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Solvent Stable UV cured Acrylic Polysulfone Membranes

M. Mian Farrukh[1], P. Bosch[2], M. Giagnorio[3], A. Tiraferri[3*], M. Sangermano[1*]

[1]Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, C.so Duca degli Abruzzi 24, 10129 Torino, Italy

[2]Departamento de Química Macromolecular Aplicada, Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas (CSIC), C/ Juan de la Cierva, 3. Madrid E-28006, Spain

[3]Politecnico di Torino, Dipartimento di Ingegneria dell'ambiente, del territorio e delle infrastrutture, C.so Duca degli Abruzzi 24, 10129 Torino, Italy

Corresponding authors (*): marco.sangermano@polito.it

alberto.tiraferri@polito.it

Abstract: A systematic investigation of the effect of the presence of acrylate resin on polysulfone-based membranes was performed with the aim to obtain chemically stable crosslinked membranes without affecting their flux performances. The membranes were prepared via UV curing of the polymer dope followed by non-solvent induced phase separation process. Two different acrylic monomers were investigated and their amount was varied in the polymer dope, to study the influence of concentration on final result. High crosslinking degrees were achieved by irradiating the solution for one minute. Morphological investigations on the active surface and on the cross-sections of the fabricated membranes, showed that typical porosity of ultrafiltration membranes was obtained starting from solutions containing at low amount of crosslinker (10 wt. %), which is consistent with the water flux values which were comparable to that of the pristine polysulfone membrane. High concentrations of crosslinker

resin in the initial polymer dope produced denser membranes with lower permeability. High rejection of 27 nm particles (> 90%) was measured on all samples having measurable flux. The addition of the crosslinker allowed to obtain stability in various solvents without affecting the flux and rejection performance of the porous membranes.

Keywords: polysulfone membranes UV Curing, acrylic resins.

1. Introduction

The most acknowledged method to fabricate porous membranes for ultra- and microfiltration is the phase inversion process [1-5], and the most common technique is that based on non-solvent induced phase separation (NIPS) [6]. In this process, the polymer solution is cast as a thin film and is subsequently immersed in a non-solvent bath. Precipitation occurs because the good solvent in the polymer solution is exchanged for the non-solvent. Among polymers, polysulfone (PSf) has been widely used to prepare microfiltration and ultrafiltration membranes, because it possesses high mechanical strength and resistance towards a relatively broad range of chemicals [7]. The main drawback of PSf-membranes is the lack of stability in certain solvents

To improve the chemical resistance of membranes prepared via non-solvent induced phase separation (NIPS), post-synthesis treatments are required to crosslink the polymer. In our previous paper, a two-step method involving NIPS and UV curing was proposed for a methacrylated PSf macromonomer [8]. The crosslinked membranes exhibited pure water permeability in the range of tight ultrafiltration membranes and adequate solvent stability. Previous important contribution from Vankelecom [9, 10] reported detailed investigations of the influence of UV curing on the morphology and performance of PSf membranes containing different acrylates with varying functional groups. In those studies, the UV curing process was performed after NIPS. However, our previous findings [8] have shown that the photocrosslinking step should precede the phase inversion process in order to obtain more uniform membranes. Furthermore, the works reported in the literature did not investigate the effect of the crosslinker content into PSf formulations.

Therefore, in this paper we build upon the previous studies by reporting a systematic investigation of the effect acrylate resin concentration on PSf-based membranes. Additionally, we establish the protocol in which the membranes are prepared via UV curing followed by NIPS process. The conversion of the pure acrylic double bond was evaluated by FTIR analysis and it was compared with the conversion obtained for the polymer dope used for membrane fabrication. The crosslinked membranes were characterized with evaluation of their viscoelastic properties, solvent stability, morphology, water flux, and selectivity, thus allowing understanding of the influence of acrylic monomer concentration on membrane structure and performance.

2. Experimental

2.1 Materials

Polysulfone (PSf, Mn=22000 g/mol), N,N, dimethyl formamide (DMF, Anhydrous, 98.8%), acetone (99.9 %), and acrylic monomers poly(ethylene glycol) diacrylate (PEGDA, Mn=700 g/mol), bisphenol-A-ethoxylate (2EO/phenol) diacrylate (BEDA, Average Mn=512 g/mol inhibited with 1000 ppm MEHQ) were purchased from Sigma–Aldrich. The photo initiator (PI) phenylbis(2,4,6-trimethylbenzoyl)phoshineoxide (BAPO) was kindly provided by BASF. A glass plate was used as casting substrate in order to prepare the membranes.

2.2 Preparation of UV cured acrylic modified PSf membranes

The modified polysulfone (PSf)-based membranes were prepared via UV curing and non-solvent induced phase separation (NIPS). A 15 wt. % of pristine PSf solution in DMF was prepared by continuous stirring at 60 $^{\circ}$C for 7 hr. Thereafter, the solution was cooled overnight. Modified PSf solutions were prepared by incorporating a diacrylate monomer crosslinker along with a photo-initiator. Two different crosslinkers were investigated, BEDA and PEGDA, which were added individually to modify the polymeric solution: the effect of three concentrations was studied, namely, 10, 20 and 30 wt. %. The photoinitiator was always added at 3 wt. % with respect to the acrylic content. The purpose of the photoinitiator was solely to induce crosslinking, thus it was not added to the pristine PSf dope. The solutions were thoroughly stirred and left to rest for 5 mins to release the trapped air bubbles. They were then cast onto a glass plate with a nominal film thickness of 100 μm. The film thickness was controlled using a wire-wound applicator. FESEM analysis confirmed that the nominal thickness was 100 μm (see below). The composition of the different casting solutions is given in Table 1.

The crosslinking was performed through UV curing and before phase separation. The UV curable films were irradiated in a static UV lamp for one min under nitrogen atmosphere. The major UV irradiation light was UVA (320 – 390 nm). The energy dose utilized to cure the membranes was 10.05 J / cm^2. The degree of crosslinking was measured via FTIR analysis. Subsequently, NIPS was carried out in a coagulation bath, containing distilled water, for 24 hr.

During the casting and phase separation of membranes, the temperature of air was 25 ± 3 ^{o}C and the relative humidity was 40 ± 10 %.

Table 1: Composition of different membrane casting solutions and operational methodologies (PSf content always 30 wt%, photoinitiator content equal to 3 wt% with respect to the amount of acrylic resin)

Membrane Code	BEDA wt. %	PEGDA wt. %
M00	-	-
M11	10.0	-
M12	20.0	-
M13	30.0	-
M21	-	10.0
M22	-	20.0
M23	-	30.0

2.3 Characterizations of modified PSf Membranes

2.3.1 Fourier Transform Infrared Analysis (FTIR)

FTIR analyses were performed in transmission mode using the spectrophotometer by Thermo Electron Corporation,. The solutions were analyzed after being applied onto a silicon wafer and UV cured. A film of 25 µm were coated on the silicone wafer and the analysis was carried out with a resolution of 4 cm^{-1} and samples were scanned 32 times in the wave number range between 650 and 4000 cm^{-1}. A background measurement was run before each of the samples was subjected to FTIR analysis. The conversion of acrylate double bonds was calculated by following the decrease of the peak area of C=C group at 810 $cm^{-1}$and normalized with the peak area of C=O group at 1730 cm^{-1}.

2.3.2 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was performed using Triton DMTA apparatus equipped with a tension – film clamp assembly and operating in frequency strain mode. The size of all samples was 6×10^{-3} m by 10×10^{-3} m. In this technique, the membrane was held in tension mode at a designated preload force equal to 0.001 N while sinusoidal stress was applied and both storage and loss modulus were obtained over the range of temperature. The ending temperature was set at 200 ^{o}C while the starting temperature was set with respect to solution composition in order to analyze the bis-phasic curves of PSf modified with acrylate monomer. The rate of increase of temperature was set as 3 ^{o}C per min.

2.3.3 Field Emission Scanning Electron Microscopy (FESEM)

The morphology of membrane surfaces and cross-sections was analyzed through FESEM. The instrument was MERLIN model FESEM, by ZEISS, equipped with state of the art GEMINIS kind of column ensuring fine control of spot and current. The samples were snapped after immersion in liquid nitrogen and mounted onto SEM stubs using carbon tape. For cross-sectional analysis, the sharp edged samples were also produced via immersion in liquid nitrogen and the samples were clamped with edges in upward position. The samples were sputter coated with Chromium (8.0 nm) so the charging effects can be counteracted. The magnification and current during imaging were adapted based on the properties of each sample.

2.3.4 Solvent resistance test

The solvent resistance of crosslinked membranes was evaluated by immersing small pieces of membranes in various solvents. The immersion was carried out at room temp for at least 120 hr. A qualitative evaluation was performed by visual inspection of the membranes. The resultant membranes were categorized into three grades: 1) stable 2) swollen 3) dissolved in the specific solvent.

2.3.5 Permeability and rejection tests

The water permeability of the membranes was tested in a stirred cell apparatus (Amicon 8010, Millipore Co) with samples having a diameter of 1 inch. In order to drive the flow, the cell was pressurized with N_2 (g) to reach a pressure drop of 15 psi, monitored using a pressure gauge. At this pressure, the membranes were subjected to pre-compaction for 10 mins. Thereafter, flux and rejection tests were performed at lower constant applied pressure of 8 psi. Flux through the membranes was determined by measuring the change of permeate mass in time and permeability was hence calculated by dividing this value by the sample area and by the applied pressure. The experiments were conducted using deionized water; obtained from a Milli-Q ultrapure water purification system, they were repeated four times for each membrane type and the values were averaged.

Rejection was tested with a solution of polystyrene latex beads with a nominal diameter from TEM measurements of 27±4 nm and average hydrodynamic diameter of 39 nm, the latter evaluated by light scattering. The nanoparticles were chosen because inert, i.e., they did not interact with the membrane material. Therefore, their rejection was solely based on size exclusion, thus providing information on the average size of the pores at the membrane/water interface. The beads were chosen based on a size typically separated by ultrafiltration. A spectrophotometer was used to measure the absorbance of both the feed solution (c_f) and the permeate solution (c_p) at a wavelength of 260 nm. A previously obtained linear correlation allowed calculation of the particle concentration from the value of absorbance. The rejection of latex particles, R, was then calculated through the following equation: $R = (1 - \frac{C_p}{C_f})$.

3. Results and Discussion

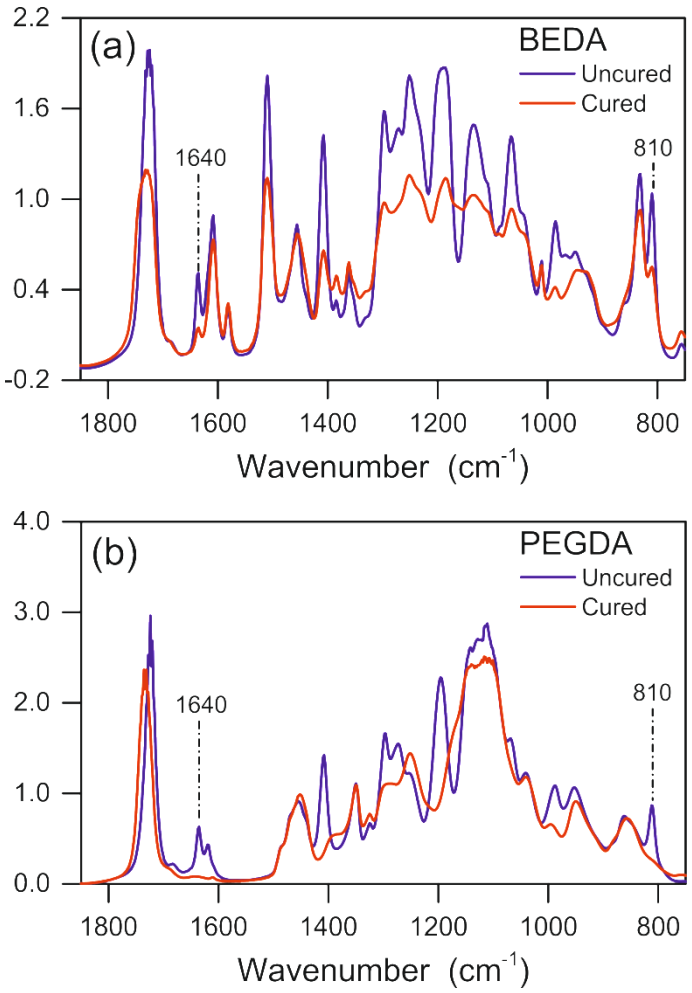
3.1 Cross linking degree of modified PSf membranes

The degree of crosslinking of both pure acrylate solutions and of the polymer dopes used for membrane fabrication was measured via FTIR. The C=O (1730 cm^{-1}) peak was taken as reference while the C=C (810 or 1640 cm^{-1}) peak was analyzed to measure the conversion percentage. Firstly, the degree of crosslinking of pure acrylate was optimized in terms of time of UV irradiation required to achieve optimum conversion of C=C.

In Figure 1a and 1b, we report the FTIR spectra before and after 1 min of UV-irradiation for pristine BEDA and PEGDA formulations with photoinitiator, respectively. After 1 min of

irradiation, the average acrylic double bond conversion for BEDA and PEGDA was 85% and 100%, respectively. The lower BEDA acrylic d.b. conversion is due to the well-known vitrification effect, since BEDA crosslinked network is characterized by a Tg that is significantly higher than room temperature (around 85 °C, as reported below). Crosslinked PEGDA also possesses a very low Tg (around –40 °C), thus assuring mobility of the macroradical growing chains and therefore reaching completeness of the addition reaction. However, the high percentage of conversion suggests that 1 min of irradiation is sufficient to obtain desired extent of crosslinking during membrane fabrication.

Figure 1: FTIR Spectra of (a) pristine BEDA and of (b) pristine PEGDA before and after 1 min of UV irradiation. Nominal film thickness of 100 µm.



Therefore, the acrylic double bond conversion was evaluated for the PSf formulations containing different contents of the acrylic monomers. All the data are reported in Table 2. As an example, Figure 2a and 2b show the FTIR spectra before and after 1 min of UV-irradiation for the PSf solution containing, respectively, 20 wt. % of BEDA (Figure 2a) and 20 wt. % of PEGDA (Figure 2b). The achieved conversion for the acrylic monomers into PSf solutions were high and in accordance with their conversion as pristine monomers.

3.2 Viscoelastic behavior of membranes

The viscoelastic behavior of membranes was characterized by dynamic mechanical thermal analysis (DMTA), which gives the evaluation of both viscous and elastic component of the modulus of the material over a large temp interval and the tan δ curves (tan δ = E'' / E': ratio of loss modulus to storage modulus) of all crosslinked membranes. The curves related to the DMTA analysis of the crosslinked membranes are reported in Figure 3.

From DMTA curves, it is evident that all the crosslinked membranes showed a biphasic nature, due to the interpenetration of the crosslinked acrylic network and the PSf polymeric chains. All the data are collected in Table 2. When BEDA was used as a crosslinker, the first tanδ curve centered at around 85 °C, while when PEGDA was used, the tanδ curve centered at around –45 °C. These Tg data are in agreement with the Tg of the corresponding pristine crosslinked acrylates [11], and therefore attributable to the UV cured acrylic network. The second tanδ curve is attributable to the PSf domains. When BEDA is used as a crosslinker, the maximum of tanδ curve related to the PSf domain is shifted to higher temperature by increasing the acrylate monomer content. This could be related to the higher croslsinking density achieved in the presence of BEDA which show a lower molecular weight between crosslinks with respect to PEGDA. When PEGDA is used as a crosslinker, the tanδ related to PSf domain is always centered at around 160 °C, which is the typical Tg of pure PSf [12].

Figure 2: FTIR Spectra of PSf solution containing (a) 20 wt. % of BEDA and (b) 20 wt. % of PEGDA before and after 1 min of UV irradiation. Film thickness 100 µm.

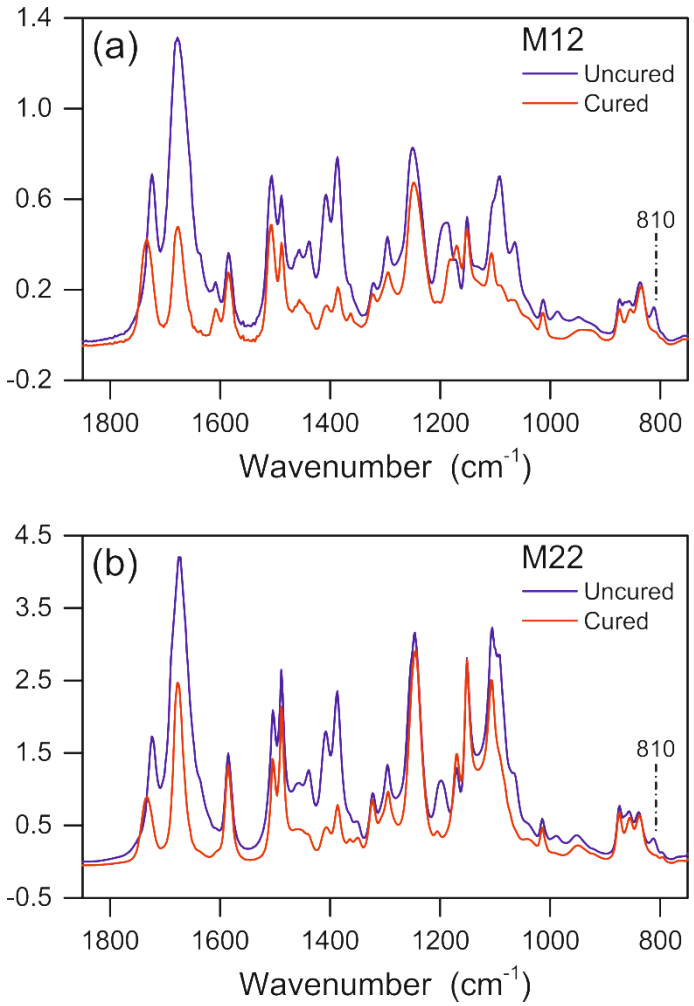
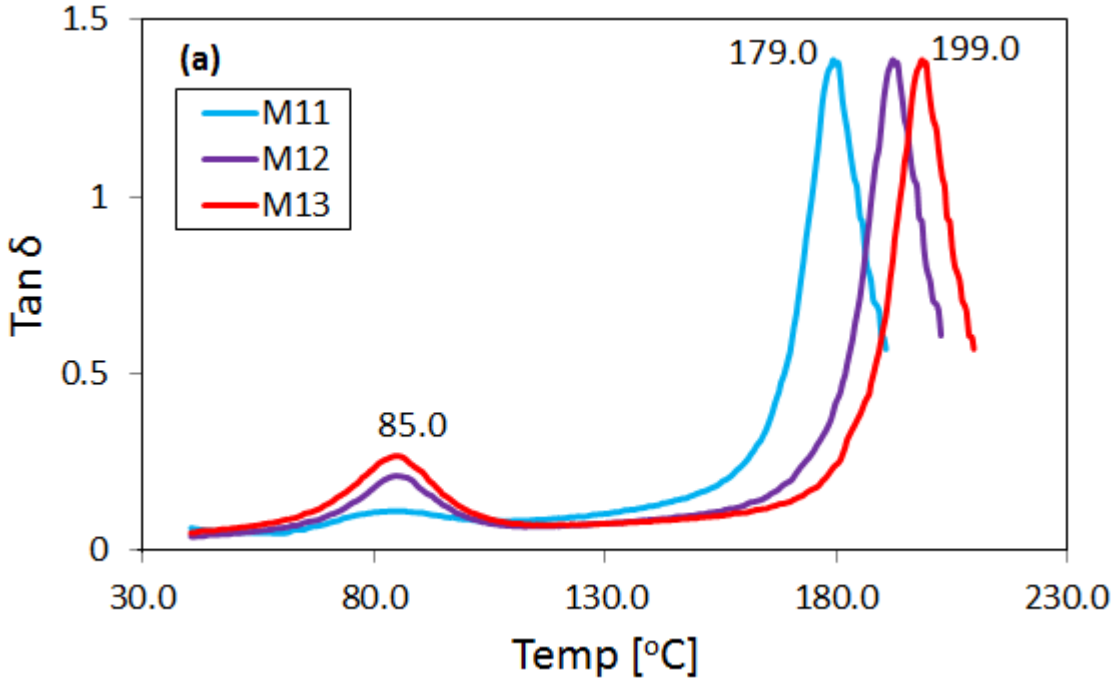


Figure 3: **3(a) DMTA curves of PSf solutions containing BEDA; Figure 3(b) DMTA Curves of PSf solutions containing PEGDA.**



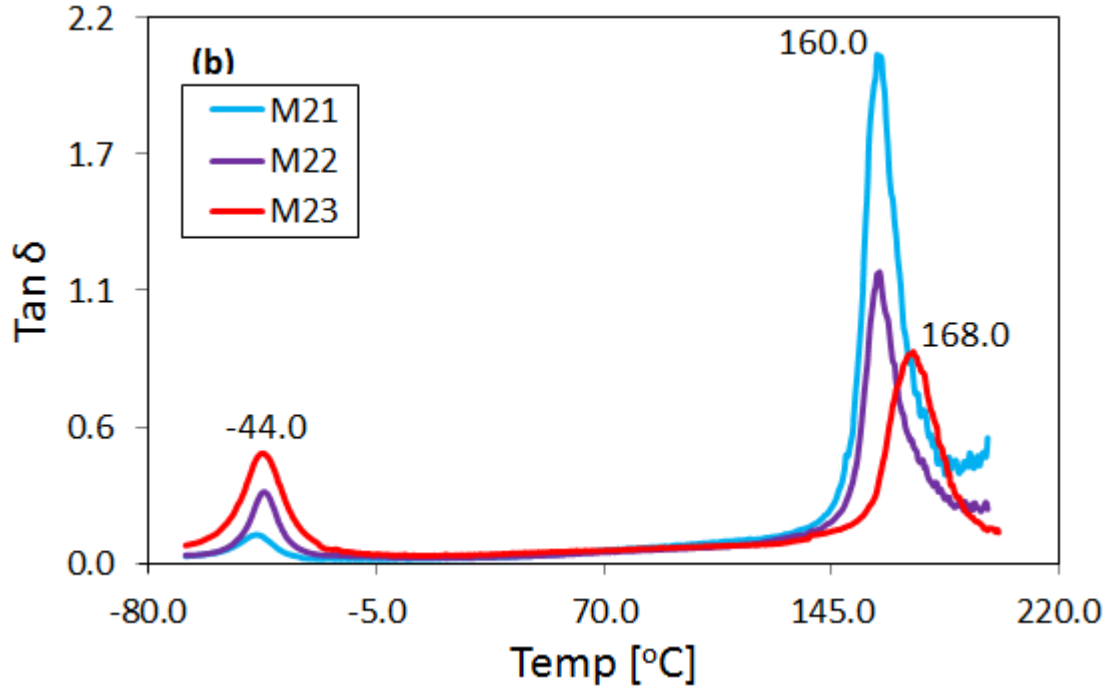


Table 2: Parametric analysis and performance evaluation of reference and UV cured membranes

Code	Wt. % of BEDA	Wt. % of PEGDA	Conversion %	First Tg [^{o}C]	Second Tg [^{o}C]	Water Flux [L $m^{-2}h^{-1}bar^{-1}$]	Rejection of 27 nm Particles [%]
M00	-	-	-	-	-	337.90	96.53
M11	10 %	-	95	85.3	179.3	238.79	92.47
M12	20 %	-	90	84.8	193.2	169.30	98.35
M13	30 %	-	90	84.8	199.4	0	-
M21	-	10 %	100	–44.0	160.0	230.81	96.75
M22	-	20 %	100	–42.0	161.0	110.90	95.84
M23	-	30 %	100	–42.0	168.0	0	-

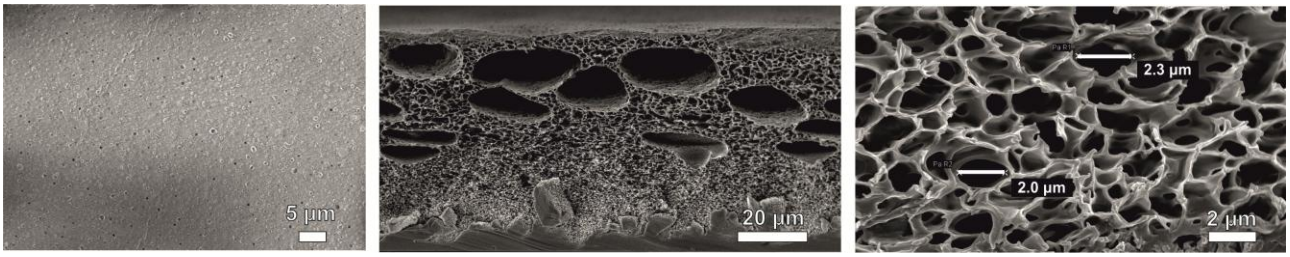
3.3 Membrane Morphology and Performance

Qualitative morphological investigations were performed by FESEM analysis on both the active surface and the cross-sections of the PSf pristine membranes and of the crosslinked membranes obtained by UV and subsequent NIPS of the PSf solution containing 10 wt. % of the two different BEDA and PEGDA acrylic resins. Representative micrographs are reported in Figure 4 (a-c).

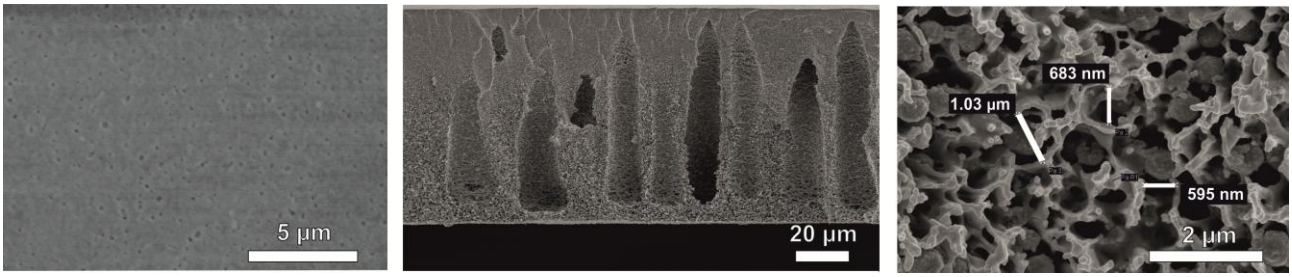
The cross-sectional images show a sponge-like structure in all cases, with pores in the micrometer range. This structure was comparable for PSf membranes and for PSf membranes modified with crosslinkers. No significant difference was observed for the two acrylic resins. On average, the micropores were smaller upon addition of the crosslinkers, but the size difference was not significant for the lowest investigated concentration of 10 wt. %. The cross-sectional micrographs also suggest that thickness did not change considerably between pristine and modified membranes. These qualitative observations were corroborated by measurement of water flux, which was used in this study as a proxy to evaluate the overall membrane porosity and to assess the potential membrane performance in ultrafiltration systems. The flux values of

membranes containing 10 wt. % of acrylic crosslinkers were lower than those of the pristine PSf membrane but they remained in the ultrafiltration range. On the other hand, when the acrylic resin content increased to 20 wt. %, a strong reduction in flux values was observed, while no flux was measured when 30 wt. % of the acrylic resins were added to the PSf formulations. Figure 5 shows the water permeability decreased in a linear fashioon with increased acrylic content in the polymer solution. When the acrylic content is high, the pores are closed by the polymer network formation. These results suggest that a tradeoff exists between the amount of acrylic agent added to the polymer dope, thus the final chemical robustness of the membrane, and its characteristics in terms of porosity and productivity. They also suggest that an optimum exists around a value of 10 wt. % of crosslinker, which still guarantees the fabrication of porous ultrafiltration membranes.

Fig, 4(a): FESEM micrographs of surface and cross section of M00 [Pristine PSf]



Fig, 4(b): FESEM micrographs of surface and cross section of M11 [PSf + 10% BEDA]



Fig, 4(c): FESEM micrographs of surface and cross section of M21 [PSf + 10% PEGDA]

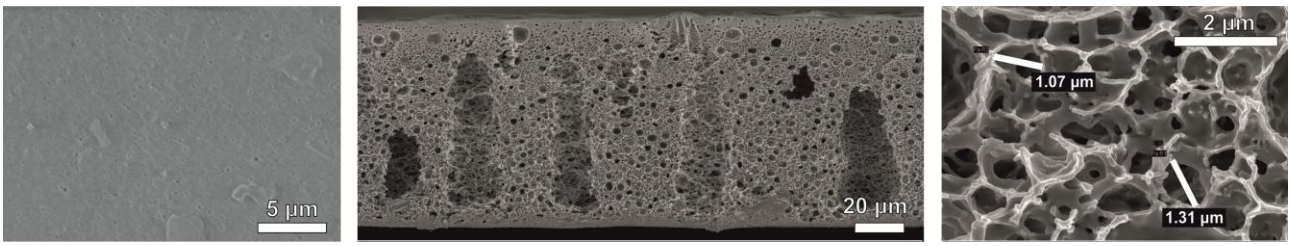
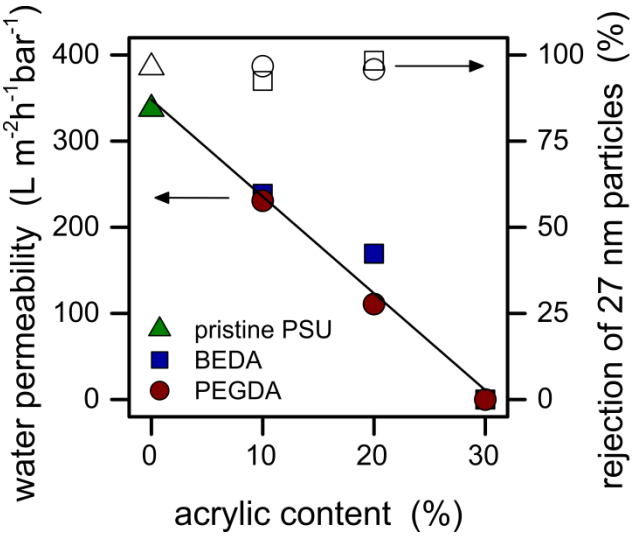


Figure 5. Influence of acrylic content on water permeability of the membranes and on their ability to reject inert particles with a diameter of 27 nm. Solid data points refer to permeability (left axis), while open points refer to rejection (right axis). The solid line is the best fit of the combined data of water permeability, having a slope of approximately –11 L $m^{-2}h^{-1}bar^{-1}$ for each percentage point of acrylic compound added.



Furthermore, high rejection of 27 nm particles (> 90%) was measured on all samples having measurable flux, suggesting that the functionalization with resins did not affect the selectivity of the membranes. No obvious correlation was observed between acrylic content and rejection of 27 nm particles, whose values are within experimental error; see Figure 5. These data suggest that, while porosity was reduced as the content of acrylic compound was increased, the change in the average pore size at the membrane surface was instead negligible. Therefore, the addition of the crosslinker did not significantly affected the selectivity of the membranes.All the crosslinked membranes were completely unsoluble in DMF, THF, Acetone, DMSO and toluene, demonstrating that the crosslinking reaction allowed to achieve solvent stable PSf based membranes. The corresponding pristine PSf membrane were readily solubilized into the above mentioned solvents, showing their good chemical stability towards solvents, thanks to the crosslinker.

4. Conclusions

We have performed a systematic investigation of the effect of the presence of acrylate resin on PSf-based membranes with the aim to obtain chemically stable crosslinked membranes without affecting their flux performances. The membranes were prepared via UV curing followed by NIPS process. The acrylic double bond conversion was evaluated by FTIR analysis and the crosslinked membranes were fully characterized. The achieved conversion for the acrylic monomers into PSf solutions were high and in accordance with their conversion as pristine monomers. The viscoelastic behavior of membranes was characterized by dynamic mechanical thermal analysis (DMTA). All the crosslinked membranes showed a biphasic nature, due to the interpenetration of the crosslinked acrylic network and the PSf polymeric chains. Morphological investigations were performed by FESEM on the active surface and on the cross-sections, both for the PSf pristine membranes and the crosslinked membranes containing 10 wt. % of the two different BEDA and PEGDA acrylic resins. Porosity suitable for ultrafiltration was obtained, which is consistent with the water flux values that were comparable to that of the pristine PSf membrane. By increasing the acrylic content above 10 wt. %, the pores were closed by the polymer network formation. High rejection of 27 nm particles (> 90%) was measured on all samples having measurable flux, suggesting that the functionalization with resins did not affect the selectivity of the membranes. All the crosslinked membranes showed stability in various solvents. In conclusion, we have found the most suitable acrylic monomer content to enhance the solvent stability without affecting the flux and rejection behavior of PSf porous membranes.

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Solvent Stable UV cured Acrylic Polysulfone Membranes

M. Mian Farrukh[1], P. Bosch[2], M. Giagnorio[3], A. Tiraferri[3*], M. Sangermano[1*]

Chemically stable UV-cured acrili polysulfone membranes have been prepared following a systematic investigation of the effect of acrylate resins on polysulfone-based membranes crosslinked membranes were prepared without affecting their flux performances.

