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Epoxy-based solvent-tolerant nanofiltration membranes prepared via non-solvent induced phase inversion as novel class of stable membranes

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ABSTRACT

A novel synthesis method of partially crosslinking a polymer solution prior to casting, has been successfully developed for the preparation of solvent-tolerant nanofiltration (STNF) membranes. STNF merges solvent resistant nanofiltration (SRNF) with aqueous nanofiltration. The feed solution consists of a mixture of solvent(s) and water, requiring a membrane with both high water permeability and solvent stability. In this work, epoxy resins are proposed to meet these requirements. The well-known epoxy curing bulk chemistry via ring-opening reactions has been applied followed by a phase inversion process, to form membranes with intermediate polarity, excellent stability and permeability, making them particularly suitable for the treatment of solvent/water mixtures.

Several epoxy monomers were screened, based on size and number of epoxide functional groups. Different amines with varying length and reactivity were chosen as curing agent. Both reagents were dissolved in dimethyl sulfoxide (DMSO) and left to react. The increasing solution viscosity was monitored as a function of time and related to the reaction rate of the epoxy-amine curing system. Integrally skinned asymmetric membranes were prepared via non-solvent induced phase inversion. Filtration experiments were carried out in 20/80 dimethyl formamide (DMF)/water mixtures with Rose Bengal (RB, 1018 g mol⁻¹), Rhodamine 6G (R6G, 479 g mol⁻¹) and Methyl Orange (MO, 327 g mol⁻¹) as solutes.

A blend of 2 epoxides, i.e. EPON 1009F (20 wt%) and EPON SU-8 (10 wt%), in DMSO resulted in RB retention of 99+% and a R6G retention of 77% in DMF/water with a permeance of 0.75 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. Addition of tetrahydrofuran (THF) as co-solvent (5/1, DMSO/THF) increased the selectivity further towards a 99% RB and R6G retention and an 85% MO retention with a permeance of 0.29 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. ATR-FTIR spectra indicated that the membranes are stable after immersion of 5 days in very harsh conditions, i.e. pH = 0–14, and in a variety of solvents.

1. Introduction

Solvent-tolerant nanofiltration (STNF) finds its origin between the already well-established fields of aqueous NF and solvent-resistant NF (SRNF). Applications for aqueous NF are found in biotechnology and food industry, but mainly in water treatment [1–4]. SRNF applications range from refining to fine chemicals and pharmaceutical industry [5,6]. STNF membranes should be able to separate solutes (with a size of 200–1000 Da) from water/solvents mixtures. The development of new

types of membranes for these applications is essential since nor aqueous NF nor SRNF membranes perform well in these conditions. Aqueous NF membranes can fail due to excessive membrane swelling and membrane degradation caused by the presence of the solvent, leading to selectivity losses. SRNF membranes on the other hand, designed to be chemically stable in less polar, organic media, commonly lead to too low fluxes in STNF. When the water fraction has a non-neutral pH, the operating conditions can even fully destroy SRNF membranes. The most frequently used membranes for aqueous treatments only have a limited pH stability

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Received 14 October 2020; Received in revised form 16 February 2021; Accepted 16 February 2021 Available online 25 February 2021 0376-7388/© 2021 Published by Elsevier B.V. (e.g. pH 2–11) [7]. A very small number of commercial membranes exists for more extreme pH environments, e.g. SelRO® MPS-34 of Koch membrane systems [8] and HYDRACoRe series by Hydranautics/Nitto Denko [9]. The ideal STNF membrane would be one that can cope with solvents present in the feed stream, is stable in a wide pH-range to tolerate as many aqueous conditions as possible, while being relatively hydrophilic so as to assure a high permeance.

In this work, membranes are prepared from multifunctional epoxy monomers and oligomers crosslinked with primary amines. Epoxy resins are used in a wide variety of applications, such as paints, coatings or adhesives [10,11]. After performing this crosslinking (in the epoxy context mostly referred to as 'curing'), they exhibit excellent chemical and thermal stability [10]. Aliphatic diamines, such as 1,6-hexane diamine (HDA) and Jeffamine D-230 (JEF), were selected as the curative because of their reactivity at low temperatures. The amines act as the nucleophiles in the nucleophilic ring opening polymerization, forming poly(β-alkanolamines). Another advantage for epoxy resins is their relatively hydrophilic nature which could provide a higher flux in solvent/water mixtures. Finally, epoxides were selected because of their well-known chemistry. The technical know-how about epoxides in bulk polymerizations could greatly speed up their feasibility in STNF membrane synthesis. Due to the wide range of applications in which epoxy resins are used, plenty of custom-made epoxides are being developed or are already commercially available [12,13]. In this work, two epoxy

compounds were selected, i.e. EPON 1009F, which was chosen for its relatively high molecular weight (MW), and EPON SU-8, which can provide a high crosslinking degree due to its high number of epoxy-groups per molecule (Fig. 1). EPON 1009F will be abbreviated to E2 and EPON SU-8 to E8, referring to the number of epoxy functional groups on each molecule.

2. Experimental

2.1. Materials

Dimethyl sulfoxide (DMSO, HPLC Grade) and 1,6-hexanediamine (HDA) were purchased from Alfa Aesar. Poly(propylene glycol) bis(2-aminopropyl ether) (JEF, MW ~230), rose bengal (RB, sodium salt, Dye content ~95%) and rhodamine 6G (R6G, Dye content ~95%), were purchased from Sigma-Aldrich. Methyl orange (MO) was purchased from Fluka. Toluene (99.5%) and tetrahydrofuran (THF, 99+%) were purchased from Acros Organics. Sulfuric acid (>95%), sodium hydroxide, acetonitrile (HPLC grade) and ethanol (analytical grade, 99.8%) were obtained from Fisher Chemical, hexane from Honeywell, EPONTM resin 1009F (pellets) and EPONTM resin SU-8 (pellets) from Brenntag. Matrimid[®] 9725 PI was obtained from Huntsman (Switzerland). The non-woven support layer which was used for casting was a polypropylene/polyethylene (PP/PE) fabric (Viledon[®] Novatexx 2471),



g) methyl orange (MO)

Fig. 1. Chemical structures of the epoxy compounds (a,b), curing agents (c,d) and solutes (e,f,g) used in this work (a) EPON 1009F (E2), (b) EPON SU-8 (E8), (c) 1,6-hexane diamine (HDA), (d) Jeffamine D-230 (e) rose bengal (RB), (f) rhodamine 6G (R6G), (g) methyl orange (MO)

kindly provided by Freudenberg Vliesstoffe (Germany).

2.2. Characterization

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were collected from the epoxy compounds and membranes (all dried prior to the measurements) using a Bruker ALPHA-P FTIR spectrometer with a diamond ATR crystal. Forty scans were collected at a resolution of 4 cm⁻¹. For every sample, at least three different positions were measured.

The epoxy compounds used in this work are produced for large scale applications that often do not require an analytical grade of purity, so it was decided to characterize them with ATR-FTIR, GPC and TGA. No significant impurities or additives were found which could influence the synthesis or performance of the membranes (Supplementary information, section S1.1-3, Fig. S1 – S2 and Table S1) and the epoxy compounds were used without further purification or pretreatment.

Gel permeation chromatography (GPC) was done on a Shimadzu 20A GPC system with a SPD 20A UV detector and a RID-20A refractive index detector. THF was used as solvent and polystyrene standards for calibration. Both epoxy compounds and curing agents were characterized with thermogravimetric analysis (TGA, TA instruments - Q500). TGA was performed under N₂ atmosphere at a rate of 5 °C/min from 30 °C to 650 °C.

Polymer casting solutions were characterized via viscosity measurements using a stress-controlled rotational rheometer (Anton Paar, MCR-501).

Membrane samples were characterized with non-contact atomic force microscopy (AFM), at ambient conditions using a Bruker, Dimension 3100D AFM. AFM was performed at ambient conditions in tapping mode using NCSHR probes from NanoAndMore GmbH. The cantilever was made out of Si with a spring constant of 40-50 N/m and a nominal tip apex radius below 5 nm. The AFM images were flattened with order 1 after scanning and after flattening, the RMS roughness (Sqroot-mean-squared roughness) and other relevant parameters were calculated using the ISO 25178-2 standard [14]. Contact angle measurements (Krüss, Drop Shape analysis system, DSA10Mk2) were performed by depositing 2 µl deionized water droplets onto the membrane surface with a syringe. At least 5 measurements were taken for each membrane sample. Scanning electron microscopy (SEM) was performed on both cross-section as surface samples with a Philips XL 30 FEG SEM. Cross-section samples were freeze-fractured in liquid nitrogen. All samples were coated with a 1.5-2 nm Au/Pd layer to reduce sample charging under the electron beam using a EDWARDS S150 sputter coater. Filtration data were obtained using a high-throughput dead-end filtration module with 16 positions $(1.54 \text{ cm}^2 \text{ filtration area per sample})$. In order to minimize concentration polarization, the feed solution was constantly stirred with a magnetic stirrer at 400 rpm. Permeance data were obtained gravimetrically and retention data with UV/VIS spectrophotometry (Shimadzu, UV-1800).

2.3. Membrane preparation

Membranes were prepared by dissolving the epoxides in DMSO. When a homogeneous solution was formed, the curing agent was added in stoichiometric quantities, unless mentioned otherwise. The solution was left to cure until it had reached a viscosity that allows for proper casting. Viscosity measurements were performed on an Anton Paar MCR501 rheometer, equipped with a Peltier system (P-PTD200) at 21 °C with solvent plate bottom and evaporation blocker. A cone and plate geometry with a cone angle of 1° and a diameter of 50 mm (CP50-1/Ti) was used.

In order to speed up the process, the samples were placed in an oven at 100 $^{\circ}$ C after addition of the curing agent. When the polymer solution reached a castable viscosity, it was removed from the oven and rapidly cooled in an ice bath to lower its reaction rate. At room temperature, the

solution was cast with an automatic casting device (Braive Instruments, Belgium) on a PE/PP non-woven, with a casting thickness of 250 μ m at a casting speed of 0.03 m s⁻¹. Coagulation occurred in a coagulation bath containing water as non-solvent to allow for phase inversion [15]. Afterwards, the samples were stored in water until further use. When THF was added as a co-solvent to the casting solution, the same procedure was followed but the curing was carried out at a temperature of 60 °C due to the low boiling point of THF and the cast film was allowed to evaporate for a fixed period of time prior to immersion in the coagulation bath. Due to partial evaporation, a locally increased polymer concentration will result in a so called "skin-layer" which will function as a resistance barrier between the bulk of the membrane and the non-solvent, hence delaying the demixing process and creating a more dense and selective membrane [16,17].

2.4. Adsorption study

Adsorption experiments were carried out by immersing 3.14 cm² membrane samples in beakers containing 50 mL of a 17.5 μ M dye in 20/80 DMF/water solution. The solutions were stirred with a magnetic stirrer at 400 rpm. All experiments were performed at room temperature (22 \pm 2 °C). The effect of contact time (0–24 h) was investigated by analysing 2 mL samples at each predetermined time with UV/VIS spectrophotometry (Shimadzu, UV-1800). The adsorption capacity was calculated from:

$$q_t = \frac{(c_0 - c_t) V}{M} \tag{1}$$

where q_t is the adsorption capacity (mg/g), c_0 and c_t are the dye concentrations in the liquid phase at time 0 and t respectively (mg/L), V is the volume of the solution (L) and M is the weight of the adsorbent (g) [18,19].

3. Results & discussion

3.1. Reaction mechanism

The curing reaction can occur via different reaction mechanisms. When a strong nucleophile, like a primary amine, is present, a nucleophilic substitution according to an S_N2-type mechanism will take place [20] (Fig. 2a). Ring opening will occur through direct attack by the nucleophile. The preferred site of attack is the sterically least hindered carbon of the epoxy ring and a β -alkanol-amine is formed. This secondary amine can follow the same reaction mechanism (Fig. 2b), but at a much slower rate. Rate constants for the (secondary amine) – epoxy reaction have been studied and are found to be 10-fold lower than for the (primary amine) - epoxy system [21]. This process eventually results in the formation of a tertiary amine which can then act as a Lewis base and initiate an anionic homopolymerization reaction of the epoxy, resulting in a poly(epoxy ether) [22]. But, due to the bulky nature of the side groups, a tertiary amine arising from this curing reaction will usually be sterically hindered, hence its catalytic effect towards the homopolymerization reaction will not be significant [21]. When it does occur, it is hypothesized that it can be initiated by 2 different mechanisms, in the absence and in the presence of hydrogen donors (Supplementary information, Fig. S3, a and b respectively). The reaction then propagates through nucleophilic attack of the alkoxide ion on the epoxy groups and is terminated through the formation of a new alkoxide ion [20,22].

3.2. Optimal reaction time before casting

In order to define when the casting solution had sufficiently cured for proper casting, the viscosity of the casting solution was monitored as a function of time. The viscosities of different concentrations of E2 in



Fig. 2. Epoxy curing mechanisms in presence of amines: (a) primary amines and (b) secondary amines react with epoxides through an S_N2 ringopening reaction.

DMSO (in absence of curing agents) were measured and compared to a reference sample of 16 wt% Matrimid® 9725 PI in DMSO, which was already known to be well castable (Table 1).

The reference sample (reference PI) has a viscosity of about 10 Pa s (Table 1, Supplementary information, Fig. S4), indicating that the epoxide solution viscosity should approach this value. The viscosity of the reference sample slightly decreases with increasing shear rates, as often observed for polymer solutions, known as 'shear thinning' [23]. The viscosity of the reference sample is situated between that of the 40 and 50 wt% E2 samples, so a first attempt in preparing a membrane was done with a 45 wt% solution. However, despite the good casting viscosity, the resulting membranes were very brittle and not suitable for filtration. This was ascribed to the low molecular weight of E2 (4600–7600 g mol⁻¹) which at this point is most likely below the critical MW required to start forming entangled polymer networks [24]. Because this entanglement would increase the toughness of the membrane, the MW of the casting solution was increased by implementing a curing step at room temperature before casting. Viscosities of the 30 and 40 wt% E2 solutions with HDA as curing agent in DMSO were measured at 21 °C as a function of time (Fig. 3). Measurements presented for 30 wt % E2 (left) were taken at a shear rate of 100 s⁻¹ close to realistic casting conditions. For the 40 wt% solution (right), oscillatory viscosity measurements were taken, thus resulting in a complex viscosity. These values can be compared with the values obtained from rotational viscosity measurements, as done with the 30 wt% sample, as long as the behavior of the solution is Newtonian [25]. For the measurements of the 40 wt% solution, an angular frequency (ω) of 1 rad s⁻¹ and a strain amplitude of 5% was chosen, assuring Newtonian and linear behavior of the solution.

For both solutions, viscosity is increasing exponentially as a function of time, proving a crosslinking reaction to occur. However, the reaction rate is low at room temperature as it takes several days for the 40 wt%

Table 1 Shear viscosity at a shear rate of 100 s⁻¹ of different concentrations of E2 in at 21 °C.

Concentration E2 (wt%)	Viscosity (Pa's)	
10	0.0147	
20	0.0845	
30	0.389	
40	3.21	
50	26.7	
Reference PI	6.71	

sample to reach a castable viscosity of around 10 Pa s. For the 30 wt% sample, the pursued viscosity is not even reached after 18 days. In further experiments, it was thus decided to use a curing temperature of 100 $^\circ$ C to speed up the process.

Oscillatory viscosity measurements were carried out to characterize the curing reaction of 26 wt% E2 with HDA in DMSO at 100 °C. Complex viscosity was measured after different reaction times, at angular frequencies varying from 0.1–100 rad s⁻¹ at a fixed strain of 5% at 21 °C. Results are presented in Fig. 4. Three main phases in the curing reaction can be distinguished: (1) Up to a reaction time of 9 h, the viscosity is low and independent of the angular frequency, resulting in Newtonian behavior [26]. (2) With increasing reaction time (9 h 30 min - 10 h) a second phase occurs, where a Newtonian plateau is found at lower angular frequencies and a drop in viscosity at higher angular frequencies, indicating a shear thinning effect [27]. (3) In a third phase (11 h–12 h), gelation has occurred due to the increased amount of crosslinks, and the solution is behaving non-Newtonian and gel-like over the entire range of angular frequencies.

Fig. 5 shows the complex viscosity at an angular frequency of 1 rad s^{-1} of the 26 wt% E2 in a DMSO casting solution at 100 °C as a function of time. An optimal casting viscosity of 10 Pa s is reached after 9 h 30 min, just after the solution passed from phase 1 to phase 2. At this reaction time, the elasticity of the sample is still limited so that the casting process will not be affected.

3.3. Filtrations

3.3.1. Influence of E2 concentration in the casting solution

Membranes were prepared from different E2 concentrations (ranging 15–30 wt%) in the casting solution. For each concentration, a stoichiometric amount of HDA was added and left to cure at 100 °C until a castable viscosity was reached. Curing times for each concentration can be found in Table 2. Filtrations were conducted with a 35 μ M RB in a 20/80 DMF/water feed solution (Fig. 6).

Increasing the E2 concentration in the casting solution results in higher retentions and lower permeances in the respective membranes. The highest retention is found with 26 wt% E2 ($R_{RB} = 86.4 \pm 2.4\%$) while the highest permeance is found with 15 wt% E2 ($P = 40.0 \pm 2.0 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$). When comparing the SEM pictures (Supplementary information, Fig. S5), lower concentrations of the casting solutions results in macrovoids in the membrane, while increased concentrations lead to more sponge-like structures. This is in agreement with earlier conducted studies on e.g. polysulfone [28] and PI [29]. Figs. S5e and S5f



Fig. 3. Viscosity increase due to epoxy curing as a function of time at 21 °C for (left) 30 wt% E2 and (right) 40 wt% E2, cured with HDA in DMSO.



Fig. 4. Oscillatory viscosity measurements at 21 $^\circ$ C of a 26 wt% E2 in DMSO solution, cured at 100 $^\circ$ C with HDA for different reaction times.



Fig. 5. Viscosity increase due to epoxy curing at 100 $^\circ C$ as a function of time (26 wt% E2 + HDA in DMSO).

Table 2

Curing times for different E2 concentrations and E2/E8 blends cured with HDA at 100 $^{\circ}$ C to reach a complex viscosity of around 10 Pa s at an angular frequency of 1 rad s⁻¹, 5% strain and at 21 $^{\circ}$ C.

E2/E8 concentration (wt%/wt%)	Curing time (h)
15/0	30
20/0	17
22/0	14.5
24/0	11.5
26/0	9.5
28/0	7
30/0	6
20/5	1.25
20/10	0.47



Fig. 6. Filtration results (10 bar, 35 μ M RB in a 20/80 DMF/water feed solution) for membranes with a varying E2 concentration cured with HDA in DMSO.

are SEM pictures from membranes prepared from high initial E2 concentrations (40 and 45 wt% respectively). Due to the high concentration, the casting solution was already at a sufficient viscosity and no pre-curing step was implemented. As a consequence, the critical MW at which entangled polymer networks can start to form was not yet reached (as mentioned in section 3.2) and these membranes were too brittle to be further tested, so no permeance nor retention data were obtained for these samples.

3.3.2. Curing time

Casting solutions were prepared containing 26 wt% E2 in DMSO and they were cured at 100 °C. The reaction was terminated at different reaction times, resulting in casting solutions with different viscosities. The complex viscosity of each sample was measured at an angular frequency of 1 rad s⁻¹, a strain of 5% and at a temperature of 21 °C



Fig. 7. Filtration results (10 bar, 35 μM RB in a 20/80 DMF/water feed solution) for membranes prepared from 26 wt% E2 with HDA in DMSO after various curing times.

(Supplementary information, Table S2). Membranes were cast from each solution and a filtration was performed (Fig. 7).

Usually, a higher viscosity of the casting solution results in a denser membrane due to delayed demixing [15,30]. However, the highest permeances are here observed for the membranes prepared from the casting solutions with the highest viscosity. As the curing reaction continues, more crosslinks are formed and a larger 3D-network is created with reduced flexibility. This leads to a more bulky, rigid structure which, when cast, results in a more open membrane morphology.

3.3.3. Curing agent type

When cured, epoxy resins become highly crosslinked thermoset polymers [31,32]. In this work, it was initially chosen to use an epoxy compound with a relatively long chain (MW between 4.6 and 7.6 kDa) and only two epoxy functional groups per macromolecule to ensure some flexibility and ease of handling of the resulting membrane. Another method to counter this brittleness could be to increase the MW of the curing agent. In this section, the effect is compared of using HDA $(MW = 116 \text{ g mol}^{-1})$ or JEF $(MW \sim 230 \text{ g mol}^{-1})$ as curing agent. Casting solutions were prepared for a range of E2 concentrations with their respective stoichiometric amounts of JEF. When compared to HDA, the reaction time is much longer for JEF (>48 h for 20 wt% and 24 h for 30 wt% E2 respectively). The lower reactivity of JEF can probably be attributed to an increase in steric hindrance as compared to HDA, making the nucleophilic attack of the amine less likely to occur. Membranes cured with JEF showed a lower permeance, and higher RB retention at lower monomer concentrations (Supplementary information, Fig. S6). This effect diminishes with higher concentrations. SEM photos (Supplementary Information Fig. S7) indicated no difference in morphology between membranes prepared with JEF or HDA.

3.3.4. Influence of curing agent concentration

The influence of the concentration of curing agent relative to the E2 concentration was studied by adding 50, 100, 200 and 500% of the stoichiometric amount, both for HDA and JEF. It was observed that adding a double amount of amine to the solution reduced the time to reach a castable viscosity (from 11 h 30 min to 7 h for HDA and from 49 h to 43 h for JEF). No castable viscosity was reached when adding 5 times the amount of curing agent. The higher reactivity of primary amines is beneficial to the reaction rate when twice the stoichiometric amount is added. When adding a 5-fold excess of the stoichiometric amount, too many epoxy-groups react with an unreacted primary amine, hence limiting the size of the created network. Also when adding only half the stoichiometric amount, the reaction time increased and no castable viscosity was achieved. Membranes were prepared from both single and double amine concentration (Supplementary information, Fig. S8). The membrane performance declined when adding more curing agent, i.e. a slight decrease in retention and a significant decrease in permeance.

3.3.5. Epoxy blends

In order to increase the membrane selectivity and its chemical stability, a second epoxy compound was added to the casting solution. EPON SU-8 (E8) was chosen because of its high number of epoxy-groups (8). Blending both compounds should provide a high crosslinking degree thanks to the high number of epoxy groups on E8, while maintaining mechanical stability thanks to the higher MW of E2. Blending both epoxy compounds also drastically reduced the necessary reaction time in order to reach a castable viscosity (Table 2). The added stoichiometric amount of curing agent is calculated as the weighted average, depending on the ratio of the epoxy compounds. Replacing E2 with E8 in the casting solution decreased the permeance while increasing the retention (Fig. 8). When replacing 10 wt% E2 with 10 wt% E8 in a 30 wt% casting solution, both permeance and RB retention increased (from 0.41 \pm 0.05 to 0.81 \pm 0.04 $\rm Lm^{-2}h^{-1}bar^{-1}$ and from 86.5 \pm 3.6 to 98.9 \pm 0.4%



Fig. 8. Filtration results (10 bar, 35 μ M RB in a 20/80 DMF/water feed solution) for membranes prepared from E2/E8 blends in different weight ratios with HDA in DMSO.

respectively).

To gain more insight in the separation performance of these membranes, a second filtration was conducted with a smaller solute. For the (20/10) E2/E8 membrane, a R6G retention of 77.0 \pm 11.6% was observed with a permeance of 0.75 \pm 0.04 $\rm Lm^{-2}h^{-1}bar^{-1}$ (Supplementary information, Fig. S9).

3.3.6. Addition of THF as co-solvent

In order to further increase the retention of the membrane, THF was added as co-solvent, which allows the introduction of an evaporation step before the cast film is immersed in the coagulation bath [33]. Based on the results from section 3.4.5, a (20/10) wt% E2/E8 blend was dissolved in a (5/1) DMSO/THF solvent mixture. Evaporation time was varied between 30 s and 3 min and the resulting membranes were filtrated with both RB and R6G as solutes (Supplementary information, Fig. S10). When the cast films were left to evaporate for 3 min, the resulting membrane (further referred to as blend_DMSO/THF) had a retention of 99.8 and of 98.9% for RB and R6G respectively. Hence, a smaller solute was tested (MO, 327 g mol⁻¹) and an 85.1% retention was found with a permeance of 0.29 Lm⁻²h⁻¹bar⁻¹ (Fig. 9). The molecular weight cut-off (MWCO) value based on these data is found to be below 400 g mol⁻¹.

3.3.7. Solvent and pH stability

Solvent and pH stability was investigated for the reference membrane (26 wt% E2 cured with HDA, further referred to as REF_26) and the blend (20/10) E2/E8 in DMSO membrane, further referred to as



Fig. 9. MWCO curve for blend_DMSO/THF, a (20/10) E2/E8 membrane prepared from a 5/1 (DMSO/THF) mixture with a 3 min evaporation time. Filtration conditions: 10 bar, 35 μ M solute in a 20/80 DMF/water feed solution; filtrations in triplo with RB, R6G and MO as solutes respectively.



Fig. 10. Filtration results (10 bar, 35 μ M dye in a 20/80 DMF/water feed solution) for blend_DMSO (left) and blend_DMSO/THF (right) after 5 days in an aqueous solution at pH = 0 or pH = 14.

blend_DMSO, by immersing them for 5 days in various solvents and aqueous solutions at pH 0 and 14. ATR-FTIR spectra were taken of the different samples. They indicated a clear improvement of solvent stability when using the epoxy blend over the reference membrane (Supplementary information, Fig. S11): where the REF_26 proved to be unstable in most solvents, almost no changes in the spectra were observed with the blend_DMSO, indicating the necessity of a better crosslinked structure when these membranes are to be used in more aggressive environments. The pH stability of the blend_DMSO and blend_DMSO/THF membranes was tested with a filtration after immersion for 5 days in aqueous solutions of pH = 0 and pH = 14 respectively. Fig. 10 confirms that the membrane performance after this treatment remains unchanged.

3.3.8. Influence of dye adsorption

To verify whether the retention of solutes can at least partly be due to adsorption side-effects, 2 anionic dyes, i.e. RB and MO, and 1 cationic dye, i.e. R6G, were selected. The adsorption experiments were carried out on the membranes REF_26, blend_DMSO and blend_DMSO/THF. Fig. 11 shows the adsorption on the blend_DMSO membrane for the 3 dyes. In all tests, an equilibrium was reached in less than 10 h (see Fig. 10 and also Supplementary Information Fig. S12). Even though there is no clear charge present on the prepared membranes, the highest adsorption capacity was found with RB, which carries a double negative charge, followed by MO with a single negative charge. R6G, with a single positive charge, hardly sorbed. This means that for R6G (479 g mol⁻¹) and MO (327 g mol⁻¹), the membrane selectivity can be almost exclusively attributed to size-exclusion rather than adsorption effects,



Fig. 11. Dye adsorption on the blend_DMSO membrane.

Table 3

Contact angle measurements with deionized water of REF_26 (26 wt% E2 + HDA), 15 wt% E2 instead of 26 wt %, JEF instead of HDA, post-treatment with pH = 0 for 5 days, 20 wt% E2 + 10 wt% E8 instead of 26 wt% E2 (blend DMSO).

Membrane	Contact angle (°)
REF_26	63.9 ± 2.1
15 wt% E2	63.7 ± 1.2
JEF	55.8 ± 1.7
pH = 0	52.4 ± 3.1
blend_DMSO	59.1 ± 3.5

while this can be a combination of both effects for RB.

3.4. Membrane characterization

3.4.1. Contact angle measurements

Membrane samples were air-dried and contact angle measurements were performed (Table 3). The reference membrane is a 26 wt% E2 membrane, pre-cured at 100 °C with a stoichiometric amount of HDA. When using JEF instead of HDA, a drop of around 8° in contact angle is observed, as attributed to the ethylene oxide blocks in JEF that render it more polar. Although less pronounced as with JEF, only blending both epoxy compounds also decreases the contact angle. The addition of E8 increases the number of epoxy functional groups, hence creating a more crosslinked structure with more polar β -alkanolamine bonds. The highest decrease in contact angle occurred when the reference membrane was first immersed in a sulfuric acid solution (pH = 0) for 5 days. Probably, the decrease can be attributed to an acidic hydrolysis of unreacted epoxy-groups [20,34], which would introduce extra hydroxyl groups.

Table 4

Summary of the AFM results: root mean square height (Sq), mean surface roughness (Sa) and peak to valley height (Sz).

Sq (nm)	Sa (nm)	Sz (nm)
5.76	3.77	67.1
6.89	5.46	62.7
12.6	10.2	72.7
5.50	3.12	70.7
	Sq (nm) 5.76 6.89 12.6 5.50	Sq (nm) Sa (nm) 5.76 3.77 6.89 5.46 12.6 10.2 5.50 3.12

3.4.2. Atomic force microscopy (AFM)

The surface morphology was analyzed for REF_26 (26 wt% E2 precured with a stoichiometric amount of HDA at 100 $^{\circ}$ C) and effects of epoxy compound concentration, curing agent type and use of blends of epoxy compounds were investigated. The same membrane sample labeling was used as for the contact angle measurements. Results are presented in Table 4 and Supplementary information, Fig. S13.

All epoxy-based membranes have a relatively high surface roughness. This could be less desired for the 15 wt% E2 membrane, which could potentially be used as a chemically robust support layer for STNF or SRNF thin film composite (TFC) membranes [35]. The influence of blending different epoxy compounds on the surface roughness is negligible. A slight increase in roughness is found when curing with JEF in comparison with curing with HDA.

4. Conclusions

A new type of integrally skinned asymmetric (ISA) membranes was developed via the process of phase inversion, based on the well-known chemistry of epoxy ringopening reactions. By partially crosslinking the casting solution prior to casting, an optimal viscosity was reached to allow preparation of defect free films, independent of the starting concentration. A whole new range of membrane materials can be prepared this way, because plenty of starting materials (epoxy resins) are commercially available and relatively cheap as they are used in a wide scope of industrial applications. Here, two different epoxy compounds (EPON 1009F and EPON SU-8) were used separately and in blends, resulting in membranes with separation performances in the UF-NF range and with excellent stability in a variety of solvents, as well as in extreme pH-conditions (from 0 to 14). NF membranes reached a RB (1018 g mol $^{-1}$) retention of 99.8 \pm 0.2%, a R6G (479 g mol $^{-1}$) retention of 98.8 \pm 0.9% and a MO (327 g mol^{-1}) retention of 85.1 \pm 15% while having a permeance of 0.29 \pm 0.16 Lm⁻²h⁻¹bar⁻¹. When using low concentrations of EPON 1009F (15 wt%) and HDA, highly permeable membranes (P = $40.0 \pm 2.0 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) were prepared which can be good candidates as support layer for the preparation of TFC membranes.

CRediT authorship contribution statement

Maarten Bastin: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization. **Jasper Raymenants:** Investigation, Validation. **Marloes Thijs:** Validation. **Anja Vananroye:** Validation, Resources. **Guy Koeckelberghs:** Validation. **Ivo Vankelecom:** Conceptualization, Methodology, Validation, Resources, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.119206.

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Epoxy-based solvent-tolerant nanofiltration membranes prepared via nonsolvent induced phase inversion as novel class of stable membranes

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Supplementary information

S1.1 ATR-FTIR

ATR-FTIR spectra were taken from both epoxy monomers (Fig S4). A characteristic peak for epoxides is located at a wave number of 915 cm⁻¹ (C-O deformation of an oxirane ring) [1]. As can be seen from the spectrum, this peak is much more pronounced for EPON SU-8 (E8) as for EPON 1009F (E2) due to the higher density of epoxy functional groups in E8 in comparison to E2 (8 epoxy groups for a MW of ~1700 g mol⁻¹ for E8 vs. 2 epoxy groups for a MW of ~6100 g mol⁻¹ for E2).



Figure S1 ATR-FTIR spectra of the epoxy monomers EPON 1009F (E2) and EPON SU-8 (E8)

S1.2 Gel permeation chromatography (GPC)

Both epoxy compounds and the curing agent JEF were analyzed with GPC. According to the technical datasheets of E2 and E8, a molecular weight of 4600 - 7600 g mol⁻¹ and of 1560 - 1840 g mol⁻¹ is expected respectively. JEF should have a MW of 230 g mol⁻¹. In table 1, the results for the three measurements are summarized. For E2, a rather large molecular weight is found and quite a high dispersity (Đ) of 1,81, indicating a wide distribution of molecular sizes. For E8, three peaks are obtained with the middle one corresponding best with the technical specifications, although the distribution is smaller than claimed by the supplier. This deviation can be attributed to the nonlinearity of E8. The hydrodynamic volume occupied by the branched polymers is smaller than occupied by linear polymers of the same size, underestimating the weight and number average MW for nonlinear polymers [2]. The results for JEF come close to the expected value of 230 g mol⁻¹ and indicate a very uniform distribution.

	Sample	M _n (g mol⁻¹)	M _w (g mol⁻¹)	Ð
E2		11108	20089	1,81
E8	peak 1	8156	9110	1,12
E8	peak 2	851	1128	1,33
E8	peak 3	266	269	1,01
JEF		277	290	1,05

Table S1 GPC results for E2, E8 and JEF

S1.3 Thermogravimetric analysis (TGA)

Both epoxy compounds and curing agents were analyzed with TGA (Fig. S5). HDA and JEF already start evaporating below the applied curing temperature of 100 °C. This emphasizes the importance of performing the curing reaction in closed containers, since the reaction can take several hours before the viscosity of the cast solution is suitable for membrane casting. For both E2 and E8, the curing temperature is far below the temperature at which a weight decrease is observed.



Figure S2 TGA of epoxy compounds and curing agents (under N_2 atmosphere at a heating rate of 5 °C/min from 30 °C to 650 °C)



Figure S3 Epoxy curing mechanisms in presence of a tertiary amine: initiation of an anionic homopolymerization reaction



Figure S4 Shear viscosity of different concentrations of E2 in DMSO and of a 16 wt% PI in DMSO reference system at 21 °C



Figure S5 (a-f) Cross-section SEM images of membranes prepared from varying E2 concentrations: (a) 15 wt%, (b) 20 wt%, (c) 26 wt%, (d) 30 wt%, (e) 40 wt% and (f) 45 wt% (at different magnification)

Table S2 Complex viscosity at 1 rad s^{-1} , 5 % strain and at 21 °C for different curing times of 26 wt% E2with HDA in DMSO

Curing time (h)	Complex viscosity (Pa ⁻ s)
6	1,6
8	2,3
9,5	11,8
10	17,2



Figure S6 Comparison of curing agent type towards membrane performance in terms of (left) permeance and (right) retention for different concentrations of E2 (10 bar, 35 μ M RB in a 20/80 DMF/water feed solution)



26 wt% E2 + JEF



Figure S7 SEM images of (top) HDA-cured E2 membranes and (bottom) JEF-cured E2 membranes: cross-sections (a - c) and surfaces (d and e)



Figure S8 Filtration results (10 bar, 35 μ M RB in a 20/80 DMF/water feed solution) for membranes prepared from casting solutions with a varying concentration of curing agents HDA (left) and JEF (right) in DMSO



Figure S9 Filtration results (10 bar, 35 μ M R6G in a 20/80 DMF/water feed solution) for membranes prepared from E2/E8 blends



Figure S10 Filtration results (10 bar, 35 μ M dye in a 20/80 DMF/water feed solution) for membranes prepared with a (5:1) DMSO / THF solvent mixture with various times of evaporation prior to coagulation. Dyes used during filtration: RB (left), R6G (right)



Figure S11 ATR-FTIR spectra of (left) REF_26 and (right) blend_DMSO after immersion in different solvents for 5 days



Figure S12 dye adsorption capacity of (left) REF_26 and (right) blend_DMSO/THF



Figure S13 (1x1)µm AFM images of (a) REF_26, (b) 15 wt% E2, (c) membrane cured with JEF and (d) blend_DMSO

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Graphical abstract

