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# Effect of $CO_2$-laser irradiation on properties and performance of thin-film composite polyamide reverse osmosis membrane

**Foad Jahangiri*, Seyyed Abbas Mousavi*,**,†, Fathollah Farhadi*, Vahid Vatanpour***, Behnam Sabzi*, and Zeinab Chenari****

*Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi Ave., Tehran, Iran
**Sharif Membrane Research and Technology Center, Sharif University of Technology, Azadi Ave., Tehran, Iran
***Faculty of Chemistry, Kharazmi (Tarbiat Moallem) University, Tehran, Iran
****Laser and Plasma Research Institute, Shahid Beheshti University, Evin, Tehran, Iran
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**Abstract**–$CO_2$-laser irradiation was used to modify the surface properties of thin-film composite (TFC) polyamide reverse osmosis (RO) membranes. These membranes were first synthesized via interfacial polymerization of m-phenylenediamine (MPD) monomers and trimesoyl chloride (TMC) over porous polysulfone ultrafiltration support, followed by a $CO_2$-irradiation. AFM, ATR-FTIR, SEM and contact angle measurements were used to characterize the surface properties of these membranes. The ATR-FTIR results indicated that $CO_2$-laser irradiation did not induce any functional groups on the membrane surface. However, it was found that the laser irradiation enhanced the NaCl salt rejection and slightly reduced the permeate flux. Moreover, the maintenance of the flux in modified membranes was much higher than untreated ones. Specially, after 180 min of filtration, the reduction in initial flux for the unmodified membranes was 22%. However, the reduction in initial flux for the modified membranes was less than 5%. Bovine serum albumin (BSA) filtration revealed an improvement in the antifouling properties of the modified membranes. The changes in the membrane surface morphology showed that the roughness of membrane surface is reduced significantly.

Keywords: $CO_2$-laser Irradiation, Polyamide Membrane, Surface Modification, Fouling Reduction

## INTRODUCTION

Membrane technology has widespread usage in different separation applications, including water industry, pervaporation, gas separation and fuel cells. However, membrane fouling in the water industry is a major problem that causes flux reduction, increases energy usage, increases membrane cleaning and reduces lifetime of membranes in long-term operation [1,2].

Surface modification of reverse osmosis (RO) membranes is a promising method towards developing antifouling membranes [3-5]. Different methods have been used to modify the antifouling ability of RO membranes [6]. These methods include physical adsorption [7,8], coating [9-12], hydrophilization treatment [13], in-situ redox initiated grafting [14-16], free-radical graft polymerization [14,17], chemical coupling [18], initiated chemical vapor deposition [19] and plasma polymerization [6]. However, most of these methods are time consuming, involve many complex steps and need chemicals, which limits their application [6]. Photochemical grafting techniques like UV-initiated grafting are very popular for modification of surfaces [20]. These techniques have wide use because of their selectivity to absorb UV light without influencing the bulk polymer and also mild reaction conditions [20,21].

†To whom correspondence should be addressed.
E-mail: musavi@sharif.edu


The most used irradiation for membrane surface modification is UV-irradiation, which is generally applied for UV-initiated graft polymerization of ultrafiltration and nanofiltration membranes [22-25]. However, the application of $CO_2$-laser irradiation for surface modification of RO membranes is not reported.

The $CO_2$-laser is widely used in the scientific investigations and within many industries. This laser family has the ability of radiation emission within the infra-red spectrum on rotational-vibrational transitions with 9 to 11 μm wavelengths [26]. Among all of the commercially available lasers, the $CO_2$ laser offers the lowest cost per watt along with good beam quality. The $CO_2$ lasers are commercially available with a wide range of average output power and also have a number of advantages, such as clean processing, high accuracy, preciseness and non-contact operation [27]. These advantages of this type of laser show that it is worth to make a distinct study on the interaction between $CO_2$-laser irradiation and TFC polyamide RO membrane. Furthermore, based on the available sources, the application of $CO_2$-laser irradiation for surface modification of RO membranes has not been observed. Hence, the main objective of the present paper is to study the effect of $CO_2$-laser irradiation on the properties of TFC polyamide RO membrane. Interfacial polymerization and modified pulsed $CO_2$-laser equipment are used to prepare the TFC polyamide RO membranes. Different $CO_2$-laser pulses were also studied. The results of the salt rejection, flux and BSA tests are reported as well as scanning electron microscopy (SEM) images, contact angles, surface roughness measurements

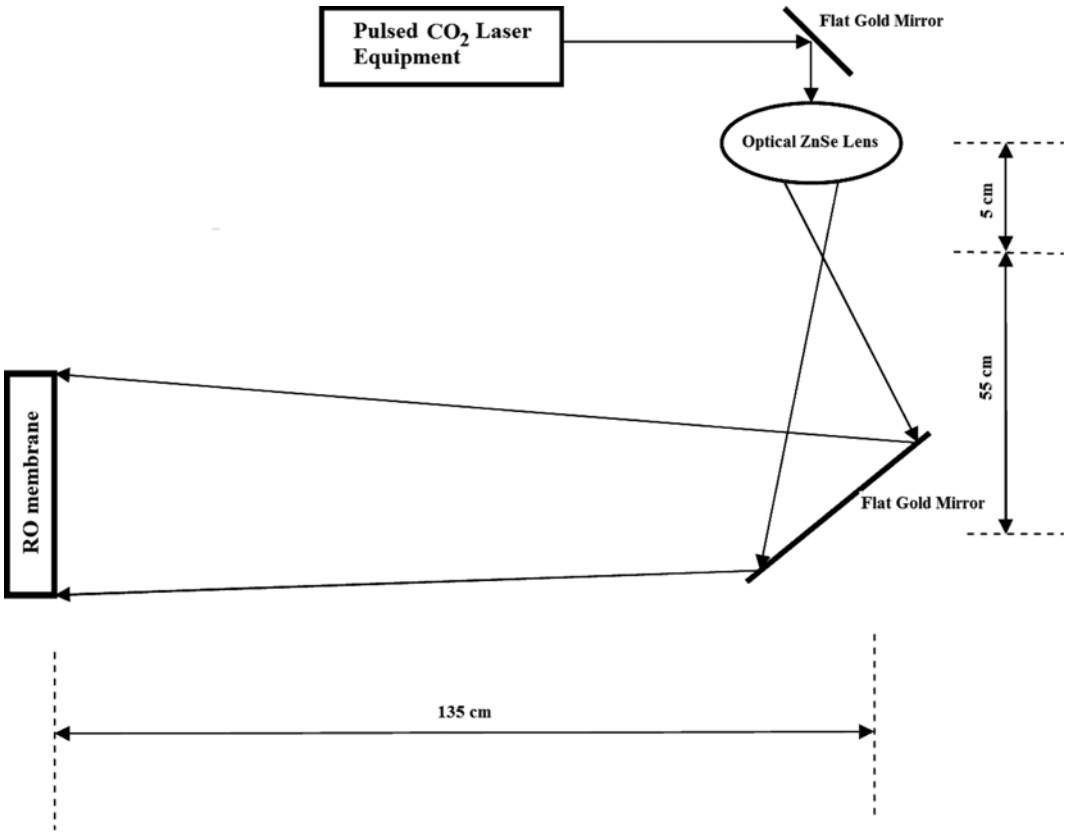



**Fig. 1. Schematic diagram of laser irradiation system used to modify TFC polyamide RO membranes.**

and attenuated total reflection - Fourier transform infrared spectra (ATR-FTIR).

## EXPERIMENTAL

### 1. Materials

The microporous polysulfone support membrane was purchased from Woongjin Chemical Co. Ltd. (Seoul, South Korea) with molecular weight cut-off 100 K. Chemicals like n-Hexane, monomers m-phenylenediamine (MPD), trimesoyl chloride (TMC), triethyl amine (TEA) and (+)-10- camphor sulfonic acid (CSA) were purchased from Merck (Germany). Bovine serum albumin (BSA) fraction V (Merck, Germany) was applied in the fouling test. The analytical grade of sodium chloride (NaCl) was used without further purification. The conductivity of pure water used was less than 5 μs/cm.

### 2. Preparation of TFC Polyamide RO Membranes

TFC RO membranes were produced via the interfacial polymerization of TMC solution (0.4 wt%) in n-hexane and MPD solution (2.0 wt%) in water. Camphor (1.0 wt.%) and TEA (2.0 wt%) were added to aqueous solution. pH adjustment and the improvement of the absorption of MPD in polysulfone support membrane were facilitated by using camphor [28]. MPD-TMC reaction was accelerated by TEA via removing hydrogen halide formed during amide bond formation [28,29]. Pure polysulfone support membranes were soaked in aqueous MPD solution for ten minutes. A rubber roller was used to remove the excess MPD solution from the surface of the support membranes. These supports were then immersed into TMC solution in n-hexane at 25 °C for 60 seconds for interfacial polymerization. Then, they were rinsed with n-hexane and heat cured at 80 °C for 10 minutes. As a result, an active layer of polyamide (PA) was formed on the polysulfone supports.

### 3. Surface Modification of TFC Polyamide RO Membranes

Laser irradiation of TFC polyamide RO membranes was carried out using a 10 W pulsed $CO_2$-laser (Synrad Inc., USA) with the spot size of 3.5 mm, providing a laser beam of wavelength 10.6 μm. To magnify the laser spot size from 3.5 mm to 7.0 cm an optical system (Fig. 1) was applied. This system consists of two flat gold mirrors and an optical ZnSe lens with the focal length of 5 cm. The TFC polyamide RO membrane samples with the effective area of 38.46 $cm^2$ (7.0 cm diameter) were mounted in the center of the laser spot. Energy reaching the membrane samples was measured by a power meter (PS-330IR, Gentec, Inc., South Korea) prior to irradiation. The applied power density per laser pulse and the number of pulses used for the investigated surface modification were 0.91 $mW/cm^2$ and 10,000-40,000 pulses, respectively.

### 4. Characterization of Unmodified and Modified RO Membranes

4-1. Spectral Analysis

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, VERTEX 80, Bruker Corp., Germany) was used for analysis of the bonds and functional groups on the near-surface region of unmodified and modified RO membranes. IR spectra of the membranes were recorded in the wavenumber range of 500-4,000 $cm^{-1}$ at 25 °C.

4-2. Contact Angle Measurement

A contact angle measurement system (OCA20, Dataphysics Instruments, Germany) was used to measure the water contact angles ($\theta$) at 25 °C. A droplet with volume of 3 µL water was put on the surface, and the contact angle of sessile drop was determined by a high speed video analysis system. Contact angle measurements were done at different points on the surface of the membrane and the average values of at least five measurements were reported.

4-3. Scanning Electron Microscopy (SEM)

The surface morphology of the unmodified and modified membranes was studied via a VEGA||(TESCAN, Czech Republic) SEM with magnification of 15,000 and 35,000. To reduce sample charging, all of them were sputter-coated with a thin layer of gold [30].

4-4. Atomic Force Microscopy (AFM)

The surface topology of the modified and unmodified membranes was structurally characterized by AFM (DualScope C-26, DME Corp., Denmark). Non-contact mode of AFM was applied to maximize the resolution and minimize the sample damage, and the scan size was 10 µm×10 µm. The surface roughness of the membrane was determined by measuring roughness parameters [31].

**5. RO Performance Tests**

Membranes with 38.46 $cm^2$ effective filtration area (7.0 cm diameter) were put into cross-flow RO cell. Pure water was used to compact these samples under 2.1 MPa for 1 h prior to permeation experiments. The selectivity and permeability of the membrane were measured by the salt rejection and water flux measurements under 2.0 MPa pressure with 2,000 ppm NaCl solutions at 25 °C. Flow rate and reservoir volume were 40 L/h and 20 L, respectively. Permeation flux (J) was determined by using Eq (1), [32]:

$$J = \frac{V}{A \times t} \tag{1}$$

where J, V, A and t stand for the permeation flux (L/$m^2$ h), permeate volume (L), membrane effective area ($m^2$) and time (h), respectively. Salt rejection was determined by using Eq. (2):

$$R(\%) = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{2}$$

where $C_P$ and $C_F$ are the salt concentrations in the permeate and feed, respectively. They were obtained with a conductivity meter (Walk Lab, Trans. Instruments Ltd., Singapore). Each experiment was repeated at least twice, and the average values were reported.

**6. Membrane Fouling Experiments**

Fouling experiments on the membranes used aqueous solution containing 200 mg/L BSA at 1.2 MPa and 25 °C by employing the stirred dead-end permeation test unit. The cell test is made of stainless steel with an active filtration area of 19.6 $cm^2$ (5 cm diameter). The stirring speed of 250 rpm was performed for all of the experiments. The dead-end cell pressure is regulated using a high-pressure nitrogen vessel equipped with a gas pressure regulator. The weight of permeate was recorded every 300 sec. The resultant water flux was used to calculate the fouling of the modified and unmodified TFC membranes. To evaluate antifouling properties of the prepared membranes, first pure water flux ($J_o$) experiments were performed for 60 min followed by 60 min of BSA solution filtration ($J_P$) with concentration of 200 mg/*l*, respectively. Then each membrane was rinsed three times by DI water and soaked in DI water for 30 min for cleaning. Finally, the DI water flux ($J_1$) was measured for 60 min. at the same pressure and the flux recovery ratio (FRR) was evaluated with Eq. (3), [29]:

$$FRR = \frac{J_1}{J_o} \times 100 \tag{3}$$

## RESULTS AND DISCUSSION

**1. ATR-FTIR Spectra Analysis**

Functional group characteristics of TFC polyamide RO membranes before and after modification were investigated by ATR-FTIR in the region 500-4,000 $cm^{-1}$. Fig. 2 represents the ATR-FTIR spectra of the modified and unmodified TFC polyamide RO mem-

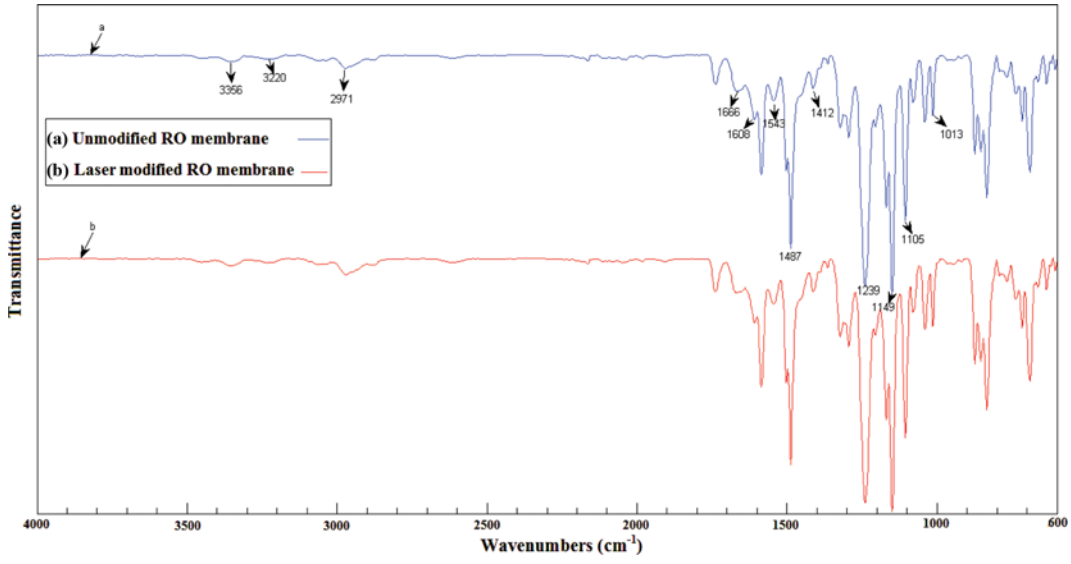



**Fig. 2. ATR-FTIR spectra of the (a) unmodified and (b) modified TFC membrane. The modification is carried out with 40,000 pulses of $CO_2$-laser irradiation.**

branes with $CO_2$-laser irradiation. The spectra in this figure show that interfacial polymerization between MPD and TMC was performed successfully onto the polysulfone support membrane. Two absorbance frequencies that appeared at 1,013 $cm^{-1}$ and 1,239 $cm^{-1}$ are characteristic of the C-O group. The absorbance frequencies responsible for the stretching mode of C=O group connected to the N-H group (HN-C=O, amide bond) appeared at 1,666 $cm^{-1}$ and the absorbance frequencies responsible for the asymmetric stretching mode of C=O group connected to the N-H group (HN-C=O, amide bond) appeared at 1,750 $cm^{-1}$. The asymmetric stretching mode is due to the interaction between functional group of amid bond and challenge of vibration in amid group. The bands appeared as a representative reaction between amine group in MPD and mesoyl group in TMC and formation of amide bond. The stretching vibration of secondary amide was observed at 3,220 $cm^{-1}$. The absorbance bands at 1,412 $cm^{-1}$ and 1,608 $cm^{-1}$ are attributed to the stretching vibration of unreacted carboxylic acid groups of TMC molecules [33,34].

As shown in Fig. 2, the ATR-FTIR spectra of the modified TFC membrane are almost the same as unmodified one. It has no new peak in the ATR-FTIR spectra of the modified polyamide membrane. All these results suggest that the chemical structure of the membrane surface is very similar before and after modification with $CO_2$-laser irradiation. Therefore, no new functional group was inserted to the surface of TFC RO membrane by $CO_2$-laser irradiation.

**2. Membrane Surface Hydrophilicity**

Contact angle measurements were used to determine the membrane surface hydrophilicity. The wetting tendency of the liquid toward the solid surface was evaluated by contact angle measurements. The higher tendency of water to wet the surface causes a lower contact angle and the greater surface hydrophilicity [35].

**Table 1. Water contact angle measurements of unmodified and modified membranes**

| Membrane | Contact angle (°) |
|---|---|
| Unmodified | 44.55 (±1.2) |
| Modified* | 44.05 (±1.1) |

*Membrane modified with 40,000 pulses of $CO_2$-laser irradiation

Table 1 shows the contact angle measurements of the modified and unmodified polyamide membranes. As shown, there is no meaningful change in the wettability of the surface of $CO_2$-laser modified reverse osmosis membranes. It suggests that the laser irradiation does not change the chemistry of the membrane surface, as approved by ATR-FTIR analysis. Accordingly, it can be concluded that the $CO_2$-laser irradiation cannot induce functional groups on the polyamide surface of the prepared reverse osmosis membranes.

**3. Surface Morphological Structure**

The surface morphological structure of the TFC polyamide RO membranes was tested before and after surface modification via the SEM and AFM measurements. Representative SEM images of the modified and unmodified TFC membrane are presented in Fig. 3. The modification was carried out with 10,000, 20,000, 30,000 and 40,000 pulses of $CO_2$-Laser irradiation with SEM magnification of 15,000 and 35,000. Similar to other investigations [35] the

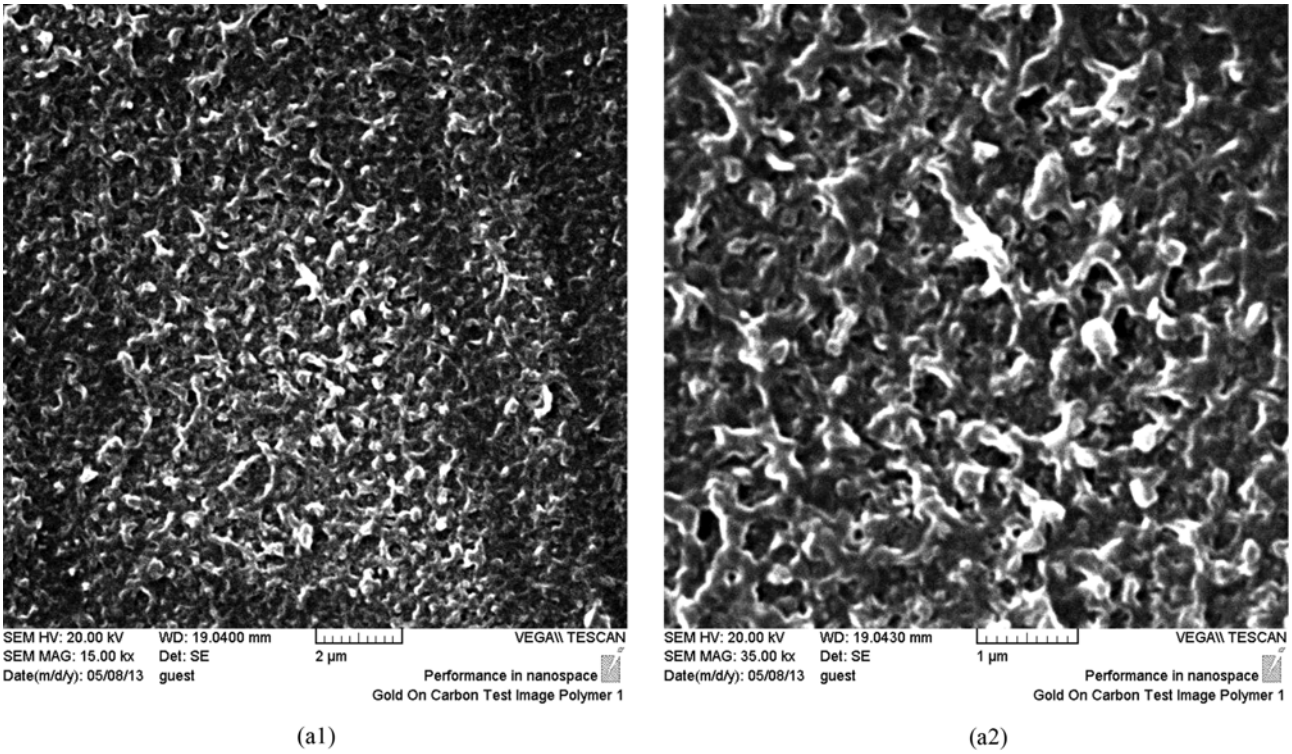
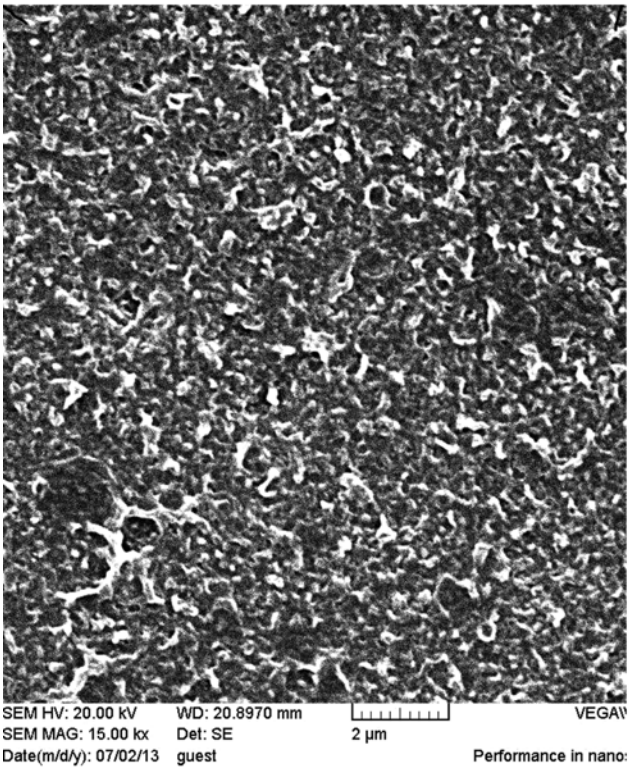
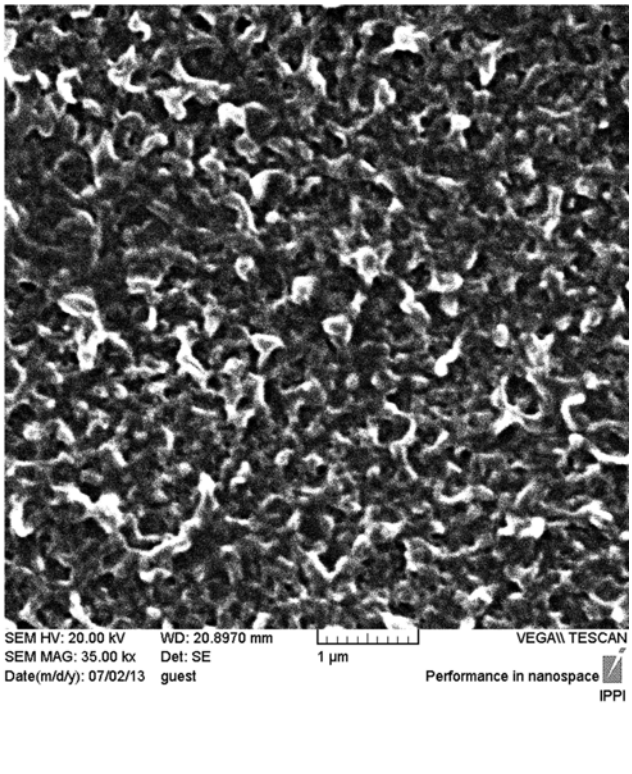


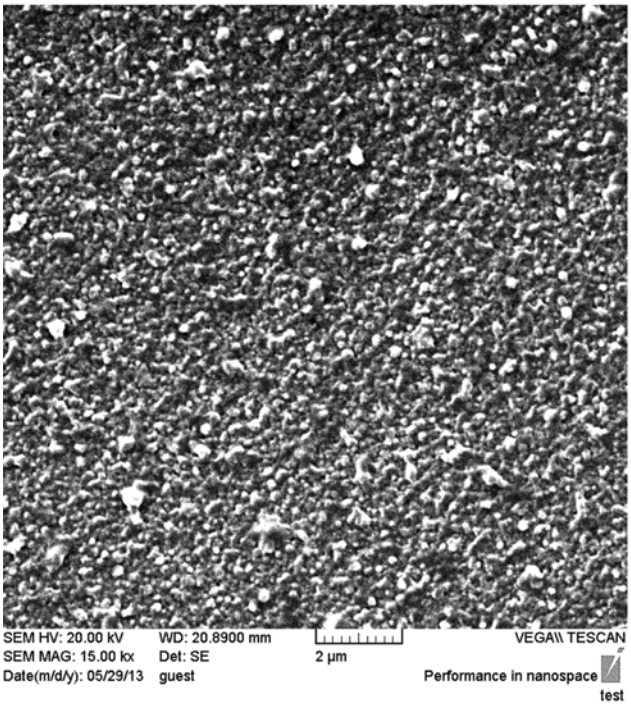

**Fig. 3. Surface SEM images of the TFC polyamide membrane: (a) Unmodified TFC membrane and TFC membrane modified with (b) 10,000, (c) 20,000, (d) 30,000 and (e) 40,000 pulses of $CO_2$-Laser irradiation (with SEM magnification of 15,000 and 35,000).**



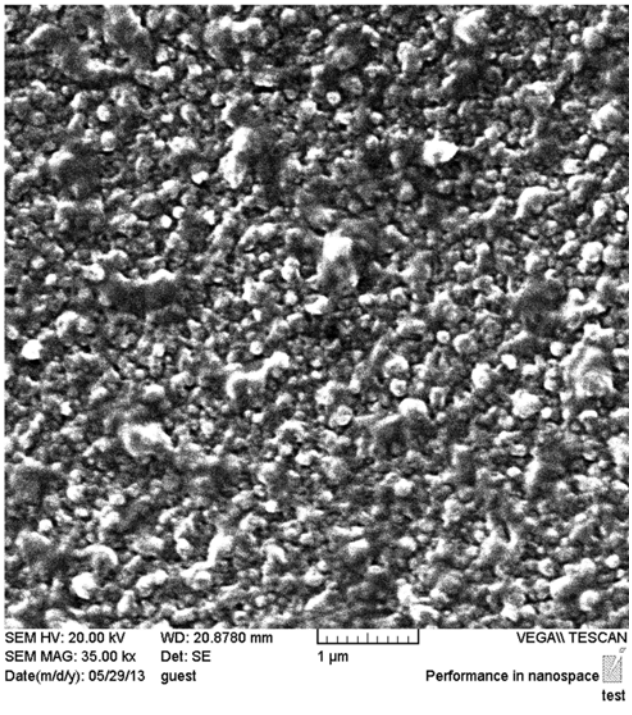

(b1)




(b2)




(c1)




(c2)

**Fig. 3. Continued.**

surface feature of the unmodified and modified TFC membrane is relatively loose and relatively compact, respectively. Fig. 3(a) shows the surface feature of the unmodified membranes, while Figs. 3(b)-(e) show this feature for the modified TFC membrane. The surface feature of the modified TFC membrane after long-term $CO_2$-laser irradiation becomes denser and more compact (Fig. 3(e)).

The three-dimensional 10 µm×10 µm AFM results of the TFC polyamide RO membranes with and without modification are pro-

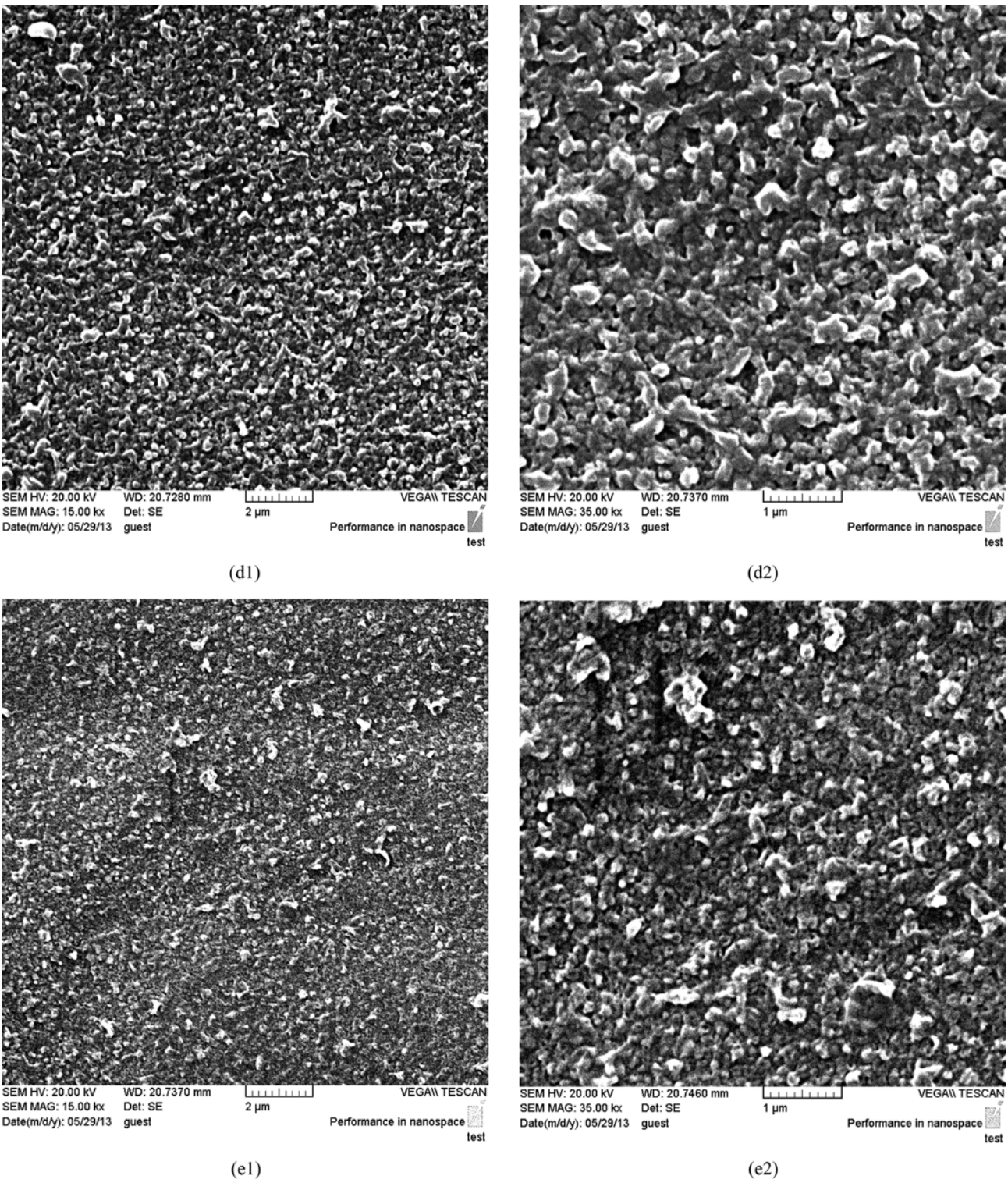



**Fig. 3. Continued.**

vided in Fig. 4. Table 2 shows the roughness parameters of the membrane surfaces which are determined with AFM. These parameters are lower for the modified TFC polyamide RO membrane relative to that of the unmodified one. These findings accompanied with the SEM results indicate a decrease in the roughness of the TFC polyamide membrane surface after $CO_2$-laser irradiation. This can be explained by the laser induced re-melting of polyamide in some regions of the membrane surface. By re-melting some regions of membrane surface, the material could then have re-solidified into a smoother surface topography, which means that the surface roughness will decrease. A similar behavior was reported by Waugh and Lawrence [36] on the studying of $CO_2$-laser irradiation effect on

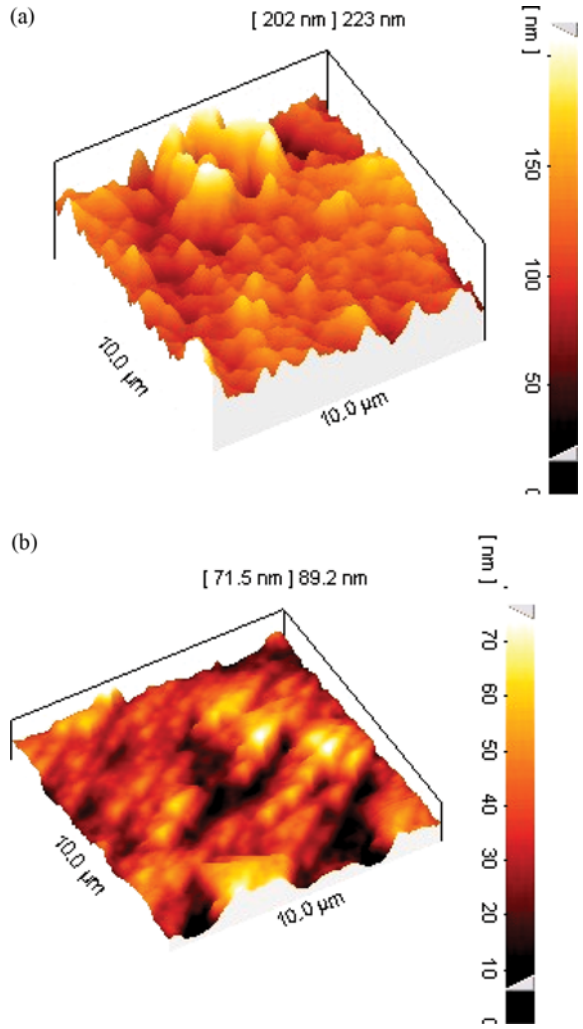



**Fig. 4. AFM images of (a) unmodified and (b) modified surface of TFC membrane. The modification is carried out with 40,000 pulses of $CO_2$-laser irradiation (scanning area 10 μm×10 μm).**

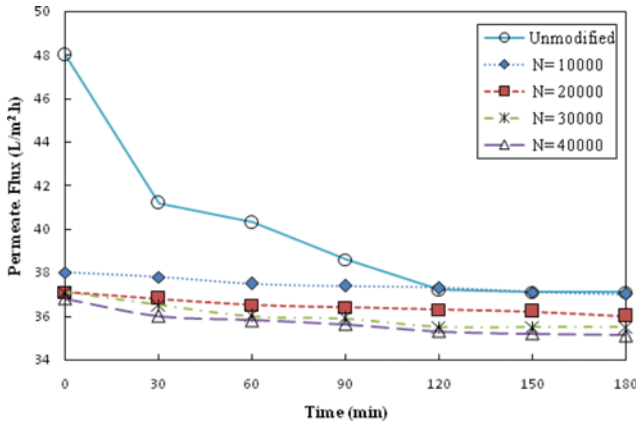



**Fig. 5. Permeate flux of the unmodified and $CO_2$-laser irradiation modified TFC membranes during 180 min of continuous filtration in water with 2,000 ppm NaCl at 2.0 MPa and 25 °C.**

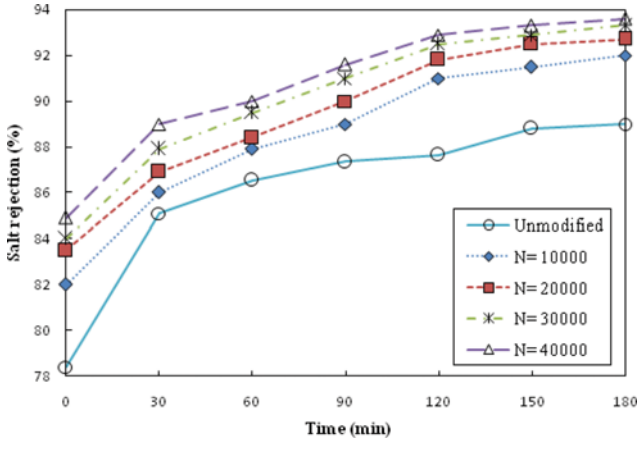



**Fig. 6. Salt rejection of the unmodified and $CO_2$-laser irradiation modified TFC membranes. Filtration continued for 180 min in water containing 2,000 ppm NaCl at 2.0 MPa and 25 °C.**

**Table 2. Surface roughness parameters of unmodified and modified membranes resulted from analyzing three randomly chosen AFM images**

| Membrane | Roughness parameters | | |
|---|---|---|---|
| | $S_a$ (nm) | $S_q$ (nm) | $S_z$ (nm) |
| Unmodified | 24.85±1.1 | 32.45±1.3 | 194.5±25 |
| Modified* | 9.94±0.9 | 12.5±1.2 | 65.4±19 |

*Membrane modified with 40,000 pulses of $CO_2$-laser irradiation
$S_a$ is average roughness (nm)
$S_q$ is root mean square of the $Z$ data (nm)
$S_z$ is mean difference between highest peaks and lowest valleys (nm)

polyamide fiber.

**4. The Performance of Reverse Osmosis**

Salt rejection and water flux were used to determine the performance of reverse osmosis for the modified and unmodified TFC membranes via cross-flow permeation tests [37]. Salt rejection and water flux values for the unmodified and modified TFC RO membranes using $CO_2$-laser irradiation with different pulses are, respectively, shown in Figs. 5 and 6. As shown, modified membranes show higher salt rejection than unmodified membrane. However, the permeation flux through the modified membranes is slightly lower than in the unmodified one. Fig. 6 shows an increase in salt rejection of the modified membranes by increasing of irradiation pulse numbers. By considering these results along with the SEM and AFM analysis, it can be suggested that salt rejection enhancement should be due to the compaction and decrease of surface roughness, which means the smoother surface in modified membranes. Also, note that a smoother surface is predicted to cause less fouling [3]. This behavior was reported by Li et al. [38], Sagle et al. [39] and Jeshi et al. [40]. In addition, increasing of the salt rejection and decreasing of the permeation flux in modified membranes seems to be due to decreasing of membrane surface roughness by increasing of the irradiation pulse numbers. As shown in Fig. 5, at the end of 180 min of RO performance test, the reduction in initial flux for the unmodified membranes was 22%. However, the reduction in initial flux for the modified membranes was less than 5%. It may be due to

**Table 3. Permeate flux of the unmodified TFC membrane and TFC membranes modified with 10,000-40,000 pulses of $CO_2$-laser irradiation during 60 min of filtration of aqueous solution containing 200 mg/*l* BSA at 1.2 MPa and 25 °C**

| Membrane | Volumetric flux (L/m$^2$ h) | | | Flux recovery ratio (FRR) |
|---|---|---|---|---|
| | $J_o^a$ | $J_p^a$ | $J_1^a$ | |
| Unmodified | 20.7 | 9.9 | 18.55 | 91 |
| 10000 | 20.25 | 11.75 | 20 | 99 |
| 20000 | 19.55 | 12.05 | 19.3 | 99 |
| 30000 | 18.75 | 12.5 | 18.7 | 100 |
| 40000 | 18.5 | 12.65 | 18.45 | 100 |

[a]60 min average flux at the end of each filtration step

improvement of antifouling ability of the modified membranes, which will be discussed in next section.

**4. Membrane Fouling with BSA**

Filtration tests with BSA solution were done to examine the performance of modified and unmodified TFC membranes against fouling. Table 3 represents the findings about flux recovery ratio and water flux. As shown, there is an initial decrease in pure water flux ($J_o$) vs. the number of pulses of $CO_2$-laser irradiation. As Fig. 3 shows, this is related to more compact structure of membrane surface irradiated by higher laser pulse numbers. It is found that the flux recovery ratio (FRR) by water washing is only 91% for the unmodified membrane. However, for all of the modified membranes, more than 99% of their initial flux was recovered after cleaning with water.

According to Table 3, the unmodified membrane has the lowest water flux ($J_P$) in BSA solution, which means that it has the highest fouling tendency. TFC membranes modified with $CO_2$-laser irradiation have higher water flux ($J_P$) in comparison with unmodified membrane, and so have lower protein deposition and absorption. Moreover, the detachment of the absorbed protein is easier in the modified membranes relative to the unmodified one. These results are consistent with FRR results which are mostly more than 99% for all of the modified membranes. This means that the antifouling properties have been increased. Finally, the antifouling properties of the TFC polyamide RO membranes were improved after modification with $CO_2$-laser irradiation. This is due to decrease in surface roughness (according to AFM results) of the TFC polyamide membranes after modification with $CO_2$-laser irradiation. However, most of the surface modification techniques such as grafting and plasma polymerization increase the membrane surface roughness [6,37]. The $CO_2$-laser irradiation technique reduces the surface roughness significantly. Vrijenhock et al. [41] and Elimelech et al. [42] studies showed a positive correlation between the surface roughness and colloidal fouling of RO membranes [3].

## CONCLUSION

$CO_2$-laser irradiation effect on the surface modification of TFC polyamide RO membranes was investigated. $CO_2$-laser irradiation with 10,000 to 40,000 pulses was employed. The contact angle experiments and ATR-FTIR spectra showed that $CO_2$-laser irradiation did not induce functional groups on the polyamide membrane surface. Therefore, membrane surface wettability was not changed. However, the SEM and AFM analysis before and after surface modification indicated that the surfaces of modified polyamide membranes are denser and more compact than unmodified membranes under $CO_2$-laser irradiation. The AFM analysis showed that the membrane surface roughness is decreased after irradiation. The reverse osmosis performance results showed higher salt rejection in irradiated membranes relative to the unmodified ones; however the permeation flux is a little decreased after irradiation.

BSA fouling experiments showed an improvement in antifouling properties of the TFC polyamide membranes after modification with $CO_2$-laser irradiation. Also, the modified RO membranes have lower protein absorption.

Finally, the antifouling ability of the modified membranes has been increased due to modification with $CO_2$-laser irradiation. In addition, a very mild environmental condition with no complex method is used to modify the surfaces of the membranes.

## ACKNOWLEDGEMENTS

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## LIST OF SYMBOLS

**Symbols & Abbreviations**

$\theta$ : contact angle
A : membrane effective area [m$^2$]
AFM : atomic force microscopy
ATR-FTIR : attenuated total reflectance- Fourier transform infrared
BSA : bovine serum albumin
CSA : camphor sulfonic acid
$C_F$ : salt concentration in the feed
$C_P$ : salt concentration in the permeate
FRR : flux recovery ratio
J : permeation flux [*l*/m$^2$ h]
$J_o$ : pure water flux [*l*/m$^2$ h]
$J_p$ : water flux [*l*/m$^2$ h]
$J_1$ : pure water flux (*l*/m$^2$ h) after cleaning
MPD : m-phenylenediamine
N : number of pulses of laser
PA : polyamide
RO : reverse osmosis
$S_a$ : average roughness [nm]
$S_q$ : root mean square of the Z data [nm]
$S_z$ : mean difference between highest peaks and lowest valleys [nm]
SEM : scanning electron microscopy
t : permeation time [h]
TEA : triethyl amine
TMC : trimesoyl chloride
TFC : thin-file composite
V : permeate volume [L]

ZnSe : zinc selenide

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