

Solvent stable UV and EB cross-linked polysulfone-based membranes

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SOLVENT STABLE UV AND EB CROSS-LINKED POLYSULFONE-BASED MEMBRANES

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LIST OF PUBLICATIONS

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V. Altun, M. Bielmann and I. F. J. Vankelecom, Study of phase inversion parameters for EB-cured PSU-based membranes, RSC advances, *6*, 2016, 110916–110921.

V. Altun, J. C. Remigy and I. F. J. Vankelecom, UV-cured polysulfone-based membranes: effect of co-solvent addition and evaporation process on membrane morphology and SRNF performance, Journal of Membrane Science, 2016, *Accepted*.

V. Altun, K. Tempelman, S. Casanova, Nieck E. Benes and Ivo F. J. Vankelecom, Effect of UV and EB cross-linking on morphology, performance, swelling behaviour, surface and mechanical properties of polysulfone membranes containing acrylates, Manuscript in preparation for submission.

ABSTRACT

The importance of membrane technology as a separation technique has increased rapidly over the past decades thanks to its broad range of applications. The expanding market brings along the requirement of advanced polymeric materials, which show resistance towards swelling and plasticization in gas separation (GS) and towards harsh solvents and extreme pH conditions in solvent resistant nanofiltration (SRNF). At this stage, cross-linking has emerged as a promising technology to overcome these issues. Chemical cross-linking is one of the most commonly used techniques and is based on a chemical reaction between a polymer (e.g. polyimide) and a cross-linker (e.g. diamine or diol). However, for polymers which do not contain chemically reactive groups in their backbone, such as polysulfones (PSU), this technique is not feasible. Additionally, chemical cross-linking involves several processing steps and causes harmful waste streams, triggering the quest for a generally applicable, fast and green curing technique.

Two new curing techniques, namely ultraviolet (UV) and electron beam (EB) curing, were explored in this thesis, in order to obtain chemically and thermally stable membranes, hence being attractive for SRNF applications. Asymmetric membranes, composed of a semi-interpenetrating polymer network (SIPN), were prepared via non-solvent induced phase separation (NIPS). PSU was chosen as polymer because of its robust thermal and mechanical properties, photosensitivity and lack of reactive groups. Cross-linked membranes with SIPN structure were obtained via UV and EB-curing.

In the first part, the influence of cross-linker functionality, radiation energy dose and polymer/crosslinker ratio on the EB-curing efficiency was investigated. Acrylate-based cross-linkers were employed. The obtained membranes were characterized with ATR-FTIR, SEM and filtration experiments, together with stability testing against harsh solvents. The best type of cross-linker and its optimum concentration under optimum EB-dose were then selected for further studies.

In the second part, the effects of solvent/co-solvent ratio and the evaporation time before precipitation of UV and EB-cured PSU SRNF-membranes were explored, using tetrahydrofuran (THF) or 1,4-dioxane (DIO) as co-solvent. Both UV and EB-cured PSU membrane morphologies differed as function of the studied phase inversion parameters. Increasing evaporation time reduced macrovoid formation with appearance of spongy structures. The flux generally remained too low for membranes to become really useful in SRNF. A post treatment was performed to increase the flux by immersing UV-cured PSU-based membranes in dimethylformamide (DMF) for 48 h. The resultant

membranes showed higher permeances and lower rejections, making them especially useful as potential candidates as stable supports in the preparation of thin film composite membranes.

In a third part, the mechanical characteristics, the effect of casting thickness and the surface properties of the membranes cross-linked by both irradiation methods were further studied. Additionally, the swelling behavior of UV-cured thin PSU films as function of different curing parameters (i.e. radiation dose and cross-linker functionality) was analyzed with ellipsometry.

In conclusion, solvent stable asymmetric PSU membranes were developed by two simple, environmentally friendly and highly effective methods. The performance and enhanced chemical resistance of the cured membranes show high potential for implementing both cross-linking procedures in adequate industrial applications after further optimization.

SAMMENVATTING

Het belang van membraantechnologie als scheidingstechniek is sterk toegenomen over de laatste decennia dankzij zijn brede toepasbaarheid. Deze groeiende markt vereist het gebruik van geavanceerde polymerische materialen, welke resistent zijn tegen zwellen en plasticisering in gasscheiding (GS) en tegen sterke solventen en extreme pH-condities in solvent resistente nanofiltratie (SRNF). Crosslinking wordt beschouwd als een veelbelovende strategie om deze problemen te overwinnen. Crosslinking wordt beschouwd als een veelbelovende strategie om deze problemen te overwinnen. Chemische cross-linking is één van de meest gebruikte technieken en is gebaseerd op een chemische reactie tussen een polymeer (bv. polyimide) en een cross-linker (bv. een diamine of diol). Echter, voor polymeren die geen chemisch reactieve groepen bevatten in hun structuur, zoals bijvoorbeeld polysulfon (PSU), is deze techniek niet toepasbaar. Daarbij komt dat chemisch crosslinken bestaat uit meerdere stappen en ook schadelijke afvalstromen genereert, wat de zoektocht initieert naar een algemeen toepasbare, snelle en duurzame behandelingstechniek.

Twee behandelingstechnieken, namelijk ultraviolet (UV) en elektronenbundel (EB) behandeling, werden daarom onderzocht in deze thesis, ten einde chemisch en thermisch stabiele membranen te bekomen, voor toepassing in SRNF. Asymmetrische membranen, bestaande uit een semiinterpenetrerend polymeernetwerk (SIPN), werden gemaakt via niet-solvent geïnduceerde fase inversie (NIPS). PSU werd gekozen als polymeer omwille van de robuuste thermische en mechanische eigenschappen, fotogevoeligheid en het ontbreken van reactieve groepen. Gecrosslinkte membranen met SIPN structuur werden bekomen via UV- en EB-behandeling en hebben verschillende voordelen ten opzichte van chemisch cross-linken, zoals minder afvalproductie, lager energieverbruik en snellere productie.

In het eerste deel werd de invloed van de cross-linkerfunctionaliteit, stralingsdosis en polymeer/cross-linker ratio op de EB-behandelingsefficiëntie onderzocht. Acrylaat gebaseerde crosslinkers werden gebruikt. De membranen werden gekarakteriseerd met behulp van ATR-FTIR, SEM en filtratie experimenten, en door stabiliteitstesten in sterke solventen. Het beste type cross-linker en zijn optimale concentratie werd dan onder optimale EB-dosis gebruikt voor verdere studie.

In het tweede deel werden de effecten van solvent/co-solvent ratio en de evaporatietijd voor faseinversie van UV- en EB-behandelde PSU-membranen onderzocht, gebruik makend van tetrahydrofuraan (THF) en 1,4-dioxane (DIO) als co-solvent. De morfologie van zowel de UV- en EB-behandelde PSU membranen varieerde afhankelijk van de bestudeerde fase-inversie parameters. Toenemende evaporatietijd verminderde de vorming van macrovoids en resulteerde in de vorming van een sponsachtige structuur. De flux was te laag om membranen te bekomen welke werkelijk toepasbaar zijn in SRNF. Een nabehandeling werd gedaan om de flux van de UV-behandelde membranen te verhogen door middel van onderdompelen van de membranen in dimethylformamide (DMF). De resulterende membranen vertoonden hogere permeanties maar lagere retenties. Het maakte hen wel geschikt als stabiele steunlagen voor het maken van dunne film composietmembranen.

In een derde deel werden de invloed van mechanische eigenschappen, het effect van gietdikte en de oppervlakte-eigenschappen van de membranen gecrosslinkt door beide methoden, verder bestudeerd. Daarenboven werd het zwellingsgedrag van UV-behandelde dunne PSU-films geanalyseerd als functie van verschillende behandelingsparameters (stralingsdosis en crosslinkerfunctionaliteit) met behulp van ellipsometrie.

Ter conclusie, solvent stabiele asymmetrische PSU membranen werden ontwikkeld met behulp van twee simpele, milieuvriendelijke en effectieve methoden. De SRNF performantie en verbeterde chemische resistentie van de behandelde membranen vertoonde een groot potentieel voor het toepassen van beide cross-linking procedures in industriële toepassing na verdere optimalisatie.

RESUME

La part des technologies membranaires en tant que technique de séparation a rapidement augmenté au cours de ces dernières années grâce à leur large gamme d'applications. Le marché en pleine expansion nécessite des matériaux polymères avancés qui montrent une résistance accrue vis-à-vis du gonflement et de la plastification en séparation de gaz (GS) ou vis-à-vis de solvants forts et des conditions de pH extrême en nanofiltration en milieu organique (SRNF). Aujourd'hui, la réticulation apparait comme une technologie prometteuse pour répondre à ces nouveaux besoins. La réticulation chimique est l'une des techniques les plus couramment utilisées et est basée sur une réaction chimique entre un polymère (par exemple un polyimide) et un réticulant (par exemple une diamine ou un diol). Cependant pour des polymères, tels que les polysulfones (PSU), qui ne contiennent pas de groupes fonctionnels chimique implique plusieurs étapes de traitement et induit des flux de déchets nocifs. La recherche d'une technique de traitement rapide et verte généralement applicable est donc d'une première importance.

Deux nouvelles techniques de réticulation, que sont les traitements par rayons ultraviolets (UV) pour par faisceaux d'électrons (EB), ont donc été explorées dans cette thèse afin d'obtenir des membranes stables chimiquement et thermiquement, ce qui est intéressant pour les applications SRNF. Des membranes asymétriques, composées d'un réseau polymère semi-interpénétrant (SIPN), ont été préparées par séparation de phase induite par un solvant (NIPS). Le PSU a été choisi comme polymère grâce à ses caractéristiques intrinsèques suivantes: propriétés thermiques et mécaniques importante, photosensibilité et absence de groupes réactifs. Les membranes réticulées à structure SIPN ont été obtenues par traitement UV et EB. Ces techniques possèdent plusieurs avantages par rapport à la réticulation chimique: une réduction de la production de déchets, des besoins énergétiques plus faibles et des temps de traitement rapides.

Dans une première partie, nous avons étudié l'influence de la fonctionnalité du réticulant, de l'énergie du rayonnement et du rapport polymère / réticulant sur l'efficacité de la réticulation par EB. Des agents de réticulation à base d'acrylate ont été utilisés. Les membranes obtenues ont été caractérisées par des expériences en ATR-FTIR, SEM et de filtration, ainsi que des essais de stabilité contre des solvants forts. Le meilleur type de réticulant et sa concentration optimale sous une dose d'EB optimale ont ensuite été sélectionnés pour les études suivantes.

Dans la seconde partie, nous avons exploré les effets du rapport solvant / co-solvant et du temps d'évaporation avant la précipitation des membranes en PSU réticulées par la suite soit par UV et soit par EB; le tétrahydrofurane (THF) ou le 1,4-dioxane (DIO) étant utilisés comme solvant. Dans les deux cas, les morphologies membranaires différent en fonction des paramètres étudiés de l'inversion de phase. L'augmentation du temps d'évaporation réduit la formation de macrovides et permet l'apparition de structures spongieuses. Les flux de solvant sont généralement restés trop faible pour que les membranes soient vraiment utiles en SRNF. Un post-traitement a été effectué pour augmenter le flux en immergeant les membranes réticulées dans du dimethylformamide (DMF) pendant 48 h. Les membranes résultantes ont des perméances plus élevées et des taux de rejets plus faibles. Elles sont alors particulièrement intéressantes pour une utilisation en tant que supports stables de membranes composites.

Dans une troisième partie, nous avons étudié les caractéristiques mécaniques, l'effet de l'épaisseur du film de collodion et les propriétés de surface des membranes réticulées par les deux procédés d'irradiation. Le comportement au gonflement de films minces de PSU durcis aux UV en fonction de différents paramètres de durcissement (dose du rayonnement et la fonctionnalité du réticulant) a été analysé par ellipsométrie.

En conclusion, des membranes en PSU asymétriques stables aux solvants ont été développées par deux méthodes simples, respectueuses de l'environnement et hautement efficaces. Les performances en SRNF et la résistance chimique améliorée des membranes réticulées montrent le fort potentiel des deux procédures de réticulation mises en œuvre dans le cadre d'applications industrielles adéquates après une optimisation supplémentaire.

LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy
AFM	Atomic Force Microscopy
CA	Cellulose Acetate
DMAc	Dimethyl acetamide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EB	Electron Beam
EIPS	Evaporation Induced Phase Separation
EtOAc	Ethylacetate
GS	Gas Separation
HSP	Hansen Solubility Parameters
IPA	Propan-2-ol
MF	Microfiltration
MW	Molecular Weight
MWCO	Molecular Weight Cut-Off
NIPS	Non-solvent Induced Phase Separation
NMP	1-Methyl-2-Pyrrolidone
PDMS	Polydimethylsiloxane
PES	Polyethersulfone
PET	Poly(Ethylene Terephthalate)
PI	Polyimide
PSU	Polysulfone
RB	Rose Bengal
RED	Relative Energy Difference
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SIPN	Semi-Interpenetrating Polymer Network
SPEEK	Sulfonated Poly(Ether Ether Ketone)
SRNF	Solvent Resistant Nanofiltration
THF	Tetrahydrofuran
TIPS	Thermal Induced Phase Separation

- TPO 2,4,6-trimethylbenzoyl-diphenyl-phosphineoxide
- UF Ultrafiltration
- UV Ultraviolet
- VIPS Vapour Induced Phase Separation

LIST OF SYMBOLS

А	Absorbance
c _f	Feed concentration
c _p	Permeate concentration
c	Concentration of the absorbing species
E	Energy
I ₀	Intensity of the incident light
Ι	Intensity of the transmitted light
L	Optical path length
Р	Permeance
Р	Pressure
R	Retention
Ra	Solubility parameter distance between two compounds (materials)
R0	Interaction radius of polymer
Tg	Glass transition temperature
δ	Total Hansen parameter
δ_d	Dispersive Hansen parameter
δ_p	Polar Hansen parameter
δ_{h}	Hydrogen bonding Hansen parameter
3	Molar extinction coefficient

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CHAPTER 1

INTRODUCTION AND SCOPE OF THESIS

1.1. MEMBRANE TECHNOLOGY

1.1.1. Membranes and membrane processes

A membrane is defined as *a selective barrier between two phases* [1]. Membranes have become essential in chemical technology and are used in a wide range of applications. The objective of a membrane separation process is to retain one (or more) component(s) of a mixture referred to as retentate, while allowing other components to pass through the membrane, referred to as permeate, under a driving force, as presented in Fig 1 [2].



Fig. 1. Basic scheme of a membrane separation process (adapted from [1]).

1.1.1.1. Membrane structures

Membranes can be categorized into symmetric and asymmetric membranes, based on their structure (Fig. 2). The morphology of symmetric membranes is equivalent across the thickness of the membrane. Both porous and dense structures can be obtained in these kinds of membranes. On the other hand, asymmetric membranes can be classified into three different types as following: porous, porous with dense top layer (integrally skinned) and composite membranes [1].

The thickness of symmetric membranes is in the range of 10 to 200 microns and their properties are constant throughout their cross-section. Asymmetric membranes consist of a thin selective top layer (thickness of 0.1 to 0.5 microns) responsible for the selective separation and a support layer (thickness of 50 to 150 microns) which provides the mechanical support to the top layer. Asymmetric membranes mostly have a higher efficiency than symmetric ones as the flux is principally determined by the thickness of the active layer [1].



composite

Fig. 2. Classification of polymeric membranes according to their morphology (adapted from [1]).

1.1.1.2. Membrane performance

The performance of a membrane is mainly described by following parameters:

$$Permeance = \frac{V}{A * t * p}, (1 / m^2 h bar)$$
(1)

Where V is the collected permeate volume (l), A is the active surface area of the membrane (m^2) , t is the collection time (h), and p is the applied pressure (bar).

$$R = \left(1 - \frac{c_p}{c_f}\right) * 100, (\%)$$
(2)

Where C_f and C_p denote the solute concentrations in the initial feed and in the permeate respectively. In addition, the molecular weight cut off value (MWCO), which states the molecular weight of a reference solute that is retained for 90%, can be further used to express the separation performance. High separation performance, chemical, mechanical and thermal stability, low fouling tendency, and defect-free production are the expected properties from an ideal membrane [1, 3].

Membrane performance can be affected negatively by two phenomena: fouling and concentration polarization. Fouling is a process that results in loss of performance of a membrane, since particles are accumulated on its surfaces or within pores [4]. Concentration polarization is a reversible phenomenon, induced by aggregation of retained particles near the membrane surface turning out in a highly concentrated layer [1].

1.1.1.3. Membrane processeses

Transport across the membrane is always induced by a driving force. Membrane processes are categorized according to the driving force which can be either a thermal, electrical, concentration or a pressure gradient. Pressure driven processes are classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Their details are given in Table 1.

Process	Pressure range	Permeance range	Pore size
	(bar)	(l/m² h bar)	(nm)
Microfiltration	0.1 - 2.0	> 50	20 - 10 000
Ultrafiltration	1.0 - 10	10 - 50	1 - 50
Nanofiltration	5.0 - 35	1.4 - 20	< 2
Reverse Osmosis	10 - 150	0.05 - 1.4	no pores

Table 1. Properties of pressure driven membrane processes [1]

1.2. PREPARATION OF SYNTHETIC MEMBRANES

Several methods are available to prepare synthetic membranes. Some of these methods can be used to prepare polymeric as well as inorganic membranes. The most common methods are sintering, stretching, treck-etching, phase inversion, sol-gel processing, vapour deposition, solution coating and interfacial polymerization [1]. As the phase inversion technique is used to prepare the membrane in this study, it will be discussed in more detail below.

1.2.1. Phase Inversion

The phase inversion process was first developed in the 1960s by Loeb and Sourirajan [5]. During the phase inversion process, a polymer film is transformed from a liquid to a solid state in a controlled manner. This transformation is mostly initiated by liquid-liquid demixing [1, 6]. Two different phases takes place after immersion into coagulation bath, a polymer-rich phase that will form the membrane matrix, and a polymer-lean phase that will form the membrane pores [7]. The phase separation may be induced in four main ways;

- by dipping the cast membrane in a coagulation bath, referred to as Non-solvent Induced Phase Separation (NIPS) [8, 9];

- by laying the cast membrane in a non-solvent vapour phase, referred to as Vapour Induced Phase Separation (VIPS) [10];

- by lowering the temperature, referred to as Thermal Induced Phase Separation (TIPS) [11];

- by vaporazing the solvent from the cast membrane, referred to as Evaporation Induced Phase Separation (EIPS) [12].

NIPS is the most common membrane formation method among the ones mentioned [13]. The membrane morphology obtained through the phase inversion process depends both on the thermodynamical behavior of the polymer solution and on the kinetic aspects of the phase separation. The polymer solution contains polymer, solvent and possibly some additives. The polymer film is prepared by a casting process and immersed into a non-solvent bath, usually water that may contain additives. Exchange of the solvent and non-solvent induces the membrane solidification. Solvent and non-solvent are required to be at least partially miscible [14, 15]. Fig. 3 shows the thermodynamic behaviour of immersion precipitation in a phase diagram of system containing solvent, polymer and non-solvent .



Fig. 3. Phase diagram with schematically shown bimodal demixing (path A) and spinodal decomposition (path B) (adapted from [1]).

The corners of the triangle represent the three components (polymer, solvent, and non-solvent), while any point within the triangle represents a mixture of three components. The system consists of two regions: a one-phase region where all components are miscible and a two-phase region where the system separates into polymer-rich and polymer-poor phases. The line which connects a pair of equilibrium compositions in the phase diagram is called a tie-line. The liquid-liquid phase boundary is the so-called binodal. The composition of the casting solution where the polymer and solvent are fully miscible is indicated in the region outside the binodal. There are two possible demixing paths for the polymer solution to phase separate. Separation can take place either by binodal demixing or spinodal decomposition. The polymer solution follows the binodal demixing (path A) and then reaches the space between the binodal and spinodal. It will then phase separate into a polymer-rich and a polymer-lean phase, of which the compositions are illustrated respectively by A' and A'' in the diagram. Liquid-liquid demixing will occur after passing the binodal. Phase separation appears in the metastable composition region in line with the nucleation and growth mechanism, generating well defined nuclei. This region corresponds to the space between the binodal and the spinodal in phase diagram. A membrane with porous structure is formed in this case. Spinodal decomposition (path B) takes place when the polymer solution passes the region between binodal and spinodal without allowing enough time to start demixing and finishes in the non-stable region inside the spinodal. In this case, two co-continuous phases are developed instead of well-defined nuclei [6, 13, 16].

The kinetic aspects of phase inversion also play an important role in membrane synthesis [6, 17]. Phase inversion can occur immediately after contact with the non-solvent, or it can be delayed and occur a while later after adding the non-solvent. A porous membrane, mostly with macrovoids, is formed by instantaneous liquid-liquid demixing (Fig. 4 a), while a more dense and mostly sponge-like membrane is formed by delayed demixing (Fig. 4 b).





Fig. 4 Examples of morphologies resulting from (a) instantaneous demixing and (b) delayed demixing.

Many phase inversion parameters, such as polymer type and concentration [17-19], solvent/co-solvent choice and ratio [20, 21], evaporation time [21, 22] etc. can influence these kinetics and are discussed in more detail in the following paragraphs.

1.2.1.1. Main parameters of the phase inversion process

Polymer type

For porous membranes, the type of polymer affects solute adsorption, membrane hydrophilicity, and the thermal and chemical stability. For nonporous membranes, the type of polymer also directly influences membrane performance because intrinsic membrane separation properties (solubility and diffusivity) depend on the polymer's chemical structure [13].

The polymer used for solvent resistant nanofiltration (SRNF) membrane is supposed to show chemical stability and solvent resistance. Commercially available polymers have been commonly employed, since they are easy to access and process. They are rendered more stable after post-treatments such as cross-linking [23, 24]. The polymers often used to obtain SRNF membranes by phase inversion will be described in the section 1.3.1.

Co-solvent

One of the simple ways to get a high separation performance with asymmetric membranes is the addition of co-solvent (e.g. tetrahydrofuran (THF) or 1,4-dioxane). A skin-layer is formed, since volatile solvent evaporates from the membrane film before entering the coagulation bath. The skin-layer on the surface of membrane behaves as a strong barrier between the bulk and the non-solvent bath. The in-diffusion of non-solvent and the out-diffusion of solvent are thus hindered and demixing gets delayed. This method was employed to synthesize polysulfone (PSU) and polyimide (PI) SRNF-membranes having enhanced separation performance [20, 24-31].

Evaporation time

In order to obtain a dense skin layer, an evaporation step can also be introduced into the phase inversion process prior dipping membrane film into the coagulation bath. The region with higher polymer concentration expands with longer evaporation time. This leads to the formation of a densified surface skin layer. Mass transfer between the non-solvent and the solvent in the polymer film slows down due to higher resistance created by top layer. As a result, delayed demixing takes place. Evaporation may be performed by simply leaving the cast film in the air for a certain time or by applying convective airflow above the cast film [6]. In general, longer evaporation time lead to denser membranes, as reported for PSU [17, 32], PI [18, 31], and CA [33].

1.3. SOLVENT RESISTANT NANOFILTRATION (SRNF)

Solvent resistant nanofiltration (SRNF) is a pressure driven technique that allows the separation of organic mixtures down to a molecular level [34]. Pressures applied are in the range of 5 to 40 bar. SRNF membranes have molecular weight cut-off (MWCO) values in the range of 200 to 1000 Da. SRNF-performance can generally be considered as reasonable when rejection of a marker compound is more than 90% and the permeance is above $1 \frac{1}{m^2}$ h bar.

SRNF is a relatively young and fast growing technology. SRNF-membranes may be applied in (petro)chemical [35], pharmaceutical [36] and fine chemicals industries [37]. Polymeric membranes are the most employed material for SRNF applications, since they are cheap and easy to handle [38]. The limited thermal and chemical stability is the critical drawback for polymeric membranes. Organic solvent-membrane interactions may lead to extreme swelling or even dissolution of the membrane. Therefore, the major challenge for SRNF is developing membranes stable in a broad range of solvents, without losing performance [6]. Nowadays, phase inversion process is generally used to fabricate asymmetric, integrally skinned SRNF membranes [29, 30].

1.3.1. Polymers for integrally skinned SRNF membranes

Membrane properties are strongly influenced by the polymer choice. The type of polymer mainly affects properties, such as degree of swelling in solvents, chemical and thermal stability and hydropilicity. The most often used polymers for SRNF applications are polyimide (PI) [25, 39, 40], poly(dimethyl siloxane) PDMS [48], poly(ether ether ketone) PEEK [9], poly(aryl sulfones) [17, 41], as well as their blends [42] and derivatives [43]. As the PSU is used in casting solutions in this study, it will be discussed in more detail below.

Polysulfone (PSU) (Fig. 5.) is often selected because of its commercial availability, favorable selectivity-permeability characteristics, and high glass transition temperature (Tg). It possesses good mechanical, thermal, and chemical properties. Futhermore, it is generally easy to prepare asymmetric membranes from PSU solution by the phase inversion method [44]. *N*-methylpyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) are commonly preferred solvents for PSU [13, 27, 28].



Fig. 5. Structure of Polysulfone (PSU).

1.4. (SEMI)-INTERPENETRATING POLYMER NETWORKS

An interpenetrating polymer network (IPN) is defined as a combination of two polymer networks where at least one polymer is synthesised or crosslinked in the presence of the other. In semiinterpenetrating polymer network (SIPN), only one polymer of the assembly is cross-linked to form network and the other polymer is linear or branched. Figure 6 shows schematically the difference between these two networks.



Fig. 6. Schematic structure of an IPN (a) and a SIPN (b) (adapted from [70]).

1.5. CROSS-LINKING

Solvent resistance is a crucial challenge in SRNF technology, since most membranes demonstrate insufficient stability in organic solvents [45]. Currently, cross-linking is getting more attention to overcome this problem by enhancing the chemical resistance of polymeric membranes. There are different ways of cross-linking membranes, such as chemical, thermal, UV or electron beam (EB) [23, 26, 46].

1.5.1. Chemical cross-linking

Chemical cross-linking is one of the most common processes, especially for polyimide (PI) SRNFmembranes. In this method, a cast PI film is first immersed into a non-solvent bath and afterwards into a solution containing the crosslinker (e.g. diamine) [24, 26, 30]. Recently, this technique was facilitated: the crosslinking reaction was combined with the phase inversion process itself by adding the crosslinker to the precipitation bath [26].

1.5.2. Thermal cross-linking

High temperatures are employed for thermal cross-linking of membrane [47]. Thermal crosslinking may be applied to polymers including diacetylene or carboxylic groups [48, 49]. Fang et al. [50] fabricated a PI membrane by first casting a poly(amic acid) (PAA) membrane, followed by room temperature drying, and finally cross-linked by the thermal imidization procedure. Final membrane had an SRNF performance and showed an enhanced resistance in many solvents. Yagci et al. [51] prepared a benzoxazine functional PSU macromonomer, which converted to cross-linked PSU-polybenzoxazine films upon application of heat.

1.5.3. UV cross-linking

UV cross-linking has been usually applied for PI membranes and for membranes consisting of polymers synthesized with photoresponsive functional groups, e.g. double bonds [52-54]. Kang et al. [55] prepared PI based polymer solutions consisting of benzophenone as a photo-initiator and N,N,N',N'-tetramethyl-1,4-phenylenediamine (N-PDA) as cross-linker and applied UV irradiation onto the cast membrane. Permeability in gas separation (GS) increased, but membrane stability was inadequate in *N*-methylpyrrolidone (NMP), even after UV exposure.

Zhong et al. [53] initially synthesized UV cross-linkable sulfonated poly(ether ether ketone) (SPEEK) with side chains comprising double bonds and then applied UV irradiation for fuel cell applications. As a result, UV-cured SPEEK membranes became stable in NMP, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), along with showing a lower water uptake compared to non-cured SPEEK membranes.

A similar procedure was used by Heo et al. [52] to develop a UV cross-linkable sulfonated poly(ether sulfone) (SPES) copolymer consisting of double bonds in the backbone of the polymer. UV-cured SPES based membranes became stable in NMP, DMSO and DMF. Synthesis of a polymer with functional groups is required for both methods.

Having a UV cross-linked membrane stable in organic solvent filtration, is still a challenge especially for membranes based on PSU. The main advantage of UV irradiation is to be more environmental friendly than other techniques [56]. However, the necessity of including photo-initiators in the casting solution makes it more difficult to obtain a membrane with the desired properties, as the phase inversion process is modified and the treatment of the waste streams becomes more delicate [57, 58].

1.5.4. EB cross-linking

An alternative approach for cross-linking is EB irradiation. Linggawati et al. [59] applied EBirradiation to prepare nanofiltration nylon-66 membranes cross-linked by γ aminopropyltriethoxylsilane via sol-gel reaction. EB-curing took place after casting the polymer/crosslinker solution. EB-cured membranes showed satisfactory permeability, excellent removal of neutral solutes and improved rejection of divalent ions.

In another study, a mixture of 4 different acrylates was mixed with an SPEEK-solution and immediately EB-cured after casting to prepare membranes for fuel cell application [60]. ATR-FTIR results confirmed the cross-linking, and EB cross-linked SPEEK membranes showed improved thermal and hydration stability.

With respect to PSU based membranes, only surface functionalization has so far been reported. Schulze et al.[61] functionalized polyethersulfone (PES) membranes with hydrophilic moieties, while Deng et al. [62] grafted acrylic acid and poly(methacrylic acid) to PES by means of EB. Similarly, 2-acrylamido-2-methylpropanesulfonic acid was grafted onto PSU membranes [63]. EB cross-linking possesses advantages, such as less waste production, lower energy requirement, fast reactions and deep penetration of the beam. Furthermore, as the photo-initiator is no longer required like in UV irradiation, the system is simplified and the process becomes environmentally safer. On the other hand, this technique requires expensive and complex electron-beam equipment [64].

1.6. UV IRRADIATION PROCESS

1.6.1. UV light

Ultraviolet (UV) radiation represents wavelengths in the range from 40 to 400 nm. There are four different regions for UV radiation; vacuum UV (VUV) (40–200 nm), UV C (200–280 nm), UV B (280–315 nm), and UV A (315–400 nm). Vacuum UV (VUV) is unsuitable for conventional radiation curing, due to the small penetration depth.

Two different ways of forming UV energy is using either electric current or microwave energy. Curing is used as a term, in general for processing of monomers, oligomers, and polymers by using an irradiation source such as UV light or EB. Curing covers chemical reactions including polymerization, cross-linking, surface modification and grafting. In these processes, electromagnetic irradiation (or light) is used mostly to influence the formation of new chemical bonds. The UV light exposed to polymeric systems typically has wavelengths ranging from 200 to 400 nm (UVC-UVA) [64].

1.6.2. Free radical photopolymerization

Photopolymerization is a technique where the free radicals are created by means of UV light absorption. There are several steps occuring during the photoinduced free radical polymerization process: UV-light absorption by photoinitiator, radical(s) formation, photopolymerization initiation by reaction of a radical with monomer or oligomer, polymer chain propagation, and termination (Scheme 1). There are also some side reactions, like oxygen inhibition, energy transfer, solvent interaction, or quenching, which are affecting each of these stages. Increase of frequency leads to higher energy radiation which induces some chemical reactions by light absorption in a photosensitive system. Eventually, radicals are formed which initiate the cross-linking reactions or polymerization.
$Phin \xrightarrow{hv} Phin^{S_1^*}$	Absorption (3)
$Phin^{S_1^*} \to Phin + h\nu'$	Fluorescence
$PhIn^{S_1^{\star}} \xrightarrow{isc} PhIn^{T_1^{\star}}$	Intersystem crossing
$PhIn^{T_1^{\star}} \rightarrow PhIn + h\nu^{\prime\prime}$	Phosphorescence
$Phln^{T_1^*} + Q \rightarrow Q^* + Phln$	Quenching
$PhIn^{T_1^*} \rightarrow R^{\cdot}$	Radical production (4)
$2R \rightarrow R - R$	Recombination
$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$	Peroxy – inhibition
$R^{\cdot} + M \rightarrow RM^{\cdot}$	Initiation (5)
$RM' + M' \rightarrow RMM' \cdot$	Propagation (6)
$RMM' \cdot + O_2 \rightarrow RMM'O_2 \cdot$	Peroxy – inhibition
$\sim \sim \sim \sim M \cdot + \cdot M' \sim \sim \sim \to \sim \sim \sim M - M' \sim \sim \sim$	Termination (7)

Scheme 1. Radiative and radiationless processes during free radical photopolymerization

The intensity of any light absorbed by a light-absorbing species (chromophores) follows Lambert-Beer's Law (eq. 8):

$$\mathbf{I} = \mathbf{I}_0 \ \mathbf{10}^{-\varepsilon cl} \tag{8}$$

Where I_0 is the intensity of the incident light

I is the intensity of the transmitted light

 ϵ is the molar extinction coefficient (L cm⁻¹ mol⁻¹)

c is the concentration of the absorbing species (mol L^{-1})

l is the optical path length (cm).

Absorbance (A) (or optical density) is indicated as $-\log (I/I0)$, thus A = $\varepsilon cl [64]$.

The Jablonski diagram is an energy level diagram which represents the different states and transitions (Fig. 6.). There are three different energy levels shown in such diagram: S0, S1 and S2. The electronic ground state is represented by S0 and the first and second singlet excited states are represented by S1 and S2 respectively. In addition, T1 and T2 stand for the first and second triplet states, respectively.

All electron spins in the singlet states are paired and the multiplicity is 1. The relative energetic position as compared to other states of the same multiplicity is indicated by the subscripts. Two electrons in the triplet states are no longer antiparallel and the multiplicity becomes 3. The stability

of the triplet state is higher compared to the singlet counterpart (S). This difference in stability is caused by the difference in the Coulomb repulsion energies between the two electrons in the two states, as well as the increase in degree of freedom of the magnetic spins. The Coulomb repulsive energy between two electrons in the singlet excited state, that are confined within the same orbital, is higher than in the triplet excited state where the electrons are now in separate orbitals. The nature of the orbital determines the splitting between these two states (S-T) [64, 65].



Fig.7. A typical Jablonski energy diagram (adapted from [65]).

1.6.3. Photoinitiators type I and type II

A photoinitiator is a compound generating reactive species that will initiate polymerization or crosslinking [64]. There are two types of photoinitators, defined as Type I (leading to photocleavage, Scheme 2.) and Type II (inducing hydrogen abstraction, Scheme 3.) photoinitators. In the case of Type I photoinitiators, a specific bond within the photoinitiator's structure undergoes homolytic cleavage to generate free radicals upon the UV-light absorption. On the other hand, Type II photoinitiators require a co-initiator which are generally a source of abstractable hydrogen to create radicals for initiating polymerization [66].

Aliphatic tertiary amines are known to rapidly transfer a H atom to the excited state of the initiator, therefore they are commonly used as H-donors. The intermolecular H-abstraction mechanism starts with a photoinitiator absorbing light to reach an excited singlet state (S1*). This is directly followed by an intersystem crossing to achieve an excited triplet state (T1*), which is sufficiently long-living to allow to be trapped by the co-initiator. The electron-proton transfer occurs through moving a hydrogen to the excited photoinitiator. As the radical of the photoinitiator is recombined, a new radical is generated on the co-initiator, which in turn initiates the reaction [67-69].



Scheme 2. Intramolecular α-photocleavage of type I photoinitiator (adapted from [69]).



Scheme 3. Intermolecular H-abstraction of type II photoinitiator (adapted from [69]).

1.7. PHOTOSENSITIVITY OF POLY(ARYL SULFONES)

Polysulfones [70] are in the category of intrinsically photosensitive polymers, like polyimides [71]. Upon absorption of UV-light (Scheme 4.) by phenoxy phenyl sulfone chromophores in the backbone of the polymer chain, two radical sites are generated at the end of each polymer chain as a result of Hemolytic cleavage of the carbon-sulfur bond (in the sulfone linkage). Consequently, the formed radicals (aryl and sulfonyl) lead to polymerization at the reactive sites of these radicals [72,73].



Scheme 4. Synthesis of free radicals in a polysulfone molecule (adapted from [70]).

1.8. EB IRRADIATION PROCESS

Electron beam irradiation is a process to obtain specific effects on materials using high-energy electrons produced by an accelerator. It is generally used in the rubber modification, specialty packaging, coating, cable insulation and sterilization [74].

1.8.1. EB-curing

The high-energy electrons production principle is rather simple. First of all, a heated cathode emits the electrons in a vacuum. Then, the acceleration of electrons takes place in the electrostatic field applied between cathode and anode. Generally, an electron optical system is employed to get focused electrons to the accelerator window plane. The electron energy gain is proportional to the accelerating voltage which is shown in electron volts (eV). The electrons pass the vacuum chamber and arrive at the process zone when they have energy high enough to penetrate foils. The thickness of the titanium window foils used ranges from 6 to 14 μ m in the lower energy applications, while it ranges from 40 to 50 μ m for higher energy applications. Extensive shielding is required due to the high energy of the emitted particles and waves.

Acceleration voltage, the EB current, and the EB power are the basic parameters of an EB processor. Efficiency of an electron accelerator is expressed by the ratio of EB power and the electrical power input. The energy of the electrons are indicated by the acceleration voltage. The acceleration voltage is described as the potential difference between cathode and anode of the accelerator. It is usually expressed in kV or MV, and obtained using a resistive voltage divider chain in the high-voltage unit. The EB current refers to the number of electrons emitted from the cathode per second. This current is expressed in mA (1 mA = 6.25×10^{15} electrons per second) at the high-voltage unit. The EB power is the product of the EB current and the acceleration voltage, and measured in kW (1 kW = 10 mA x 100 kV or 10 mA x 0.1 MV). The absorbed dose is the mean value of the ionizing radiation energy that the unit of mass of the processed material absorbs. The unit of the dose is 1 Gray (Gy) = 1 J kg⁻¹ or 1 kGy = 1 J g⁻¹. The dose rate is defined as the dose with respect to unit time, expressed in Gy s⁻¹ = J kg⁻¹s⁻¹. The dose rate is proportional to the EB current when the accelerating voltage is kept constant [75].

Some chemical transitions may occur in the substance used in EB-curing due to the fast electrons and this fact construct the principle of the curing process. The accelerated electrons which have usually energies in the range of keV and MeV are absorbed in the material. After that, the energy degradation process lead to secondary electrons. Coulomb interaction appears among these electrons and absorber molecules. Eventually formation of radicals, ions, trapped electron and excited state of molecules takes place [76].

1.8.2. Free radical polymerization

Electon beam radiation may be used to realise many different processes in polymeric systems, such as grafting, cross-linking and polymerization. Various reactive species have a part in each process. In EB-curing, the most significant reactions are initiated by radicals formation. Inhibition is very crucial in this point. This can be induced by radical scavengers, such as oxygen with unpaired electrons. The free radical mechanism is typically followed in acrylate cross-linking reactions and can easily be inhibited by the same reason. Therefore, nitrogen blanketing is required in most curing applications to avoid the direct oxygen contact with the surface of materials irradiated by EB [75].

Free-radical polymerization is usually applied in most of the EB-curing treatments. There are four steps in this reaction mechanism, as illustrated in in Scheme 5. There is no need for a photoinitiator in formulations treated by EB, since the the free radicals are directly generated by the beam. The cleavage of an organic chemical bond to generate two radicals is induced by EB irradiation in the first step. After that, the start reaction takes place during a radical reaction with the first monomer unit to generate a new radical species. In the third step, formation of a polymer occurs when the additional monomer unit reacts with the new radical in a chain reaction. In the last step, if two radicals cluster, they recombine and the termination reaction takes place [74].

Chapter 1

		EB		
1. Initiation	R-R∙		\longrightarrow	2R
2. Start reaction	$R\cdot + M$		\longrightarrow	RM·
3. Propagation reaction	$RMn\cdot + M$		\longrightarrow	RM_{n+1}
4. Termination reaction	$R\cdot + R\cdot$		\longrightarrow	R-R

Scheme 5. Reaction mechanism of the radical polymerization process.

Formation of a hydrogen atom via the C–H bond cleavage on polymer chain and abstraction of a second hydrogen atom from a next chain are the facts happens during typical postulated mechanism. The H_2 molecule is generated by two hydrogen atoms. Subsequently then the two adjacent polymeric radicals combine to form a cross-link leading to branched chains until, ultimately, a three-dimensional polymer network is formed when each polymer chain is linked to another chain [75].

1.9. SCOPE

Membrane applications are increasingly being introduced in many chemical processes. Due to the expanding market, advanced polymeric materials with broad resistance towards solvents in solvent resistant nanofiltration (SRNF) are strongly demanded. Chemical cross-linking is the most commonly employed method to create such stability. However, for polymers which do not contain functional, chemically reactive groups in their backbone, such as polysulfones (PSU), this technique is impractical. Additionally, harmful waste streams and several processing steps make it mandatory to develop alternative techniques which are generally applicable, more simple and environmentally friendly. This PhD thus focuses on the synthesis of solvent stable PSU-based membranes, prepared via UV or EB cross-linking.

1.10. THESIS OVERVIEW

This thesis, consisting of six chapters including this introduction chapter, defines two radiation based (UV and EB) curing techniques to synthesize membranes composed of a semi-interpenetrating network of polysulfone (PSU) and cross-linked polyacrylate with enhanced solvent stability and SRNF performance. The environmentally friendly character, high reaction rate, low energy demand, and deep penetration capability render UV and EB irradiation most attractive the methods for curing polymeric membranes.

Chapter 2 describes a new method to prepare such SRNF membranes with enhanced solvent resistance via EB radiation. Various parameters, including the cross-linker functionality, radiation

energy dose and polymer/cross-linker ratio, are explored to optimize the curing efficiency. SRNF performance and solvent stability of the EB-cured membranes are presented.

Chapter 3 involves the study of polymer concentration, evaporation time before precipitation and co-solvent/solvent ratio as phase inversion parameters for EB-cured PSU-based membranes to tune their properties. The influence of the studied parameters on the morphology and separation performance is analysed.

Chapter 4 discusses the influences of phase inversion parameters on a UV-cured PSU system for the preparation of SRNF-membranes via NIPS. Evaporation time before immersion into the non-solvent bath as well as co-solvent content are selected as parameters to tune the separation performance of the UV-cured membranes.

Chapter 5 presents the effect of UV and EB cross-linking on mechanical and surface properties of PSU-based membranes containing acrylates. Additionally, the swelling extent of UV-cured PSU thin films is investigated varying the radiation dose and cross-linker functionality.

Finally, general conclusions and future work are given in chapter 6.

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CHAPTER 2

EB DEPTH-CURING AS A FACILE METHOD TO PREPARE HIGHLY STABLE MEMBRANES

Based on: Veysi Altun, Michael Bielmann and Ivo F. J. Vankelecom, RSC Advances, 6, 2016, 55526-55533.

Graphical Abstract



Abstract

Solvent resistant polymeric membranes were prepared via electron beam (EB) curing after adding acrylate monomers to existing membrane casting solution. Various parameters including the cross-linker functionality, radiation energy dose and polymer/cross-linker ratio were investigated to optimize the curing efficiency. Resulting EB-cured polysulfone (PSU) membranes showed excellent solvent stability with 96% Rose Bengal (1017 Da) retention at isopropanol permeance of 0.062 l/m² h bar in a typical solvent resistant nanofiltration (SRNF) system. Using the same technique, membranes with much higher permeances and lower rejections could be obtained, with excellent potential use as stable support layers for subsequent deposition of denser selective layers or for applications under harsh conditions.

2.1. INTRODUCTION

Polysulfone (PSU) possesses robust thermal and mechanical properties due to its high glass transition temperature [1, 2]. It is frequently employed in the synthesis of asymmetric membranes with porous structure prepared via non-solvent induced phase separation (NIPS) [3-7]. However, PSU dissolves in many solvents, especially in aprotic solvents, and is therefore not very suitable for preparation of membranes for Solvent Resistant Nanofiltration (SRNF) nor for use as support layers for thin film composites (TFC) where coating solutions contain harsh solvents [8-16]. Polymer cross-linking can overcome this problem. Chemical cross-linking is one of the most frequently used processes to increase solvent stability of membranes, e.g. for polyimide (PI) membranes, where diamines and diols are employed as cross-linkers [17-19]. However, due to the lack of functional groups, this method cannot be applied to PSU membranes and, in addition, this method requires several steps and leads to harmful waste streams [20].

UV cross-linking could overcome these issues. It has so far mainly be applied in membrane technology to modify membrane surfaces [6, 21, 22]. Recently, a solvent-resistant semiinterpenetrated network was created via photo-irradiation by using polyfunctional acrylates in a PSU matrix [23]. The necessity of including photo-initiators in the casting solution makes it more difficult to obtain a membrane with the desired properties, as the phase inversion process is modified and the treatment of the waste streams becomes more delicate [24, 25]. Another alternative approach for obtaining solvent stable membranes is electron beam (EB) irradiation, possessing advantages, such as less waste production, less energy requirement, fast reactions and deep penetration of the beam. Furthermore, as the photo-initiator is no longer required, the system is simplified and the process becomes environmentally safer. EB can be classified into three types, based on the irradiation dose which signifies the penetration depth: these are low (100–500 kV), medium (500–5000 kV) and high energy EB (5000–10000 kV) [26-28]. In the EB-irradiation process, electrons in the polymers are excited and start the initiation of cross-links [29, 30].

EB-irradiation has been employed earlier to cure polymeric membranes [31-34] and to modify their surfaces. With respect to PSU based membranes, only surface functionalization has so far been reported. Schulze *et al.* [35] functionalized poly(ethersulfone) (PES) membranes with hydrophilic moieties, while Deng *et al.* [36] grafted acrylic acid and poly(methacrylic acid) to PES by means of EB. Similarly, 2-acrylamido-2-methylpropanesulfonic acid was grafted onto PSU membranes [37]. Different types of cross-linkers are commercially available. Viscosity of the polymer solution and

cross-linking degree of the final product are influenced by the cross-linker chemical structure and its relative content. Acrylate based cross-linkers are preferred generally for UV and EB cross-linking thanks to their fast polymerization and short time exposure [38].

In this study, EB depth-curing is applied as a simple and effective way to cross-link asymmetric PSU membranes in a one-step procedure to render them solvent stable. Using acrylate-based cross-linkers, effects of EB-dose, cross-linker type and cross-linker concentration on curing efficiency, membrane performance, morphology and solvent stability are explored.

2.2. EXPERIMENTAL

2.2.1. Materials

PSU (Udel P-1700 LCD, $Mn = 21000 \text{ g mol}^{-1}$) was kindly supplied by Solvay and dried overnight at 100 °C prior to use. The polyethylene terephthalate non-woven fabric Novatexx 2413 was kindly provided by Freudenberg (Germany). The multifunctional acrylate monomers trimethylolpropane triacrylate (SR351, Sartomer), pentaerythritol tetra-acrylate (SR295, Sartomer) and dipentaerythritol penta-acrylate (SR399LV, Sartomer) were used as cross-linkers. Table 1 shows the details of the cross-linkers used. Rose Bengal (RB) was purchased from Sigma-Aldrich. *N*-methylpyrrolidone (99%, NMP), tetrahydrofuran (99.5%, THF), acetone (99.8%), *N*,*N*-Dimethylacetamide (99%, DMAc), toluene (99.8%, Sigma-Aldrich), cyclohexanone (99%,Sigma- Aldrich), butylacetate (99%, Acros), ethylacetate (EtOAc, 99.5%, Acros), xylenesmixture (ACSreagent, Sigma-Aldrich) and *N*,*N*-dimethylformamide (99.5%, DMF) were obtained from Acros and used as received.

Code	Name	$MW (g mol^{-1})$	Structure
3AC	Trimethylolpropane tri-acrylate (Sartomer™ SR351)	296	
4AC	Pentaerythritol tetra-acrylate (Sartomer [™] SR295)	352	
5AC	Dipentaerythritol penta-acrylate (Sartomer™ SR399LV)	524	H ₂ C =

Table 1 List of cross-linkers and their main properties.

2.2.2. Membrane synthesis

Integrally skinned asymmetric PSU membranes were prepared via NIPS. Polymer casting solutions were prepared containing 21 wt% PSU in NMP and THF (with a constant ratio of 85/15) and an acrylate cross-linker with varying concentrations 10 to 20 wt%. The solutions were cast onto an NMP-saturated PET non-woven fabric (Novatexx 2413) using an automated casting knife set at 200 μ m (1.81 m/min, Braive Instruments, Belgium). The film was left in ambient air for 30 s in order to evaporate THF and form a denser top layer. Membranes were stored in deionized water until EB cross-linking. Table 2 shows the compositions of all membranes prepared with different polymer concentration, cross-linker functionality and concentration.

2.2.3. EB-curing

Membranes were cross-linked using EB-curing set-up (COMET, EBLab200, Switzerland) at 200 kV accelerating voltage and 9.3 mA beam current with a maximum dose of 100 kGy given during each pass. Three different irradiation doses were applied of 100, 300 and 500 kGy. Some cured PSU membranes were impregnated after EB-curing to enhance the flexibility and avoid pore collapse, by soaking them in a solution comprising 40%(v/v) of glycerol in propan-2-ol for 48 h at room

temperature, and subsequently air-dried. ATR-FTIR and SEM was applied to the non-impregnated part of the membranes.

2.2.4. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR was performed to monitor the conversion of acrylate double bonds using a Varian620-FTIR equipped with a diamond ATR crystal. The conversion was measured based on the IRabsorbance received by non-cured and EB-cured membranes for the C=C group at 810 cm⁻¹ and the C=O group at 1728 cm⁻¹, following Equation 1.

$$Conversion = \left(1 - \frac{\left(\frac{C=C}{C=O}\right)cured}{\left(\frac{C=C}{C=O}\right)non-cured}\right) \times 100$$
(1)

Membrane	PSU	NMP	THF	Cross-linker	Cross-linker
	(wt%)	(wt%)	(wt%)	(wt%)	Туре
M0	21	59.25	19.75	-	-
M1	21	51.75	17.25	10.00	3AC
M2	21	49.87	16.63	12.50	3AC
M3	21	48.00	16.00	15.00	3AC
M4	21	44.25	14.75	20.00	3AC
M5	21	51.75	17.25	10.00	4AC
M6	21	49.87	16.63	12.50	4AC
M7	21	48.00	16.00	15.00	4AC
M8	21	44.25	14.75	20.00	4AC
M9	21	51.75	17.25	10.00	5AC
M10	21	49.87	16.63	12.50	5AC
M11	21	48.00	16.00	15.00	5AC
M12	21	44.25	14.75	20.00	5AC
M13	9	86.00	-	5.00	5AC

Table 2 Membrane compositions (all cured with a 300 kGy EB-dose).

2.2.5. Scanning electron microscopy (SEM)

Membrane cross-section images were obtained by using a Philips XL30 FEG scanning electron microscope. The membrane samples were freeze-cracked in liquid nitrogen. Samples were coated with a 1.5–2 nm gold layer using a Cressington HR208 high-resolution sputter coater to reduce sample charging under the electron beam.

2.2.6. Swelling/solvent stability test

The solvent stability of the prepared and cured PSU-membranes was determined by visual inspection after immersing membrane samples in various solvents at room temperature for at least 24 h.

2.2.7. Filtration experiments

Filtrations were carried out at room temperature and selected pressure in a high-throughput filtration module (HTML, Belgium) [39, 40], allowing for simultaneous filtrations of 16 membranes. Membrane discs were supported by a porous stainless steel disc and sealed with Viton[®] O-rings. The active membrane surface area was 0.000452 m². Solutions of 17.5 μ M Rose Bengal (1017 Da) in IPA, THF and acetone were used as feed solutions and stirred magnetically at 400 rpm to reduce concentration polarization. Permeance (P, 1/m² h bar) was determined gravimetrically by weighing the collected permeate. Rejection (R, %) is defined as (1–C_p/C_f)×100, where C_f and C_p denote the solute concentrations in the initial feed and in the permeate respectively. Permeate and feed concentrations were measured on a Perkin-Elmer Lambda 12 UV–vis spectrophotometer at a wavelength of 555 nm.

2.3. RESULTS AND DISCUSSION

2.3.1. Cross-linker conversion

2.3.1.1. Effect of cross-linker functionality and concentration

As the efficiency of EB cross-linking can be improved by selecting the appropriate cross-linker and its concentration, the effect of different cross-linker concentrations and types was studied in detail. Casting solutions were prepared by using three types of cross-linker (3AC, 4AC and 5AC) with different acrylate functionalities and concentrations. The EB cross-linking efficiency of the cured compared to non-cured membranes was verified qualitatively by ATR-FTIR analysis as shown in Fig. 1.

In addition to this, Fig. 2 demonstrates the acrylate double bond conversion of the different crosslinkers as a function of their concentration in the casting solution quantitatively as calculated according to equation 1.



Fig. 1. ATR-FTIR spectra from 500 to 2000 cm⁻¹ of non-cured and EB-cured membranes containing 15 wt% of the 3AC, 4AC and 5AC cross-linker.



Fig. 2. Influence of the cross-linker type and its concentration in the casting solutions on the conversion of the C=C bond of the membrane under EB radiation.

It can be seen that the double bond conversion increased with increasing acrylate functionality and with increasing concentration in the casting solution. The lowest double bond conversion of 36% was observed for the 10% tri-acrylate cross-linker (3AC). For the tetra (4AC) and penta-acrylate (5AC) cross-linkers, the double bond conversion rate increased to 57% and 86%, respectively, for the same concentration. The best cross-linking was achieved for 5AC at a 20% concentration.

2.3.1.2. Effect of EB-dose

Another important parameter affecting EB cross-linking performance is the irradiation dose. The EB cross-linking efficiency of the cured membranes was verified qualitatively by ATR-FTIR analysis as shown in Fig. 3 as a comparison with non-cured membranes.

Fig. 4 illustrates how the double bond conversion of formed membranes changes by increasing the applied EB-dose quantitatively as calculated according to equation 1. Three different doses (100, 300 and 500 kGy) were applied to all 21 wt% membranes. For any casting solution, an EB-dose of 100 kGy was insufficient to create the required double bond conversion to keep the membranes stable in solvents, like NMP, DMF and THF (Table 5).The double bond conversion increased from 71% at 100 kGy to 86% and 95% at 300 and 500 kGy, respectively, for the 5AC-membrane. As the stability increased, membranes became more brittle, but it was still possible to use them in filtration.



Fig. 3. ATR-FTIR spectra from 500 to 2000 cm⁻¹ of non-cured and EB-cured membranes containing 15 wt% of the 5AC cross-linker cured at 100, 300 and 500 kGy.



Fig. 4. Influence of the EB-dose on the conversion of the C=C bond of the membranes cast from 21 wt% solutions.

2.3.2. Membrane morphology

Based on above results, 5AC was selected as cross-linker for further analysis of network structure and membrane performance. SEM cross-section images of the different PSU membranes are shown in Fig. 5. As the NIPS process is changed by the presence of the additives in the cast film, the membrane microstructure shows some small changes: finger-like macrovoids become somewhat longer in the membranes prepared with additive compared to the reference membrane (Fig. 5 a to c).

Earlier studies indicated that macrovoid formation is associated with instantaneous demixing [41-44]. In present case, this can probably be linked to the more hydrophilic nature of the cross-linkers which act as a kind of non-solvent additive in the casting solution. The limited compatibility between PSU and the acrylate cross-linkers thus results in thermodynamically less stable solutions [45]. The non-cured and EB-cured membranes demonstrated a more defined top layer compare to reference membrane (Fig. 6 a–c).

Fig. 5d to f shows that casting solutions prepared with cross-linkers with higher acrylate functionality lead to formation of slightly larger macrovoids. Fig. 5g to i shows the dependence of membrane morphology on irradiation dose. The macroscopic structure of the membranes was not affected significantly within the range of the applied irradiation dose. Similar behavior with the same acrylate has also been observed in morphology of PSU-based membranes by UV irradiation.[23] The SEM images also reveal that EB radiation did not damage the membrane structure at the resolution reached in these SEM-images.[37]



Fig. 5. SEM pictures of cross-sections of reference and EB-cured membranes: (a-c) influence of additive and EB-curing; (d-f) influence of cross-linker functionality; (g-i) influence of EB-dose.



Fig. 6. SEM pictures of cross-sections of reference and EB-cured membranes: (a-c) influence of additive and EB-curing (high magnification, 3000x).

2.3.3. Membrane performance

The separation performance of the membranes was highly affected by the EB-irradiation. Table 3 shows a sharp decrease in IPA permeance from 1.90 to 0.02 l/m^2 h bar and an increase in rejection from 78 to 90% upon curing (comparing M0 and M1). These results suggest that a distinct densification of the selective layer occurred during EB-curing, which is obviously not observable at this SEM-resolution. The use of strong irradiation or the intense cross-linking effect could both form a possible explanation of this membrane performance change, as both processes create a local

polymer rearrangement [23]. Another membrane composition (M13) was employed to achieve membranes which are, upon irradiation, not reduced to membranes without useful fluxes. Under the same curing conditions, membrane M13 ended up with a performance of 8.06 l/m² h bar with 33.9% RB rejection, opening the possibility to use these very stable and easy to prepare membranes as supports for TFC-membranes.

	1	
Membranes	Permeance (l/m ² h bar)	Rejections (%)
Non-cured (M0)	1.90 ± 0.30	78.1 ± 4.2
EB-cured (M1)	0.02 ± 0.01	90.3 ± 3.5
EB-cured (M13)	8.06 ± 0.20	33.9 ± 1.2

Table 3 Filtration performance of the reference and EB-cured.

2.3.3.1. Effect of cross-linker functionality and concentration

Fig. 7 illustrates the influence of the acrylate functionality and the acrylate concentration in the casting solution on membrane performance. IPA permeance was reduced from 0.020 to 0.015 l/m^2 h bar, while the RB retention increased from 90.4% to 93.9% when increasing the 3AC-concentration from 10 to 20%. A stepwise decrease of IPA permeance and an increase of RB retention was observed when replacing the 3AC by the tetra- or penta-functional acrylates in the casting solution. A similar trend was for 3AC observed for 4AC and 5AC when increasing the concentration from 10 to 20%. These results show that by increasing the cross-linker functionality and its concentration, a semi-interpenetrated network was created [46], which increased the retention and lowered the permeance.



Fig. 7a. Influence of the cross-linker type and concentration in the casting solution on the permeance of EB-cured (300 kGy) PSU membranes.



Fig. 7b. Influence of the cross-linker type and concentration in the casting solution on the rejection of EB-cured (300 kGy) PSU membranes.

2.3.3.2. Effect of EB-dose

It can be seen that by applying a dose of 100 kGy, the membrane permeance immediately dropped to 0.05 l/m^2 h bar (Fig. 8a) with a RB retention of 89.9% (Fig. 8b) coming from 1.90 l/m² h bar and 78.1% respectively for the untreated reference membrane. An additional decrease in permeance was

observed by further increasing the irradiation dose to 300 and 500 kGy. The rejections seemed to show a little increase for 500 kGy, but all within experimental error. Although the membranes cured at 100 kGy showed a higher permeance, the double bond conversion is comparatively low, making these membranes probably less suitable for SRNF application or for later coating procedures when applied as a support for TFCs. The solvent stability was explored below.



Fig. 8a. Influence of EB-dose on permeance of EB-cured PSU membranes (all membranes include 15 wt% cross-linker in the casting solution).



Fig. 8b. Influence of EB-dose on rejection of EB-cured PSU membranes (all membranes include 15 wt% cross-linker in the casting solution).

2.3.3.3. Performance of EB-cured membranes in acetone and THF

To assess the solvent stability of EB-cured membrane, further filtrations were performed with RB in THF and acetone, solvents in which PSU membranes are normally prone to undergo very strong swelling and/or dissolution. The EB-cured membrane (M11), containing 15 wt% 5AC cross-linker and cured with 300 kGy was used for these filtrations. The membranes exhibited stable performance with RB rejections >80% (Fig. 9). The permeability order of acetone >THF >IPA reflects the different solvent-membrane interactions and physico-chemical properties of the solvents, such as viscosity and molar volume [47, 48]. Table 4 shows the correlation of these 2 parameters with the solvent permeances [49]. The separation of organic mixtures is a complex process. There are various models describing transport through SRNF membranes [3, 13]. In this study, the Bhanushali model was used [47] to explain membrane performance change when the feed solution is based on different solvents.

Table 4 The physico-chemical properties of the solvents used for filtrations.

			Molar
Solvents	Molar volume	Viscosity	volume/viscosity
	(cm^3/mol)	(cP)	(cm ³ /mol cP)
IPA	76.46	2.00	38
THF	81.09	0.48	168
Acetone	73.42	0.31	232



Fig. 9. Filtration performance of EB-cured membrane (M11) for RB in acetone and THF.

2.3.4. Solvent stability

Tables 5 and 6 demonstrate the stability of the reference (M0) and the EB-cured membranes in different solvents. All membrane types were stable in propanol. The reference membrane exhibited some visible swelling in acetone and butyl acetate, while the EB cross-linked membranes were almost all fully stable in these solvents. The reference membrane was soluble in other solvents (toluene, THF, NMP and DMF), while EB-cured membranes prepared with cross-linker 3AC were soluble in THF, NMP and DMF. Similar behavior was observed for the membranes prepared with cross-linkers 4AC and 5AC and cured with the lowest energy dose of 100 kGy. Membranes prepared with cross-linkers 4AC or 5AC and cured at irradiation dose of minimum 300 kGy showed a significantly increased stability in most of the solvents. It is thus mandatory to use at least tetra-functional acrylate cross-linkers and an irradiation dose of 300 kGy to have a full solvent stability.

 Table 5 Solvent stability of membranes as a function of cross-linker functionality and concentration cured at 300 kGy.

			3A	кС			4 <i>A</i>	AC				5AC		
Solvent	M0	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13
		10	12.5	15	20	10	12.5	15	20	10	12.5	15	20	5
IPA	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Acetone	Х	+	+	+	+	+	+	+	+	+	+	+	+	+
Butyl acetate	Х	Х	+	+	+	Х	+	+	+	Х	+	+	+	+
Toluene	-	х	Х	+	+	х	+	+	+	х	+	+	+	+
THF	-	-	-	-	-	-	-	-	-	Х	-	-	Х	Х
NMP	-	-	-	-	-	-	-	-	-	Х	-	-	Х	Х
DMF	-	-	-	-	-	-	-	-	-	Х	-	-	Х	Х
DMAc	-	-	-	-	-	-	-	-	-	Х	-	-	Х	Х

+stable, X swelling, - dissolution

Solvent	100 kGy	100 kGy	100 kGy	500 kGy	500 kGy	500 kGy
Solvent	(3AC)	(4AC)	(5AC)	(3AC)	(4AC)	(5AC)
IPA	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
Butyl acetate	Х	Х	+	Х	+	+
Toluene	-	-	+	Х	+	+
THF	-	-	-		Х	Х
NMP	-	-	-	-	Х	Х
DMF	-	-	-	-	Х	Х
DMAc	-	-	-	-	Х	Х

Table 6 Solvent stability of membranes containing 15 wt% of cross-linker as a function of EB-dose.

+ stable, X swelling, - dissolution

2.4. CONCLUSION

EB-curing was used successfully for the preparation of solvent-stable, cross-linked PSU-based membranes. Appropriate combinations of acrylate functionality, preferably penta-functional, and EB-dose of at least 300 kGy, were essential in order to enhance the chemical stability of the membranes. In general, increasing the cross-linker functionality and the EB-dose led to a decrease in IPA permeance and increase in RB retention. The decrease in permeance was unfortunately so significant that practical use of the EB-cured membranes in SRNF is excluded. Morphological analyses showed that macrovoids became slightly larger by adding more cross-linker and by increasing the acrylate functionality. Compared to UV-curing, exclusion of the photo-initiator thus makes EB treatment an attractive and reliable new depth-curing method for stable PSU membranes, but only for use in UF. These membranes seem especially attractive as an ultra-stable supports for later preparation of TFC membranes for e.g. NF or gas separation.

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CHAPTER 3

STUDY OF PHASE INVERSION PARAMETERS FOR EB-CURED PSU-BASED MEMBRANES

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Graphical Abstract



Abstract

Asymmetric EB-cross-linked polysulfone (PSU) membranes suitable for solvent resistant nanofiltration (SRNF) were prepared via the phase inversion method. The influence of phase inversion parameters including polymer concentration, evaporation time prior to immersion and co-solvent/solvent ratio was investigated to optimize the separation performance. When the PSU concentration increased from 15% to 21%, Rose bengal (RB) rejection varied from 84.7 to 94.3% and isopropanol (IPA) permeance decreased from 0.051 to 0.015 l/m² h bar. Rejection increased from 88.6 to 94.7%, while permeance decreased from 0.039 to 0.007 l/m² h bar with increasing evaporation time from 0 to 100 s for the PSU membranes cast from a solution that contained a THF/NMP ratio of 16/48. A similar impact was also obtained when the co-solvent/solvent (THF/NMP) ratio was increased from 0/100 to 30/70 at 30 s evaporation time: rejection increased from 86.3 to 96.1%, while permeance decreased from 0.042 to 0.011 l/m² h bar. The EB-cured PSU membranes were further characterized by scanning electron microscopy (SEM) and solvent resistance tests.

3.1. INTRODUCTION

Cross-linked PSU-based membranes have been studied for a wide range of applications. In gas separation membranes, cross-linking is mainly introduced to prevent plasticization and to enhance separation performance [1-3]. Cross-linked PSU-based membranes have also been employed in pervaporation [4] and used in thin film composites as support layer [5]. Moreover, solvent resistant nanofiltration (SRNF) is specifically a very attractive field for these highly stable membranes as they exhibit excellent stability in most organic solvents, such as acetone, toluene, tetrahydrofuran (THF), *N*-methylpyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF) [6-9].

Chemical cross-linking is the primary technique to improve the solvent stability of polymeric membranes [10, 11]. However, it has to be replaced with other cross-linking methods in the case of PSU, due to the intrinsic limited chemical reactivity resulting from the absence of reactive groups [12]. Radiation-based cross-linking via UV or electron beam (EB) in that case is a more suitable process for PSU cross-linking [13-15]. Stream of electrons that moves in same direction forms EB. Rapid reactions, low energy demand, high radiation dose and deep penetration capability render the EB-curing method most attractive. Moreover, the cross-linking procedure becomes simple and environmentally friendly since photo-initiators are not required [16, 17]. EB-irradiation has been mainly applied earlier for surface modification of PSU membranes [14, 18, 19]. Recently, we have developed an EB-depth curing method to prepare highly stable PSU-based membranes [20]. In that approach, EB-irradiation was performed to PSU-membranes containing acrylate cross-linkers, synthesized via non-solvent induced phase separation (NIPS) [6]. Membrane performance, morphology and solvent resistance were investigated using various acrylate functionalities and EB-doses.

Even small variations in the composition of the casting solutions and synthesis procedures may have strong effects on the final SRNF-membrane performance and morphology [6, 21-29]. A detailed investigation of the phase inversion parameters was thus performed here to obtain better performances, i.e. higher permeances combined with improved rejections, with EB cross-linked PSU-based membranes via this method. From the previous study, a spesific EB-depth cured membrane was thus selected for further optimization by tuning following crucial phase inversion parameters: the polymer concentration in the casting solution, evaporation time prior to immersion, and solvent/co-solvent ratio. The SRNF performance, cross-section morphology and solvent stability of the resultant EB-cured PSU membrane were analyzed.

3.2. EXPERIMENTAL

3.2.1. Materials

PSU (Udel P-1700 LCD, $Mn = 21000 \text{ g mol}^{-1}$) was kindly supplied by Solvay and dried overnight at 100 °C prior to use. The polyethylene terephthalate non-woven fabric Novatexx 2413 was kindly provided by Freudenberg (Germany). Dipentaerythritol penta-acrylate (SR399LV, Sartomer) was used as cross-linker. Rose Bengal (RB) was purchased from Sigma-Aldrich. Isopropanol (99.5%, IPA), *N*-methylpyrrolidone (99%, NMP), tetrahydrofuran (99.5%, THF), acetone (99.8%), N,N-dimethylacetamide (99%, DMAc), toluene (99.8%), *N*,*N*-dimethylformamide (99.5%, DMF) were obtained from Acros and used as received.



Fig. 1. Chemical structure of the Dipentaerythritol penta-acrylate.

3.2.2. Membrane synthesis

Three different series of membranes were prepared to determine the influence of the polymer concentration, evaporation time and role of co-solvent as phase inversion parameters on the performance and morphology of the EB-cured PSU-membranes. In the first series, the influence of the polymer concentration was analysed by using an NMP-based solution with 15, 18 and 21 wt% of PSU. In the second series, the influence of the evaporation time was analysed by using an NMP-based solution containing THF as a co-solvent in a 85/15 ratio. Evaporation times of 0, 10, 20, 30, 60 or 100 s were applied. It has to be mentioned that all cast films were evaporated for roughly about 5 s extra, which was the required time to move the cast film from the casting equipment to the coagulation bath. In the third series, the influence of co-solvent was analyzed by using an NMP (boiling point, 202 °C) based solution with THF (boiling point, 66 °C) as a co-solvent keeping a constant evaporation time of 30 s, but with various ratios of THF/NMP: 0/100, 5/95, 10/90, 15/85, 20/80 and 30/70. All samples were prepared at room temperature under atmospheric conditions. In the second and third series, the polymer concentration was kept constant at 21 wt%. All samples were prepared by using cross-linker an amount of 5 wt%. The solutions were cast onto an NMP-saturated PET non-woven fabric (Novatexx 2413) using an automated casting knife with a thickness

of 200 μ m (1.81 m/min, Braive Instruments, Belgium). Membranes were stored in deionized water until the EB cross-linking process.

3.2.3. EB-curing of asymmetric PSU-based membranes

Membranes were cross-linked using EB-curing (COMET, EBLab200, Switzerland) at a 200 kV accelerating voltage and 9.3 mA beam current with a maximum dose of 100 kGy given during each pass. In accordance with previous study [20], an energy dose of 300 kGy was chosen to cure the membranes. Some cured PSU membranes were impregnated after EB-curing to enhance the flexibility and avoid pore collaps by soaking them in a solution comprising 40%(v/v) of glycerol in propan-2-ol for 48 h at room temperature, and subsequently air-dried. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and SEM were applied to the non-impregnated parts of the membranes.

3.2.4. Viscosity measurements

The viscosity of the casting solutions measurements was measured with an Anton Paar MCR501 rheometer with a cone-plane geometry with solvent trap at 20 oC. The sample temperature was controlled by a Peltier element with high accuracy. Viscosity at different shear rates was measured in steady-shear flow from 0.01 to 100 1/s. Data acquisition and analysis was done using RheoPlus software (Anton Paar GmbH, Austria).

3.2.5. Scanning electron microscopy (SEM)

Membrane cross-section images were obtained using a Philips XL30 FEG scanning electron microscope. The membrane samples were freeze-cracked in liquid nitrogen. Samples were coated with a 1.5–2 nm gold layer using a Cressington HR208 high-resolution sputter coater to reduce sample charging under the electron beam.

3.2.6. Solvent stability

The solvent resistance of the PSU-membranes was determined by visual inspection after immersing membrane samples in various solvents at room temperature for at least 24 h.

3.2.7. Filtration tests

Filtrations were performed at room temperature at selected pressures in a high-throughput filtration module (HTML, Belgium) [24, 30], allowing for simultaneous filtrations of 16 membranes. Membrane coupons were supported by a porous stainless steel disc and sealed with Viton[®] O-rings. The active membrane surface area was 0.000452 m². A solution of 17.5 μ M Rose Bengal (1017 Da) in IPA was used as feed and stirred magnetically at 400 rpm to reduce concentration polarization. Permeance (P, 1/m² h bar) was determined gravimetrically by weighing the collected permeate. Rejection (R, %) is defined as (1–C_p/C_f)×100, where C_f and C_p denote the solute concentrations in the initial feed and in the permeate respectively. These concentrations were measured on a Perkin-Elmer lambda 12 UV–Vis spectrophotometer at 555 nm.

3.3. RESULTS AND DISCUSSION

3.1. Influence of PSU concentration

3.1.1. Filtration performance

Fig. 2 represents the IPA permeance and RB rejection data obtained with EB-cured PSU-membranes prepared from casting solutions with polymer concentrations between 15 wt% and 21 wt%. The NMP/THF ratio and evaporation time of the cast films were kept constant as 85/15 and 30 s respectively prior to immersion precipitation. The IPA permeances decreased with higher PSU concentration from 0.051 to 0.015 $1/m^2$ h bar, while the RB rejections slightly increased with increasing PSU concentration, hardly above experimental error. Overall, especially the changes in rejection were not as significant as expected. This might be explained by the excessive cross-linking of all prepared membranes that takes place due to the intrinsic energy of EB as was reported in our previous study [20]. This seemingly densifies all skin layers of the membranes to a very large extend. The general effect of polymer concentration in the casting solution is in accordance with literature where it has been studied already for *e.g.* polyimidie (PI) and PSU-based SRNF membranes [26, 31]. Due to the increasing initial polymer concentration in the casting solution, a higher concentration is present at the polymer/non-solvent interface which retards the diffusion of non-solvent. Thus, demixing is delayed and a denser or thicker skin layer is formed which especially results here in a lowered permeance, which is obviously not desired [1].



Fig. 2. Effect of PSU concentration in the casting solution on the separation performance of EBcured PSU-membranes (conditions: 30 s of evaporation time and 15/85 ratio of THF/NMP).

3.1.2. Membrane morphology

Fig. 3 illustrates the cross-sections of the membranes consisting of 15 wt%, 18 wt% and 21 wt% of PSU. It is clear that the number of macrovoids decreases and their size increases with increasing polymer concentration. Increasing the polymer concentration in the casting solution leads to elevated polymer concentrations at the interface of the cast membrane and the precipitation bath. As shown in Table 1, the viscosity of casting solution increases from 2.17 to 2.93 Pa.s by increasing the PSU concentration from 15 to 21 wt%. In this way, the higher viscosity of the film slows down the non-solvent diffusion and thus limits the macrovoid formation [21, 32].



Fig. 3. Effect of the PSU concentration in the casting solution on the morphology of the resulting EB-cured PSU membranes as observed in SEM cross-section images: (a) 15 wt%, (b) 18 wt%, (c) 21 wt% in THF/NMP (15/85).

PSU concentration	Viscosity		
(wt%)	(Pa.s)		
15	2.17		
18	2.49		
21	2.93		

Table 1 Viscosity of the casting solutions containing various PSU concentration.

3.2. Influence of evaporation time

3.2.1. Filtration performance

One of the commonly used methods to have a denser membrane skin layer is evaporation of volatile (co-)solvents from the casting solution before coagulation [21, 22, 26, 31]. This process leads to the formation of a thin layer at the surface of the membrane which creates a locally elevated polymer concentration. The resultant film layer induces delayed demixing as the mass transfer resistance between the non-solvent bath and the bulk of the membrane increases [33].

Literature related to this parameter in SRNF-membranes seems very system dependent. Evaporation times of 0 to 40 s for PI (P84) membranes based on DMF/DIO casting solutions did not influence the dense top layer formation [21]. On the other hand, increasing evaporation time from 0 to 120 s for another PI (Matrimid) membrane based on an NMP/THF casting solution resulted in a higher rejections and lower permeances [31]. In the case of PSU-based SRNF-membranes, a constant decrease in permeance was observed with higher evaporation time, but the rejection increase stopped after a certain time and remained stable afterwards [26].

Six different evaporation times of 0, 10, 20, 30, 60 or 100 s were applied for evaporation of THF before dipping the cast membranes in the water bath. The IPA permeance decreased from 0.039 to 0.007 l/m² h bar, while RB retention slightly improved from 88.6 to 94.7% by increasing the evaporation time (Fig. 4). After 30 s, effects on rejection and flux became less pronounced, especially the rejection. Evaporation times longer than 30 s are thus not beneficial for this system, while shorter times show a typical trade-off between flux and rejection, hence creating an application dependent optimum.



Fig. 4. Effect of evaporation time before immersion in the non-solvent bath on the separation performance of EB-cured PSU/THF-based membranes in terms of rejection and permeance for a RB/IPA feed (conditions: 15/85 ratio of THF/NMP).

3.2.2. Membrane morphology

Varying the evaporation time remarkably affected the membrane morphology, as illustrated in the SEM pictures (Fig. 5). Only membranes prepared very short evaporation times showed small macrovoids immediately under the surface layer. At the highest evaporation times (100s), even an almost full disappearance of macrovoids could be observed. The reason to turn the macrovoid structure into a more sponge-like structure is generally attributed to delayed demixing, here provoked by the formation of a stronger mass transfer resistance for the non-solvent penetrate the film after the evaporation step.



Fig. 5. Effect of evaporation time before immersion in the non-solvent bath on the morphology of the EBU-cured PSU membranes: (a) 0 s, (b) 10 s, (c) 20 s, (d) 30 s, (e) 60 s, (f) 100 s.

3.3.3. Influence of co-solvent concentration

3.3.3.1. Filtration performance

The distinct influence of co-solvent addition on the performance and morphology of asymmetric membranes has been investigated by several researchers [21, 31, 34]. Fig. 6 demonstrates the effect of the co-solvent/solvent ratio (THF/NMP) on the separation performance of EB-cured PSU-membranes. THF evaporates considerably during the evaporation step, owing to its low boiling point (66 °C). In general, it is observed that adding more THF to the casting solution results in reduced IPA permeances and increased RB rejections. The ideal THF/NMP ratio can be assumed roughly to be 15/85, since beyond this ratio, permance still decreased, but rejection stayed almost constant. It can be seen that the higher THF concentration in the PSU casting solution increased the rejection (Fig. 6). However, IPA flux was still very low to fulfill SRNF applicability [9].



Fig. 6. Effect of co-solvent (THF) amount on the separation performance of the EB-cured PSUmembranes (conditions: 30 s of evaporation time).

3.3.3.2. Membrane morphology

The increase in THF/NMP weight ratio from 0/100 to 30/70 in the casting solutions notably influenced the membrane morphology, as shown in the SEM pictures (Fig. 7). The number of macrovoids decreased gradually with increasing THF content. In line with 3.1.2, this could be explained by an increased mass transfer barrier at higher THF concentrations leading to delayed demixing, inducing less macrovoids in the membranes [35, 36].



Fig. 7. Effect of co-solvent/solvent ratio (THF/NMP) in the PSU casting solution on the morphology of the EB-cured PSU membranes: (a) (0/100), (b) (5/95), (c) (10/90), (d) (15/85), (e) (20/80), (f) (30/70).

3.3.4. Solvent resistance

Tables 2 illustrates the stability of the non-cured and the EB-cured membranes in various solvents. All membranes were stable in IPA. The EB cross-linked PSU membranes were stable in acetone and butyl acetate, while the non-cured membrane swelled upon immersion in these solvents. The EBcured PSU membranes were also stable in toluene, while the reference membrane fully dissolved. Furthermore, the EB cross-linked PSU membrane swelled without dissolving after immersion in DMF, THF and NMP, while the reference membrane dissolved fully. Hence, the EB irradiation obviously enhanced the solvent stability of the PSU membranes.

Table 2 Solvent stability of the non-cured (without additive) and EB-cured PSU membranes(conditions: 85/15 ratio of co-solvent/solvent and 30 s of evaporation time).

Solvent	Non-cured	EB-cured
IPA	+	+
Acetone	Х	+
Butyl acetate	Х	+
Toluene	-	+
THF	-	Х
NMP	-	Х
DMF	-	Х
DMAc	-	Х

+ stable, X swelling, - dissolution

3.4. CONCLUSIONS

This study focused on the impact of various phase inversion parameters for the preparation of solvent stable EB-cured PSU membranes via NIPS in an attempt to create useful SRNF-membranes combining high rejection with high flux. Polymer concentration, evaporation time before immersion and co-solvent/solvent ratio were varied during membrane preparation to control the EB cross-linked membrane performance. Higher polymer concentrations in the casting solution led to a slight increase in RB rejection but a strong decrease in IPA permeance. Longer evaporation times prior to the precipitation continuously lowered the permeance till 0.007 l/m² h bar (at 100 s), while no significant change was observed in rejection. Depending on the targeted final application of the EBcured membranes, evaporation times may be limited to 10 s or even totally eliminated. Addition of a more volatile co-solvent (THF) to the casting solution caused constant decline in permeance up to 0.011 l/m^2 h bar, while the rejection increased to 96.1%. The morphological analysis demonstrated that synthesized membranes were influenced markedly by the phase inversion parameters as anticipated. The most distinct change was detected by varying the time of the evaporation step, as the macrovoid structure turned to a totally spongy structure with increasing evaporation time. In conclusion, despite varying all these phase inversion parameters, the flux generally remained too low for membranes to become really useful in SRNF. However, these membranes still may be used for applications where more dense structures are required, like in gas separation or pervaporation.

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CHAPTER 4

UV-CURED POLYSULFONE-BASED MEMBRANES: EFFECT OF CO-SOLVENT ADDITION AND EVAPORATION PROCESS ON MEMBRANE MORPHOLOGY AND SRNF PERFORMANCE

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Abstract

Membranes consisting of a semi-interpenetrating network of polysulfone (PSU) and cross-linked polyacrylate were synthesized via non-solvent induced phase inversion followed by UV-treatment. Tetrahydrofuran (THF) or 1,4-dioxane (DIO) was added as co-solvent to the N,Ndimethylformamide (DMF)-based polymer solutions and cast films were subjected to evaporation prior to coagulation. Effects of synthesis variables on the membrane morphology and solvent resistant nanofiltration (SRNF) performance were investigated by using a Rose Bengal solution in isopropanol. By increasing the evaporation time from 0 to 100 s for the membranes prepared with THF and DIO as co-solvent respectively, rejections increased from 65.3 to 94.2% and 60.1 to 89.1%, while permeances decreased from 0.29 to 0.01 l/m^2 h bar and 0.41 to 0.08 l/m^2 h bar. A similar effect was observed when the co-solvent/solvent ratio was increased from 0/100 to 100/0: rejections increased from 63.1 to 94.9% and 59.2 to 90.6%, while permeances decreased from 0.43 to 0.01 l/m^2 h bar for THF-based membranes and to 0.07 l/m^2 h bar for DIO-based membranes respectively. A post-treatment was performed to increase the flux by immersing UV-cured PSU-based films in DMF for 48 h. The resultant membranes showed higher permeances and lower rejections, making them especially useful as potential candidates for stable supports to apply selective layers upon, such as e.g. in thin film composite (TFC) membranes. As observed in scanning electron microscopy, higher evaporation times and lower initial co-solvent concentrations resulted in less or even no macrovoids.

4.1. INTRODUCTION

Polymeric membranes are extensively employed in gas and liquid separations due to their good processability and low cost [1-3]. These membranes mostly demonstrate an asymmetric structure and are fabricated via the phase inversion process where a polymer solution is cast on a support, followed by immersion in a non-solvent bath where polymer precipitation and membrane formation appears [4-11]. Solvent resistant nanofiltration (SRNF) is a contemporary process that allows the separation of organic mixtures down to a molecular level by applying a pressure gradient over a membrane [12, 13]. It is entering as an innovative technology in petrochemical, food & beverage, pharmaceutical industries where organic solvent streams need to be treated. Besides permeability and selectivity, the chemical stability of the membranes is of great importance for such applications. In SRNF, both polymeric and inorganic membranes are used with molecular weight cut-offs in the range of 200 to 1000 Da [9, 14-19].

Polysulfone (PSU) has strong thermal and mechanical properties which makes it an ideal candidate for broad membrane applications [20-25]. However, performance of these membranes and many others, such as polyimide (PI) and polyether ketone, are still inadequate in the SRNF process because of their low resistance in aprotic solvents, such as N-methylpyrrolidone (NMP) and N,Ndimethylformamide (DMF) [26, 27]. This problem can be solved by introducing cross-linking. The most common method to realize this is via chemical cross-linking [26, 28-31]. However, it is less suitable for PSU due to its limited chemical reactivity. Additionally, chemical cross-linking generally requires a series of reaction steps which induce toxic contaminants such as diamines[26]. Therefore, radiation treatment via UV or electron beam (EB) can be a preferred alternative procedure for PSU [32-34]. The high cost and relative complexity of EB-curing units render UV-curing generally preferred [35]. Usually, surface modification of PSU-membranes is targeted via UV radiation to realize grafting [36, 37]. Very recently, a simple and effective method was developed to depth-cure PSU-membranes via UV-curing [38]. In this approach, UV-irradiation was applied to PSU membrane films containing cross-linker and photo-initiator, prepared via non-solvent induced phase separation (NIPS) process. Combinations of various photo-initiators and cross-linkers were investigated to find a practically useful system [39, 40]. As well-known, the final SRNF performance and membrane morphology can be modified easily through even slight changes in synthesis protocol or composition of the casting solution. In-depth analysis of the phase inversion parameters is thus still necessary to achieve the best performance with UV-cured PSU-membranes via this method.

Among the most effective parameters to tune phase inversion parameters [9, 41-45], evaporation time prior to immersion, choice of co-solvent and solvent/co-solvent ratio are easily accessible and well understood [40, 45-50]. In present study, the influence of evaporation time and the role of co-solvent (tetrahydrofuran (THF) or 1,4-dioxane (DIO)) on the formation, performance and morphology of UV depth-cured PSU-based is thus investigated to further optimize this type of interesting membranes with respect to use in SRNF.

4.2. EXPERIMENTAL

4.2.1. Materials

Polysulfone (PSU) (Udel P-1700 LCD, $Mn = 21\ 000\ g\ mol^{-1}$) was kindly provided by Solvay (Belgium) and dried for 24 h at 100 °C prior to use. The polyethylene terephthalate non-woven fabric (PET Novatexx 2413) was kindly supplied by Freudenberg (Germany). Dipentaerythritol pentaacrylate (SR399LV, Sartomer) was used as cross-linker. 2,4,6-Trimethylbenzoyl-diphenyl-phosphine oxide was purchased from Sigma-Aldrich and used as photo-initiator. **Table 1** shows details of photo-initiator and cross-linker used. Rose Bengal (RB) was obtained from Sigma-Aldrich. *N*,*N*-dimethylformamide (99.5%,DMF), tetrahydrofuran (99.5%, THF) and 1,4-dioxane (99%, DIO) were purchased from Acros and used as received.

Name	MW (gmol ⁻¹)	Structure	
2,4,6-Trimethylbenzoyl- diphenyl-phosphine oxide (Darocur TM TPO)	348	CH ₃ CH ₃ CH ₃ C	
Dipenta-erythritol penta-acrylate (Sartomer™ SR399LV)	524	H_2C O CH_2 OH OH CH_2 OH OH CH_2 OH OH CH_2 OH OH OH OH OH OH OH OH	

Table 1. Photo-initiator and cross-linker used in this study.

4.2.2. Membrane synthesis

Two different series of membranes were prepared to determine the influence of evaporation time and the role of co-solvent as phase inversion parameters on the performance and morphology of the UVcured PSU-membranes. In the first series, the influence of evaporation time was analyzed by using a DMF-based solution, based on ref. [38], with two different co-solvent (THF and DIO) with a ratio of DMF to co-solvent equal to 85/15. As evaporation times 0, 10, 20, 30, 60 or 100 s were used. It has to be mentioned that all membranes were evaporated for roughly about 5 s extra, which is the required time to move the cast film from the casting equipment to the coagulation bath. In the second series, the influence of co-solvent was analyzed by using a DMF (boiling point, 153°C) based solution with the same THF (boiling point, 66 °C) and DIO (boiling point, 101 °C) as co-solvent keeping evaporation time constant (30 s), but with various ratios of DMF to these co-solvents: 100/0, 75/25, 50/50, 25/75 and 0/100. All samples were prepared at room temperature under the atmospheric pressure. In both series, the polymer concentration was kept constant at 21 wt%. Crosslinker and photo-initiator were used at 5 wt% and 3 wt%, respectively. After obtaining a homogenous polymer solution, membranes with a wet thickness of 200 µm were cast at a speed of 1.81 m/min onto a glass plate or a polypropylene/polyethylene non-woven fabric (Novatexx 2413) impregnated with DMF. Before immersion into the coagulation bath, the membrane was kept in ambient air for a certain time. The membranes were stored in distilled water prior to the UV treatment.

4.2.3. UV-curing of asymmetric PSU-based membranes

The PSU-based membranes were passed through a UV-curing set up (UVAPrintS200, HonleUV France) on a conveyor belt at a line speed of 10 m min⁻¹. UVA (320–390 nm) was used as the main irradiation light. According to our previous study [39], the dose of energy to cure the membranes was chosen as 5 J/cm².

To increase the flexibility and prevent pore collapse for better filtration, some of the cross-linked PSU-membranes were impregnated after the UV-curing. The membranes were stored in a solution including 40% (v/v) of glycerol and 60% (v/v) of propan-2-ol for 48 h at room temperature, and subsequently air-dried. ATR-FTIR and SEM were performed to non-impregnated UV-cured PSU-membranes.

4.2.4. Viscosity measurements

Viscosity measurements were carried out with an Anton Paar MCR501 rheometer with a cone-plane geometry with solvent trap at 20 °C. The polymer solution was loaded onto the plate, and the cone was lowered onto the sample. It was then covered by a lid to avoid solvent evaporation. The sample temperature was controlled by a Peltier element with high accuracy. Viscosity at different shear rates was measured in steady-shear flow from 0.01 to 100 1/s. Data acquisition and analysis was done using RheoPlus software (Anton Paar GmbH, Austria).

4.2.5. Scanning electron microscopy (SEM)

Philips XL30 FEG scanning electron microscope has been employed to obtain membrane crosssection images. The membrane samples were freeze-cracked in liquid nitrogen. To reduce sample charging under the electron beam, samples were coated with a 1.5-2 nm gold layer using a Cressington HR208 high-resolution sputter coater.

4.2.6. Solubility parameters

The Hansen solubility parameters (HSP) are useful to check the solvent strength and the solubility of polymer. Based on the thermodynamics of the solubility equilibrium, Hansen calculated the enthalpy of miscibility using the three Hansen solubility parameters of the solvent and polymer. This HSP δ_D , δ_P , and δ_H are the partial HSP attributed to dispersive forces, polar forces, and hydrogen bonding, respectively. Thus the HSP are properties of a polymer or a solvent. The total solubility parameter δ is the geometric mean of the three components given by the following equation [51]

$$\delta = \left(\delta_D^2 + \delta_P^2 + \delta_H^2\right)^{1/2} \tag{1}$$

The three partial HSP are used to define a space where the solubility volume (modelled as a sphere of radius R0 and center δ_D , δ_P , and δ_H of polymer) a polymer is plotted. This solubility volume includes of the solvents of a polymer and Ro is also called the critical radius of interaction of a polymer. A solubility parameter distance (Ra) is a measure of affinities between polymer (1) and solvent (2) and is based on their individual Hansen solubility parameters by the following equation;

$$Ra = \left[4\left(\delta_{D2} - \delta_{D1}\right)^2 + 4\left(\delta_{P2} - \delta_{P1}\right)^2 + 4\left(\delta_{H2} - \delta_{H1}\right)^2\right]^{1/2}$$
(2)

The relative energy difference, RED, is equal to Ra/R0. Solubility of the polymer in the solvent is expected in case of RED value is smaller than 1. Solubility increases when the RED value is below 1.

4.2.7. Swelling/solvent resistance test

The solvent resistance of prepared and cured PSU-membranes was analyzed by visual inspection after keeping membrane samples in various solvents at room temperature for at least 24 h.

4.2.8. Filtration Experiments

Filtrations were performed in a dead-end filtration cell with a high throughput filtration module (High Throughput Membrane Systems Leuven, Belgium) [12, 52], at room temperature and under pressures ranging from 10 to 30 bar allowing for simultaneous filtrations of 16 membranes. Membrane samples were placed in the module and sealed with Viton[®] O-rings. The active membrane surface area was 0.000452 m². A solution of 17.5 μ M Rose Bengal (1017 Da) in propanol (IPA) was used as feed. It was stirred magnetically at 350 rpm to reduce concentration polarization. Permeances, expressed in (l/m² h bar), were determined gravimetrically by weighing the collected permeate. Rejections (R, %) were defined as (1–C_p/C_f) × 100, where C_f and C_p denote the dye concentrations in the initial feed and in the permeate respectively. Dye concentrations were recorded on a Perkin-Elmer Lambda 12 UV–vis spectrophotometer at a wavelength of 555 nm. Filtration measurements lasted an average 20 h and 4 membrane coupons were tested for each membrane sample. Typically 3 samples were taken for analysis per coupon after having reached steady state conditions.

4.2.9. Post-treatment of UV-cured PSU-based membranes with immersion in DMF

A solvent activation post-treatment step was performed on a selection of UV-cured membranes in order to increase the solvent flux according to Solomon et al. [63]. Selected membranes were immersed in DMF for 48 h. The performance of treated membranes was evaluated through filtrations using IPA/RB and DMF/RB as feed solutions.

4.3. RESULTS AND DISCUSSION

4.3.1. Influence of evaporation time

4.3.1.1. Filtration performance

In the membrane fabrication process, an evaporation step is frequently applied to get a more dense membrane surface layer when the casting solution includes volatile (co-)solvents [41, 45, 49]. Consequently, a thin layer is created at the surface of the cast film with a locally increased polymer concentration. The formed layer acts as a resistance barrier between the deeper membrane regions and the coagulation bath, leading to delayed demixing [53]. Longer evaporation times remove more co-solvent from the surface of the cast film, thus the region with increased polymer concentration at the top of the film enlarges and turns into a more concentrated nascent skin layer [48, 49]. Consequently, asymmetric membranes with a dense and thick skin layer are formed and with less chances for macrovoid creation.

Literature with respect to SRNF-membranes is in this respect not unambiguous however. For a certain type of PI-SRNF membrane (Matrimid - NMP - THF), a longer evaporation time (0 to 120 s) increased rejections and decreased permeances [49], while moderate evaporation (0 to 40 s) of a volatile solvent before the immersion in a coagulation bath was found needless to create a selective skin layer in another PI-system (P84 - DMF - DIO) [46]. For PSU-based SRNF membranes, an increased evaporation time caused a continuous decline in permeance while it took the rejection to a certain ultimate level [45].

Six different evaporation times of 0, 10, 20, 30, 60 or 100 s were allocated for evaporation of THF and DIO before immersion of the cast films in the water bath. As seen from Fig. 1, increasing the evaporation time changes the membrane performance most notably for THF series. The flux of IPA decreased from 0.29 to 0.01 l/m² h bar, while the RB retention increased from 65.3 to 94.2% by increasing the evaporation time from 0 to 100 s. Additionally, rejections increased distinctly till an evaporation time of 30 s to a maximum value of 89.3%, while IPA permeances further decreased continuously with evaporation time. The ideal time for evaporation of THF as co-solvent before immersion in the precipitation bath can thus be assumed to be around 30 s as beyond 30 s, rejection stayed almost constant but permeance dropped down to zero.

For DIO containing membranes, the flux of IPA decreased from 0.41 to 0.08 l/m² h bar while RB retention increased from 60.1 to 89.1% by increasing the evaporation time from 0 to 100 s (Fig. 2). Similar to THF-based membranes, 30 s seemed to be the optimum evaporation time to apply for DIO-based membranes, as RB rejections were then close to the maximum value.

In general, THF containing membranes showed lower permeance and higher rejection for each applied evaporation time due to the faster THF evaporation rate arising out of lower boiling point (Fig. 1).



Fig. 1. Effect of evaporation time on the separation performance of the UV-cured PSU/THF-based membranes with a THF/DMF ratio of [15/85], in terms of rejection and permeance for a RB/IPA

feed. Permeance is indicated as blue diamonds and rejection as red triangles.



Fig. 2. Effect of evaporation time on the separation performance of the UV-cured PSU/DIO-based membranes with DIO/DMF ratio of [15/85], in terms of rejection and permeance for a RB/IPA feed. Permeance is indicated as blue diamonds and rejection as red triangles.

Additionally, the weight loss of the DIO and THF-containing cast films was measured as a function of evaporation time. THF-containing films lost more weight compared to DIO-containing films (Fig. 3), as a consequence of the low boiling point of THF.



Fig. 3. Effect of evaporation time on the weight loss of the PSU/DMF/DIO and PSU/DMF/THF cast films with co-solvent/solvent ratios of [15/85]. THF is indicated as blue diamonds and DIO as red squares.

4.3.1.2. Morphology

Membrane morphology is notably influenced by changing evaporation time, as demonstrated in the SEM pictures (Fig. 4). For both co-solvents used, the number of macrovoids under the skin layer decreased by increasing the evaporation time. Their size also decreased, and the macrovoids finally even fully disappeared at the longest evaporation times (100s). This can all be related to the delayed demixing induced by creating a tougher mass transfer barrier during the evaporation step.

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Fig. 4. Effect of evaporation time on the morphology of the UV-Cured PSU-membranes: a-f: THF; g-l: DIO containing membranes with [15/85] co-solvent/solvent ratio (0, 10, 15, 20, 30, 60 and 100 s respectively).

4.3.2. Influence of co-solvent type

4.3.2.1. Filtration performance

Many studies showed that the addition of a co-solvent to casting solutions could significantly influence the performance and morphology of asymmetric membranes for [46, 49, 54].

Fig. 5 and 6 show the effect of co-solvent/solvent ratio (THF/DMF and DIO/DMF respectively) on the separation performance of UV-cured PSU membranes. THF was expected to evaporate well during the evaporation step because of its low boiling point. Fig. 5 shows that increasing the THF/DMF weight ratio induced lower IPA permeances and higher RB rejections due to the densification of the membranes. The membranes prepared from solutions containing DIO as cosolvent showed a similar behavior as the THF-based membranes: IPA permeance decreases continuously while the RB rejection increases distinctly till a certain ratio, and then further remains rather stable with increasing DIO/DMF ratio (Fig. 6). It can be seen that THF-based membranes have lower permeance than DIO-based membranes at the same co-solvent/solvent ratio. This can be explained by the higher volatility of THF compared to DIO which leads to formation of a denser skin layer at a certain evaporation time due to the loss of more co-solvent, as earlier mentioned in the discussion of the evaporation time. Varying the THF/DMF and DIO/DMF ratio in the casting solution showed us that it is possible to have a higher rejection with optimum ratio, but permeance stayed too low in all cases to become satisfactory (>1/1 m² h bar) for SRNF-applications [55].



Fig. 5. Effect of co-solvent/solvent ratio (THF/DMF) on the separation performance of the UV-cured PSU-membranes given 30 s of evaporation time. Permeance is indicated as blue diamonds and rejection as red triangles.



Fig. 6. Effect of co-solvent/solvent ratio (DIO/DMF) on the separation performance of the UV-cured PSU-membranes given 30 s of evaporation time. Permeance is indicated as blue diamonds and rejection as red triangles.

4.3.2.2. Morphology

By increasing the THF/DMF and DIO/DMF weight ratios from 0/100 to 100/0 in the casting solutions, finger-like macrovoids appeared in Fig. 7 [56]. The solvent/non-solvent exchange rate is lowered after the formation of a dense top layer on top of the cast polymer film which slows down the demixing deeper in the membrane. Therefore, macrovoids have longer time to be formed and grow in size in membrane with a higher THF concentration [39, 57].



Fig. 7. Effect of co-solvent/solvent ratio on the morphology of the UV-cured PSU-membranes given 30s of evaporation time.

4.3.2.3. Viscosity change

Apart from thermodynamics, the kinetic aspects of the phase inversion process also affect the membrane formation process. The viscosity of the casting solution can be changed by adding cosolvent which alters the phase inversion process in terms of a slower diffusion of solvent into the non-solvent bath and of non-solvent into the polymer film. Fig. 8 demonstrates the change in viscosity upon addition of co-solvent to the casting solution. The viscosity of the polymer solution is mainly fixed by the quality of the solvent. Dissolution of polymer is easier in the presence of a solvent of high affinity. In a good solvent, polymer chains stretches where as in a poor solvent the polymer chain collapses. As a result of the stretched chains, polymer solution becomes more viscous [58]. According to HSP interaction distance (Table 4), it can be estimated that DIO (5.4 MPa^{1/2}) is better solvent than THF (6.4 MPa^{1/2}) for PSU. Thus, in studied systems, the addition of DIO leads higher viscosity than addition of THF. The viscosity values presented in Fig. 7 are rather just indicative, since it was hard to perform the precise measurements, especially for the samples containing THF, due to the partial solidification caused by fast evaporation during the actual viscosity measurements. Nevertheless, it is clear that addition of THF decreased the viscosity of the polymer solutions, while the addition of DIO increased the viscosity. Macrovoid formation is accepted to be suppressed by increasing the casting solution viscosity as demixing becomes more delayed [59, 60]. Fig. 7 confirms this, since macrovoids disappeared when viscosity increased with higher DIO concentration, while they became more apparent when viscosity decreased at higher THF levels. However, increasing the co-solvent amount showed the same tendency in separation performance for both membranes. This thus proves that flux and rejection are controlled by the skin layer and that existence of macrovoids is not the dominating factor for the performance of these SRNF-membranes under the applied filtration conditions [61].



Fig. 8. Effect of co-solvent/solvent ratio concentration on the viscosity of the casting solutions of the UV-cured PSU-membranes (21 wt%).

4.3.3. Solvent activation of UV-cured PSU membranes by immersion in DMF

To further evaluate the solvent stability and to increase the SRNF flux, UV-cured membranes were immersed in DMF for 48 h [62, 63]. The membranes with highest and lowest permeances were selected to check the effects of the DMF immersion (Table 2). The performances were measured first in IPA/RB to see the improvement in flux. Afterwards, the same membranes were tested in DMF/RB solution, which is a feed that would normally dissolve PSU membranes immediately. As shown in Fig. 9, the IPA permeances increased distinctly compared to the results summarized in Table 2 (factors of 3 to 4) upon the treatment, while RB rejections decreased. Higher permeances were systematically observed for thr DMF/RB filtration, as commonly observed in previous studies [62, 63]. The membranes stayed stable despite the decreasing selectivity.

Membrane	Co-solvent	Evaporation time Co-solvent/solvent		Permeance
		(s)	(wt/wt)	
M1	THF	0	85/15	highest
M2	THF	30	100/0	lowest
M3	DIO	0	85/15	highest
M4	DIO	30	100/0	lowest

Table 2 Properties of UV-cured PSU membranes that were selected for the immersion in DMF.

 Permeance column indicates the IPA/RB filtration results obtained before immersion in DMF.

Table 3 The physico-chemical properties of the solvents used in the filtrations.

Solvents	Molar volume	Viscosity	Molar volume/viscosity	
	(cm^3/mol)	(cP)	$(\text{cm}^3/\text{mol cP})$	
IPA	76.46	2.00	38.46	
DMF	77.43	0.82	94.43	



Fig. 9. Filtration performance of UV-cured membranes for RB in IPA and in DMF after solvent activation by immersion in DMF for 48 h. The composition of membranes (M1-M4) is given in Table 2.

4.3.4. Solvent stability

The reference and UV-cured membranes were immersed in various solvents commonly used in processing, to prove the efficiency of UV treatment with respect to solvent stability. Table 4 shows the solvent stability of the reference and cured membranes with calculated HSP interaction distance of various solvents used for stability experiment. As expected, all membranes were stable in IPA. The reference membrane swelled after immersion in butyl acetate and acetone, while the UV-cured PSU membrane remained unaltered in these solvents. The reference membrane dissolved in toluene and xylene, while the UV-cured PSU membrane was stable and hardly swelled. After immersion in DMF, THF and NMP, the reference membrane dissolved completely while the UV-cured PSU membrane swelled slightly here, but without dissolving. Regarding the outcome of the solvent stability test and the HSP interaction distance, it can be concluded that the cross-linked membranes could be used with solvents having an interaction distance higher than 8.8 safely (no swelling). However, this hypothesis seems invalid for two outlier solvents, since the reference membrane dissolves in toluene and xylene mixtures (interaction distance >8.8). This could be attributed to π interactions between PSU and aromatic solvents which are not properly taken in account in calculation of HSP. Furthermore, the reference membrane just swells in aliphatic solvents such as acetone and butyl acetate. As a result, it was monitored that the UV irradiation distinctly improved the solvent stability of the PSU-based membranes.

Solvent	Reference	UV-cured	δd	бр	δh	Interaction distance (Ra)
			(MPa ^{1/2})	(MPa ^{1/2})	(MPa ^{1/2})	solvent/reference PSU
						(MPa ^{1/2})
IPA	0	0	15.8	6.1	16.4	11.5
Toluene	1	0	18	4	2	9.9
Xylene	1	0	17.8	1	3.1	9.7
mixture						
Butyl acetate	Х	0	15.8	3.7	6.3	9.3
Acetone	Х	0	15.5	10.4	7	8.8
DMF	1	Х	17.4	13.7	11.3	7.7
THF	1	Х	16.8	5.7	8	6.4
NMP	1	Х	18	12.3	7.2	5.4

Table 4 Solvent stability of the reference (without photoinitator and cross-linker) and UV-cured(5j/cm²) PSU (21 %wt) membranes with interaction distance (Ra) of solvents used.

0-stable, X-swelling, 1-dissolution

4.4. CONCLUSIONS

This study describes the effects of phase inversion parameters on a UV-cured PSU system for the fabrication of SRNF-membranes via NIPS. Co-solvent content and evaporation time before immersion into non-solvent bath were selected as parameters to tune the separation performance of the membranes. Longer evaporation times before coagulation of a cast membranes consistently decreased the permeance till 0.01 and 0.08 l/m^2 h bar (at 100 s) for the membranes containing co-solvent THF and DIO as respectively. Meanwhile, the rejection of the same membranes increased to 89.3% (THF-based) and 84.9% (DIO-based) till evaporation times around 30 s and then remained almost constant when further extending the evaporation process. Too long evaporation times (>30 s) should thus be avoided.

When adding a more volatile co-solvent to the casting solutions, permeances steadily declined to 0.01 and 0.07 $1/m^2$ h bar and rejections increased to 94.9 and 90.6% for the membranes containing

co-solvent THF and DIO as respectively. The morphology of the prepared membranes was affected strongly by the phase inversion parameters. The appearance of finger-like macrovoids could be explained via viscosity changes in the casting solution when co-solvent was added. An increase in evaporation times to 100 s reduced macrovoid formation with appearance of spongy structures, ascribed to the formation of a more concentrated polymer layer on top of the cast membranes at extended evaporation times. Finally, post-treatment with DMF significantly improved the permeances but reduced rejections. These membranes could still be useful as support layer in TFC membrane preparation processes.

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CHAPTER 5

EFFECT OF UV AND EB CROSS-LINKING ON MORPHOLOGY, PERFORMANCE, SWELLING BEHAVIOUR, SURFACE AND MECHANICAL PROPERTIES OF POLYSULFONE MEMBRANES CONTAINING ACRYLATES

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Abstract

Ultraviolet and electron beam radiation have been used to cross-link polysulfone-based asymmetric solvent resistant nanofiltration membranes. The influence of the casting thickness and the radiation dose on the cross-section morphology, the isopropanol flux and Rose Bengal retention, the surface features, and mechanical properties have been investigated. The cross section of all membranes comprises a dense layer, atop a more open sub-layer with macro-voids or with a spongy structure, depending on the exact casting conditions. The casting thickness only affects the thickness of this open sub-layer, and not that of the dense layer and hence neither flux nor retention. The surface roughness decreases gradually with an increasing radiation dose. Increasing the energy dose in the radiation-based cross-linking process leads to an increase in tensile strength and decrease in elongation at break of cured samples. With spectroscopic ellipsometry, the swelling of ultravioletcured thin polysulfone films, obtained via spincoating, in toluene-satured water has been investigated. Non-cured thin films show excessive swelling (63%). A monotonic decrease in swelling is observed with the radiation dose and the cross linker functionality, to <2 % for 3 J/cm² and 5 acrylate groups. Increasing the radiation dose to 5 J/cm² causes a higher swelling degree (8%) as compared to the radiation doses <3 J/cm². There is thus a negative effect of excessive crosslinking on the polymer network.

5.1. INTRODUCTION

Polysulfone (PSU) can be applied as a membrane material for a broad range of applications thanks to its strong mechanical and thermal characteristics [1]. However, the chemical stability of PSU-based membranes is insufficient for using them in aggressive solvent applications, either as a support layer or as a nanofiltration membrane [2]. Cross-linking is an attractive approach to enhance the stability of the polymeric membranes as polymer chains are joined together to form a three-dimensional network leading to the formation of insoluble polymers [3-5]. Chemical cross-linking is one of the most preferred methods to improve the solvent stability of the polymeric membranes [6, 7]. However, chemical cross-linking becomes ineffective for polymers such as PSU, which have a limited chemical reactivity due to the absence of functional groups [8]. In this case, radiation based cross-linking either via UV or electron beam (EB) is an attractive and emerging alternative approach [9-11]. In UV-curing, a photoinitiator added to the polymer solution consisting of cross-linker, is triggered by UV light to form initiating species for the cross-linking reaction. The distinctive feature of the EB-curing system is no requirement of a photoinitiator. In this case, polymerization is initiated by electrons and high cross-linking degrees are achieved at the end of the process [12]. Radiationbased cross-linking is a very fast process and causes intense changes in the separation and mechanical properties of the cured membranes [13, 14]. UV-curing is more favored compared to EBcuring, due to its relatively low costs and simple equipment. On the other hand, EB-curing is a more environmental friendly technique, as there is no need of a photoinitiator in the formulation [15]. Although both treatments are commonly used for surface modification of the polymers [16, 17], only very recently, UV and EB based depth cross-linking in the PSU membranes has been achieved [18, 19].

In our previous studies, UV and EB-curing of PSU-based films resulted in asymmetric membranes consisting of a semi-interpenetrated network with a densified skin layer. The cured PSU membranes exhibited a high solvent stability, but on the other hand showed a lower flux and became more brittle compared to non-cured membranes [14, 19]. For both UV and EB curing, the powerful radiation energy required to achieve cross-linking, has to be balanced to protect the selective layer of membrane [20, 21]. For example, the cross-linked membrane might become fragile, which complicates its use in pressure driven applications, like nanofiltration [22]. In order to prepare the cured membranes suitable for industrial applications, these negative impacts of the cross-linking process on the mechanical stability of the membrane should be minimized without reducing the chemical stability. Hence, the degree of cross-linking which is strongly dependent on the chemical

nature of the cross-linker and the applied radiation dose, is supposed to be tuned to obtain optimal cured membranes [11, 23].

It is important to understand the swelling behavior or dissolution dynamics of the cross-linked membranes to tune the cross-link density in applications such as solvent resistant nanofiltration (SRNF) where feed solutions consist of organic solvents [24]. To understand this phenomenon, spectroscopic ellipsometry is a suitable in-situ characterization technique, since it has a very high precision, accuracy and non-intrusive character [25].

In this study, the swelling behavior of UV-cured PSU thin films was analyzed by in-situ spectroscopic ellipsometry. The influence of the cross-linker type and energy dose on the swelling degree of UV cross-linked films has been investigated separately. The effect of wet thickness on separation performance and morphology has been studied for UV and EB-cured membranes. Tensile testing was performed to analyze the mechanical properties of both UV, EB-cured and non-cured membranes, while varying the radiation dose.

5.2. EXPERIMENTAL

5.2.1. Materials

PSU (Udel P-1700 LCD, $Mn = 21000 \text{ g mol}^{-1}$) was kindly provided by Solvay and dried overnight at 100 °C prior to use. The polyethylene terephthalate non-woven fabric Novatexx 2413 was kindly provided by Freudenberg (Germany). 2,4,6-Trimethylbenzoyl-diphenyl-phosphine oxide was purchased from Sigma-Aldrich and used as photo-initiator. The multifunctional acrylate monomers trimethylolpropane tri-acrylate (3AC, SR351 Sartomer), pentaerythritol tetra-acrylate (4AC, SR295 Sartomer) and dipentaerythritol penta-acrylate (5AC, SR399LV Sartomer) were used as cross-linkers. *N*-methylpyrrolidone (99%, NMP), tetrahydrofuran (99.5%, THF), toluene (99.8%, Sigma-Aldrich), *N*,*N*-dimethylformamide (99.5%, DMF) were obtained from Acros and used as received. Rose Bengal (RB) was obtained from Sigma-Aldrich.

5.2.2. Membrane synthesis

PSU membranes were prepared via phase inversion [24]. The polymer concentration (21 wt%) and solvent/co-solvent ratio (85/15) were kept constant for all membranes. 5 wt% of cross-linker and 3 wt% of photoinitiator were used for UV-cured membranes. 15 wt% of cross-linker was added for EB-cured membranes. PSU films with various wet thicknesses (50, 100, 200 and 300 μ m) were cast to investigate the influence of the casting thickness on the performance and morphology of the cured

membranes. Membranes were kept in the air for 30 s prior to immersion in the water non-solvent bath.

5.2.3. Thin film preparation

3 wt% of PSU was dissolved in cyclopentanone. The obtained homogenous polymer solution was spin coated on a fresh silicon wafer (2 nm native SiO_2 layer) using a Laurell WS-400B-6NPP-Lite Spinner. Spin coating was performed in two steps: 500 rpm for 5 s and 1000 rpm for 5 min successively. As a result, polymer films with thickness around 200 nm were obtained. Prepared samples were left in a furnace under N2 to remove the remaining solvent for 8 h at 215°C with a 5°/min ramp starting from room temperature.

5.2.4. UV-curing

The PSU-based membranes and spin-coated thin films were passed through a UV-curing unit (UVA PrintS200, HonleUV, France) on a conveyor belt at a line speed of 0.16 m/s. UVA (320–390 nm) was used as the main irradiation light. The energy doses from 0 to 5 J/cm² were chosen to cure the prepared samples containing penta-acrylate as the cross-linker. Additionally, a fixed UV dose (3 J/cm²) was applied to cure the films prepared for studying the influence of acrylate functionality using 3AC, 4AC and 5AC.

5.2.5. EB-curing

The PSU-based membranes were passed through an EB-curing unit (COMET, EBLab200, Switzerland) at 200 kV accelerating voltage and 9.3 mA beam current with a maximum dose of 100 kGy given during each pass. The EB doses applied in this study were 100, 300 and 500 kGy. Three different EB doses were applied of 100, 300 and 500 kGy

5.2.6. Filtration experiments

Filtrations were conducted at room temperature and selected pressure in a high-throughput filtration module (HTML, Belgium), allowing for simultaneous filtrations of 16 membranes [26, 27]. Circular coupons were cut from the membranes, mounted in the high-throughput filtration module, and sealed with Viton[®] O-rings. The active membrane surface area was 4.52 cm². Solutions of 17.5 μ M Rose Bengal (1017 Da) in IPA were used as feed solutions and stirred magnetically at 300 rpm to reduce concentration polarization. The permeance was determined gravimetrically by weighing the collected permeate and expressed in (l/m² h bar). Rejection (*R* (%)) is determined according to following equation:

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right) \cdot 100\tag{1}$$

where C_f and C_p represent the solute concentrations in the initial feed and in the permeate respectively. A Perkin-Elmer Lambda 12 UV–vis spectrophotometer was employed to measure permeate and feed concentrations at a wavelength of 555 nm.

5.2.7. Atomic force microscopy (AFM)

The surface morphology and roughness of dry non-cured and dry cured membranes were monitored by AFM (BioScope Catalyst) operating in tapping mode at ambient conditions. The root mean square of the Z data (Sq) was used to express the membrane surface roughness. The measurements were performed with scan areas of 2 μ m × 2 μ m at 3 different locations for each of the samples.

5.2.8. Mechanical tests

The tensile strength at break and elongation at break were measured according to the ISO 37 standard method using a tensile test machine (Zwick Roell Z100). The samples were analyzed at a crosshead speed of 10 mm/min.

5.2.9. Scanning electron microscopy (SEM)

Cross-section morphologies of the membrane were observed by using a Philips XL30 FEG SEM. The membrane samples were freeze-cracked in liquid nitrogen. Samples were sputtered with a thin gold layer using a sputter coater (Cressington HR208) to reduce sample charging under the electron beam.

5.2.10. Spectroscopic ellipsometry measurements

Spectroscopic ellipsometry (SE) is an optical technique, which can be used to investigate the optical properties of thin films in-situ. SE provides information on the thickness and density (refractive index) of polymer films. SE is based on the measurement of the change in polarization of a light beam upon reflection on a sample, given by Psi (Ψ) and Delta (Δ), defined as in the following equation:

$$\tan(\Psi)e^{i\Delta} = \rho = \frac{r_p}{r_s} \tag{2}$$

where r_p and r_s are the parallel and perpendicular reflectivities, respectively.

The ellipsometry measurements are very precise, since the current optical devices allow a very accurate quantification of changes in the polarization state light. It is achieved by the measurement of polarization light intensity ratios instead of the absolute intensities as for instance is done for

refractometry [28]. As the introduction of a fluid ambient generally leads to losses in the absolute intensity, spectroscopic ellipsometry is preferred.

In order to interpret the change in the polarization in terms of thickness and refractive index, an optical model is required. Since most of the polymers are transparent is the visible wavelength range, their optical dispersion can be modeled according to Cauchy dispersion formula (eq.2).

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$
(3)

where *A*, *B* and *C* are adjustable fitting parameters, *n* the refractive index and λ is the wavelength. The model-generated data is fitted numerically to the measured spectrum. The fit quality is most commonly measured by the root mean square error (*MSE*), which quantifies the error between the measured and model-generated spectra. In general, *MSE* values between 1 and 2 are considered as a good fit for samples having thickness in the range of 100-200 nm. Higher values of *MSE* (10 to 20) are acceptable for thicker films in-situ measurements where polymer-solvent interaction lowers the accuracy of optical modeling.

The swelling of a thin polymer film in a solvent can be quantified by the swelling degree (*SD*) and the normalized refractive index (n_{norm}):

$$SD = \frac{d}{d_0} - 1 \tag{4}$$

$$n_{norm} = \frac{n - n_s}{n_0 - n_s} \tag{5}$$

where d_0 is the dry polymer film thickness and d is the swollen polymer films thickness, n_0 is the refractive index of the dry polymer film, n is the total refractive index of the swollen film and n_s is the refractive index of the ambient.

A spectroscopic ellipsometer (Woollam α -SE) was employed to observe the swelling of ultra-thin polysulfone films. All measurements were done at a fixed angle of incidence (70°) in the wavelength range from 370 to 900 nm. Samples were placed in a 500 µL Woollam Liquid Cell. First, the dry sample thickness and refractive index were measured. Then the cell was filled with water that is saturated with toluene. The measurement was continued, until an equilibrium swelling was reached. Delta-offsets were determined for both dry measurements and liquid measurements using a 25 nm SiO₂ calibration wafer. The optical dispersion of the saturated toluene in water solution was determined using a Schmidt Haensch ATR-L multi-wavelength refractometer at wavelengths of 365 nm, 400 nm, 450 nm, 500 nm, 590 nm, 700 nm and 800 nm at 22°C.

5.3. RESULTS AND DISCUSSION

5.3.1. Casting thickness

The effect of casting thickness on morphology and separation performance of UV and EB-cured membranes was studied using various casting thicknesses (100, 250 and 400 μ m). In Fig. 1, the SEM images of both UV and EB cured films at the different casting thicknesses are shown. For both UV and EB cured films, a film of 100 μ m resulted in a spongy structure while the macrovoids started to appear and grow with a thickness of 250 μ m. Upon increasing the thickness up to 400 μ m, the finger-like macrovoids were clearly present. This phenomenon can be correlated with the macrovoid formation mechanism [1]. The solvent/non-solvent exchange rate is hindered after the formation of a dense skin layer on the membrane. As a result, demixing of the deeper parts across the membrane becomes slower. Thus, this gives the opportunity for the formation and growth of macrovoids in thicker membranes due to the longer available time with enhanced polymer flexibility. A similar cross-section structure with macrovoids was already observed for PSU, cellulose acetate (CA) and poly(etherimide) by increasing the cast film thickness [29, 30].

In Fig. 2 (UV-cured) and 3 (EB-cured), filtration results of the cured membranes in a Rose Bengal in IPA solution (RB/IPA) are shown. In our previous studies, a sharp decrease in permeance of the PSU membranes was observed after either a UV or EB cross-linking step [14, 19]. In general, the EB-cured membranes showed the lower permeances of the RB/IPA solutions compared to UV-cured membranes. As mentioned above, this might be the consequence of the relatively higher intrinsic energy of EB radiations leading to a higher cross-linking degree. The casting thickness itself shows no significant influence on the separation performance of the membranes for both UV-cured and EB-cured membranes. However, the membranes cured with same energy source (UV or EB) showed some morphological difference (Fig. 1). It can thus be concluded that the casting thickness did not affect the skin layer which controls the separation and just had an impact on the morphology of the sublayer [31].



Fig. 1. SEM images of cross-sections of the UV (above) and EB-cured (below) PSU membranes with casting thicknesses of 100 μm, 250 μm and 400 μm.



Fig. 2. Influence of casting thickness on SRNF performance in RB/IPA solution of UV-cured PSU membranes. Permeance is indicated as blue diamonds and rejection as red triangles. Error bars represent standard deviation (n = 3).

EB-cured



Fig. 3. Influence of casting thickness on SRNF performance in RB/IPA solution of EB-cured PSU membranes. Permeance is indicated as blue diamonds and rejection as red triangles. Error bars represent standard deviation (n = 3).

5.3.2. Surface morphology

The surfaces of the non-cured, UV and EB-cured PSU membranes were analyzed by Atomic Force Microscopy (AFM). The areal roughness parameter (Sq) was used to show differences in the morphology quantitatively (Fig. 4). The non-cured membrane showed a lower surface roughness than the cured membranes. It was noticed that the additives, which were required for the cross-linking process, caused a higher surface roughness [32]. Upon increase of the radiation dose, the average surface roughness decreased gradually. This might be attributed rearrangements of the polymer chains present in the skin layer, as they get increased mobility upon UV or EB-irradiation. Curing process indeed result in a substantial temperature increase of the membrane during the irradiation.



Fig. 4. AFM images of membranes top surface and calculated areal roughness parameters (Sq): (a) non-cured, (b-d) UV-cured with radiation doses of 1,3 and 5 j/cm² respectively, (e-f) EB-cured with radiation doses of 100, 300 and 500 kGy.

5.3.3. Mechanical properties

To determine the influence of the radiation dose on the mechanical properties of the cured PSU, tensile tests were performed for both UV-cured and EB-cured PSU membranes. In Fig. 5 and 6, the tensile strength and the elongation at break are shown as function of the curing dose for both UV and EB cured membranes respectively. For both UV cured and EB cured membranes, the tensile strength increased linearly with increasing radiation dose leading to a higher cross-linking density. Membranes treated by the highest UV (5 J/cm²) and EB (500 kGy) radiation dose showed the highest tensile strength, 7.79 and 6.53 Mpa, respectively. In terms of elongation properties, a higher radiation dose reduced the elongation at break values for the cured samples. This decrease might be attributed to the rigidity caused by a higher cross-linking density. In general, intrinsically softer radiation of the UV treatment led to the alignment of the components of the cross-linked system to form a network that accomplishes maximum polymer film strength at equilibrium during polymerization. This process probably became disturbed in EB-curing applications due to its intrinsically higher energy. Nevertheless, the tensile strength of EB-cured polymeric films also showed an increasing trend, but less pronounced than for UV-cured films. This general enhancement in tensile strength and decrease

in elongation of cured films was due to the formation of cross-linked networks, hence inducing restricted mobility of the polymer chains.



Fig. 5. Tensile strength and elongation at break of cured PSU membranes as a function of UV dose. Tensile strength is indicated as circles and elongation at break as diamonds. Error bars represent standard deviation (n = 5).



Fig. 6. Tensile strength and elongation at break of cured PSU membranes as a function of EB dose. Tensile strength is indicated as circles and elongation at break as diamonds. Error bars represent standard deviation (n = 5).

5.3.4. Swelling behavior

In order to determine the solvent stability behavior of the UV and EB cured PSU membranes, swelling studies were performed. A mixture of water saturated with toluene was used in this analysis to observe the stability of the membrane as function of the cross-linking effect, since a fast dissolution of PSU was previously observed in the water-toluene mixture.

The *SD* and n_{norm} of a UV-cured PSU membrane for different UV dose rates, are shown respectively in Fig. 7 and 8. For the PSU cross-linked films, the increase in both radiation dose and cross-linker functionality induced a higher cross-link density as it was shown in our previous studies [19, 33]. In general, the UV treated membrane exhibited improved swelling resistance for the water-toluene mixture compared to a non-cured membrane sample. The non-cured sample reached a SD of 54% within 3 hours, while for low UV doses, the maximum SD obtained was 7% after 16 hours for UV doses up until 3 J/cm². Showing that the UV-curing stabilized the membrane. However, when the UV dose was further increased to 5 J/cm², the SD increased to 17%. This increase at the high radiation dose might destroy the polymer network that stimulates swelling.

For both the non-cured membranes with additives and that prepared with a UV dose of 5 J/cm², an initial increase in the refractive index could be observed followed by a decrease in the index. This indicates an excess free volume filling by toluene followed by a dilation of toluene. This phenomenon of an initial increase in the refractive index followed by a decrease was not observed for the UV-cured films with a radiation dose of 3 J/cm². Instead, the refractive index increased slowly but steadily over the whole measurement period. This would indicate that due to the rigidity of the cross-linked films, toluene diffused into the film very slowly and was still filling up the excess free volume of the cross-linked film.

The fact that both the non-cured samples and the sample cured with a radiation dose of 5 J/cm² have a n_{norm} below 1 at t=0, can be explained by the accuracy of the system. As n_{norm} is based on both the dry and swollen refractive index of the polymer, one is dealing with two different models to determine the refractive index. Where the dry refractive does not include an ambient in its model, the swollen refractive index does. Hence the discrepancy in the refractive index. Therefore, one can conclude that the trend that is observed for n_{norm} is qualitatively accurate, but not quantitatively.



Fig 7. Swelling degree comparison of UV-cured (with various UV dose) and non-cured PSU (without and with additive) thin films containing 5AC. The vertical axis is logarithmic for a better visualization.



Fig 8. Normalized refractive index comparison of UV-cured (with various UV dose) and non-cured PSU (without and with additive) thin films containing 5AC.

In Fig. 9 and 10, the increase of acrylate (AC) functionality as cross-linker is demonstrated as function of the SD and n_{norm} respectively. A higher functionality decreased the SD substantially. The lower functionality of 3AC induced a 40% higher SD than 4AC and neither of them resembled the excessive swelling of the non-cured sample. Further increase of cross-linker functionality lowered

the SD due to the inducing higher cross-linking degree. Also the trend observed in n_{norm} is consistent with the increased cross-linking degree induced by a higher cross-linker functionality, as observed in SD.



Fig 9. Swelling degree comparison of UV-cured (with fixed UV dose of 3 J/cm² and various crosslinkers) and non-cured PSU (without and with additive) thin films. The vertical axis is logarithmic for a better visualization.



Fig 10. Normalized refractive index comparison of UV-cured (with fixed UV dose of 3 J/cm² and various cross-linkers) and non-cured PSU (without and with additive) thin films.

5.4. CONCLUSIONS

The mechanical properties, separation performance, morphology and casting thickness effect of the UV and EB-cured PSU membranes were investigated in the present study. Additionally, the swelling extent of UV-cured PSU thin films was analyzed varying the radiation dose and cross-linker functionality. The mechanical characterization results demonstrated that increasing the energy dose in the radiation-based cross-linking process, elevated the tensile strength and lowered elongation at break of cured samples. At higher radiation dosages, the surface roughness of the samples decreased for both types of radiation-curing methods. Increasing the thickness of the cast film led to the appearance of macrovoids. Separation performance of the radiation-cured membranes also did not change distinctly with variation of casting thickness. In general, the swelling degree of UV-cured thin films reduced with higher radiation dose and acrylate functionality. UV radiation dose should be restricted up-to 3 J/cm² for cross-linking of prepared thin films, since a higher radiation dose increased the swelling degree.

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CHAPTER 6

CONCLUSIONS AND PERSPECTIVES

6.1. GENERAL CONCLUSIONS

This PhD thesis mainly focused on the preparation of solvent stable membranes via UV and EB irradiation-based cross-linking methods. Cured PSU membranes with robust chemical properties compared to non-cured membranes were achieved. Their excellent separation performances allow their implementation in SRNF applications.

6.1. 1. EB-curing

EB-curing was developed as a new and easy method for the synthesis of solvent stable membranes. The most effective parameters for EB-curing efficiency were the acrylate functionality and radiation dose. The highest cross-linking degree obtained with membrane consisting of penta-acrylate as a cross-linker cured under 500 kGy EB-dose. The double bond conversion increased with higher acrylate functionality and radiation energy. For any casting solution, at least an EB-dose of 300 kGy was necessary to keep the membranes stable in different solvents, such as NMP, DMF and THF. As their chemical stability increased, the membranes became more brittle, although they could still withstand high pressures during filtration. In general, higher cross-linking density induced lower IPA permeance and higher RB retention. The permeance decreased distinctly upon radiation which unfortunately complicated the use of EB-cured membranes in SRNF applications. With higher cross-linker amount and functionality, relatively larger macrovoids were observed via morphological characterization techniques.

6.1.2. Influence of phase inversion parameters in UV and EB-cured PSU-membranes

To optimize the separation performance of EB-cured PSU membranes, the effect of phase inversion parameters, including polymer concentration, evaporation time prior to immersion and co-solvent/solvent ratio, was explored. A slight decrease in permeance and an increase in rejection took place with higher polymer concentrations in the casting solution. Longer evaporation times prior to the precipitation continuously lowered the permeance, while no significant change was observed in rejection. Addition of a more volatile co-solvent THF to the casting solution caused constant decline in the permeance up to 0.011 l/m² h bar with increase in RB rejection up to 96.1% in IPA. The most significant morphological change was detected by increasing the time of the evaporation step, as the macrovoid structure turned into a spongy structure.

Additionally, cross-linked PSU membranes for solvent resistant nanofiltration (SRNF) were prepared similarly via the NIPS method, followed by UV-curing. The effect of phase inversion parameters

such as solvent/co-solvent ratio and evaporation time on SRNF membranes was investigated employing THF or DIO as co-solvent. Viscosity measurements were applied in order to explain precipitation kinetics of PSU solutions. Double bond conversion was observed by ATR-FTIR. Higher evaporation times and lower initial co-solvent concentrations resulted in less or even absence of macrovoids, according to morphological analysis via SEM. UV-treated PSU membranes showed enhanced stability after immersion in aprotic solvents at room temperature. Linking solvent resistance results with HSP interaction distances showed that the cross-linked membranes could be used with solvents having an interaction distance larger than 8.8 safely, without swelling problem. The performance of the membranes was evaluated in SRNF conditions. In general, as the evaporation time was increased from 0 to 100 seconds, permeances declined. The ideal evaporation time of the co-solvent before immersion in the coagulation bath assumed to be around 30s, after which the rejection remained almost constant around 90% and the permeance dropped to zero. To increase the flux, UV-cured membranes were post treated by immersion in DMF for 48 h. Higher permeance (up to a factor of 4) and lower rejection (up to 26.6%) was obtained after solvent activation. The membranes were stable which makes them useful as stable supports for preparation of TFC-membranes.

6.1.3. Comparison of UV and EB-curing

In the final part, the effect of casting thickness and radiation dose on the separation performance, morphology, mechanical and surface properties of UV and EB-cured membranes were compared. The tensile tests illustrated that higher energy doses in both radiation-based cross-linking processes resulted in superior tensile strength and inferior elongation at break of the cured membranes. UV– irradiated PSU films showed higher tensile strengths than EB-irradiated films due to the relatively soft radiation. Surface roughness of cured membranes diminished gradually with increased radiation doses for both procedures. Casting thickness had no remarkable effect on separation performance, but induced morphological changes. Cured films with 100µm wet thickness exhibited a spongy structure, while macrovoids started to appear and grow at thicknesses of 250 µm and 400 µm. The swelling behavior of UV-cured PSU thin films was also analyzed by in-situ ellipsometric analysis. The influence of acrylate functionality and radiation dose on the swelling degree of UV cross-linked films was investigated separately. Cross-linking had an immense impact on the membrane's swelling behavior. The swelling degree of PSU thin films decreased from around 63% to only 5% after UV exposure. Increase of radiation dose and acrylate functionality showed a similar tendency, namely

favoring higher cross-linking degrees. However, "excessive cross-linking" of the polymer network needs to be taken into account as it causes a partially negative effect on swelling.

In conclusion, both UV and EB cross-linking methods successfully enhanced the chemical resistance of PSU-based membranes. These new irradiation-based processes are greener, faster and consume less energy, compared to conventional chemical cross-linking techniques. The UV and EB-cured PSU membranes were stable in various solvents such as toluene, ethyl acetate and acetone. Their stability in other solvents such as NMP, THF, and DMF was lower due to the high swelling degree and increased fragility. EB-cured membranes were more convenient for use in UF due to their flux capacity. These membranes may also be considered practically employable for gas separations or as ultra-stable supports for TFC membranes for e.g. NF. On the other hand, UV cross-linked membranes showed good SRNF performance. With less complex and cheaper installations, UV-curing technique relatively stands outs more. However, exclusion of the photo-initiator (needed in UV-curing) and high radiation energy capability, renders EB-curing an attractive alternative technique for depth-curing of stable PSU membranes. After further optimization, UV and EB-curing could thus play an important role in industrial solvent stable membrane applications.

6.2. FUTURE PERSPECTIVES AND CHALLENGES

Fabrication of the solvent stable UV and EB-cured NF/UF membranes via NIPS are new emerging techniques and many aspects are still required to be explored deeply which is the main objective of the present study. The cross-linked membranes already showed satisfactory chemical resistance in harsh solvents. Therefore, future research should mainly focus on improving the curing parameters, increasing the membrane separation performance and its mechanical properties. Later stage research should ultimately focus on broadening the field of application further than merely SRNF.

Unfortunately, only few EB irradiation dose rates could be tested in the present study, due to the limited accessibility of the EB-curing unit. Nevertheless, it is known that the exposure of energy is a crucial parameter in radiation-based cross-linking, and therefore, tuning of different EB-doses is needed. A similar investigation is also desired for the UV-curing method. Although the membranes were lit mainly with UVA, other wavelengths of the UV-Vis spectrum (UVB and UVC) also reached the polymer. Presumably, these secondary wavelengths, owing to their intrinsic higher energy, caused partial PSU degradation, hence influencing the membrane's mechanical properties. This can be prevented by employing a LED UV-curing system, which gives the possibility to perform irradiation with well defined, narrow wavelengths (typically 30-40nm). On the other hand, traditional

mercury lamps emit a broad spectrum of light (200-800nm) and roughly 20% of this spectrum is used for UV curing, while more than 50% of the total energy is present in the infrared range. In addition, the post-treatment with DMF is worth to explore in more detail as flux shows a remarkable improvement following such simple treatment.

NIPS, the most commonly used phase inversion method, was employed in this study to synthesize integrally skinned membranes. An alternative technique could be vapor induced phase separation (VIPS), which could overcome to limitations of NIPS, such as use of insoluble cross-linkers and photo-initiators in the coagulation solvent bath. In this manner, the potential of other suitable additives for cross-linking could likewise be addressed.

The obtained fluxes decreased significantly after both curing processes. This problem can probably be solved with finding the optimum radiation dose for each method separately. In addition, all filtration experiments were carried out with a feed solution of IPA with RB. Screening of other solvents and solutes would definitely provide more insight on their interactions with the polymer, and hence on their transport mechanisms across the membrane.

The mechanical properties of the cured membranes are poor and should thus be further optimized. Impregnation baths with various impregnation agents (glycerol, dimethyl ethylene glycol or poly(propylene glycol) and solvents (isopropanol and other proper alcohols) could for example be investigated to achieve higher polymer flexibility and thus easier membrane handling. The UV LED curing system as expressed above could be another solution to this problem. Moreover, the process time and the way of washing subsequent to impregnation could also be explored in more depth.

Once the phase inversion parameters are optimized and different polymer types are screened, it is worth to investigate whether these curing techniques could also be applied in the synthesis of support membranes for gas separation (GS), nanofiltration (NF) and reverse osmosis (RO) membranes.

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