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Ink-jet printing assisted fabrication of patterned thin film composite membranes

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ABSTRACT

Thin film composite membranes are used worldwide especially for desalination and water treatment. However, for effective water permeation, and to minimize fouling, feed water must be pre-treated before membrane treatment. Moreover, polymer degradation by oxidizing agents and the presence of undesirable elements such as boron in the permeate are persistent challenges. Novel membrane fabrication methods based on modern technologies may facilitate the creation of robust and selective polymer compositions and coatings. Here we explore the hybridization between ink-jet printing technology and the interfacial polymerization process. In this study, the patterned incorporation of a fluorinated diamine into an m-phenylenediamine-based polyamide yielded improved salt rejection that was explained in terms of increased selective layer hydrophobicity. Incorporation of the new fluorinated monomer, observed using FTIR and XPS, resulted in a more hydrophobic surface whose morphologies were similar to membranes lacking fluorine. The combination of printing technology with interfacial polymerization facilitated the fabrication of unique selective layers and demonstrated to be a potentially useful new laboratory membrane fabrication tool. Further development may accelerate the discovery of more efficient and robust membranes and promote the exploration of new material combinations, the potential of patterned compositions, and polymer morphologies that are not possible with conventional methods.

1. Introduction

Ink-jet printing technology enables the highly efficient and accurate deposition of substances onto different substrates, from micro-scale to macro-scale applications. In the last two decades, this technology has expanded rapidly into many industrial sectors and research activities. For example, development has led not only to large-scale ink printing, but also to the printing of electronics, ceramics, biological cells, biological molecules, nanoparticles, and catalysts [1–5]. In addition, this technology has been adapted for the three-dimensional printing of polymers and functional structures, and it is revolutionizing design and prototyping methods [6–8].

Due to its current versatility to print a variety of solutions on different substrates, ink-jet printing technology is well suited to the flat sheet polymer membrane fabrication process, in which accurate resolution of coatings of monomer or polymer solutions are critical. The incorporation of such a flexible coating method may lead to advances in membrane manufacturing due to the ability to design and precisely control what is deposited on the substrate surface, towards defect-free membranes. It could also be potentially useful as a new fabrication tool to study novel membranes, which cannot be fabricated using conventional methods based on novel material combinations of, for example, incompatible components and the achievement of unique, selective layer morphologies [9]. In this study, we explored the possibility of incorporating ink-jet technology in the interfacial polymerization reaction for thin film composite (TFC) membranes.

Used in many different applications, TFC membranes are currently manufactured using interfacial polymerization, a technique in which an ultra-thin, selective polymer layer is applied on top of a porous support [10–13]. The polymerization reaction occurs between two relatively reactive monomers at the interface of two immiscible solvents on the surface of a supporting membrane. Typically comprising an ultrafiltration (UF) asymmetrical membrane, the support layer is immersed in an aqueous solution containing a hydrophilic reactive monomer, generally an aliphatic or aromatic amine. The resulting aqueous amine film is subsequently immersed in a second bath containing a water-immiscible solvent in which a reactive hydrophobic monomer, often an aliphatic or aromatic di- or tri-acid chloride, has been dissolved. After interfacial polymerization occurs between the monomers,

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the solution is often subjected to further heat treatments to complete the interfacial reaction and to cure the resulting thin polymeric film. Commercially, this process has been optimized for roll-to-roll fabrication facilities, in which the advantage of using interfacial polymerization is that the reaction is self-controlled without the need for exact stoichiometry, through diffusion control of a limited supply of reactants through the initially formed interfacial polymer layer. The resulting film is extremely thin, with a thickness in the 50–200-nm range.

At first glance, this process may seem straightforward, but in practice, vast efforts have been invested in elucidating the reaction with the ultimate goal of optimizing it [14–16]. For instance, parameters that can affect the outcome and the membrane performance (selectivity and flux) are the nature of the support layer, including pre-treatment, the solvents and monomers, the monomer concentrations, the monomer solution composition, including additives and pH, the soaking time in the aqueous monomer solution, the method used to remove excess droplets from the support surface, the time between soaking and interfacial polymerization, the interfacial polymerization reaction time, the temperature, the method and temperature of post-fabrication heat curing, and chemical post-treatments [17]. Subtle differences in these parameters define the porosity, pore size, thickness, and morphology of the selective layer.

The rationale for using ink-jet printing in membrane fabrication is that it enables the creation of membranes with spatially controlled properties or compositions to confer on them novel separation capabilities and performance. In addition, the ink-jet printing technique can be used to combine incompatible components for which there is no common solvent or that prematurely react upon mixing [9].

Ink-jet technology can be incorporated into the interfacial polymerization process in many different ways. For example, as a coating technique the printer could apply the aqueous amine monomer solution to the surface of the support, it could deposit additional substances on the monomer-soaked support, or it could apply multiple monomers in different compositions or patterns as for example in a mosaic morphology. In principle, multiple solvents could also be applied using multiple printing heads, a protocol that could result in a completely reacted polymer coating and in which complete control could be maintained over each step of the process.

In this study, as a first step to analyze the incorporation of the ink-jet coating procedure into the membrane fabrication process and to demonstrate its capabilities, we printed a diamine monomer that contained fluorine on an ultrafiltration membrane presoaked in an aqueous solution of m-phenylenediamine (MPD), a commonly used membrane polyamide building block. The rationale for choosing to print a fluorinated diamine was to facilitate the analysis of the different monomers. Furthermore, its application by ink-jet printing allowed membranes with spatially distributed chemical compositions and properties to be examined. The resultant membrane exhibited improved performance and is a first example of TFC membranes with patterned physical properties via printing assisted fabrication (PAF) methods.

2. Experimental

2.1. Materials and reagents

The UF membrane support was asymmetric polysulfone (PSf, model PS35, MWCO 20 kDa) supplied by Ultura Water (Oceanside, CA, USA). The following reagents and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA): m-phenylenediamine (MPD, ≥99%), trimesoyl chloride (TMC, 98%). n-hexane (anhydrous, ≥99%) was purchased from Bio-Lab (Jerusalem, Israel). 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane, (HFP-mAP), (≥99%, cat. #PC1224) was purchased from Apollo Scientific (Denton, Manchester, UK). All chemicals and solvents were used as received, unless otherwise noted. Deionized (DI) water was generated by a Milli-Q Advantage A10 water purification system (Millipore, Billerica, MA, USA). Glass plates (16 cm × 16 cm × 0.4 cm) were used to support the UF membrane during TFC membrane preparation, and plastic frames and rubber gaskets to fit the plates (inner size: 12 cm × 12cm) were custom made. A soft rubber roller (cat. #R1275) was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). An Epson piezoelectric ink-jet L110 printer was purchased from a local Epson retailer (Jugend, Tel Aviv, Israel). The front paper feed roller was removed to prevent damage to the membrane surface, and the middle portion of the rear roller was also removed (see Fig. S1, Supporting information).

2.2. Patterned TFC membrane preparation via ink-jet printing of MPD and HFP-mAP

Several key steps of the general preparation process for an interfacial polymerization membrane were adapted from Xie et al. [18]. The printer was used to apply the aqueous solutions to UF membrane surfaces. An aqueous alkaline solution comprising HFP-mAP (5%, w/v) was prepared using 2 mol of NaOH per mol of HFP-mAP monomer to completely dissolve the monomer (pH ~12). This solution was added to the black ink reservoir (K), while the C, M and Y ink reservoirs contained DI water. Before printing on the UF membrane surface, we performed print head cleaning, power ink flushing (5 times) and nozzle checking to prime the printer with solution. The printer settings were high quality printing and glossy paper. The UF membrane supports (PS35, MWCO 20 kDa) were soaked in DI water overnight, drained, and were then soaked in an aqueous solution of MPD (2%, w/v) for 5 min, after which the MPD solution coated UF supports were rolled with a rubber roller to remove excess solution. The soaked support was taped to an A4-sized paper and loaded into the printer. Black and white checkerboard patterns generated by Adobe Photoshop software were printed one time on the membrane surface. The frame and gasket were reassembled on top of the printed ultrafiltration membrane, which was then treated with TMC in *n*-hexane (0.1%, w/v) in the frame for 1 min. The TMC/n-hexane solution was drained from the frame, and the frame and gasket were disassembled. After drying for 5 min at ambient temperature, the membrane surface was rinsed with an aqueous solution of Na_2CO_3 (0.2%, w/v) for 5 min, and the membranes were immersed in DI water until further use. Unprinted control membranes were obtained by soaking the UF membrane supports in MPD (2%, w/v) or premixed aqueous solutions of MPD:HFP-mAP in ratios 1:1, 9:1, 99:1 (total concentration 2%, w/v) and performing interfacial polymerization as described above. Membrane surfaces, in both printed and non-printed areas, were analyzed by Fourier transform infrared spectroscopy (FTIR), contact angle, and scanning electron microscopy (SEM). Performance was assessed by measuring pure water flux and NaCl rejection at a pressure of 27 bar.

2.3. TFC membrane characterization

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed on a VERTEX 70/80 spectrophotometer (Bruker Optiks GmbH, Ettlingen, Germany) using a Miracle ATR attachment with a one-reflection diamond-coated KRS-5 element for membrane characterization. Six replicate ATR-FTIR spectra were obtained for every membrane type, with each spectrum averaged from 40 scans collected from the spectral range of 4000–400 cm^{-1} at a 4 cm^{-1} resolution. The