DETERMINATION OF SURFACE CHARACTERISTIC OF ATMOSPHERIC PRESSURE PLASMA MODIFIED POLYMERIC ULTRAFILTRATION MEMBRANE VIA CONTACT ANGLE MEASUREMENTS

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Abstract: The aim of this study was to improve the surface hydrophilicity of ultrafiltration membrane (UP150, PES, MWCO; 150 kDa) by using atmospheric pressure argon plasma jet (APAPlJ) modification system. Argon was selected as a precursor gas and three different distances between nozzle and substrate surface (25-30-35 mm) and three different exposure period (1-5-10 times) was applied during APAPlJ modifications. The effect of APAPlJ modifications on the membrane surface evaluated by contact angle measurements, surface free energy (SFE) method and xVDLO theory. APAPlJ modification was able to change membrane surface properties. More hydrophilic surface properties were obtained by APAPlJ modifications using 25 mm of distance of nozzle to substrate surface and 5 times of exposure period. Under these conditions, the water contact angle was decreased from 63.5 to 34.6°. The base component of SFE was increased 5 times and Giwi value was increased from -45.0 to 28.7 mJm^{-2}.

Keywords: Ultrafiltration membrane, atmospheric pressure argon plasma jet, modification, contact angle measurement, SFE, xVDLO theory

Introduction

The membrane separation processes is widely used today for separation of wide varying mixtures, purification and concentration of valuable components from industrial wastewater in petrochemical (Ravanchia et al., 2009), textile (Ciardelli et al., 2000), and food (Baldasso et al., 2011; Onsekizoglu 2013) industries. Especially, polimeric commercial membranes such as polyethersulfone (PES), polysulfone (PS), polyvinylidene fluoride (PVDF) are widely used in the pressure-driven membrane processes due to their high thermal, mechanical and chemical resistance (Mulder, 1996) However, they have hydrophobic surface properties, so that it severely limits its long-term membrane separation processes. Therefore, they need to surface modification to enhance hydrophilicity (Demirci et al., 2014).

Plasma modification is one of the modification method to change surface properties of membrane. It has many important advantages such as uniformity, reproducibility, short reaction time, and environmental safety. Plasmas, often considered as the fourth state of matter, are composed of an ionized gas containing a mixture of ions, electrons, neutral and excited molecules, and photons (Kull et al., 2005; Gulec et al., 2006). Plasma treatments can alter the surface energy of most polymers, changing their surface polarity, wettability, and adhesive characteristics without affecting the overall bulk properties. Helium, oxygen, nitrogen, argon plasma are used to modify polymeric membrane surfaces from hydrophobic to hydrophilic increasing the surface polar groups (Saxena et al., 2009). In addition, the changes in the polymeric surface depend directly on the plasma treatment conditions (Wavhal and Fisher, 2005).

The hydrophobicity or hydrophilicity of a solid surface can be determined by contact angle measurement which is a simple, useful and very sensitive method (Gulec et al., 2006). The surface free energy (SFE) and SFE components of membrane can be calculated with different approaches such as Zisman Plot, Equation of State, Fowkes/WORK, Wu and van Oss, Good and Chaudhury. van Oss, Good and Chaudhury's acid–base method is widely used by researchers, because it provide more detailed information about electron-acceptor and electron–donor interactions through membrane and test liquid interface (Cantin et al., 2006; Zenkiewicz, 2007; Damar Huner and Gulec, 2016). xVDLO theory is also used to evaluate interaction between foulant and membrane and it shows surface characteristic and fouling tendency of membrane surface (Subhi et al., 2012; Zuo and Wang, 2013).

Steen et al. (2002) reported that low temperature H_2O plasma treatment improved the hidrophilicity of PES membrane. Their study revealed that the contatct angle of unmodified membrane decreased from 69.5 to nearly

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0°. They obtained highly hydrophilic surface. Saxena et al. (2009) used argon–oxygen ($Ar–O_2$) plasma to modify the PES membrane. Unmodified PES membrane water contact angle value degreased from 56.9 to 8.6° by using $Ar–O_2$ plasma (%60 O_2 concentration) at 10 min exposure time. These results clearly demonstrated that the plasma treated PES membrane was more hydrophilic surface. Wavhal et al. (2002) modified PES membranes using low temperature Ar plasma, followed by grafting of hydrophilic monomers in the vapor phase. After 90 s plasma treatment, water contact angle of PES decreased from 90 to 40°. In literature, there is limited investigation report about the PES membrane modification using atmospheric pressure plasma jet (APAPlJ) system. And also, this study contributes by using contact angle measurement to determine surface hydrophilicity.

The objective of this study was to improve the surface hydrophilicity of UP150 PES ultrafiltration membrane, by using atmospheric pressure argon plasma jet (APAPlJ) modification system. Initially, different APAPlJ parameters (plasma treatment period: 1, 5 and 10 times, distance between nozzle and membrane surface: 25, 30, 35 mm) were used. The effects of APAPlJ modification on the membrane surface were determined using contact angle measurements. Surface free energy of unmodified and APAPlJ modified membrane were calculated using acid-base methods. The hydrophobicity/hydrophilicity characteristic of membrane was evaluated accordingly xVDLO theory.

Material and Methods

Material

Flat sheet commercial polyethersulfone ultrafiltration membrane (UP150) was used. Specific properties of the ultrafiltration (UF) membrane are summarized in Table 1. Before the plasma treatments and contact angle measurements, membrane was cut into rectangular shapes having size of 76 x 20 mm manually and they were fixed to glass support with double-sided tape.

Table 1: Specific properties of commercial microfiltration membrane

Supplier	Membranes	Material	MWCO (KDa)	Maximum Temperature	pH	Permeability (L m^{-2} $h^{-1}$$bar^{-1}$)
Micrody n-Nadir	UP150	PES	150	95 °C	0–14	286[a]

[a]: according to the indicative properties by the membrane manufacturer

Atmospheric pressure plasma jet system

The atmospheric pressure plasma jet system (OpenAir) manufactured by PlasmaTreat GmbH (Steinhagen, Germany). OpenAir plasma system (Fig. 1.) is equipped with plasma rotary jet (nozzle-RD2004), metallic carrier platform (10 x 20 cm) which allows x-direction of the moving at a parallel speed of 0 to 60 m min^{-1}, manual y-direction of moving column adjust the distance between substrate and nozzle, and plasma generator (FG5001). The membrane was placed in a distance of 25, 30 and 35 mm to the nozzle on metallic carrier platform that was moved with a speed of 1.5 m min^{-1}. Three different treatment times (1, 5, 10 times) were chosen for the plasma surface modification. The precursor gases to be used for plasma modification were selected argon at an input pressure of 3 bar. UP150 membrane was soaked ultra-pure water at 24 h to ensure wetting of membrane structure before and after modification.

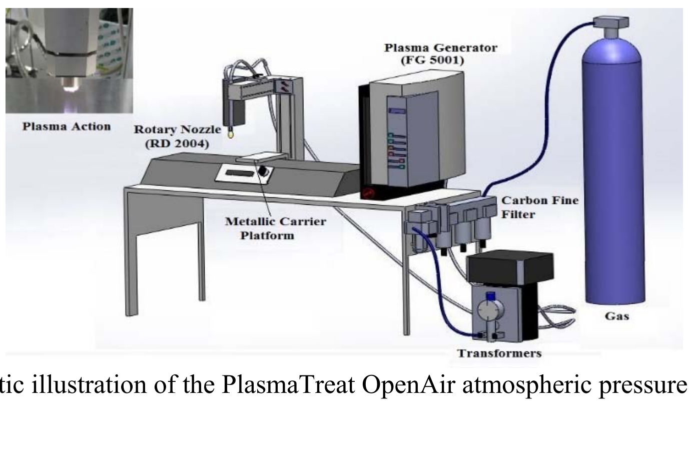

Figure 1. Schematic illustration of the PlasmaTreat OpenAir atmospheric pressure plasma jet system

Contact angle measurements

Theta Optical Tensiometer (KSV Attension Instruments, Helsinki, Finland) was to measure the contact angle. It was equipped with an automated droplet dispenser, a high speed digital camera (60 fps), and image analysis software (OneAttension). OneAttension used Young-Laplace three-phase system consisting of standard test liquid, solid surface and air for contact angle determination (Fig. 2.). Contact angles measurement was performed by sessile drop technique using three standard liquid (ultra-pure water, formamide, diiodomethane). The droplet volume of standard liquids was 2.5 µl and the drop image was captured during 60 s. The contact angle measurements were performed at 5 random locations at room temperature (25 ± 3 ºC).

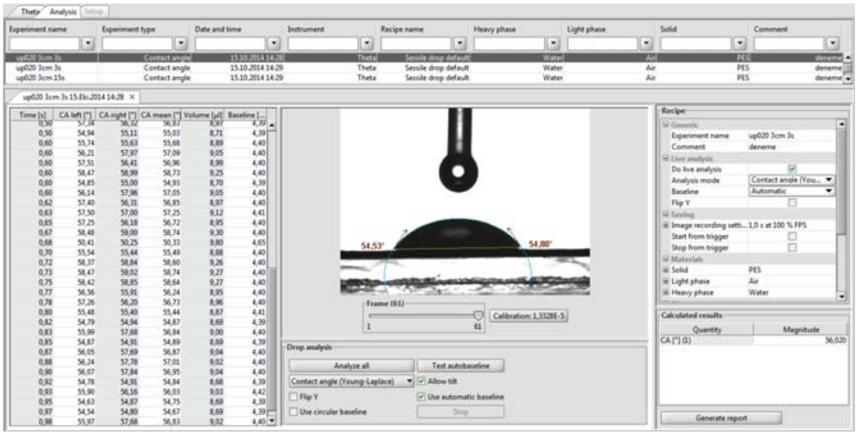

Figure 2. Contact angle in a three-phase system consisting of solid surface, liquid, and air (from OneAttention software)

Calculation of surface free energy

Surface free energy of membrane was calculated van Oss, Good and Chaudhury's acid–base method (van Oss et al., 1988). The surface free energy (SFE) was the sum of two components (Eq. 1), Lifshitsz van der Waals interactions (LW) and Lewis acid–base interactions (AB) according to this method. While, γ^{LW} represents apolar interactions such as London dispersion forces, dipole-dipole Debye and Keesom interactions, γ^{AB} also mentioned as the "polar component" contains, hydrogen bonding, π bonding and ligand formation (Cantin et al., 2006; Rieke 1997).

$$\gamma_{SV}^{TOT} = \gamma_{SV}^{LW} + \gamma_{SV}^{AB} \tag{1}$$

Lewis acid–base interactions are divided within itself, including the electron acceptor (Lewis acid, γ_i^+) and electron donor (Lewis base, γ_i^-) components and expressed as a geometric mean of acid and base force components.

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-} \tag{2}$$

The solid-liquid interface tension can be expressed as

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\left[\sqrt{\gamma_{SV}^{LW}\gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{+}\gamma_{LV}^{-}} + \sqrt{\gamma_{SV}^{-}\gamma_{LV}^{+}}\right] \tag{3}$$

Combining this equation with Young-Dupre equation (Eq. 3) obtains van Oss, Good and Chaudhury's acid–base equation. The SFE of unmodified and modified membranes was calculated by this equation.

$$\gamma_{LV}(1 + \cos\theta) = 2\left[\sqrt{\gamma_{SV}^{LW}\gamma_{LV}^{LW}} + \sqrt{\gamma_{SV}^{+}\gamma_{LV}^{-}} + \sqrt{\gamma_{SV}^{-}\gamma_{LV}^{+}}\right] \tag{4}$$

At least 3 different standard liquids of known surface tension components are needed to determine the unknown surface free energy components (γ_{SV}^+, γ_{SV}^-, γ_{SV}^{LW}) of the membrane surface. Generally, to solve the equation should be used one dispersive and two polar liquid. In this study, polar liquids ultrapure water, formamide; and non-polar liquid diiodomethane were used as a standard liquid (Table 2).

Table 2: Specific properties of the test liquids used in this study (OneAttention software)

	γ^{tot} [mN/m]	γ^{d} [mN/m]	γ^{+} [mN/m]	γ^{-} [mN/m]	g [g/cm^3]	η [mPa.s]	T [°C]	Mw [gmol]
Water	72.80	21.80	25.50	25.50	0.998	1.00	20.00	18.01
Formamide	58.00	39.00	2.28	39.60	1.133	3.30	20.00	45.04
Diiodomethane	50.80	50.80	0.00	0.00	3.325	2.80	25.00	267.84

xVDLO theory

In this study, Derjaguin, Landau, Verwey and Overbeek (xDLVO) theory was used to determination of hydrophilicity and hydrophobicity of membrane surface after plasma modification. According to, the total free energy of cohesion (ΔG_{iwi}^{Tot}) between foulant (i) and water (w) is the sum of apolar Lifshitz–van der Waals (LW) and polar acid–base (AB) forces (van Oss, 1993). ΔG_{iwi}^{Tot} can be written as

$$\Delta G_{iwi}^{Tot} = -2\left[\left((\gamma_i^{LW})^{\frac{1}{2}} - (\gamma_w^{LW})^{\frac{1}{2}}\right)^2 + 2\left((\gamma_i^{+}\gamma_i^{-})^{\frac{1}{2}} + (\gamma_w^{+}\gamma_w^{-})^{\frac{1}{2}} - (\gamma_i^{+}\gamma_w^{-})^{\frac{1}{2}} - (\gamma_w^{+}\gamma_i^{-})^{\frac{1}{2}}\right)\right] \quad (5)$$

If ΔG_{iwi}^{Tot} is lower than zero ($\Delta Giwi < 0$), the membrane is considered hydrophobic surface properties. In contrast, if ΔG_{iwi}^{Tot} is larger than zero ($\Delta Giwi > 0$), the membrane shows hydrophilic properties and has less fouling tendency (Subhi et al., 2012; Zuo and Wang, 2013).

Results and Discussion

Contact angle measurements

The aim of this study was to investigate the influence of the treatment parameters on the hydrophilicity and hydrophobicity properties of the membrane surface. The surface properties of the unmodified and APAPlJ modified membranes were characterized by contact angle measurements. Three different treatment times (1-5-10 times) and three different distances between nozzle and membrane surface (25-30-35 mm) were chosen as plasma treatment conditions.

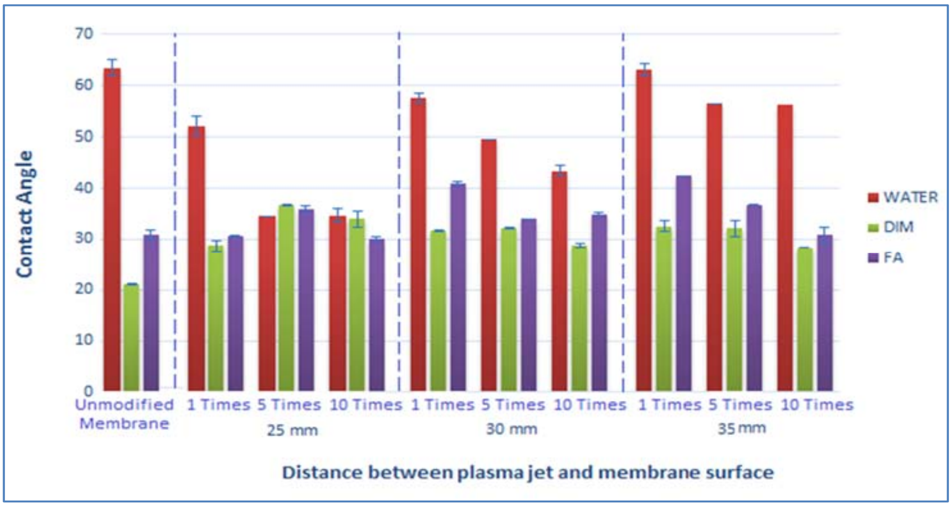

Figure 3. The contact angle measurements according to plasma jet modification conditions

If the water contact angle (θw) is higher than 65°, the surface is considered hydrophobic and if θw is lower than 65°, it is considered hydrophilic (Sadiki et al., 2014). According to the results presented in Fig. 3., θw showed that unmodified UP150 PES membrane has moderately hydrophobic surface (θw = 63.5 ± 1.6°). Similar results were reported by Steen et al., (2002); Kim et al., (2009). They were evaluated the hydrophobic character of the PES membrane (θw = 69.5°, θw = 69.0° respectively).

The contact angle results of unmodified membrane were changed depending on plasma treatment conditions (Fig. 3.). The results revealed that, θw decreased with plasma treatment in all parameters. However, a slight decrease of θw was observed at the distance of 30 and 35 mm. In addition, θw decreased with increasing treatment times for the same distances. This can be attributed to high interaction between plasma ions and membrane surface with increasing treatment times. For plasma treatment, the lowest θw (θw =34.6±0.0°) was obtained at the distance of 25 mm and 5 times treatment (Fig. 4.).

Although, many other studies explained that the surface hydrophilicity related to the water contact angle value (Steen et al., 2002; Wavhal et al., 2002), diiodomethane and formamide contact angle values also can give an information about hydrophilicity. The surface hydrophilicity increases with decreased formamide contact angle (θf) and increased diiodomethane contact angle (θd). In this study, while θd increased in all plasma treatment conditions, the significant increase was observed at 25 mm 5 times (θd =36.6±0.1°). The lowest contact angle of formamide was obtained at 25 mm distance 10 times (θf =30.1±0.5°).

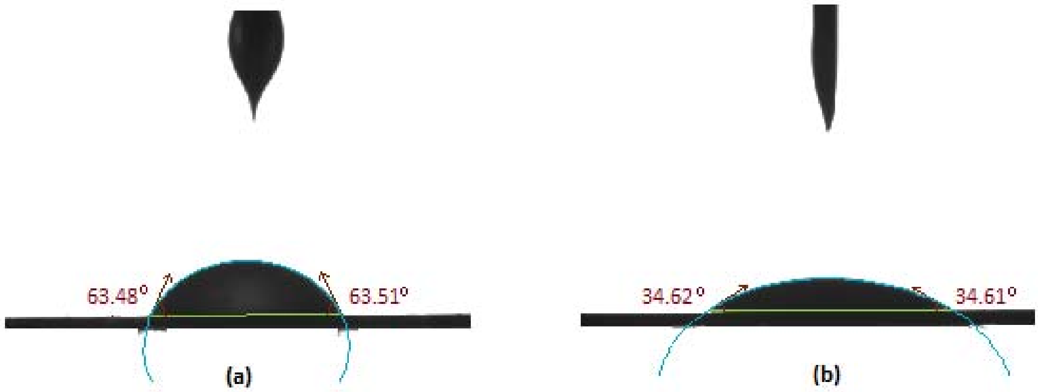

Figure 4: Water droplet image on UP150 PES unmodified (a) and APAPlJ modified membrane 5 times at 25 mm (b)

Saxena et al. (2009) used argon–oxygen (Ar–O2) plasma to modify PES membranes. They found that the contact angle decreases from 57.0° (untreated membrane) to 8.6° (Ar–O2 plasma treated membrane). Their study revealed that higher exposure time increases the hydrophilicity. Contrarily, in this study, the highest exposure period (10 times) did not decrease the water contact angle value as in 5 times treatment condition. This was mainly attributed to using only argon as a precursor gas in this study.

Calculation of surface free energy

The surface free energy was calculated from acid-base method. Total (γ_S^{tot}), disperse (γ_S^{d}), polar (γ_S^{p}), acid (γ_S^{+}) and base (γ_S^{-}) components of unmodified and modified membrane were given Table 3.

Table 3: The SFE components of unmodified and APAPlJM membrane

Distance (mm)	Times	γ_S^{tot} [mJm^{-2}]	γ_S^{d} (γ_S^{LW}) [mJm^{-2}]	γ_S^{p} (γ_S^{AB}) [mJm^{-2}]	γ_S^{+} [mJm^{-2}]	γ_S^{-} [mJm^{-2}]
Unmodified Membrane		64.9±1.2	47.6±0.2	17.3±1.4	1.2±0.3	8.1±2.4
25	1	73.8±0.4	44.8±0.4	29.1±0.8	0.7±0.1	21.4±2.2
	5	50.7±1.8	41.3±0.0	9.4±1.8	0.1±0.0	47.5±0.5
	10	69.0±4.2	42.5±0.7	26.5±4.8	0.3±0.1	42.9±1.5
30	1	52.0±0.2	43.5±0.1	8.6±0.3	0.2±0.0	20.5±1.0
	5	66.7±0.1	43.3±0.0	23.4±0.2	0.4±0.0	26.3±0.0
	10	52.0±1.4	44.7±0.2	7.3±1.6	0.1±0.0	35.4±0.3
35	1	52.9±0.1	43.1±0.5	9.8±0.6	0.3±0.0	14.5±1.2
	5	63.2±1.8	43.3±0.7	19.9±2.5	0.5±0.0	19.3±1.4
	10	74.3±4.0	44.9±0.0	29.5±4.1	0.9±0.2	16.6±0.7

According to van Oss, Good and Chaudhury's method, especially higher base component value (γ_S^-) shows hydrophilicity character of surface (Sadiki et al., 2014). The results presented in Table 3, the γ_S^- component of SFE of UP150 showed a significant increase at 25 mm distance and 5 times treatment conditions. The γ_S^d component decreased from 47.6 to 41.3 mJ m^{-2} at the same treatment conditions. These results clearly indicated that APAPlJ modified membrane had more hydrophilic surface than unmodified membrane.

xDVLO theory
xVDLO theory was performed to state the change of surface hydrophilicity. While positive Giwi value indicates the hydrophilic surface, negative Giwi value refers hydrophobic surface properties. The effects of plasma modification on Giwi value were evaluated by MINITAB and presented in three dimensional graphs (Fig. 5.).

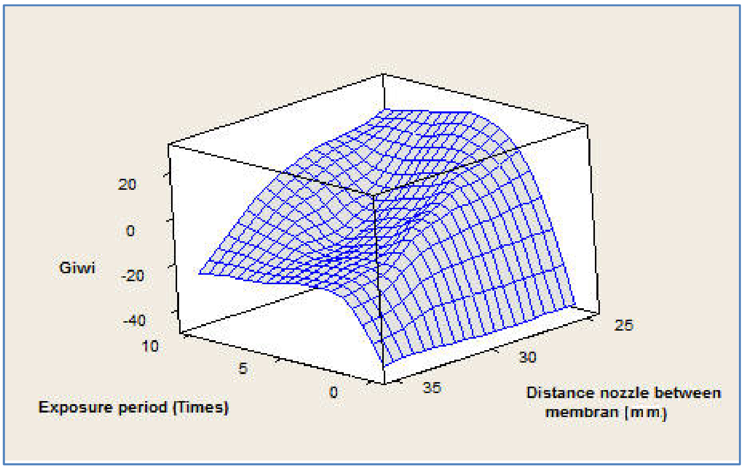

Figure 5: 3D graph depicts exposure period - distance nozzle to membrane surface - Giwi value

As shown in Fig. 2, Giwi value of unmodified membrane was lower than zero (Giwi=-45.8), it had a hydrophobic surface. While the treatment provided a positive effect on hydrophilicity of membrane in exposure period at 35 mm distance, Giwi did not take a positive value for this condition. This may be attributed to the weak interaction between the ions and electrons generated by plasma and the membrane surface. In contrast to this, the ions and electrons generated by plasma reacted easily with reactive groups on PES membrane surface at 25 mm distance. The highest positive value (Giwi=28.7) which indicates the hydrophilic property was observed at 5 times of exposure period and 25 mm of distance.

Conclusion

The main goal of this study was to determine change of hydrophilicity of UP150 PES membrane surface under various APAPlJ treatment conditions. The contact angle measurements, SFE method and xVLDO theory were used to evaluate the APAPlJ modification effect on the UP150 PES membrane surface. The results revealed that the use of APAPlJ to modify the PES membrane is an effective way to improve its surface hydrophilicity. The more hydrophilic surface properties (the lowest water contact angle, the highest base value of SFE and the highest Giwi value) were obtained by APAPlJ modifications using 25 mm of distance between nozzle and substrate surface and 5 times of exposure period.

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