of voids using SEM images taken from membrane cross-section, a program has been developed by mean of MATLAB programming. The program, under supervision of the user, would extract voids; then, for each void, would calculate the area, centroid, and properties of the fitting ellipse (axis length, eccentricity, and orientation). The fitting ellipse has the same second-moments as the void. Percent of void area concentration, void equivalent diameter distribution, void area distribution, and void fitting ellipse eccentricity distribution have been calculated.

3.1. Pre-processing

Raw SEM images are not suitable for analysis. They contain the scale, needs contrast enhancement for more accurate results and in some images, the surface of the membrane is not horizontal. The images should be stripped of the scale. So, before stripping, the user should scale the image by clicking on both of the ends of the scale line. To reliability of orientation data, images have been rotated to straighten the surface of the membrane. The scale extraction process is a user-assisted process, because it's difficult for a machine to detect the scale line and it may have bigger errors if does by mean of the program.

3.1.1. Image Enhancement

The program treats connected region of pixels with low luminance as voids. Therefore, before analysis, two phases of contrast stretching have been applied. In first phase, 1% of the intensity of pixels saturated at low and high intensities of the original image. This indicates the values in the intensity of original image to new values in enhanced images, such that 1% of data is saturated at low and high intensities of original images. This increases the contrast in the new image. In second phase, the contrast enhanced by using Contrast-Limited Adaptive Histogram Equalization (CLAHE) algorithm [120].

3.2. Void detection

Thresholding is used for image segmentation. Unlike Weina et al.[121] that used region growth algorithm for image segmentation, this program uses thresholding. The image will process by the light intensity that is very more user friend than the old method. The results were from standard deviation of at least 5 thresholds at the estimated area (default threshold that the software suggested). As the user can change the light intensity in the program and consequently the software calculates voids properties after each threshold change, it will be very more user friend than clicking on the void area and growing the region. The old method could have more errors than standard deviation of plenty of threshold results in the estimated area (default threshold from enhancement methods).

3.2.1. Segmentation

Gray-scale image converted to a binary image (black and white). An initial value for the threshold proposed by the program using Otsu's method [122]. User can change threshold value using a slider control (Figure 6).

In Figure 7e, colorized image of extracted voids has been illustrated (adjacent voids have different colors). Whole void extraction process is illustrated in Figure 7a-d.

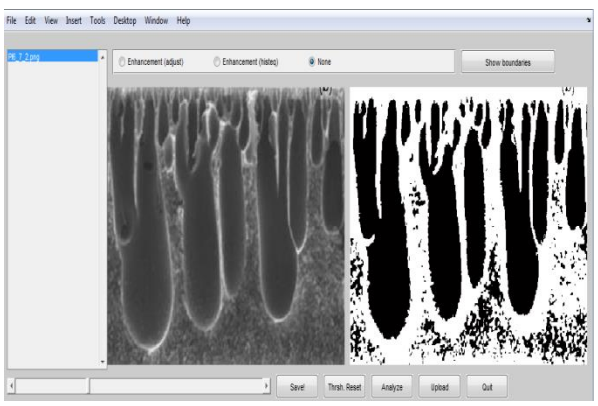


Figure 6. Screenshot of GUI (thresholder).

3.3. Analysis

Void area concentration (in percent) is calculated using the following formula:

$$Void\ area\ concentration = \frac{\sum(area\ of\ voids)}{\sum(\text{area of whole image (voids} + \text{non} - \text{voids))}}$$

Weina et al. [121] used (a + b) as the definition of equivalent diameter, but in this paper, the diameter of a circle with the same area as the void, used as equivalent diameter:

$$\text{Equivalent diameter of circle} = \sqrt{4\frac{area\ of\ voids\ (\mu m2)}{\pi}}$$

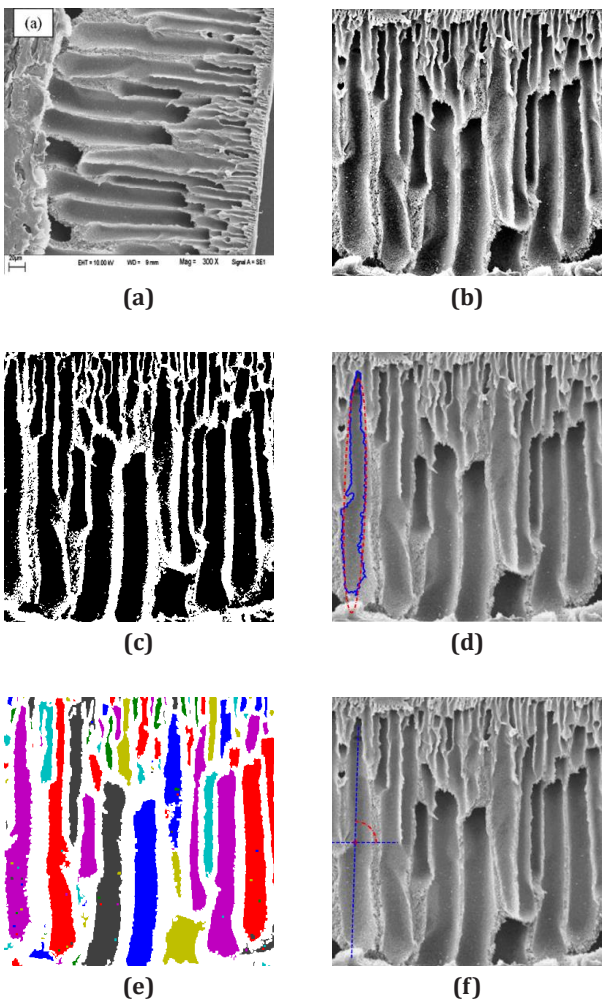


Figure 7. SEM analysis of polyethersulfone SRNF membrane in deferent stages of image processing: a) original image, b) pre-processed image, c) thresholded image, d) Boundary of void and fitting ellipse on original image, e) colorized voids, f) Orientation of the void (88.3°) [21].

Orientation of void is defined as the angle between the x-axis and the major axis of the fitting ellipse, see Figure 7-f. Whole image processing process steps and results have shown in the Figure 8.

All mentioned properties of each detected void, plus mean, median, and standard deviation of them, have been saved on disk for further analysis.

At last, the circle equivalent diameter distributions (histogram) have been calculated for images. Data and curves achieved form above process all have been used to define the properties of voids in cross-section SEM images of SRNF membranes and to find relations between these properties and other parameters in membrane preparation methods.

4. A survey of different morphologies of SRNF membranes by image processing and study on their relations with other properties of membrane

4.1. Morphological characterization of membranes with scanning electron microscopy (SEM)

Scanning electron microscopy is one of the most convenient methods to observe the materials morphology in micro scales and even in nano scales in some cases [19, 123-132]. In membrane technology, prepared membranes should observe morphologically to achieving a good see from relations between the shape of membrane and its other properties. It could help to development of methods for membrane preparation and also prediction of membranes properties. It also could be useful for detection of membrane applications. SEM micrographs in membrane morphological studies

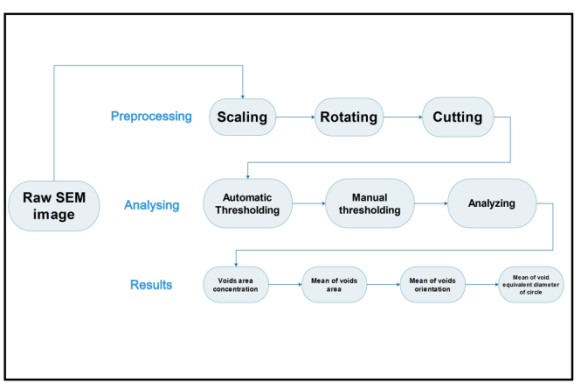


Figure 8. Whole SEM images computing with image processing process.

are taken from the surface of membranes or cross section of them. For determination of void properties in the membranes, the cross sectional view of SEM images is very useful. This view also can show the thin skin layer and different morphologies exist in the membrane [133-135]. It also illustrates particles and additives in the structure [136-139]. Important parameters in a membrane morphology which could relate to other properties and can detect by image processing method are void sizes (diameters and area), cross sectional porosity index of membranes, void size distributions and void orientations.

4.2. Phase inversion parameters VS. Void properties

It's clear that the method of membrane preparation affects the morphology of the membrane. In this case and for the phase inversion method there are some parameters that have effects on void properties of SRNF membranes which were discussed before. Accordingly, there are some image processing assisted reviews on some research studies on SRNF membranes with different polymeric materials and on the effect of phase inversion parameters on their voids properties. They will discuss below.

A survey of some research works on phase inversion and morphology

One of the most popular groups of SRNF membranes that studied up to now are polyimide based membranes. So focus of this review is on these types of polymeric membranes.

Polyimide is among most useful materials to prepare SRNF membranes. Some research on this polymer has morphological studies that investigated different parameters on morphology of membranes. P. Vandezande et.al [140] studied on phase inversion parameters of polyimide-based SRNF membranes and their effect on morphological properties changes which illustrated by SEM micrographs. Figure 9 shows the effect of polymer concentration on void size, void area percentage and mean of the void equivalent diameter of the circle in the SEM micrographs. Data have been achieved by image processing program. As this is clear from the curves, the void area percentages have been decreased by increasing the polymer concentration in the casting solution. This result confirms the author claim and it has correspondence to predictions about changes in morphology against polymer concentration in the casting solution. Mean of voids area in micrometer and voids circle equivalent diameters have also been illustrated in the figure. These parameters show the void extents in the structure of the membrane. It can be seen that void sizes decreases by increasing of polymer concentration at the first step and then a meaningful increment is obvious in the sizes. It's because of decreasing in buoyant forces for bubbles of solvent that can decrease the rate of solvent and non-solvent exchange in the phase inversion process [141]. In this study THF was used as volatile co-solvent. Augmentation of THF in the solution has decreased void concentration in the structure. The THF makes a dense layer on the top of membrane in pre-evaporation step. This layer acts as a resistant layer against counter diffusion of solvent and non-solvent, so the void concentration, mean of void area and mean of equivalent diameter, all decrease by increasing the THF concentration in the casting solution. The image processing results have shown in the Figure 10. The pre-evaporation time effect on the morphology of membranes has been shown in the Figure 11 curves. Void concentration in the structure has decreased by increasing of pre-evaporation time. The pre-evaporation time leads to create a dense layer on top of the membrane and a resistance against diffusion of solvent and

non-solvent. It results less voids with bigger sizes. But at the first step by addition of time from zero to 30s a decrement in void sizes is because of lower velocity compared to sample with no pre-evaporation and also the lower thickness of top resistant layer than samples with higher time of pre-evaporation. Lower velocity leads to slower diffusion and naturally smaller voids also in the cases with higher pre-evaporation times the process has lower velocity, but addition of resistant layer thickness has effects as same as addition of polymer concentration that leads to higher viscosity and so bigger void sizes. To investigate of change in morphology of membranes with change in coagulation bath composition, the research team added 2-propanol to the bath. This leaded to lower area percentage of voids and lower void sizes in diameter and also area. In 80% concentration of 2-propanol in the coagulation bath there is a visible increment in void sizes and this raise has disappeared in 2-propanol concentration of 100% that almost there are no voids in the structure in this concentration. The increment in 80% percent may causes by low diffusion rate and attraction of solvent globes during the diffusion time that leads to higher void sizes.

Figures 13 to 16 show the population histograms of voids in the structure of SRNF membranes prepared by P. Vandezande et.al. In the

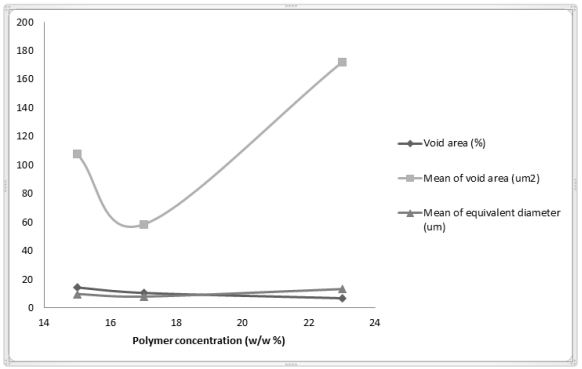


Figure 9. Void area (%), mean of voids area and mean of circle equivalent diameter of polyimide-based SRNF membranes against polymer concentration [142].

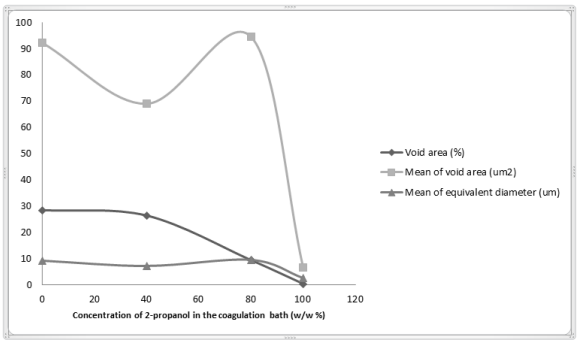


Figure 12. Void area (%), mean of voids area and mean of circle equivalent diameter of polyimide-based SRNF membranes against concentration of 2-propanol in the coagulation bath [142].

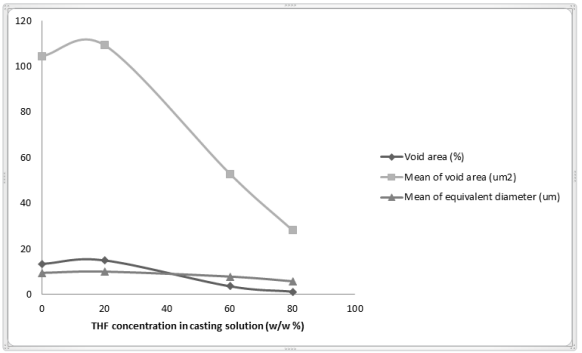


Figure 10. Void area (%), mean of voids area and mean of circle equivalent diameter of polyimide-based SRNF membranes against THF concentration in casting solution [142].

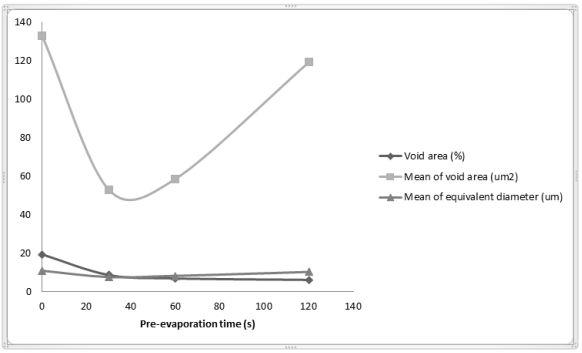


Figure 11. Void area (%), mean of voids area and mean of circle equivalent diameter of polyimide-based SRNF membranes against pre-evaporation time [142].

Figure 13 it's completely obvious that the voids diameter shifts to higher amounts by the addition of polymer concentration. On the other hand, by addition of the volatile co-solvent to the casting solution, bigger voids will exist in the structure of membranes (Figure 14). Void populations in different pre-evaporation times are shown in the Figure 15. In this case number of voids with bigger diameters increased by increments of evaporation time, but in time of 120s most of the voids have small diameters. This may be because of very low rate of diffusion in the phase inversion step that don't lead the bubbles to attract together to form bigger macro-voids. By the addition of 2-propanol to the coagulation bath higher amounts of voids goes to the higher diameters. As before mentioned, lower diffusion rate results bigger voids, but very low diffusion rate can disperse very small bubbles in the membrane and don't let them to attract. This matter is illustrated in Figure 16 that in pure 2-propanol coagulation bath there are small voids with a uniform distribution in the membrane cross sectional SEM image.

Voids orientation is one of the most important and most novel data that image processing program gives us. It could be predicted that voids orientations could have effects on membrane performance and is controllable by selecting proper phase inversion parameters. About void orientations, image processing shows results with a decrement on orientation by increasing of polymer concentration that caused by higher viscosity of casting solution and higher resistance against counter diffusion of solvent and non-solvent and in more concentrations of polymer the mean of orientation has increased. It means that high concentrations of casting solution and accordingly higher viscosities lead to very low diffusion rate. Upper viscosity roles as a barrier on top of the membrane similar to the membranes prepared by addition of pre-evaporation step or addition of volatile sol-

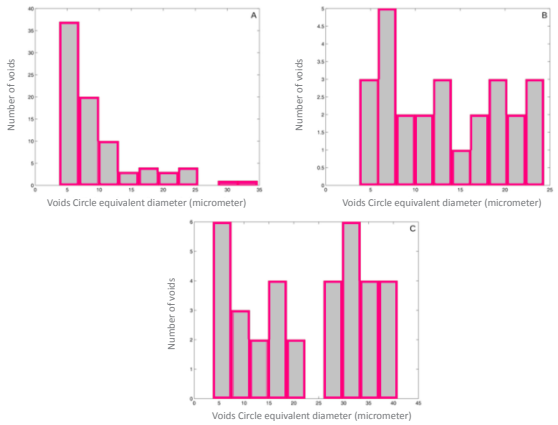


Figure 13. Population histogram of voids in different polymer concentrations in NMP as solvent: A) 15% B) 17% C) 23% [142].

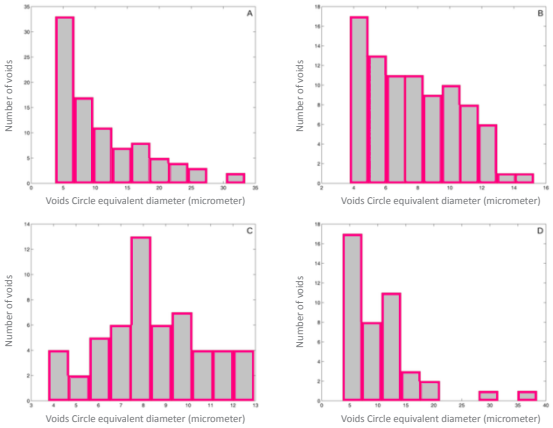


Figure 15. Population histogram of voids in different air velocities in pre-evaporation step: A) 0s B) 30s C) 60s D) 120s [142].

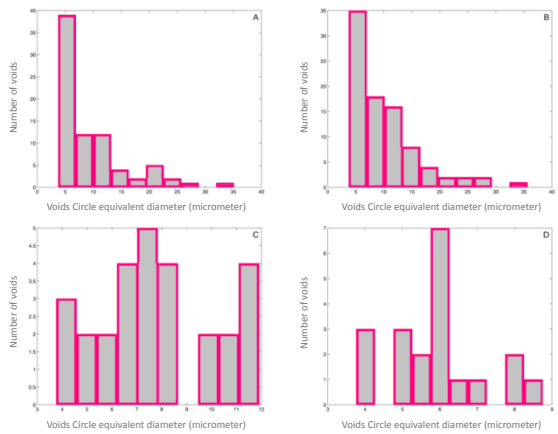


Figure 14. Population histogram of voids in different volatile co-solvent (THF) concentrations in the casting solution (base solvent was NMP): A) 0% B) 20% C) 60% D) 80% [142].

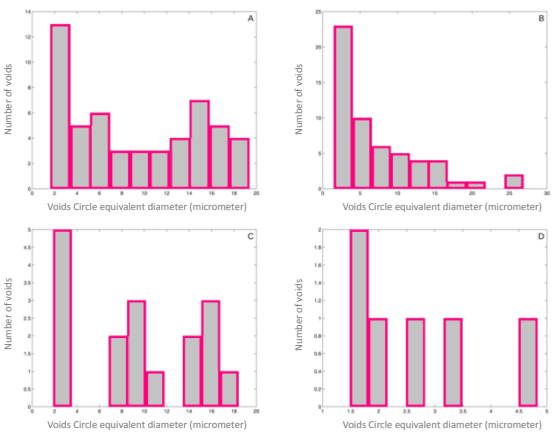


Figure 16. Population histogram of voids in different 2-propanol concentrations in the coagulation bath: A) 0% B) 40% C) 80 D) 100% [142].

vent to the casting solution. This barrier prevents from relax transfer for solvent globes in the casted membrane. In conclusion, for lower polymer concentrations the way for transfer is open because of lower viscosity, also there is lower speed by addition of concentration up to a specified level, so the globes of solvent will be more uniform with lower stray by addition of concentration up to this level. After this level addition of polymer concentration roles as a barrier and there is less open ways for solvent to exit from casting solution and diffuse in the non-solvent bath, so the globes will stray more that causes higher orientation.

Increment of the orientation of voids is resulted by increasing volatile co-solvent in casting solution. Addition of volatile co-solvent in high concentrations prepares a very dense and thin layer above the membrane. It leads to low velocity of phase inversion and acts as a barrier that has assumed in high polymer concentrations. This high resistance against diffusion results crooked set of macro voids in the membrane.

Change in evaporation time has effect as like as polymer concentration on voids orientations. It can be postulated that the barrier that creates by addition of pre-evaporation time is not as dense as barrier resulted by the addition of volatile co-solvent. So, this has open ways for diffusion in low

evaporation times and by increment of time it becomes denser and less uniform voids is resulted by this action. As a result void orientations become lower in high evaporation time.

Addition of 2-propanol to the coagulation bath made the voids to have higher orientations. This action lowers the rate of counter diffusion and orients the voids to the sides and at pure 2-propanol coagulation bath almost there are no voids.

Data of above discussed research work and also other studies are gathered together in Table 4. There are 6 columns in this table that shows data achieved from image processing of SEM images from different articles. The data are about voids concentration (area percentage of voids in the SEM micrographs), voids area, voids orientations and voids diameters.

Vandezande et al [108] has worked on different casting solutions (with different solvent compositions) and effect of addition of NMP-based nano-sized silicalite-1 precursor suspension (NMP-S) was seen in different properties of membrane includes morphological characteristic measured by SEM. Our investigation on SEM micrographs of this study shows that the void concentration (%) has decreased by increasing the additive to the casting solution. It's because of the emulsification effect of NMP-S that leads the membrane morphology to sponge-like that there are lower macro-voids in the structure of membrane in this type of morphology. Mean area of voids in higher concentrations of NMP-S has decreased. It's also because of suspension that exists on these high contents of NMP-S that leads to sponge-like morphology. Equivalent diameter of the circle for voids has increased by increasing of NMP-S in low concentrations because suspension in the casting solution resists against phase inversion. But in the high concentrations that lead to sponge-like morphology there are voids with lower diameters. Orientation of voids has decreased by addition of NMP-S to the casting solution in low concentrations and by increasing the concentration of additive, the orientations have increased and horizontal voids have existed. The reason is also the resistance of suspension solution against diffusion of solvent and non-solvent that increased in high concentrations of additive and let solvent globes to orient as much as possible.

The SEM analysis of polyimide-based SRNF membranes in different polymer concentrations has been investigated by Cano-Odena et al [143]. The results showed that there is a decrease in voids area (%) as like as previous changes in polymer concentration. Also the mean of voids area has a trend just like polymer concentration part of Vandezande et al [140] study. On the other hand, at first by increasing the polymer concentration void equivalent diameters of the circle has decreased and after the addition of more polymeric material to the solution it increased just like a behavior that discussed before for another study on PI SRNF membranes [140]. But about orientation of voids in the cross sectional area image, there is a reverse trend compared to addition of PI concentration. This could be because of lack of enough quality in SEM micrographs or lack of enough number of voids in the area that captured by instrument. These doubts can be repaired by an original research work with higher numbers of SEM micrographs from each sample. The research team is working on a study in this field.

In a previous study by our research team a novel nano composite membrane with polyimide base that incorporated with functionalized TiO2 particles has been studied [13]. As a result from SEM micrographs processing, the prepared membrane has area percentage of about 37%, mean of area of about 34μm2, orientation of about 11 degree from the horizontal axis and the equivalent diameter of circle of about 4μm.

In a study by Vanherck et al [111] cross-linked polyimide SRNF membranes have investigated and morphological properties of membrane before and after cross-linking and after filtration in DMF was observed. Results from image processing program are available in Table 4. Voids area concentration has increased after cross-linking and also after filtration in DMF. The reason of higher void area concentration after DMF filtration is gelation of the polymer during the process. The mean of voids area and circle equivalent diameter of voids also increased after filtration and cross-linking. But about orientation of voids, there are voids very near to circle in the structure of membranes. But at all there are a few bigger horizontal diagonal in the voids and this matter results a high orientation in the voids. Also orientation has decreased after gelation by the solvent filtration. It seems to be because of freer environment for voids to form across the vertical axis during the gelation process.

A polyimide SRNF membrane has been prepared by a two-step method by Fang et al [112]. PI has synthesized by pyromellitic dianhydride (PMDA) and 4, 4- diaminodiphenyl ether (ODA) with more aromatic heterocyclic structures. As a result a membrane with below void behavior has obtained: void area concentration 33.94%, mean of void area 363.75 μm2, equivalent diameter of circle of about 11.46 μm and orientation from hor-

izontal axis of about 16.87 degree.

Morphology of cross section of membranes could be affected by nano particles addition. In a research done by Vanherck et al [144] addition of gold nano particles to PI-based SRNF membranes has been studied. The membranes void area concentration has increased by addition of 0.1, 0.2, and 0.4 (w/w %) of gold nano particles at first and then it decreased by addition of 0.4 percent of particles. The nano particles provide a resistant in phase inversion process that leads to lower count of macro-voids in the structure. In the other hand the void diameters and also mean of voids area has decreased by increasing of nano particles and it confirms the claim. Orientation of voids for 0.1 and 0.4 percent of nanoparticle are almost the same, but by addition of 0.2% of gold nano particles to the membrane casting solution the mean of orientation has decreased. It illustrates that the gold nano particle modified the membrane in 0.2% that is the optimum amount to achieve nearest degree to the vertical axis between the samples.

Jansen et al [145] has investigated polyphenylsulfone/polyimide solvent resistant nanofiltration membranes. Effect of addition of PI on the casting solution and also concentration of polymer on the morphology of membranes has been observed by mean of SEM images. The results showed that the addition of PI to the solution of 25% to 75% increased the void area concentration up to 50% and after this content amount of voids decreased significantly. Mean of void area and void diameters have decreased by increasing of PI. Also, there is less orientation from vertical axis in the 50/50 sample. So the 50% of the PI in the sample is the optimum amount that increment of this composition in the casting solution has also studied. The void area concentration has increased and then decreased by increment of polyphenylsulfone/polyimide 50/50 in the solution. The increment of voids area concentration in the structure is relates to higher resistant in phase inversion process by addition of polymer concentration. Mean of void area and voids diameters are also increased by increment of polymer concentration. On the other hand the voids orientation from vertical axis is lower after addition of more polymers to the solution. It shows that addition of polymer concentrations in this case resulted bigger and more uniform voids.

Vanherck et al [146] was used gold nano particles in the PI-based SRNF membranes in two different methods, using pre-synthesized gold nano particles (PRE) and in situ chemical reduction (ISR). The SEM micrographs have been processed by image processing program and the results have been shown in the Table 4. The images have high zoom and have shown almost the top layer of membranes. In both of the methods the voids area concentration (%) was very low caused by high zoom and very small scale pores in the top layer of membranes. The sponge-like structure has been detected on the membranes for all images in this region. In comparison between the ISR and PRE method the samples without any additional material have been studied by mean of SEM images. Processes of images shows higher void area concentrations and also mean of area for voids in PRE membrane that has PVP in its structure. This is because of PVP effect as a void former. It cloud increase the viscosity of the membrane casting solution and accordingly it forms bigger voids with a higher concentration in the structure. Equivalent diameters of voids are very small. It's because of the high magnification of SEM images that shows only very small voids. The orientations of voids are almost zero because of sponge-like structure that has ellipses near to circle as voids and the orientation of the circle is zero.

5. Conclusion

There are some logical trends in the parameters of phase inversion process and change in the morphological properties of polymeric membranes. Polyimide is one of those polymers that has used in many investigations to prepare SRNF membranes. The quantitative study of SEM images on these types of membranes in different conditions can proof the trends and relations between phase inversion and morphology. New parameter that has introduced in this review is orientation of voids which is correlated with phase inversion parameters. In the current work, the highest void concentration was for membranes prepared by a void area percentage of about 37%, the most mean of void area was for a research by Angels Cano-Odena et.al with an area of about 166 square micrometer (the membrane was 19% PI in NMP and THF solution with evaporation time), the highest diameter of voids (equivalent diameter of circle) was for PI in N,N-dimethylformamide (DMF) that studied by P. Vandezande et.al. At last the lowest area concentration of voids (%), lowest mean of voids area, lowest equivalent diameter and highest orientation was for a sample that prepared by 2-propanol coagulation bath. As a result, it's clear that different parameters in phase inversion technique have different effects on the morphology of

PI membranes. Increasing of some of them could increase some important properties of membrane morphology and in some cases it happens up to a level. For the future studies, optimization of these parameters recommended to achieve a controlled morphology SRNF membrane.

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Table 4. Effect of different parameters on PI-based SRNF membranes morphological properties (references shows by the following pattern: reference number_figure number_figure section).

Reference*	Voids area concentration (%)	Mean of voids area (µm2)	Mean of voids orientation (degree)	Mean of voids equivalent diameter of circle (µm)	Type of SEM micrograph	Investigated parameter
[140]_3_a	14.330185	107.491673	-36.678477	9.784704	cross	Polymer concentration: 15%
[140]_3_b	10.551438	58.476275	68.40057	8.005024	cross	Polymer concentration: 17%
[140]_3_c	6.814865	172.044485	-50.076415	13.246061	cross	Polymer concentration: 23%
[140]_5_a	13.431247	104.4719	60.951352	9.512254	cross	Volatile co-solvent: 0%
[140]_5_b	14.965326	109.256972	-48.925062	10.033561	cross	Volatile co-solvent: 20%
[140]_5_c	3.624373	52.907106	47.824008	7.855378	cross	Volatile co-solvent: 60%
[140]_5_d	1.25322	28.179996	46.171718	5.832491	cross	Volatile co-solvent: 80%
[140]_9_a	19.446861	132.793743	52.050336	10.997372	cross	Pre-evaporation time: 0%
[140]_9_b	8.764721	52.977521	68.089843	7.708597	cross	Pre-evaporation time: 30%
[140]_9_c	6.973494	58.60791	73.734199	8.329973	cross	Pre-evaporation time: 60%
[140]_9_d	10.249888	118.998897	-42.199482	10.354424	cross	Pre-evaporation time: 120%
[140]_11_a	28.498789	92.211269	55.889494	9.251714	cross	Additives in coagulation bath: 0%
[140]_11_b	26.449275	69.012605	31.706117	7.255194	cross	Additives in coagulation bath: 40%
[140]_11_c	9.470099	94.504376	-31.656578	9.55555	cross	Additives in coagulation bath: 80%
[140]_11_d	0.4593	6.516724	-2.304791	2.644975	cross	Additives in coagulation bath: 100%
[108]_2_a	22.661741	45.972612	-28.080634	5.372409	cross	Addition of NMP-S: 0%
[108]_2_b	19.410511	47.265856	-48.037245	6.718715	cross	Addition of NMP-S: 9%
[108]_2_c	12.728751	13.417397	8.239594	3.092415	cross	Addition of NMP-S: 30%
[108]_2_d	5.667574	8.217234	6.934717	2.798631	cross	Addition of NMP-S: 43%
[143]_3_1	30.086274	137.388427	46.098114	9.492048	cross	Polymer concentration: 14%

Reference*	Voids area concentration (%)	Mean of voids area (µm2)	Mean of voids orientation (degree)	Mean of voids equivalent diameter of circle (µm)	Type of SEM micrograph	Investigated parameter
[143]_3_2	17.72101	61.116892	25.36114	6.552759	cross	Polymer concentration: 16%
[143]_3_3	31.745015	166.190407	18.103295	11.21153	cross	Polymer concentration: 19%
[143]_3_4	16.140233	119.006326	32.023003	9.818485	cross	Polymer concentration: 21%
[13]_10_a	37.426868	34.341762	11.048138	3.977089	cross	-
[111]_7_1	8.241035	0.351151	-3.256	0.483611	cross	Before cross-linking
[111]_7_2	14.821038	0.650774	2.409162	0.608065	cross	After cross-linking
[111]_7_3	20.687313	0.883252	-5.015996	0.739638	cross	After filtration in DMF
[112]_7_2	33.985578	363.750678	16.874066	11.467056	cross	-
[144]_7_a	10.642347	132.128229	-10.819162	10.608953	cross	Gold nano particles: 0.1%
[144]_7_b	15.086069	98.776322	-62.88171	9.593718	cross	Gold nano particles: 0.2%
[144]_7_c	6.882383	75.826166	-9.797247	7.451004	cross	Gold nano particles: 0.4%
[145]_5_1	14.976594	34.27906	-23.653684	4.630379	cross	polyphenylsulfone/polyimide: 100/0
[145]_5_2	17.465645	48.630591	14.889118	5.914906	cross	polyphenylsulfone/polyimide: 75/25
[145]_5_3	25.335141	91.246094	40.706784	8.245493	cross	polyphenylsulfone/polyimide: 50/50
[145]_5_4	19.61308	121.268506	-22.382217	8.696853	cross	polyphenylsulfone/polyimide: 25/75
[145]_5_5	9.270355	37.438679	25.48484	5.168425	cross	polyphenylsulfone/polyimide: 0/100
[145]_7_1	24.233948	81.337018	15.222692	6.011627	cross	Polymer concentration: 20%
[145]_7_2	31.358077	43.056431	21.220283	3.978277	cross	Polymer concentration: 25%
[145]_7_3	27.41349	121.840967	21.907688	5.412003	cross	Polymer concentration: 30%
[146]_3_1	0.01193	0.004455	3.456985	0.075317	cross	ISR method
[146]_3_2	0.387838	0.008208	2.221202	0.097054	cross	PRE method

*References shows by the following pattern: reference number_figure number_figure section.