

Effect of NH₃ plasma on thin-film composite membrane: Relationship of membrane and plasma properties

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(Received September 22, 2012, Revised February 15, 2013, Accepted March 08, 2013)

Abstract. Surface modification by low-pressure ammonia (NH₃) plasma on commercial thin-film composite (TFC) membranes was investigated in this study. Surface hydrophilicity, total surface free energy, ion exchange capacity (IEC) and zeta (ζ)-potentials were determined for the TFC membranes. Qualitative and quantitative analyses of the membrane surface chemistry were conducted by attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy. Results showed that the NH₃ plasma treatment increased the surface hydrophilicity, in particular at a plasma treatment time longer than 5 min at 50 W of plasma power. Total surface free energy was influenced by the basic polar components introduced by the NH₃ plasma, and isoelectric point (IEP) was shifted to higher pH region after the modification. A ten (10) min NH₃ plasma treatment at 90 W was found to be adequate for the TFC membrane modification, resulting in a membrane with better characteristics than the TFC membranes without the modification for water treatment. The thin-film chemistry (i.e., fully-aromatic and semi-aromatic nature in the interfacial polymerization) influenced the initial stage of plasma modification.

Keywords: thin-film composite; modification; membranes; NH₃ plasma; physico-chemical properties

1. Introduction

Polymeric membrane has been recently applied to various industries, such as chemical plants, biological systems, gas separation units, and drinking water and wastewater treatment applications (Bhut 2008, Ishitsuka 2008, Tian 2008, Turan 2004). Membranes are categorized by separation mechanisms, polymer structures and size of targeted molecules, and common membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The NF and RO membranes can be made of thin-film composites (TFC) with high water flux and salt rejection, as well as high mechanical strength (Manttari 2006, Prakash Rao 1997, Xu 2006). TFC membrane has three major layers: a non-woven layer to provide mechanical strength, a support layer with high porosity, and a thin-film layer for selectivity. Each layer consisted of different polymers and could be modified separately; therefore, independent optimization is possible (Freger 2002, Korikov 2006). Particularly, treatment of thin-film layer is not only critical to improve the membrane performances, but also to understand the advanced TFC technology in general (Kwon 2006).

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Physico-chemical properties of membrane surface largely determine the water permeability, selectivity, membrane hydrophilicity, as well as membrane fouling characteristics. Several methods have been developed to change the surface properties and enhance membrane performances. Grafting polymerization, chemical treatments, flame, radiation or plasma treatments are all explored for the membrane modification (Wavhal 2003), among which *in-situ* plasma reaction can easily introduce various functional groups onto the membrane surface and coat a layer without contamination (Zhou 2010). The plasma treatment uses highly energized particles, ions, radicals and electrons to activate the surface (Chen 1997, Gancarz 2002). The quality of plasma and its performances depend on the source gas and operating parameters including treatment time, pressure, power, and distance between sample and plasma electrode (Ciszewski 2007, Pozniak 2002). In this study, a low-pressure NH_3 plasma treatment is selected for the membrane modification because polymeric membranes could be easily damaged by thermal and chemical treatments, and the plasma treatment is biocompatible as the NH_2 , NH and N radicals in the plasma will be decomposed after the treatment (Castro Vidaurre 2001, Lazea 2005). Surface hydrophilicity and fouling tendency could be changed by the incorporation of nitrogen functional groups (amino, imino or cyano) on membrane surfaces (Tusek 2001).

Both the membrane modification method (i.e., low-pressure plasma) and the material (i.e., TFC membrane) are frequently investigated to improve the water purification performance. Previously we have demonstrated that the low-pressure NH_3 plasma can increase the pure water flux and the salt rejection at a set of plasma generation parameters (i.e., treatment time and applied power) (Kim 2011). Upon the plasma treatment, the membrane fouling by Bovine serum albumin (BSA) and Aldrich humic acid (AHA) fouling was decreased. However, while the overall performance of the NH_3 plasma modified membrane was found improved for water treatment, the specific changes of membrane physico-chemical properties have not been evaluated. The objective of this study is to characterize the commercial TFC membranes following the low-pressure NH_3 plasma treatment in terms of hydrophilicity, total free energy, and electro-kinetic properties. Different commercial TFC membranes are evaluated and compared including the plasma treatment efficiency, membrane types, post-treatment conditions, and thin-film layer chemistry. Plasma treatment time and applied power are two testing variables. Membranes are characterized for hydrophilicity by the sessile drop method, measurements of surface roughness and surface free energy, acid-base titration for ion exchange capacity (IEC), and tangential streaming potentials (TSP) analysis for the zeta (ζ)-potential. Surface functional groups are analyzed by the attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy.

2. Experiments

2.1 Membrane properties

Six commercial TFC membranes - three nanofiltration (NF) (NF90, NF270 and DK) and three reverse osmosis (RO) membranes (XLE, BW30 and SG) - were evaluated in this study. Membranes were purchased from Dow/Filmtec (NF90, NF270, XLE and BW30) and GE Osmonics (SG and DK) as dry rolled flat-sheet forms. The NF membranes have salt rejections of 94.4%, 56.9% and 66.4% for NF90, NF270 and DK, respectively, lower than those of RO membranes with salt rejections of more than 95% (Tang 2009b). However, RO membranes normally require higher transmembrane pressure (TMP) than NF membranes. Thin-film layer

chemistry could be changed based on if a fully- or a semi-aromatic polyamide (PA) was used for interfacial polymerization. The fully-aromatic PA layer was prepared by the polymerization of *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC) and the semi-aromatic PA layer by the polymerization of piperazine and TMC (Freger 2002). Some of the TFC membranes are post-treated to protect membrane surface or to improve their performance by adding a coating layer (Tang 2007a). The fully- and semi-aromatic PA membranes and various post-treated membranes were used in this study, and their characteristics are summarized in Table 1. Membranes were cut into less than 100 cm^2 for further treatment and washed with Milli-Q deionized water ($18.2 \text{ M}\Omega\text{-cm}$, Millipore Corp.) to remove impurities and detergents. Cleaned membranes were dried in room temperature at least 48 h prior to use and stored at 4°C .

2.2 Low-pressure NH_3 plasma treatment

The experimental setup and configurations of low-pressure plasma system were described elsewhere (Kim 2009). Briefly, two electrodes were vertically aligned in a Pyrex bell-jar reactor and same sized membranes on aluminum holder were placed between the electrodes. The reactor was pre-vacuumed to remove any residual moisture. The mechanical and booster pumps evacuated the reactor to below 3 mTorr. At the steady-state, pure NH_3 source gas (anhydrous 99.99%, Scott specialty gases) was introduced into the reactor at a given pressure (50 mTorr). Plasma was generated by 13.56 MHz radiofrequency (RF) power (RFX-600, Advanced Energy Industries, Inc.), and source gas flow and pressure of the plasma reactor were controlled by needle valve and gas channel module (Type 247, 252 channel readout modules), respectively. The RF power was set at 10, 50 and 90 W and the plasma treatment time at 1 to 10 min. After the plasma modification, the membrane samples were split and stored separately, one portion in a Teflon-sealed vacuum

Table 1 Characterization and physical parameters of membrane

Membrane	XLE	BW30	SG	NF90	NF270	DK
Manufacturer	Dow/FilmTec	Dow/FilmTec	GE	Dow/FilmTec	Dow/FilmTec	GE
Types	RO	RO	RO	NF	NF	NF
PA ^a chemistry	Fully-aromatic	Fully-aromatic	Semi-aromatic	Fully-aromatic	Semi-aromatic	Semi-aromatic
Surface coating ^b	Uncoated	Coated	Modified	Uncoated	Uncoated	Modified
Permeability ^b ($\text{l m}^{-2} \text{ h}^{-1} \text{ bar}$)	$6.04\text{E} + 00$	$3.96\text{E} + 00$	$2.32\text{E} + 00$	$1.12\text{E} + 01$	$1.45\text{E} + 01$	$5.51\text{E} + 00$
Contact angle ^c (degree)	53.7 ± 2.9	45.9 ± 3.1	57.6 ± 6.0	48.8 ± 2.7	36.6 ± 5.3	43.1 ± 3.6
Salt rejection ^b (%-NaCl)	96.5	97.9	95.2	94.4	56.9	66.4
Zeta potential ^c (mV @ pH 7)	-18.3 ± 2.3	-9.2 ± 3.9	-19.4 ± 1.8	-14.1 ± 4.1	-29.5 ± 1.6	-10.5 ± 3.7
RMS ^c (nm)	139.2 ± 5.4	53.1 ± 9.2	20.5 ± 5.8	128.4 ± 10.4	49.8 ± 2.1	19.2 ± 8.0

^a PA: polyamide

^b Tang (2007a)

^c Measurements were performed in this study. Contact angles were averaged values and zeta potential was evaluated in 10^{-3} KCl solution by different pressure gradients.

desiccators to minimize atmospheric effect, and the other under the ambient atmosphere, which was used to evaluate the aging effect of the plasma-treated membranes.

2.3 Characterization of physico-chemical properties

2.3.1 Contact angle measurement by the sessile drop method

Prior to the contact angle measurement, the membranes were cleaned to remove impurities and completely dried. Pure water contact angle on the membrane surface was measured by a goniometer (Video contact angle system 2500 XE, ASC products). 1 to 5 μL of deionized water was dropped using gas-tight syringe on the membrane surface, and water droplet image was captured by the video imaging system. Measurements were conducted at least at 10 different positions on the membrane surface and the contact angle was reported as the average values. The contact angles measured immediately after the plasma treatment and those measured after 30 days.

2.3.2 Total surface free energy

Surface free energy originated from Young's equation has been used for evaluating equilibrium between liquid and solid (Cantin 2006). Lifshitz-van der Waals and Lewis acid-base (*LW-AB*) approach (Van Oss 2006, Van Oss 1988) was selected to calculate the surface free energy of the membranes. In brief, *LW-AB* approach shows two parts of surface free energy components: apolar electro-dynamic *LW* components (i.e., London dispersion, Keesom orientation and dipole-dipole Debye inductions) and polar *AB* components (i.e., electron accepting and electron donating properties of Lewis acid-base theory, Eq. (1)). Total surface free energy is defined as the sum of *LW* and *AB* components, and it can be transferred by Young's equation (Eq. (2)).

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \quad (1)$$

$$\gamma^T = \gamma^{LW} + \gamma^{AB} = \left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}} \right)^2 + 2 \left(\sqrt{\gamma_S^+} - \sqrt{\gamma_L^+} \right) \left(\sqrt{\gamma_S^-} - \sqrt{\gamma_L^-} \right) \quad (2)$$

where, γ^T is the total surface free energy, *S* means the solid interfaces and *L* means the liquid interfaces. γ^+ and γ^- are the parameters related to the electron acceptor and electron donor, respectively. Three testing liquids are required in *LW-AB* method for unknowns (Van Oss 1988): deionized water and formamide (HCONH_2 , Sigma-Aldrich) were employed for two polar components and diiodomethane (CH_2I_2 , Sigma-Aldrich) was used for an apolar component. Chemicals were all over 99% purities and stored in a desiccating system to avoid contamination. Contact angles of each liquid were measured by the sessile drop method as previously discussed.

2.3.3 Acid-base titration

Non-woven polyester film (i.e., mechanical support layer) of TFC membranes was removed, and 500 mg of dried membrane strips per sample was prepared. The titration followed a procedure reported in the literature (Afonso 2006). Membrane samples were equilibrated with 1 N of HCl to achieve a free acidic surface. After 24 h at pH 3, membranes were titrated by 0.1 N NaOH to pH 10. Membrane strips and solution were mixed by a magnetic stirrer and the system was purged with N_2 to prevent the carbonate interference. The membrane strips were collected by a 0.45 μm vacuum filter and weighted for mass after drying in an oven. Ag/AgCl glass electrodes in 798 MPT Titrino (Metrohm AG, Switzerland) automatically recorded electrical potential, volume of consumed titrant and pH. IEC was calculated with the Eq. (3) (Hu 2007)

$$\text{IEC}(\text{mequiv./g}) = \frac{V_{\text{HCl}} \cdot N_{\text{HCl}} - V_{\text{NaOH}} \cdot N_{\text{NaOH}}}{m} \times 1000 \quad (3)$$

where V_{HCl} and V_{NaOH} represent the volume of consumed HCl and NaOH, respectively. N is the normality of the solution, and m is the mass of membrane. IEC is the milli-equivalent of protons per gram of dry membrane.

2.3.4 Tangential streaming potential (TSP) and ζ -potential

ζ -potential is an important parameter showing the electrical charge characteristics of a material. ζ -potential cannot be determined directly, instead, it is calculated from the streaming potential measurement (Childress 1996). Due to the overlapping of electrical double layer and concentration polarization, the streaming potentials of NF and RO membranes were often measured by the TSP method (Afonso 2006). A customized TSP measuring device is illustrated in Fig. 1 (Fievet 2006, Matsumoto 2007, Wang 2006).

The TSP device was consisted of two sets of glass chamber with two Ag/AgCl wire electrodes. Glass chambers were connected by a streaming channel. Two membrane coupons (effective surface area of 200 mm^2) were separated by a polytetrafluoroethylene (PTFE) spacer with $250 \mu\text{m}$ thickness and membrane coupons with spacer was positioned in the streaming channel. Electrolyte solutions (10^{-2} and 10^{-3} M of KCl) (Fisher Scientific, ACS reagent) were flowed through the inlet port of chamber. N_2 gas in a dispensing pressure vessel (4-L, Millipore Corp.) was used to control the flow rate and system pressure. Direction of electrolyte flow was alternated to prevent concentration polarization. Deionized water was circulated outside of chambers to maintain system temperature. pH values (3–10) were controlled by 0.1 M of acid (HCl) and base (NaOH). Streaming potential, pH, conductivity and temperature were measured by a digital multimeter (Fluke Electronics) and conductivity meter (HACH pH and conductivity meter) at a scheduled time interval. Pressure gradient (0–1300 mbar) was applied to determine the streaming potential coefficient via linear regression, and ζ -potential was calculated with the alternative Helmholtz-Smoluchowski (H-S) equation (Eq. (4)) (Wang 2006)

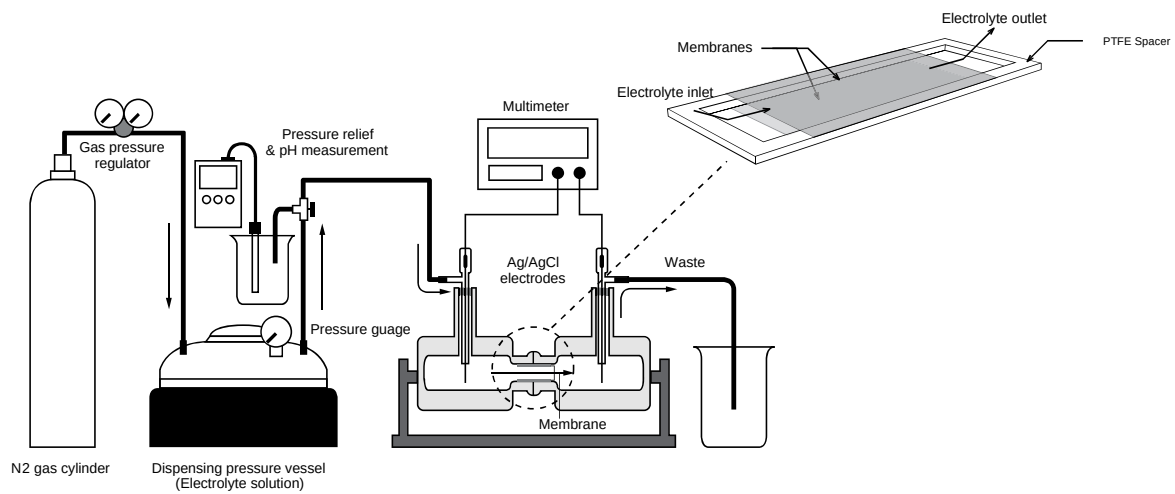


Fig. 1 Schematic diagram of tangential streaming potential (TSP) device

$$\zeta = \frac{\Delta E}{\Delta P} G_t \frac{\eta}{\varepsilon_0 \varepsilon_r} \frac{L}{hD} \quad (4)$$

where, ΔE is the tangential streaming potential, ΔP is the pressure gradient, G_t is the total conductance of the membrane and system, η is the liquid viscosity, ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant, L , h and D are the length, height and width of the slit, respectively.

2.4 Surface roughness and chemistry

Membrane surface roughness was analyzed by the atomic force microscopy (AFM) (MFP-3D, Asylum Research) using a silicon cantilever in tapping mode. The root mean square (RMS) values were determined by the scan size of $4 \mu\text{m}$ by $4 \mu\text{m}$ of the sample and 500 nm depths. Qualitative and quantitative membrane chemistry after the plasma modification was observed by ATR FT-IR spectroscopy (Nicolet 4700 FT-IR with multi-reflection Smart Performer[®] ATR, Thermo Electron Corp.). The germanium (Ge) crystal plate with a nominal incident angle of 45° was used in the ATR accessory. The dried membrane sample was placed on the Ge crystal and pressed carefully with noise reduction. Spectra in the wave numbers from 650 to 4000 cm^{-1} with 128 scans at a resolution of 2.0 cm^{-1} were collected. The peak area was integrated by the OMNIC software (ver. 7.2, Thermo Scientific) with standardized baseline for quantitative analysis.

3. Results and discussion

3.1 Surface hydrophilicity of TFC membranes

The membrane surface hydrophilicity is a significant factor controlling the water permeability, solute separation and/or membrane fouling (Kull 2005). Fig. 2 shows the contact angles of membranes immediately after plasma treatment (θ_0). Treatment time was varied from 1 to 10 min at 50 mTorr fixed system pressure and 50 W RF power. The range of treatment time was determined through preliminary experiments, which indicated that a plasma treatment time of 15 min and 20 min did not change the contact angle in comparison with 10 min treatment. This is consistent with the results of previous research (Yan 2008, Yu 2007).

The contact angles of NH_3 plasma treated membrane were decreased with increasing plasma treatment time. A steep decrease in the contact angle was observed in the initial 3 min, and the contact angle reached a steady value after 5 min of treatment. The smallest contact angle measured was 9° with NF270 following a 10 min treatment. The decrease in the contact angle was caused by the formation of hydrophilic surface functional groups, and radical interaction with oxygen (Yasuda 2005). The percentage decreases in NF270, NF90 and XLE were 76, 75 and 81%, respectively. NF270 and NF90 are the NF series membrane and XLE is the RO series membrane. Nevertheless they have similar contact angles with similar decrease following the NH_3 plasma treatment. DK, SG, and BW30 membranes (solid line-closed symbols) are less affected by the plasma treatment.

NF270, NF90 and XLE membranes are uncoated but DK, SG, and BW30 are coated with a proprietary coating layer (Tang 2009b). Uncoated membranes have lower contact angles than the coated ones in general, in particular with increasing plasma treatment time. Plasma-treated

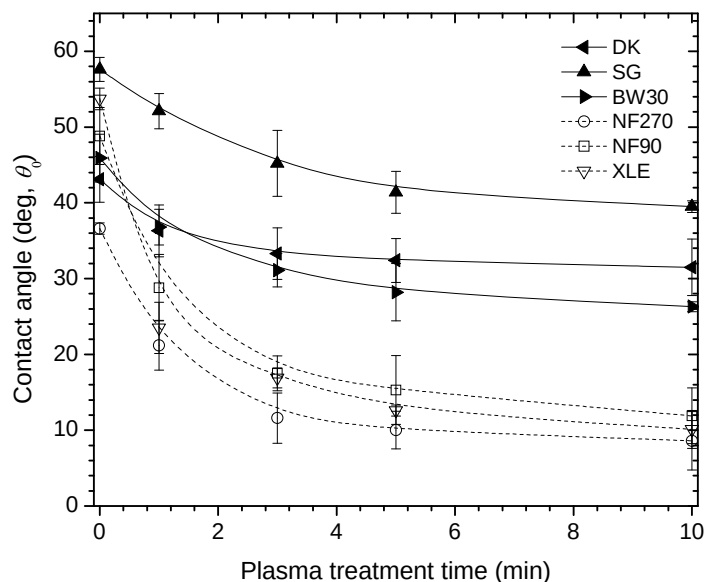


Fig. 2 Contact angle changes as a function of plasma treatment time. Open symbol: uncoated membranes and closed symbol: coated or modified membranes. Plasma operational parameters are 50 mTorr of pressure with 50 W of 13.56 MHz-RF power

membranes contained lower nitrogen contents, and it could reduce surface roughness because a coating layer can cover peak-and-valley features of the membrane (Tang 2007a, 2009b). The decreased surface roughness reduces the effective contact area of membrane (Kim 2003). Therefore, the effectiveness of NH_3 plasma treatment is more pronounced on rough membranes compared to the smooth membranes. AFM roughness and RMS values of tested membranes are shown in Fig. 3 and listed in Table 1, respectively.

Under the interfacial polymerization condition, the decreases in contact angle for the fully-aromatic membranes (XLE, NF90, and BW30) were larger than those for the semi-aromatic membranes except for NF270. The fully-aromatic membranes have much higher RMS values than semi-aromatic membranes (Table 1). Therefore, a lower effective contact area of membrane can decrease the efficiency of the plasma treatment.

Contact angles after 30 days of NH_3 plasma treatment were examined to evaluate potential for the hydrophobic recovery of the membrane. The different mobility and reorientation property of polymer chains at different depths of membrane (e.g., top surface and bulk polymer) could recover the membrane's original hydrophobic property (Wavhal 2003). Fig. 4 shows the normalized result of θ_0 and contact angle after 30 days of aging (θ_{30}). Changes in θ_{30} as a function of plasma treatment time and a correlation between the θ_0 and θ_{30} by different treatment times (1 and 10 min) are presented in Fig. 4(a) and 4(b), respectively. Fig. 4(c) shows the θ_0 and θ_{30} by different applied powers (10, 50, and 90 W) at a fixed plasma treatment time (10 min). Experimental parameters of the plasma treatment and the sessile drop method are the same with the initial tests.

The 30 days-old samples showed an increased contact angles than contact angles measured immediately after the NH_3 plasma treatment. The θ_0 of 1 min treated samples showed a steep decrease in the contact angles (Fig. 2); however, they were restored to the original hydrophobic

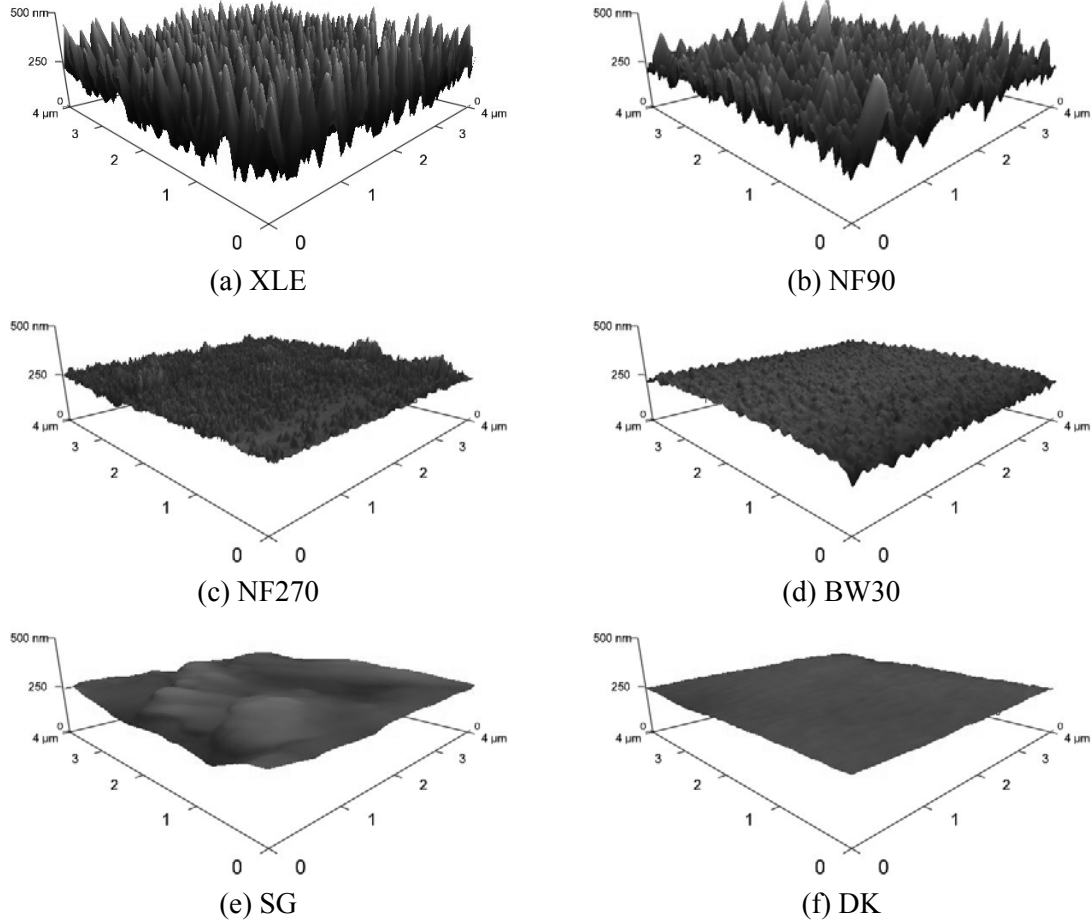


Fig. 3 AFM images of membranes: (a) XLE; (b) NF90; (c) NF270; (d) BW30; (e) SG; and (f) DK. Dimensions of x and y are $4\ \mu\text{m}$ and z is $500\ \text{nm}$

surface after 30 days (Fig. 4(a)). The θ_{30} of uncoated membranes showed lower contact angles (i.e., higher hydrophilicity) compared with the untreated membranes. Hydrophobic recovery was observed on 5 and 10 min treatments of uncoated samples, but their magnitudes were smaller than coated or modified membrane samples. NH_3 plasma treatments on the uncoated membranes are more stable against the hydrophobic recovery.

Fig. 4 showed that the hydrophobic recovery was less severe in the uncoated membranes (NF270, NF90 and XLE) under a longer plasma treatment. It is correlated with the contact angle changes in uncoated membranes. The effect of plasma treatment time is explained by different stabilities of surface bonding. Activated species from initial plasma discharge can reach an early stage of ion bombardment process; therefore, there is a lower holding strength of surface functionalities under a longer plasma treatment time (Castro Vidaurre 2001).

Fig. 4(c) shows the effect of plasma powers through the correlation of θ_0 and θ_{30} . Different plasma powers change the properties of hydrophobic recovery. 10 and 50W treatments of uncoated membranes recovered 41.7% and 39.5% of hydrophobicity, respectively, and 90 W treatments of

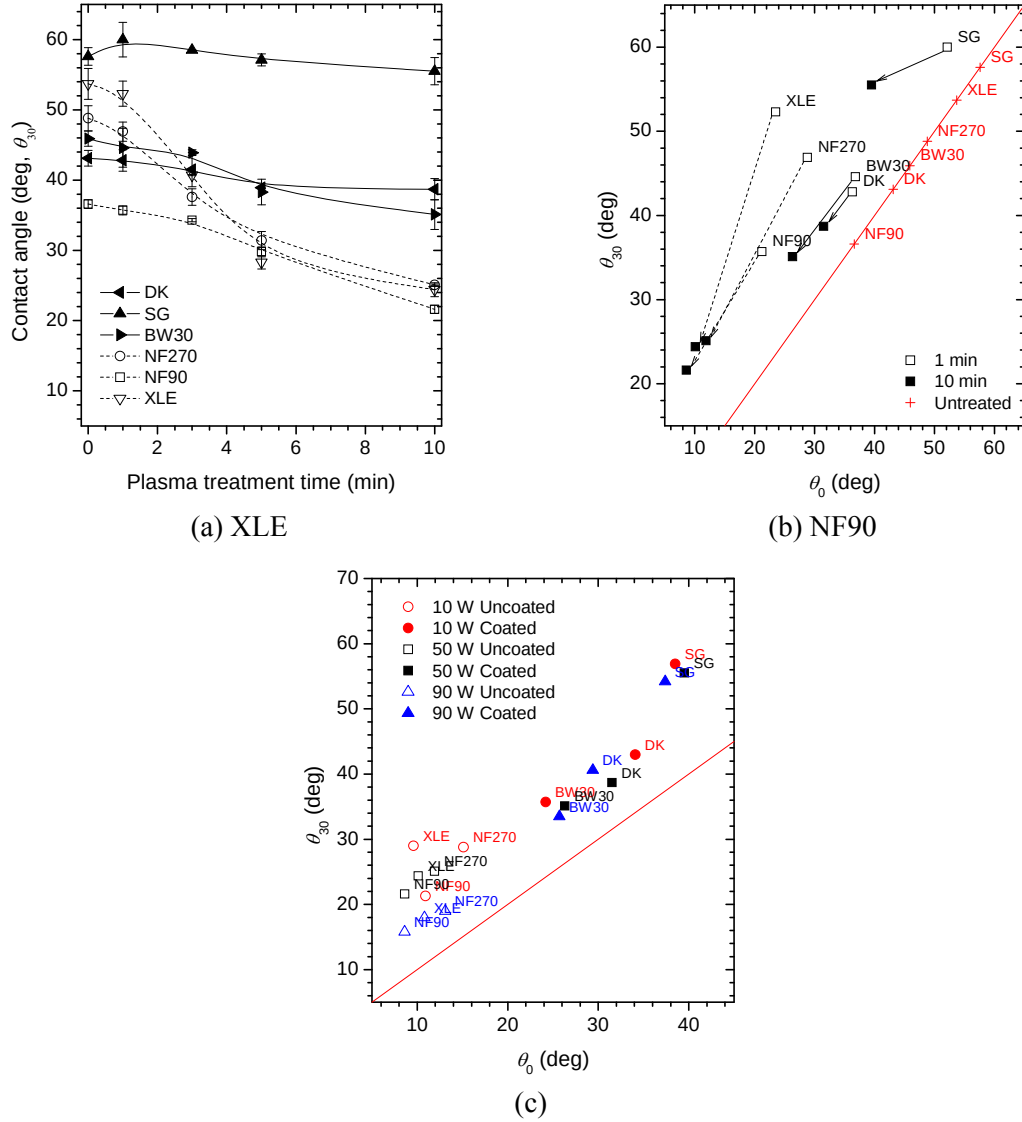


Fig. 4 Contact angles after 30 days (θ_{30}) of NH_3 plasma treatment: (a) θ_{30} as a function of plasma treatment time; (b) comparison of hydrophobic recovery of 1 min and 10 min treated samples (solid-arrow: change of coated or modified membranes, dashed-arrow: change of uncoated membranes, and cross symbol: the initial contact angles of untreated membrane); and (c) contact angle distributions as a function of plasma treatment powers

uncoated membranes showed 19.7% of hydrophobic recovery. Coated and modified membranes had 82.7, 65.1 and 67.8% of hydrophobic recovery at 10, 50 and 90 W treatments, respectively. Higher power generates higher plasma energy between surface functional groups and membrane (Yasuda 2005); therefore, stronger interaction between surface and functional group can result in a lower hydrophobic recovery.

3.2 ATR FT-IR characterization

Our previous results on the survey peaks and high resolution peaks of X-ray photoelectron spectroscopy (XPS) indicated that NH_3 plasma treatment increased the intensity of N 1s and O 1s peaks, and generated nitrogen-containing functional groups combined with oxygen (N–O at 401.5 eV) and carbon (N–C/N = C at 399.0 eV) (Kim 2011). The differences of NH_3 plasma treatment of uncoated and coated membranes are quantified here through ATR FT-IR analyses. The ATR FT-IR spectra of untreated and the plasma treated membranes with different times (1 min and 10 min) and applied powers (10, 50 and 90W) are presented in Fig. 5. Low-pressure plasma is able to modify several tenths or hundreds nanometers of the top membrane surface; therefore, the comparison of ATR FT-IR spectra at high wave number region (2700 to 3700 cm^{-1}) were considered to represent a penetration depth less than 200 nm (Tang 2009a).

The uncoated membranes show a large peak area with increasing treatment time and applied powers (Figs. 5(a), 5(b) and 5(c)). The coated membranes show a smaller change in the peak areas (Figs. 5(d), 5(e) and 5(f)). The TFC membrane spectra from the wave numbers of 3500 to 3100 cm^{-1} overlapped for N–H, O–H, and C–H stretching modes (Tang 2009a). The N–H bond was detected at 3400 to 3300 cm^{-1} range in the untreated samples, and aromatic and aliphatic C–H bonds were positioned in 3100 to 2900 cm^{-1} . The coated samples possess a broad band of O–H stretching in 3300 cm^{-1} and C–H stretching band in 2900 cm^{-1} (Belfer 1998, Tang 2007a). The absorption intensities increased after the plasma treatment; however, there was no new peaks detected which could be due to the overlapping of chemical properties induced by the NH_3 plasma treatment and TFC membrane in high wave numbers. The peak area at 3400 to 3300 cm^{-1} was increased by 114% for the uncoated membranes, and 40.0% for the coated membranes after 10 min of treatment. Increased peak intensities were caused by the broad stretching of H–N–H and N–H absorption associated with the amine and amide groups from the NH_3 plasma treatment (Bryjak 2002). The wave numbers of 3300 cm^{-1} represented the increase in oxygen by the radical reaction. Free radicals on the polymer surface can react with oxygen in the atmosphere after plasma treatment (Tusek 2001).

The impact of plasma treatment on membranes was assessed based on the normalized ratios of spectroscopic peak areas (Mason 2000) as presented in Fig. 6. Overall, the peak area increased with increasing plasma energy applied in the treatment, and the impact was more dramatic for the uncoated membranes (open symbols). It is known that higher plasma energy generates more free

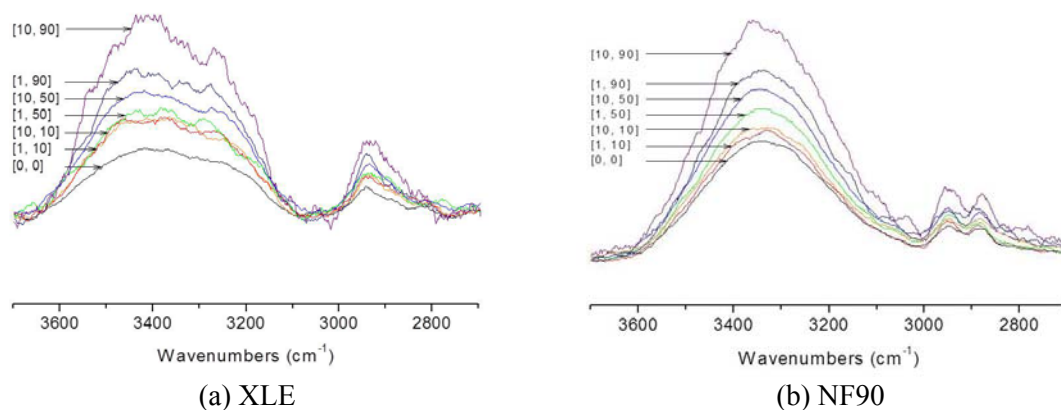


Fig. 5 Continued

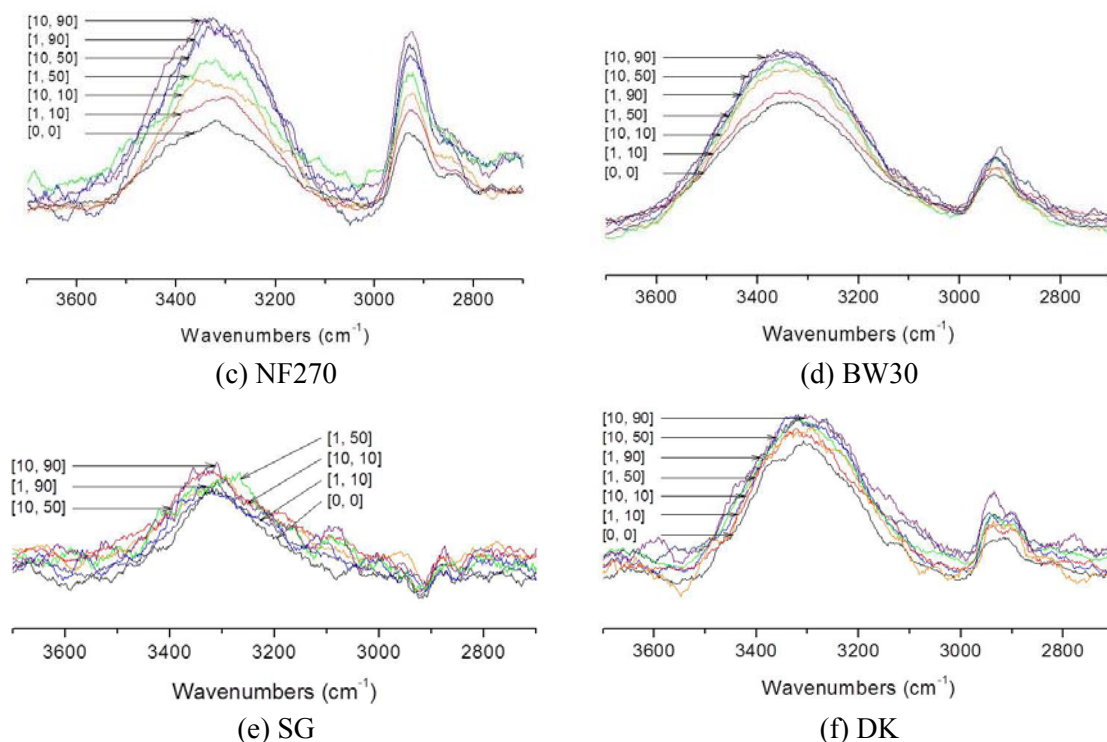


Fig. 5 High region (2700 to 3700 cm^{-1}) ATR FT-IR spectra of NH_3 plasma treated membranes: (a) XLE; (b) NF90; (c) NF270; (d) BW30; (e) SG; and (f) DK. Each spectrum shows different conditions of plasma treatment: left number in the bracket is the plasma treatment time in min, and right number is the applied power in W. [0, 0] is an untreated membrane.

radicals and denser surface functional groups (Tusek 2001). Our results are consistent with those reports and indicate that plasma energy is an important parameter to create tailored functionalized surface on the membrane.

3.3 Total surface free energy

The contact angles of three liquids (i.e., deionized water, formamide and diiodomethane) with the membranes were measured by the sessile drop method and polar and apolar components were calculated by the *LW-AB* method. The obtained total surface free energy of (a) fully-aromatic thin-film, and (b) semi-aromatic thin-film is shown in Fig. 7.

TFC membranes have high *LW* components due to the intrinsic hydrophobic property (Brant 2006). The surface free energy of TFC membranes tested here was slightly increased after the plasma treatment. In comparison with the total surface free energies of raw TFC membranes ranging from 41 to 52 mJ/m^2 , the total surface free energy of BW30, NF90 and XLE (fully-aromatic membrane) after 10 min of the plasma treatment increased by 6.9, 16.0 and 24.9%, respectively (Fig. 7(a)). For the semi-aromatic membranes, NF270, SG and DK, the increase was 29.0, 7.8 and 6.8 %, respectively (Fig. 7(b)). The membranes can be categorized into two groups

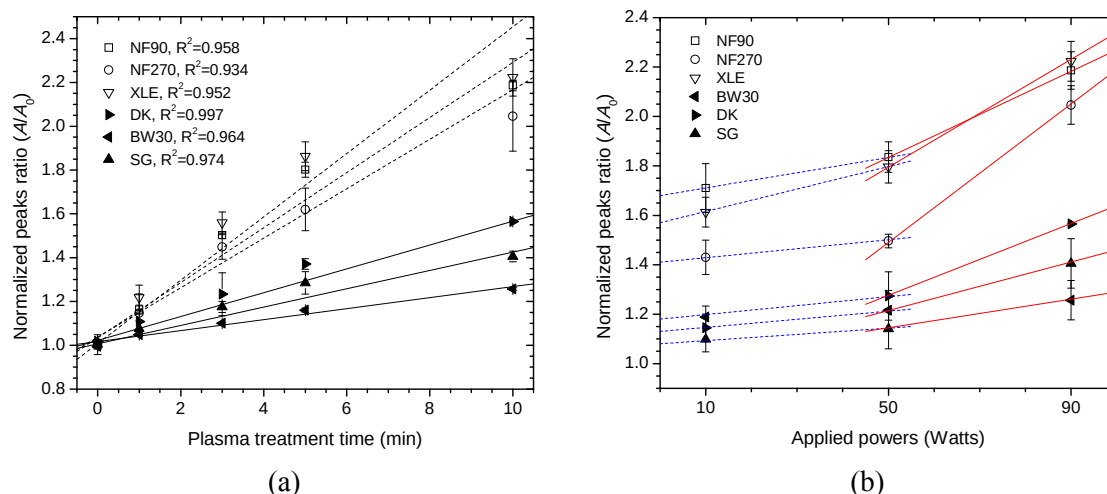


Fig. 6 Normalized peak ratio of ATR FT-IR for tested TFC membranes as a function of (a) plasma treatment time; and (b) applied power. A_0 is the peak area of untreated membranes and A is the peak area of each interval of treatment time and power. Peaks are identified by OMNIC software and integrated by the Gaussian with minimum baseline

based on their susceptibility to the plasma treatment: highly impacted group (increased by more than 16.0 %) and lowly impacted group (increased less than 7.8 %). NF270, NF90 and XLE are among the highly impacted group and the others (DK, SG, and BW30) are among the lowly impacted group. The highly impacted membranes are all uncoated and their AB components increased significantly after the plasma treatment. For semi-aromatic membranes (NF270, SG and DK), the AB components were enhanced initially by the plasma treatment but additional time did not further change the surface energy much (Fig. 7(b)). The semi-aromatic polymer has a weaker aliphatic backbone and lower density than the fully-aromatic polymer, so it could more easily form free radicals under the plasma treatment initially (Zhao 2006). The change of the total surface free energy after the NH_3 plasma treatment is dominated by the AB components.

3.4 Acid-base titration and ζ -potential measurement

Acid-base titration measures the interaction of surface functional groups with proton or hydroxyl group, and the density of ionizable hydrophilic groups on membrane surface could be described by the ion exchange capacity (IEC) (Gohil 2006). As shown in Fig. 8, the average IEC increases with increasing plasma treatment time.

The initial IEC was 0.0–0.2 mequiv./g for uncoated membranes, and 0.2–0.3 mequiv./g for coated membranes. The IEC was increased rapidly at the initial treatment, but reached saturation after 3 to 5 min of treatments. The maximum IEC was 0.90 (NF90) among the uncoated membranes, and 0.69 (DK) among the coated membrane after 10 min of NH_3 plasma treatment. The higher reactivity of the uncoated membrane observed here is consistent with the results of hydrophilicity, total surface free energy, and ATR FT-IR spectra discussed earlier. It is clear that the NH_3 plasma treatment created nitrogen-containing functional groups that are responsible for the observed changes in the surface membrane characteristics.

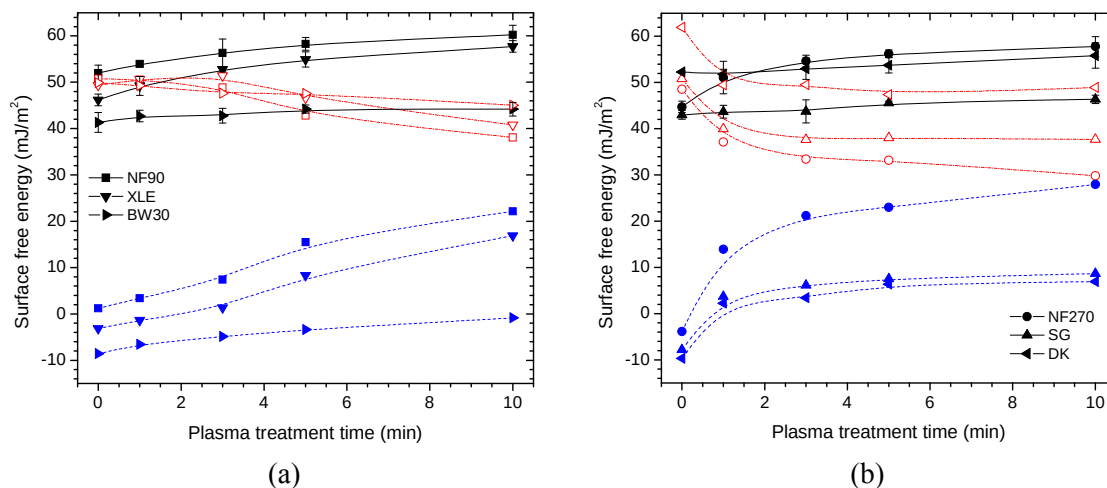


Fig. 7 Total surface free energy of membranes: (a) fully-aromatic thin-film; and (b) semi-aromatic thin-film. Closed symbols with solid line are the total surface free energy, and open symbols with dash-dot line and closed symbols with dash line are the LW and the AB components, respectively

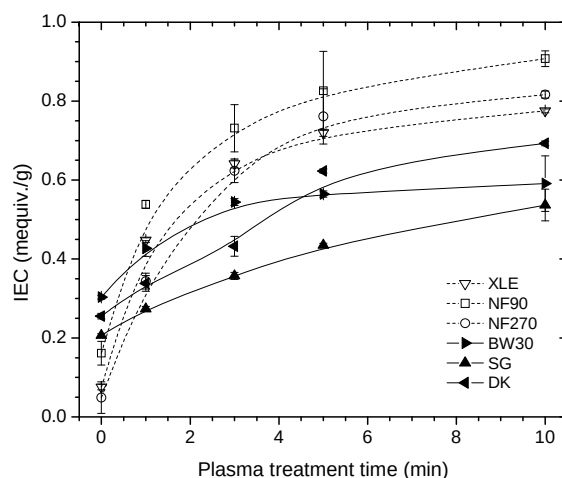
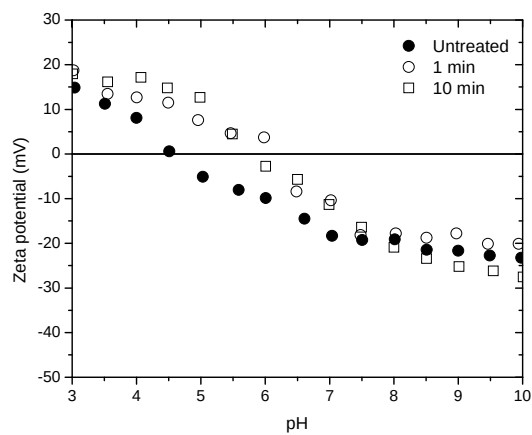


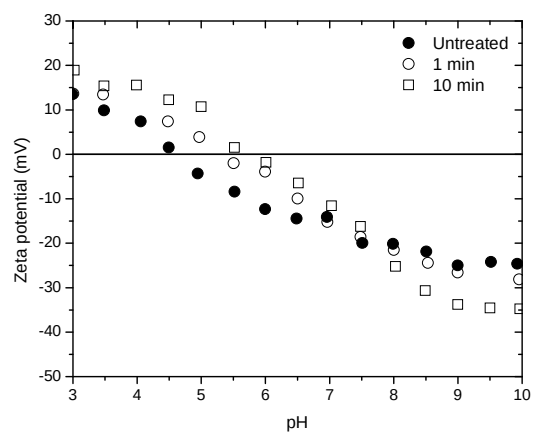
Fig. 8 The average ion exchange capacity (IEC) values as a function of the plasma treatment time for uncoated (dashed-open symbols) and coated (solid-closed symbols) membranes

The pH dependence of ζ -potential for each membrane is shown in Fig. 9. Closed symbols indicate ζ -potential of untreated membranes, and open symbols of circle and square represent the membranes after 1 min and 10 min of NH_3 plasma treatment, respectively.

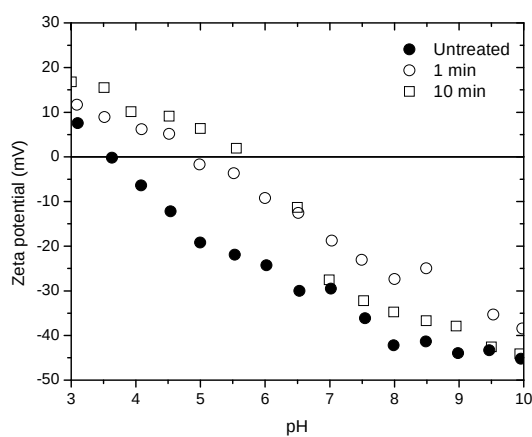
The results indicate that the raw membranes are amphoteric with an isoelectric point (IEP) from pH 3.6 to 4.6, a characteristic typical of the residual monomer after the interfacial polymerization (Matsumoto 2007). Protonation of an amine group creates a positive charge on the surface and deprotonation of a carboxylic group results in a negative charge. The changes of IEP as a function of the plasma treatment time are summarized in Table 2.



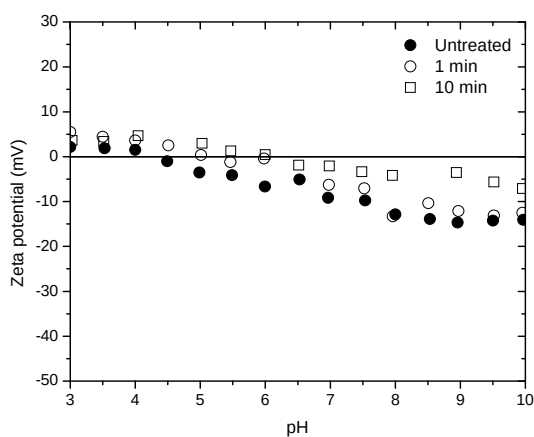
(a) XLE



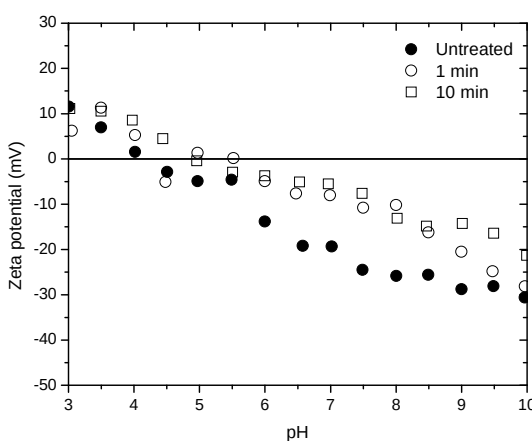
(b) NF90



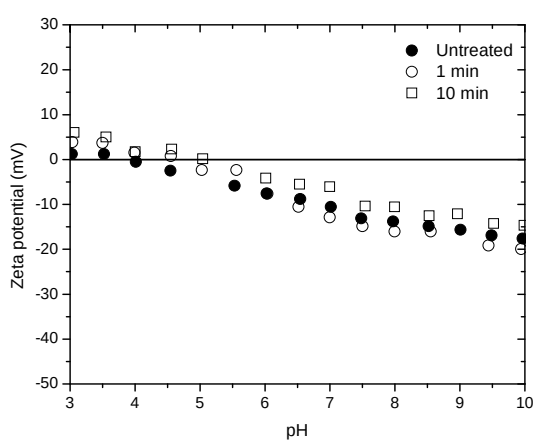
(c) NF270



(d) BW30



(e) SG



(f) DK

Fig. 9 Zeta-potential of untreated, 1min, and 10 min NH_3 plasma treated membranes: (a) XLE; (b) NF90; (c) NF270; (d) BW30; (e) SG; and (f) DK

Table 2 Changes of IEP at different plasma treatment times

Membranes		IEP		
		Untreated	1 min treated	10 min treated
Uncoated	NF270	3.63	4.85 (+1.22)	5.61 (+1.98)
	NF90	4.50	5.09 (+0.59)	5.84 (+1.34)
	XLE	4.61	5.59 (+0.98)	5.76 (+1.15)
Coated	BW30	4.24	4.94 (+0.70)	4.98 (+0.74)
Modified	SG	4.07	4.76 (+0.69)	4.87 (+0.80)
	DK	3.98	4.22 (+0.24)	4.75 (+0.77)

The IEP of NF270 after 10 min of treatment was shifted 2.0 pH units higher due to the introduction of amine groups by the NH_3 plasma treatment (Tusek 2001). The other two uncoated membranes were also significantly affected. The IEPs of coated or modified membranes (BW30, SG and DK) were increased too but to a much lesser degree. They demonstrate the non-polar surface characteristics having a near linear decrease of ζ -potential with increasing pH (Lappan 1999). The uncoated membranes have lower ζ -potential value (higher negativity) in the high pH range than those of the coated or modified membranes. The total surface free energy could be explained by that uncoated membranes had higher polar components. The results suggested that NH_3 plasma treatment significantly changes the surface electrical property of the uncoated membranes, and coated membranes are less subject to such plasma modifications.

4. Conclusions

Thin-film composite membrane is widely used for water purification. Here low-pressure NH_3 plasma was applied to modify various commercial TFC membranes, and the importance of various plasma parameters was evaluated on their impact to the membrane characteristics. The physico-chemical properties are characterized by surface contact angle, roughness, total surface free energy, surface functional groups, IEC, and ζ -potential. Surface hydrophilicity as measured by the contact angle is found to increase with increasing plasma treatment time, and uncoated membranes (NF270, NF90 and XLE) are more susceptible to the plasma treatment. In terms of the surface energy, the AB components (polar property) dominate the total surface free energy after the NH_3 plasma treatment. ζ -potential and ATR FT-IR results of the plasma treated membranes show formations of dissociable nitrogen functional groups. Overall, the thin-film layer chemistry, condition of membrane surface coating, membrane types, plasma treatment time and applied powers all affect the efficiency of NH_3 plasma treatment to the TFC membranes.

Acknowledgments

The assist of plasma modification by Professor Qingsong Yu at the Center for Surface Science and Plasma Technology in University of Missouri is greatly appreciated. Financial support for this research was partially provided by the U.S. National Science Foundation (no. BES-0296109).

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