Journal of Membrane Science 450 (2014) 174–180

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Surface modification of thin film composite polyamide membrane using atomic layer deposition method

Juha Nikkola [a,*], Jenni Sievänen [b], Mari Raulio [b], Jing Wei [c,d], Jyrki Vuorinen [e], Chuyang Y. Tang [c,d]

[a] VTT Technical Research Centre of Finland, PO Box 1300, 33101 Tampere, Finland
[b] VTT Technical Research Centre of Finland, PO Box 1000, 02044 Espoo, Finland
[c] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
[d] Singapore Membrane Technology Centre, Nanyang Technological University, Singapore 639798, Singapore
[e] Department of Materials Science, Tampere University of Technology, PO Box 589, 33101 Tampere, Finland

ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form
30 August 2013
Accepted 4 September 2013
Available online 10 September 2013

Keywords:
Thin-film-composite (TFC) polyamide (PA)
Reverse osmosis membrane
Inorganic surface modification
Atomic layer deposition (ALD)
Aluminium oxide (Al_2O_3)

ABSTRACT

We present surface modification of thin-film-composite (TFC) polyamide (PA) reverse osmosis (RO) membrane by atomic layer deposition (ALD) process using trimethylaluminium ($AlMe_3$). The aim of the inorganic ALD coating is to improve the anti-fouling performance of TFC PA membranes. The ALD processing parameters were systematically studied because of the lack of previous investigations of the ALD coated RO membranes. Two different processing temperatures (70 °C and 100 °C) and three different ALD cycles (10, 50 and 100) were used to deposit the Al_2O_3 ALD coatings on TFC PA membranes. The ALD process parameters affected on the hydrophilicity and the surface polarity as well as on the surface roughness of the coated membranes. The bacteria attachment test results indicated that the lowest number of *Pseudomonas aeruginosa* cells was adhered on the most hydrophilic and polar surface, among the ALD coated membranes. RO tests showed the effect of ALD coating on the water and salt permeability as well as on the salt rejection of the membranes.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Membrane fouling, such as scaling, colloidal fouling (inorganic and organic) and biofouling, has remained a critical issue in the reverse osmosis (RO) process [1]. For example, thin-film-composite (TFC) polyamide (PA) membranes have shown to be vulnerable to fouling in the RO process. Several surface properties of TFC PA membranes, including hydrophilicity and low surface roughness, have shown to play a key role in reducing the membrane fouling [2]. Researchers have developed various approaches to modify the surfaces of TFC PA membranes to introduce anti-adhesion and antimicrobial surface [3]. Indeed, many commercial “low fouling” TFC PA membranes contain an additional polymeric coating layer to enhance their anti-fouling performance [4]. Compared to the vast literature on organic/polymeric surface coatings or modifications, there are few studies on inorganic coatings as a surface modification of RO membranes [5], despite their great potential to increase the mechanical and the chemical stability as well as to decrease the fouling tendency.

Atomic layer deposition (ALD) technology has been used almost four decades for manufacturing inorganic coating layers, such as oxides, nitrides and sulphides, with thickness down to the nanometre range [6]. Manufacturing of Al_2O_3 thin films using the self-terminating reaction of trimethylaluminium ($AlMe_3$, Me$=$CH), with water or ozone, is considered as an ideal example of the ALD process [7]. Recent advancement in ALD technology has increased its potential to produce functional thin films on flexible and temperature-sensitive polymeric materials [8,9]. The technology has also been applied to coat various fibrous polymers [10–13].

In recent years, a few research groups have investigated ALD technology as surface modification of porous microfiltration and ultrafiltration, including both polymeric and ceramic membranes [14–18]. These studies suggested that ALD processing parameters, such as temperature and number of ALD cycles, have clear impact on membrane performance. For example, they have shown an effect on the pore size of membrane, which have affected on solute permeability and rejection properties [16,17]. Furthermore, hydrophilic and smooth polymeric membranes have been obtained using $AlMe_3$ based ALD technology [15], which increases its potentiality to create low-fouling membrane surface. However, hydrophilicity and low surface roughness have been typically obtained using a relatively thick ALD coating, such as 300–500 ALD cycles [14,16]. In addition, the change in the ALD processing

* Corresponding author. Tel.: +358 405358169; fax: +358 207223498.
E-mail address: juha.nikkola@vtt.fi (J. Nikkola).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.09.005

temperature has affected on reactivity of $AlMe_3$ [11]. For example, the most hydrophilic membrane surface has been obtained at 150 °C [14]. The increase of ALD coating thickness and temperature may negatively affect the RO membrane performance by tightening the rejection layer of temperature-sensitive polymeric membrane. Therefore, further understanding of the ALD process is needed in order to overcome the current drawbacks and to develop new low-fouling RO membrane using the ALD technology. To the best knowledge of the authors, the ALD method has not been applied for modifying RO membranes, and therefore systematic study is needed to introduce ALD technology to the RO membranes.

Our aim was to investigate the surface modification of TFC PA membrane using the $AlMe_3$ based ALD process. Two different processing temperatures (70 °C and 100 °C) and three different number of ALD cycles (10, 50 and 100) were used to apply the ALD coatings on TFC PA membranes. The ALD process parameters were shown to have effect on the surface roughness as well as on the hydrophilicity and surface polarity of TFC PA membranes. The bacterial attachment test simulated the effect of ALD coating on the biofouling tendency. Furthermore, RO tests showed their effect on the water permeability and salt rejection.

2. Experimental

2.1. Materials

The commercial TFC PA membrane DOW™ FILMTEC™ LE-400 (The Dow Chemical Company, Midland, MI, USA) was used as-received as a substrate for the ALD coatings. Trimethylaluminum ($AlMe_3$) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and it was used as received.

2.2. ALD coatings

The ALD-Al_2O_3 depositions were carried out in a Picosun SUNALE™ reactor (Picosun, Espoo, Finland) on substrates that were $10 \times 10\ cm^2$ in size. $AlMe_3$ and H_2O were used as precursors. The ALD process parameters were selected according to our previous investigations on low-temperature ALD process for temperature-sensitive substrates [9,19,20]. Two different processing temperatures (70 °C and 100 °C) and three different ALD cycles (10, 50 and 100) were used to deposit the ALD coatings on the TFC PA membranes. Table 1 summarises the ALD coated specimens with their processing parameters. The coated membranes are named according to the coating cycles and temperature (e.g., c10_t70 denotes a membrane with 10 coating cycles at 70 °C).

Furthermore, our previous investigations have shown the effect of physical and chemical pre-treatment on the ALD layer growth, which has occurred due to the changes in surface morphology and chemistry of temperature-sensitive substrate [9]. Because RO membrane is sensitive to the changes in its surface morphology, it was decided to deposit the ALD coatings on virgin TFC PA membranes without further pre-treatment.

The precursor pulsing sequence was 0.1 s $AlMe_3$ pulse, 10 s N_2 purge, 0.1 s H_2O, 10 s N_2 purge and the number of ALD cycles was adjusted according to the targeted Al_2O_3 coating thickness. The nominal thicknesses of the coating was estimated based on the growth rate 0.1 nm/cycle measured from films grown on a silicon wafer with a Nanospec AFT 4150 reflectometer [19,20]. ALD coatings have shown a minor variation of the actual film thickness, because of the difference in surface chemistry and roughness of different polymers, in comparison to a silicon wafer. Although, the aim was to deposit the ALD film on PA side, the film growth cannot be totally prevented on reverse side of the membrane.

Table 1
Summary of the ALD coated specimens with their processing parameters.

Sample ID[a]	Number of cycles	Processing temp. (°C)	Nominal coating thickness[b] (nm)
c10_t70	10	70	1
c50_t70	50	70	5
c100_t70	100	70	10
c10_t100	10	100	1
c50_t100	50	100	5
c100_t100	100	100	10

[a] Al_2O_3 coating.
[b] Nominal thickness according to the growth rate 0.1 nm/cycle [19,20].

2.3. Membrane characterisations

ATR-FTIR measurement was carried out to analyse the surface chemistry of uncoated and coated membranes. Perkin Elmer spectrum BX II FT-IR (Fourier transform IR) system was equipped with vertical-Attenuated total reflectance (ATR) and KRS-5 (Thallium Bromoiodide) crystal. In a typical analysis 50 scans were collected from 500 to 4000 cm^{-1} at 4 cm^{-1} resolution. A background spectrum of pure KRS-5 was collected before running the samples.

The microscopic imaging of uncoated and coated membranes was conducted using scanning electron microscope (SEM) JEOL JSM-6360 LV 11 kV on high vacuum mode. All SEM samples were sputter coated with gold before imaging.

The surface topography of uncoated and coated membrane samples were characterised using non-contact mode atomic force microscopy (NC-AFM). The NC-AFM analysis was performed using Park Systems XE-100 AFM equipment (Suwon, South-Korea), with cantilever 905M-ACTA (AppNano Inc., Santa Clara, CA, USA). Typically, the scan rate was 0.4–0.6 Hz and the measured area was $5 \times 5\ \mu m^2$. Six replicate measurements were performed to determine the root-mean-square roughness value, R_{RMS}.

The contact angle measurements were conducted by using Optical Tensiometer Theta T200 device (Attension, Biolin Scientific). The measurements were performed in a controlled atmosphere (RH 50%, temperature 23 °C) and the results are given as an average of five parallel measurements. The water contact angle values, expressed as deg, are presented at the time of 30 s from the moment the drop contacts the surface. The surface energy values were obtained by measuring the contact angle of three different probe liquids, including water (H_2O, $\gamma = 72.80$ mN/m), diiodomethane (CH_2I_2, $\gamma = 50.80$ mN/m) and formamide (CH_3NO, $\gamma = 58.20$ mN/m). The total surface energy values, as summary of polar and dispersive surface energies, were determined from the measured contact angle data using the Fowkes theory [21].

2.4. Bacterial anti-adhesion performance

Biofilm formation was demonstrated by analysing the attachment of *Pseudomonas aeruginosa* on uncoated and coated membranes. *P. aeruginosa* is Gram-negative, aerobic, rod-shaped bacterium, which is widely used as the model microbe for biofilm formation studies [22–25]. Therefore, *P. aeruginosa* was selected as model bacterium in our study to provide comparable data related to the attachment of bacteria.

Bacteria attachment test was conducted according to our previous studies [3]. The membranes (⌀ 4.7 cm) were submerged in bacterial suspension consisting of standard seawater ASTM D1141-98 (2008) [26]. Furthermore, the suspension was inoculated with overnight culture of *P. aeruginosa* (VTT E-96726) cultivated in 37 °C Trypticase soy broth solution, harvested by centrifugation

Download English Version:

https://daneshyari.com/en/article/633837

Download Persian Version:

https://daneshyari.com/article/633837

Daneshyari.com