Journal of Membrane Science 548 (2018) 73–80

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

UV initiated surface grafting on polyethersulfone ultrafiltration membranes via ink-jet printing-assisted modification

Roy Bernstein*, Clare E. Singer, Swatantra P. Singh, Canwei Mao, Christopher J. Arnusch*

Department of Desalination and Water Treatment, Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede-Boqer Campus 84990, Israel

ARTICLE INFO

Keywords:
Graft polymerization
Ultrafiltration
Ink-jet printing
Biofouling

ABSTRACT

An efficient graft polymerization method for modification of polymeric membranes was developed using ink-jet printing. The method for grafting was investigated by printing a zwitterionic acrylate monomer on a polyethersulfone UF membrane with subsequent UV irradiation. The successful grafting was confirmed by ATR-FTIR and XPS. This printing-assisted grafting method required 5-10X less reactant chemicals compared to known dip-coating methods, while a similar degree of grafting could be achieved. Furthermore, the grafting resulted in polymer brush morphological features, which increased with the reaction time. In addition, the membrane permeability following modification was maintained even at high degree of grafting, and rejection of PEG was only slightly affected, indicating that the grafting was predominantly on the surface and not in the pores. Static protein adsorption measurements confirmed that the modified membrane acquired low protein fouling properties, and reduced biofilm growth was observed using *Pseudomonas aeruginosa* as the model biofilm forming bacteria. These new tools for modification of membranes will enable optimization of surface coatings and could facilitate advances in water treatment technology.

1. Introduction

Ink-jet printing has been used in various applications that involve the directed deposition of materials on surfaces and it has been demonstrated for membrane fabrication. For example, ink-jet printing was used in order to assist with the fabrication of thin film composite membranes [1,2]. In these examples, aqueous monomer solutions were printed on porous polymer membrane substrates with a subsequent interfacial polymerization reaction step, which produced dense polyamide coatings. Others have also demonstrated the utilization of ink-jet for polymer deposition, for example deposition of nafion ionomers as an effective alternative to spray coating [3,4], fabrication of a catalyst-coated membrane [5], and deposition of anti-bacterial nanoparticles [6] or polyelectrolytes toward the generation of mosaic-like membranes [7]. A recent example utilized ink-jet printing for grafting on silicon surfaces via an advanced grafting technique [8]. However, the modification of polymeric membrane surfaces using ink-jet printing and graft polymerization has never been reported.

Graft polymerization has been consistently shown to be a powerful method to reduce the surface fouling propensity and usually involves the use of aqueous monomer solutions [9–11], which are suitable to print. Membrane grafting is usually accomplished by radical polymerization using various methods to initiate the polymerization reaction. Nonetheless, most of the free radical grafting methods require excess reagents in larger volumes of solution and thus are not very efficient [12]. As a result, new advanced techniques are being developed such as enhanced radical graft polymerization using monomer filtration, in situ surface chemical modification or initiated chemical vapor deposition [12–15], which allow a more effective use of reagents. In this present study we explored for the first time the use of ink-jet printing to achieve surface grafting onto a polymeric membrane by free radical polymerization by UV-photoinitiation. The grafting was studied using a well-known fouling resistant zwitterionic polymer, a product of the polymerization of an sulfobetaine acrylate monomer [13,16,17], for the coating of polyethersulfone ultrafiltration membrane surfaces (Fig. 1). A grafted layer could be obtained when multiple layers were printed and irradiated, and the modification was characterized using ATR-FTIR and XPS. The degree of grafting (DG) was evaluated using ATR-FTIR, and increased with increasing UV irradiation time. The amounts of chemicals that were needed for sufficient grafting in the printing method was very low compared to other grafting methods, which can lead to much lower materials costs and less chemical waste, and is a major advantage of the presently reported printing method. Furthermore, membrane surface modifications typically affect the

---

* Corresponding authors.
E-mail addresses: royber@bgu.ac.il (R. Bernstein), arnusch@bgu.ac.il (C.J. Arnusch).

https://doi.org/10.1016/j.memsci.2017.10.069
Received 15 August 2017; Received in revised form 26 September 2017; Accepted 28 October 2017

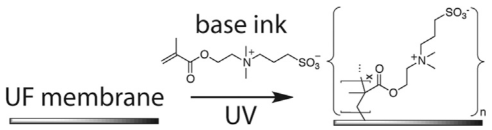

Fig. 1. Polyethersulfone ultrafiltration membrane surfaces were coated with [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide dissolved in base ink (an aqueous solution of 35% glycerol, ~ 3% propylene glycol, and ~ 1% Triton X-100) and irradiated using UV light for 0–30 min.

permeability and MWCO. The permeability of the modified printed-assisted membranes remained high following modification while the MWCO did not significantly change, whereas a large decline in permeability was measured for the dip-coated grafted membranes at similar grafting degrees. Moreover, the grafted polymers obtained by printing had a brush morphology, which was not observed on grafted modification layers using the dipping method or other free radical grafting methods [12,18–20]. Furthermore, the printing-assisted coating procedure can facilitate chemically patterned surfaces, and might enable other types of membranes, for example mosaic membranes.

2. Experimental section

The 150 kDa molecular weight cut-off ultrafiltration PES membranes (UP150) were supplied by Microdyn-Nadir (Germany). [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SPE), was purchased from Sigma Aldrich (Israel). Paul Roark's C6A Base ink for optimal jetting was obtained from www.inksupply.com. This solution was composed of 61% water, 35% glycerol, ~ 3% propylene glycol, and ~ 1% Triton X-100 (based on the manufacture's specifications). Monomer deposition was done using the Fujifilm Dimatix Materials Printer (DMP-2800 series). Polyethylene glycol (PEG) 35 kDa, 100 kDa and 200 kDa was procured from Sigma Aldrich (Israel). Membranes were irradiated in a UVACUBE oven to initiate radical polymerization and graft the polymers to the PES surface.

2.1. Ink-jet printed graft polymerization

Prior to modification, the commercial membranes were washed for 24 h in an aqueous solution of 50% ethanol (by volume) at 40 °C while stirring. Subsequently, the membranes were rinsed thoroughly with Milli-Q water and stored in Milli-Q water at 4 °C until use. Water soaked membranes were taped to a glass plate for printing and the excess water was removed from the membrane surface. The monomer-ink was made by dissolving SPE monomer, for a final concentration of 0.5 M, in the C6A base ink. The monomer solution was filtered using a 0.22 µm syringe filter (cellulose acetate, Millipore) prior to being loaded into the cartridge, which delivers 10 pL for each droplet, supplied with the Dimatix printer. To print fully covered rectangular membranes of size 1 cm × 4 cm, or circular membranes with a diameter of 2.4 cm, the drop spacing was set to 10 µm, which ensured sufficient drop overlap in order to prevent evaporation before UV irradiation. The waveform for droplet ejection was set to the preset Dimatix Model Fluid settings with voltages adjusted to ensure uniform jetting with droplet speeds of 7–9 $\mathrm{m\,s^{-1}}$ as recommended in the printer manual. Membranes were printed with 1, 2, or 4 layers of monomer solution by repeating the print sequence for each layer. The amount of ink ejected was measured by weighing a sample before and immediately after printing. Immediately after printing, the membranes were irradiated as printed for 10, 20, or 30 min using a UV oven with a UVA intensity of 16 $\mathrm{mW\,cm^{-2}}$ (measured using UV power puck® II radiometer, EIT, USA). After irradiation, membranes were washed for 3 h in 50% ethanol at 40 °C to remove un-grafted monomers and then thoroughly rinsed with Milli-Q water.

2.2. Dip-coating graft polymerization

Previously published standard dipping techniques were used [21]. Briefly, washed membranes were cut into 50 mm diameter circles and placed in a glass Petri dish. A rubber ring was placed on top of the membrane and the monomer solution containing SPE (0.5 M in C6A base ink) was poured on the top face of the membrane so that the membrane was completely submerged in the solution. Approx. 4 mL of monomer solution was used. The submerged membrane was then irradiated for 10–20 min in the UV oven. After irradiation, membranes were washed for 3 h in 50% ethanol at 40 °C to remove un-grafted monomers and then thoroughly rinsed with Milli-Q water.

2.3. Membrane characterization

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR): Membranes were dried completely in a 40 °C oven for 1 h before measurement. Measurements were carried out using a Vertex 70 spectrometer (Bruker Optics, Ettlingen) equipped with a one reflection diamond covered KRS-5 crystal (Pike); 30 scans were taken for each spectrum at a resolution of 4 $\mathrm{cm^{-1}}$. Three membranes were measured for each condition and an average was calculated for at least three spectra measured in different areas of each sample. The data were evaluated using the spectral analysis software (OPUS 6.5). The ratios and standard deviation of the signal intensities at different wavelengths were calculated. *Contact Angle*: The contact angle (θ) was measured by the captive bubble method with OCA-15 contact angle analyzer (DataPhysics, Filterstadt, Germany). Membranes were soaked in Milli-Q water prior to measurement, taped to a glass cover slip, and placed with the modified side facing down in a container of Milli-Q water. An air bubble, 7 ± 3 µL, was injected under the membrane and the images were analyzed using the SCA 2.0 software. *High resolution X-ray photo-electron spectroscopy (HR-XPS)*: Experiments were carried out using an ESCALAB 250 apparatus (Thermo Fisher Scientific) ultrahigh vacuum (10^{-9} bar) apparatus with an AlKα X-ray source and a monochromator. The X-ray beam size was 500 µm, and survey spectra were recorded with a pass energy (PE) of 150 eV and high energy resolution spectra were recorded with a PE of 20 eV. The spectral components of the C1s, N1s, O1s and S2p signals were found by fitting a sum of single component lines to the experimental data by means of nonlinear least-squares curve-fitting. To correct for charging effects, all spectra were calibrated relative to a carbon 1s peak positioned at 285.0 eV. *Scanning Electron Microscopy (SEM)*: The samples measured included the modified membranes in which 2 layers of printed SPE monomer solution were irradiated for 10, 20 and 30 min. Controls included a washed untreated membranes. The surfaces were examined at standard high-vacuum conditions. The samples were sputtered with gold before examination. *Atomic Force Microscopy (AFM):* Surface topography of the membranes was observed with AFM (MFP-3D-Bio setup from Asylum Research) in DDW for the samples in which 2 layers of printed SPE monomer solution were irradiated for 10, 20 and 30 min.

2.4. Membrane performance

Permeability: The water permeability of membranes was tested using a customized microfluidic cell system [22–24]. Milli-Q water was pumped through cells with channels of cross-sectional area 1 × 30 mm. Membrane samples were cut to 5 × 40 mm, placed across these channels and tested at 0.8 bar. Tests ran for 1 h and effluent was collected and weighed every minute. The membrane permeability (L_p) was calculated in 10 min intervals using:

$$L_p = \frac{V}{A \times t \times P}$$

where V is the water volume collected (L), A is the surface area of the membrane tested ($\mathrm{m^2}$), t is the elapsed time (hours), and P is the applied