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Ink-jet printing assisted fabrication of thin film composite membranes

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ABSTRACT

Modern printing techniques may facilitate membrane fabrication methods for the creation of novel polymer compositions and coatings. The interfacial polymerization reaction between diamine and triacyl chloride monomers is a highly efficient method to achieve currently used RO and NF thin film composite membranes. Here we present our investigation of the interfacial polymerization process using an ink jet printer for the application of an amine monomer to an ultrafiltration (UF) support as part of the polymerization method. In this study, single and multiple coatings of m-phenylene diamine (m-PDA) were applied to the UF support, without a draining step, before application of trimesoyl chloride (TMC). The resulting polymer films were characterized using FTIR and correlated to the amount of m-PDA printed on the UF support. The amount of crosslinking in the polyamide thin film increased as more m-PDA was printed on the support as indicated by XPS oxygen/nitrogen ratios. Also, the hydrophilicity of the surfaces could be explained with respect to the amount of polyamide crosslinking. SEM images of the membrane surfaces showed the progressive morphological changes to the surface as more m-PDA was printed. Salt rejection increased and the flux decreased as the amount of printed m-PDA increased, and was explained by amount of polymer crosslinking, surface hydrophobicity, and polyamide layer thickness. Further development of ink-jet printing within the context of interfacial polymerization methods, or for other membrane coating applications may accelerate the discovery of novel membranes, and lead to deeper understanding of membrane processes. Printing as a coating method exhibits higher accuracy and controllability compared to dip coating methods, that require removal of excess liquid or droplets via difficult to control draining or other steps, and which may eventually result in an overall more efficient fabrication process.

1. Introduction

For over 30 years, the fabrication of thin film composite (TFC) membranes has been intensively studied due to their broad practical utility. Since their inception, highly efficient TFC membranes with variable salt rejections, and other pollutant rejections have been used in many industrial and large scale applications such as sea and brackish water desalination [1–6]. Due to scarcity in water stressed regions, membrane based desalination capacity has exceeded 17,000 plants worldwide producing over 80 million cubic meters of potable water per day. TFC membranes are composed of three polymer layers: a non-woven polymer for mechanical support, upon which a second porous UF support layer commonly consisting of polysulfones is cast, and upon which a third thin skin layer is formed [7–10]. This skin layer is usually a thin, dense polyamide (PA) and is the selective layer in reverse osmosis (RO) or nanofiltration (NF) membranes. This PA layer is commonly fabricated using the interfacial polymerization method between a diamine compound dissolved in an aqueous medium, and a triacyl chloride present in an organic solution. These two components will react at the interface of the two phases forming a PA layer between 10 nm to more than 100 nm thick. Generally, interfacial polymerization of m-phenylenediamine (m-PDA) and trimesoylchloride (TMC) is believed to involve an incipient fast stage that forms a dense core barrier layer followed by a slow growth stage that is monomer diffusion limited [11,12]. The fast reaction upon contact of both monomers at the organic solvent-water interface in the incipient stage provides the dense core layer that is significantly thinner than the extended loose layer formed later as monomer diffuses through the dense core layer [13]. The growth of the polyamide layer essentially stops when the mass transfer resistance of the polyamide layer becomes great enough to decrease m-PDA transport into the organic phase to very low rates.

The versatility of ink-jet printing to coat surfaces with multiple

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liquids, including spatially controlled liquid deposition warrants investigation into its hybridization with polymer membrane fabrication and modification. A coating device that has the ability to precisely control the amounts and location of deposited material may be a valuable advance in membrane manufacturing especially in the laboratory, compared to dip coating, where hard to regulate factors such as temperature or solution composition affect the solution viscosity, cohesion and adhesion, thereby leading to variable coating thicknesses.

A major advantage of membrane printing methods may be realized in the laboratory for membrane development and understanding of new membranes. Precise control inherent in the printing method may result in a more efficient and environmentally friendly membrane research process, with respect to the amounts of chemical used, and the design of novel membranes that are yet difficult to achieve with the current methods. This could include the use of costly specialty materials such as nanoparticles fillers, or additives, and printing could facilitate high throughput strategies where multiple formulations or modifications are desired. Ink jet printing is very versatile and may print many types of materials or solutions, for example ceramics, metals, nanoparticles or proteins, on multiple types of porous or non porous substrates [14], underlining the potential of the method for facilitating new research in membranes.

Recently, we have begun to explore the possibilities of using ink-jet printing as a coating method in the fabrication and modification of membranes [15]. In principle, printing assisted fabrication (PAF) could be incorporated in many different ways to assist the fabrication of the membrane. Previously, we showed that a chemically different amine monomer could be coated on top of a membrane soaked in m-PDA, for the creation of a skin polymer layer that was composed of different regions of different chemical and physical properties. Due to the many variables and steps in the membrane fabrication process, ink-jet printing as a coating method may be incorporated in many different ways. Select examples may include altering the nature of the support layer with printed coatings, varying the monomer concentrations, the monomer solution composition, including additives and pH, and chemical post-treatments. In the present study, we explored formation of a polyamide layer by printing on a wetted membrane support not previously imbibed with m-PDA. Printing multiple layers of m-PDA with subsequent treatment of the membrane surfaces with a solution of TMC in hexane formed a series of membranes that were characterized and showed subtle differences in membrane thickness, crosslinking, and hydrophilicity depending on the number of printed layers.

2. Experimental

2.1. Materials and reagents

Polyamide polymer films were generated on hydrophilic polyethersulfone asymmetric ultrafiltration (UF) supports (PESH, MWCO 50 kDa, Microdyn-Nadir, Wiesbaden, Germany). The following reagents and solvents were purchased from Sigma–Aldrich (St. Louis, MO, USA): m-phenylenediamine (m-PDA, $\geq 99\%$), trimesoyl chloride (TMC, 98%). The solvent n-hexane (anhydrous, $\geq 99\%$) was purchased from Bio-Lab (Jerusalem, Israel). 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 ($7.8\ \text{cm} \times 10.2\ \text{cm} \times 0.4\ \text{cm}$) were used to support the UF membrane during TFC membrane preparation and plastic frames and rubber gaskets (inner size: $5.7\ \text{cm} \times 8\ \text{cm}$) were custom made in order to fit the plates. An Epson L110 ink-jet printer was used for applying aqueous solutions on the substrate. The front paper feed roller and the middle portion of the rear roller of the printer were removed to prevent damage to the membrane surface, and the volume printed was estimated to be 0.25 $\mu L/cm^2$ by weighing the membrane before and immediately after printing as described previously [15].

2.2. Printed TFC membrane preparation via ink-jet printing of m-PDA

The printer was used to apply the diamine aqueous solutions to the UF membrane's surfaces. An aqueous solution of m-PDA (2.5%, w/v) containing Na_2CO_3 (100 ppm) and ethylene glycol (5%, w/v) was used. This solution was added to all the ink reservoirs in the printer. Print head cleaning, tubing flushes (5 times) and nozzle checking was performed to prime the printer with the solution. The printer was set on high quality printing and glossy paper. Using these settings, the printer was previously characterized to print ca. 0.25 $\mu L/cm^2$ [15]. The UF membrane supports were soaked in DI water overnight, drained, and residual droplets on the top surface were removed with a paper towel. The wetted support was taped to an A4-sized paper and loaded into the printer. A black square image generated by Adobe Photoshop software was printed 1–5 times on the membrane surface to generate a series of membranes with variable amounts of m-PDA. A frame and a gasket were assembled on top of the printed ultrafiltration membrane to prevent leaking of the TMC solution, and the m-PDA printed membrane was treated for 1 min with TMC in *n*-hexane (0.13%, w/v). The TMC/n-hexane solution was drained, and the frame and gasket were disassembled. The membranes were placed in an oven at 70 °C in air at ambient pressure for 10 min. After the heat treatment the membranes were immersed in DI water until further use. Unprinted control membranes were obtained by soaking the UF membrane supports in the same aqueous m-PDA solution as above, rolling with a rubber roller to remove the excess droplets, and performing interfacial polymerization by treatment with TMC in *n*-hexane (0.13%, w/v) as described above and previously [15,16]. Membrane surfaces were analyzed by Fourier transform infrared spectroscopy (FTIR), contact angle, and scanning electron microscopy (SEM) as previously described [15]. Performance was assessed by measuring pure water flux and NaCl rejection at a pressure of 15.1 bar using a previously described dead-end filtration unit [15].

2.3. Viscosity and density measurements of ink and amine solutions

Ink jet performance depends on the properties of the solution. The viscosities of pure water, of the four original ink solutions of the Epson printer and the precursor amine monomer aqueous solutions were measured using the Anton-Paar rolling-ball viscometer (Lovis 2000 M/ME). Densities of the measured solutions were tested by density meter (Densito 30 PX, Mettler Toledo). Both density and viscosity measurements were performed at 21 °C.

3. Results and discussion

3.1. Ink-jet printing assisted fabrication of TFC membranes using m-PDA and TMC

We applied multiple coatings of the amine monomer (m-PDA) on the UF support using ink-jet printing for fabrication of thin film composite membranes. An aqueous solution was printed in order to be compatible with the printer, which was originally designed to use aqueous based inks. The aqueous amine solution was observed to print well, and its viscosity and density were close to those of the original ink solutions of the printer (Supporting