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PEER REVIEWED

UV-Cured ultrafiltration membranes

KEYWORDS: Ultrafiltration, photopolymerization, non-solvent induced phase separation, solvent-stable membranes, polydopamine coatings, sustainability.

ABSTRACT

In this work, we present a review of recent results in the design of ultrafiltration membranes by using photopolymerization. Non-solvent induced phase separation (NIPS) was coupled with photopolymerization and the starting polysulfone polymer (PSU) was either modified with methacrylated photocurable functionalities (PSU-DM) or the PSU was mixed with an acrylated resin. The resulting membranes showed an enhancement of solvent resistance, due to the crosslinking matrix. Finally, the solvent-resistant membranes were coated them with polydompamine in order to couple ultrafiltration and removal of contaminants by adsorption.

INTRODUCTION

The UN Agenda 2030 has put the sustainable use of water as a top priority among its sustainable development goals. In this perspective, the treatment of wastewater is a challenging task that requires the adoption of new innovative solutions and calls researchers to investigate new processes and materials. Among these, membrane separation technologies have gained widespread attention because of their ability to treat wastewater at the highest standards using modules that operate in continuous mode over broad operational regimes (1, 2).

Ultrafiltration (UF) is a pressure-driven membrane filtration process in which raw water flow is forced to pass through a porous membrane while excluding pathogens, colloids, and macromolecules from the feed (3). UF is widely used for drinking water purification, seawater desalination, and urban and industrial wastewater treatment. Chemical, food, pharmaceutical, and textile industry use large quantities of water or discharge toxic effluents that can be treated efficiently and cost-effectively by using UF. Moreover, the effluent water quality is stable and reliable, the process is streamlined and continuous, no chemicals are required, and the UF plants are much more compact compared to traditional processing plants (4).

Most of commercially-available UF membranes are made of polymeric materials such as polysulfone (PSU), poly(ether sulfone), cellulose acetate, poly(ether imides), aromatic polyamides, poly(vinylidene fluoride) and poly(vinyl pyrrolidone). A standard method for generating a porous membrane consists of inducing the precipitation of the polymeric phase from its solvent by adding a non-solvent; this technique is known as non-solvent induced phase separation (NIPS). The porous structure plays a fundamental role in the separation performance of the membrane as well as in the water permeance. Other fundamental characteristics that a membrane should meet are the mechanical resistance to pressure due to the water flux, chemical resistance to solvents, and antifouling/antimicrobial properties.

Here, we present a review of recent results from our group in the design of ultrafiltration membranes by using photopolymerization. The aim of the review is to show the strategies followed to produce solvent-stable and multifunctional ultrafiltration membranes.

RESULTS AND DISCUSSION

Coupling non-solvent induced phase separation with photopolymerization

The NIPS is a common method for producing porous membranes and consists of separating the polymer from its solvent by using a second solvent, which has a good affinity with the first solvent but is a bad solvent for the polymer. Other ways for inducing polymer precipitation, such as thermal gelation, are discussed in (4).

The membranes produced via mere NIPS may not have enough chemical resistance to solvents, such the case of PSU membranes to many aprotic solvents (5). Here, we have solved that problem by coupling NIPS with photopolymerization.

Photopolymerization, also known as UV-curing, uses UV irradiation to trigger the chain reaction mechanism that leads monomers to create a crosslinked polymer network. The three main components of a photopolymerizable formulation are (a) a photoinitiator that absorbs the light and generates the active species, (b) a reactive multifunctional monomer, and (c) a reactive diluent to adjust the viscosity of the formulation (6). Photopolymerization presents the advantages of a fast reaction.

Two different procedures were tested for the membrane preparation, namely, (a) phase inversion followed by UV curing (Figure 1a) and (b) UV curing followed by phase inversion (Figure 1b). UV curing was performed by irradiating the membrane with a UV lamp for 1 min under nitrogen. For all the cases discussed in this article, the good solvent for the polymer was N, N-dimethylformamide (DMF), and the bad solvent was deionized water. Since pristine polysulfone is a thermoplastic polymer that is not able to be crosslinked, we have followed different strategies for creating a crosslinked network:

1. Synthesis of dimethacrylated polysulfone (PSU-DM)
2. Mixing pristine polysulfone and an acrylate resin.

Dimethacrylated polysulfone membranes

The first approach consisted of modifying polysulfone to incorporate methacrylic functionalities that can be used as crosslinking sites during the photopolymerization (7), see Figure 2a. The synthesis proposed in (8) produced UV-curable (meth)acrylate telechelic polymers with polysulfone backbones. The production of membranes from PSU-DM started from the synthesis of the monomer to have PSU with the desired molecular weight and functionalities.

Contrary to pristine polysulfone, PSU-DM was able to form a crosslinked network through a classical photoinduced-radical chain-growth reaction. The fabrication of the membranes followed two different methods, i.e., (i) phase inversion followed by UV-curing and (ii) UV-curing followed by phase inversion. The sequence of production affected the properties of the material. In the first case, the conversion of the acrylic double-bound was about 41%, as the mobility of the growing chains in the solid phase was very limited. On the other hand, in the second method, UV-curing occurred when PSU was solubilized in DMF, implying higher mobility of the growing chains and resulting in a double-bound conversion of about 61%. The presence of the crosslinked network determined a high chemical resistance of the membranes, which were insoluble in DMF, and boiling water.

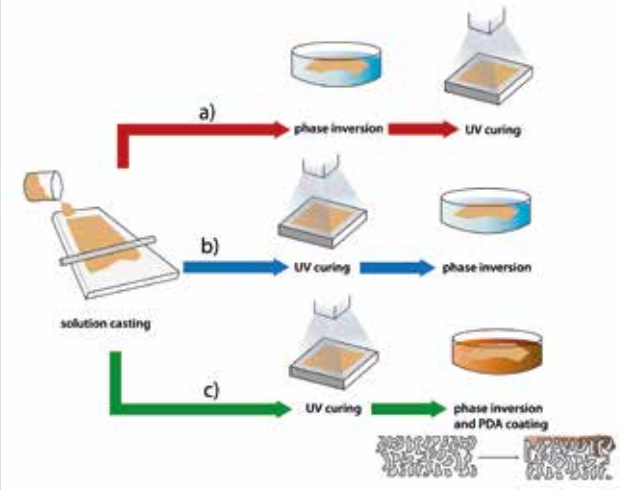

Figure 1. Schematic representation for producing photopolymerized membranes and photopolymerized coated membranes: (a) NIPS followed UV-curing, (b) UV-curing followed by NIPS and (c) UV-curing followed by NIPS in dopamine solution.

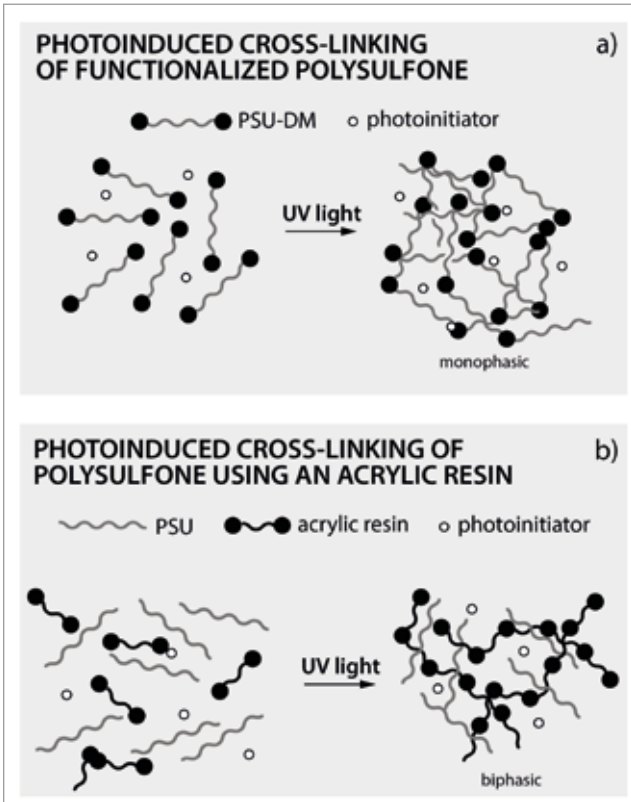

Figure 2. Photoinduced crosslinking of (a) polysulfone with two methacrylate functionalities which forms a monophasic network and (b) acrylic resin in solution with non-reactive polysulfone which forms a biphasic network.

From the morphological point of view, these membranes presented a porous structure, with pores below 2 µm in dimension. Some differences in terms of pore uniformity were observed between the membranes produced via NIPS-UV or UV-NIPS. UV-NIPS membranes presented a more uniform pore distribution than those produced via UV-NIPS. Probably, the first step of curing and the consequent formation of a crosslinked structure limited the anisotropic effect produced because of the different rates of diffusion of non-solvent and polymer precipitation. The main drawbacks of this approach are the need for the synthesis of a methacrylate polysulfone monomer and the very low values of water flux, which were three order magnitude lower than the non-crosslinked polysulfone membranes.

Acrylic polysulfone membranes

A second strategy consisted of using non-reactive polysulfone and a diacrylate monomer crosslinker, as shown in Figure 2b. In this case, the photopolymerization of the diacrylate monomer produces the crosslinked polymer network that confers mechanical and chemical stability to the membrane, whereas the polysulfone is used to create the porous structured via NIPS (9). A diacrylate monomer crosslinker, i.e., BEDA or PEGDA and the photoinitiator were added to the Polysulfone/DMF solution.

These membranes presented two phases, i.e., the crosslinked acrylic network and the PSU polymeric chains interpenetrated into it. As shown in Figure 3, the water flux through the membranes decreased almost linearly as the acrylic content increased, reaching no flux when 30% of the acrylic resins were added. On the other hand, the rejection of particles with a diameter of 27 nm was high (>90%) and remained almost constant. Contrary to the membranes fabricated using the pristine polysulfone, the crosslinked membranes were completely insoluble in DMF, tetrahydrofuran, acetone, dimethylsulfoxide, and toluene. These results demonstrate that a small amount of acrylic resins guarantees the fabrication of porous membranes that present similar filtration properties of the non-crosslinked membranes but with much higher chemical resistance.

Coupling ultrafiltration and adsorption

After the production of solvent-resistant membranes, we coated them with PDA in order to couple ultrafiltration and removal of contaminants by adsorption (10), see Figure 1c. While large colloids and macromolecules are rejected because of their size, smaller molecules are removed by adsorption on the surface of pores.

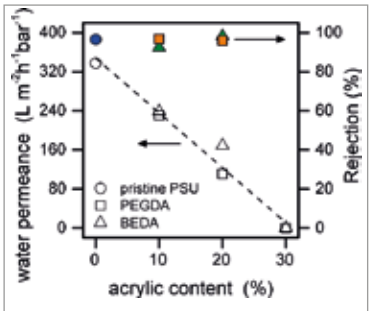

Figure 3. Influence of acrylic content on water permeance and selectivity of the tested membranes. Selectivity tests were performed with particles with a diameter of 27 nm. Filled data points refer to rejection (right axis), while open points refer to permeance (left axis).

From the morphological point of view, PDA coating seemed not to change the cross-sectional porosity but only the pores at the membrane surface. As a result of these morphological changes, the water flux decreased only of one order of magnitude with respect to the non-functionalized membranes while the rejection of particles with a diameter of 27 nm remained high, about 90-96 %.

The adsorption capability of the PDA membranes was tested using a model molecule, the cationic dye methylene blue, at different pH values, see Figure 4c. In fact, due to its zwitterionic character, PDA is negatively charged in basic conditions and, so, is able to absorb positively-charged molecules; the opposite effect can be achieved in acid conditions. As PDA functionalization duration increased (figure 4a), the specific mass of dye adsorbed at saturation increased as well (test performed at ph 10). This may be ascribed to the large amount of PDA self-polymerized during the functionalization process Moreover, the zwitterionic character of PDA gives the membranes the possibility to be regenerated effectively by change pH conditions.
As shown in Figure 4b, membranes were subjected to several cycles of dye adsorption at pH 10 and desorption at pH 3 without loss of adsorption performances. Furthermore, depth filtration tests were also conducted using the typical condition of the ultrafiltration process. The breakthrough curves of methylene blue shown in Figure 4d were fitted using an advection-convection model in order to better understand the potentiality of such membranes in industrial systems (9). To give an example, for a feed stream with an extremely high concentration of contaminant of 0.5 g/L, a spiral-wound module having a filtration area of 40 m^2 and applying a pressure of 2 bar would allow the filtration of about 300 L of permeate (taking the breakpoint concentration equal to the 10% of the feed concentration).

NEWS

IMPROVED SUSTAINABILITY FOR CHEMISTRY LABORATORIES

Asynt reports on how chemistry labs, seeking to minimise water wastage, are electing to replace Liebig-style water condensers with their **CondenSyn waterless air condenser,** for both reflux and distillation reactions.

Synthetic experiments often include reflux and distillation steps, making a reflux condenser an essential tool for both research and teaching chemistry. Traditional condensers, cooled by a circulating fluid, are effective and widely used, however they are often operated directly with tap water. This not only creates an environmental and cost issue but also increases the risk of a laboratory flood. The use of an Asynt CondenSyn air condenser negates the need for any recirculating coolant during standard reflux and distillation conditions, saving time, money and water.

Dr Ffion McKeague - Technology Manager at Asynt commented "Our CondenSyn waterless condensers are rapidly becoming a necessity in laboratories all over the world, driven by their ease of use and massive associated water savings benefits compared to using traditional water condensers". She added "Not only has the CondenSyn proved itself as a sustainable alternative for reflux reactions but increasingly also for distillation experiments using the **CondenSyn Distillation Adapter**. A typical Chemistry laboratory replacing their standard water condensers with CondenSyn units can expect to see a return on its investment in as little as 6 months".

The CondenSyn waterless air condenser's unique design uses a special borosilicate glass manufacturing technique and this, together with a proprietary multiple hyperbolic profile, ensures optimum heat removal as vapors pass along its length. Offering clear visibility of ongoing experimental reflux, the Asynt CondenSyn is also easy to clean and maintain, whilst the incorporation of a non-roll feature helps prevent accidents if left on a lab bench. Asynt offers a range of CondenSyn to optimally suit different capacity round bottom flasks.

For further information on CondenSyn please visit **https://www.asynt.com/product/asynt-condensyn-air-condenser/** or contact Asynt on +44-1638-781709 / enquiries@asynt.com.

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CondenSyn in reflux mode



CondenSyn in distillation mode

NEWS

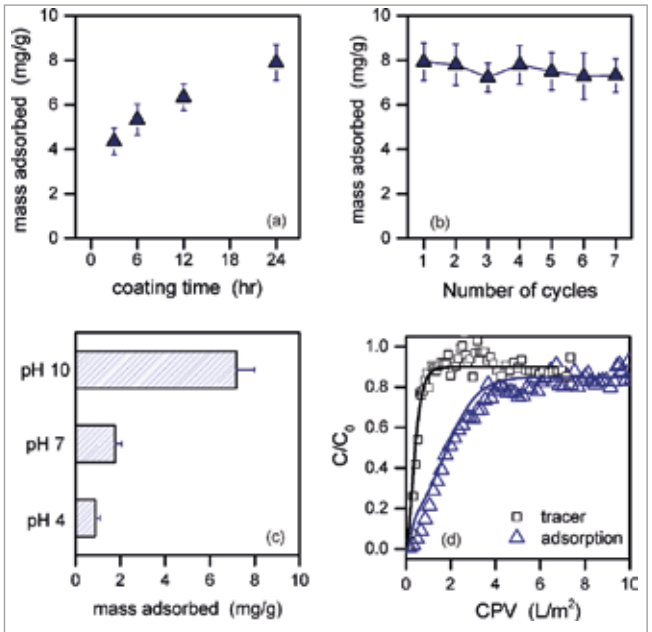

Figure 4. Specific mass of methylene blu adsorbed per gram of membrane as a function of (a) functionalization duration, (b) adsorption/desorption cycles and (c) (d) Breakthrough curves of methylene blue obtained in depth filtration tests for (triangles) clean membrane and (squares) already saturated membranes.

MATERIALS AND METHODS

Hydroxyl-functionalized PSU (PSU-DM) of different molecular weights were prepared by condensation polymerization followed by esterification of the oligomers with methacryloyl chloride in the presence of triethylamine as the base (details reported in ref. 7). PSU-DM monomer having a weight average molecular weight of about 23000 and a number average molecular weight of 15000 (polydispersity index of 1.53) was chosen among the various monomers synthesized because of its high molecular weight. PSU-DM can be UV-cured directly in the presence of photoinitiator, i.e., phenyl bis(2,4,6-trimethyl benzoyl)phosphine oxide (BAPO).

Polysulfone (15%wt, Mn=22000 g/mol) was used as based polymer for the membrane preparation, Ethylene glycol diacrylate (PEGDA; Mn=700 g/mol) and bisphenol A ethoxylate (2EO/phenol) diacrylate (BEDA; average Mn=512 g/mol) were used as crosslinker monomers and phenyl bis(2,4,6-trimethyl benzoyl)phosphine oxide as a photoinitiator.

Polydopamine functionalization was performed by UV curing the thin film and, finally, performing phase inversion inside a dopamine water solution (Figure 1c). Dopamine, under alkaline conditions, tends to self-polymerize spontaneously into PDA and strongly adhere to almost every substrate (11).

CONCLUSIONS

In this paper we review our recent results in the design of ultrafiltration membranes by using photopolymerization. Typically, we have prepared our membranes inducing the precipitation of the polymeric phase from its solvent by adding a non-solvent. The non-solvent induced phase separation (NIPS) was coupled with photopolymerization and the starting polysulfone polymer (PSU) was either modified with methacrylated photocurable functionalities (PSU-DM) or the PSU was mixed with an acrylated resin.The resulting membranes showed an enhancement of solvent resistance, due to the crosslinking matrix. Finally the solvent-resistant membranes were coated them with polydompamine in order to couple ultrafiltration and removal of contaminants by adsorption.

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Marco Sangermano *is an Associate Professor of polymer science and technology and the director of the interdepartmental laboratory Graphene@PoliTo at Politecnico di Torino. His research activity is focused on photopolymerization and its application on the fabrication of advanced hybrid materials, coatings, gas sensors, membranes, 3D printing, tissue engineering, and nanostructured polymeric coatings. He is also working on the development of new monomers from biorenewable resources to be used in the production of more environmentally-friendly materials. He currently collaborates with numerous academic and the R&D of many corporate partners worldwide. He is co-author of over 250 papers and several patents, and, in 2016, received the IBM University Award for the development of polymeric gas sensors for the fabrication of an electronic nose.*