Improvement of Gas Separation Properties of Polyurethane Membrane Using Plasma Grafting

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ARTICLE INFO	ABSTRACT
	In recent years, plasma treatments have presented good results since they offer high-tech efficiency with low waste generation. One of the most important characteristics of plasma methods is their action only on a thin surface layer, whereas the bulk of sample remains unchanged and the modified material keeps its chemical and mechanical properties. In this research, polyurethane membrane surface was modified by low-frequency plasma grafting with methacrylic acid and acrylamide monomers to alter solution-diffusion mechanism. We chose different parameters of plasma treatment and studied their effects toward maximum solubility, permeation, and selectivity. The grafting on the surfaces was characterized by water contact angle measurement and atomic force microscopy. After confirming a successful grafting, we studied the effect of surface modification on permeation of CH_4 and CO_2. Significant increase in CO_2 permeation and about 32 percent increase in CO_2/CH_4 selectivity were observed. Better results were obtained for low powers and acrylamide grafted surface.

1. Introduction

Natural gas is one of the most fundamental resources of energy. The amount of world natural gas production at the end of 2015 was 3538.6 billion cubic meters [1]. Fig. 1 reveals the world natural gas production and consumption from 1990 to 2015. Results show a nearly 2.2 % increase of the world natural gas production rate for the time period of 2014 to 2015.

The crude natural gas contains the average amount of 20 percent of carbon dioxide as an important sour gas with toxic influences on both transition pipelines and industries [2].

Large consumption of natural gas all around the world shows that a small increase in sour gas separation leads to large economic benefits in the case of lower toxic conditions. In addition, acid gases must be removed from crude natural gas to achieve the higher heating value, lower corrosion situations, in addition to lower environmental hazards through the emission of CO_2 and SO_2 [2-4].

The current separation technology, involving absorption by amine solution, has some disadvantages such as thermodynamic limitation, the large value of solvent purge and recycling problem, and the environmental

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effects of toxic amine solvents. Consequently, alternative technologies with higher efficiency, in addition to the lower effects on the environment, sometimes called the solvent-free technologies, need to fulfill these two important criteria [4-6].
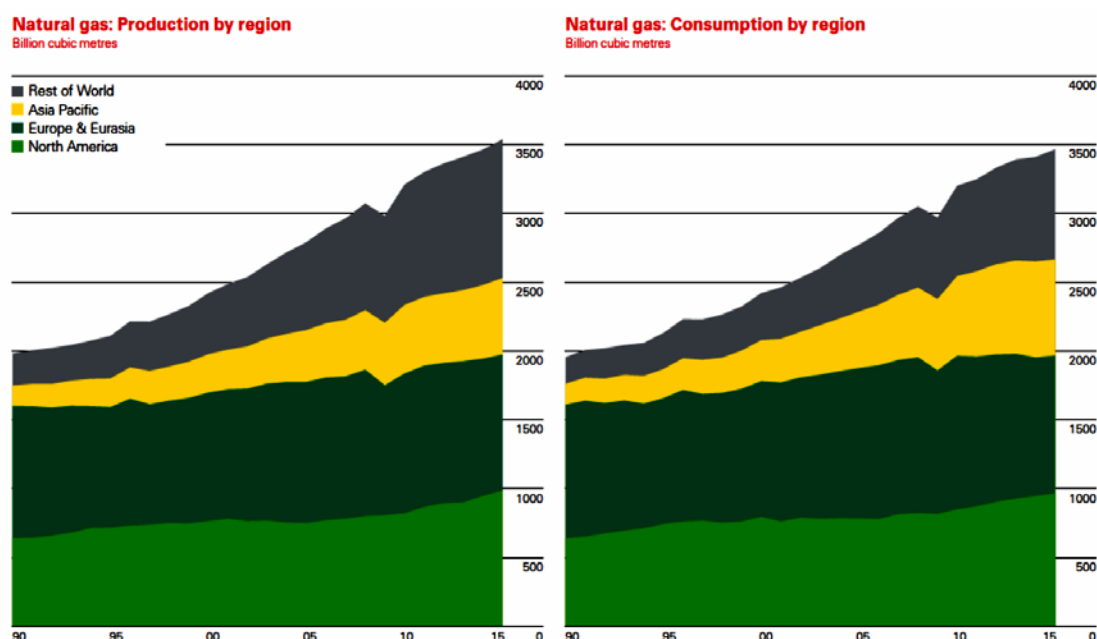
Figure 1. World natural gas production and consumption from 1990 to 2015 [1].

Gas separation by the technology of selective membranes can be efficiently used to separate acid gases from the raw natural gases. Membrane purification technology has some advantages such as being potentially energy efficient. Other advantages are: easy module design, ease of scale up, easy to work, being environmentally-friendly, good flexibility regarding the module design ability, reliability to work with different situations of natural gas flow rate, gas composition, process conditions involving process temperature and pressure, low space and weight, and finally easy to replace the membrane modules [2].

Crude natural gas involved different molecules with different molecular sizes and polarities. The most proportion of natural gas contains CH_4, CO_2, H_2S, and water vapor. The later three molecules permeate faster through the polymer membranes rather than the methane molecule; as a result, CH_4 is concentrated in the high pressure stream without high pressure drop for the sweetened gas stream.

The early purification of natural gas by cellulose membranes was investigated in the late 1960s, where the first technical research for the removal of carbon dioxide and hydrogen sulfide was realized by the cellulose acetate membranes. The spiral module of dry cellulose acetate membrane reveals the selectivity for the gas mixture, which is dramatically below the selectivity calculated for pure gases [4,7]. Studies show that the plasticization by CO_2 and heavier hydrocarbons deals this significant low selectivity [3, 13, 25].

Other polymers, such as polysulfones, polycarbonates, polyamides, and polyimides, were investigated during 1980s. These types of polymers show the higher selectivity and permeability for acid gases. But, polymeric membranes are still restricted by the trade-off

trend between gas permeability and selectivity [3, 13, 25]. For this reason, some procedures have been suggested to improve the selectivity of membranes. The prime techniques for polymer modifications are grafting, crosslinking, blending, and composite formation, which are all multicomponent polymer [20]. Grafting is a method wherein monomers are covalently bonded (modified) onto the polymer chain [26]. The membrane surface affects under two conventional types of grafting, the chemical reaction, and irradiation. Plasma modification, the sub-step of irradiation procedure of polymer membranes, has attracted researcher's attention to change the surface properties of materials, while the bulk properties remain unchanged [4, 8,20].

Plasma treatment can create a concentration of the generated functional groups on the surface leading to chemical and physical modifications of the membrane's surface to prepare highly selective ones for gas separation [21, 23]. Polyurethanes (PUs) are types of polymers with rubbery behavior that have been used as membranes. In case of gas separation, the nature of flexible chain structure in PUs allows for the transportation of gas, hence providing a good permeability [10]. Taking into account the high gas permeation of PUs, it seems reasonable to examine the effect of plasma modification on polyurethane membranes for the gas separation. Acrylic acid is the monomer most easily grafted to plasma treated polymer surface [22]. In the present work, methacrylic acid (MAA) and acrylamide (AA) were grafted to the surface of PU membranes by plasma. The changes in the surface properties of the membranes were evaluated using contact angle measurements and atomic force microscopy (AFM). The permeation

properties of the membranes for CH_4 and CO_2 were examined. Then, the effects of pressure, plasma power, and grafted monomer were compared.

2. Materials and method
2.1. Materials
In this experiment, ether-based polyurethane granule was available from Coim S.p.A Co. Ether polyol as a soft segment included poly (oxytetramethylene), and the hard segment was composed of 4,4-diphenylmethanediisocyanate and 1,4-butanediol with content of 35 %. Dimethylacetamide as solvent, methacrylic acid, and acrylamide monomers were provided by Merck Co., Germany. CO_2 gas cylinder with 99.9 % purity was available from Aboughaddareh Co., Shiraz, Iran. 99.995 % pure CH_4 gas was purchased from Air Products Co. All materials were used as received and no further modifications were needed.

2.2. Membrane preparation
13 pure polyurethane membranes were prepared by solution casting. Polyurethane were first dried in vacuum oven, then 1.5 g granule was dissolved in 60 ml DMA solvent by stirring for 2 h at 70 °C to form a homogeneous solution. This solution was filtered by a stainless steel mesh, casted on a glass petri-dish and heated in an oven for 12 h at 78 °C to vaporize the solvent. The film was then removed from the dish and heated in vacuum oven for 3 h at 78 °C to remove trace solvent. The process repeated until all needed membrane films were prepared. Thicknesses of films were between 70 to 90 microns.

A 400 kHz low-frequency diener electronic plasma reactor with maximum power of 1000 watt was used to modify surface of

membranes. Two polyurethane films were placed in chamber faced up and vacuumed for 2 minutes. Then, O₂ flowed into the chamber at a rate of 1 sccm/min, and chamber pressure was maintained at 0.66 mbar. Plasma was then generated with given power and time and created active sites on polymer surface. After that, films were exposed to air for 5-10 minutes so that oxides and peroxides could be formed.

The films then were immersed in aqueous solution of MAA and AA. After degassing containers were sealed and kept at 60 °C for 90 minutes, grafted films were then rinsed with toluene and deionized water for several times to remove excess copolymers, dried in room temperature for 24 h and stored in sealed packages.

Table 1
The nomenclature and plasma treatment conditions of the PU membranes.

Sample	Power (watt)	Radiation time (min)	Grafted monomer
250-2-MAA	250	2	Methacrylic acid
250-2-AA	250	2	acrylamide
250-5-MAA	250	5	Methacrylic acid
250-5-AA	250	5	acrylamide
500-2-MAA	500	2	Methacrylic acid
500-2-AA	500	2	acrylamide
500-5-MAA	500	5	Methacrylic acid
500-5-AA	500	5	acrylamide
750-2-MAA	750	2	Methacrylic acid
750-2-AA	750	2	acrylamide
750-5-MAA	750	5	Methacrylic acid
750-5-AA	750	5	acrylamide
Pure PU	-	-	-

2.3. Characterization

Contact angle measurement was done by a Kruss DSA-100 apparatus to approve hydrophilicity effect, and thus, the monomer was grafted on polymer surface. Deionized water was the liquid selected for this measurement. Droplets were placed on each sample (at least 3 different locations) and water contact angle was measured three times at each location to lay down an accurate and acceptable result. An average of these values was then expressed as the contact angle for each sample.

Topography and morphology of membrane surface were examined by Atomic Force Microscopy (AFM). Different locations of modified membranes were selected and tested by an Autoprobe CP AFM. Image sizes were 1×1 µm and RMS values were measured. An average roughness was then calculated for comparison.

2.4. Permeation test

Permeation of gases was measured using an apparatus shown in (Fig. 2a). The setup consists of a coil followed by the permeation cell (Fig. 2b) located in a plexy-glass chamber kept at constant temperature using an industrial hot air gun. Permeated gas flows out of the cell at the front, and the rate of gas was calculated by measuring the travel of a water drop in a column at specific time intervals.

Permeation of pure gases through plasma grafted membranes was measured at a temperature of 30 °C with constant pressures of 6, 9, and 12 bars, and the permeate side of membrane was kept at atmospheric pressure. Test cell area for membranes was 12.5 cm^2. Permeability of membranes for each gas was then calculated from the following equation:

$$P = \frac{ql}{A(p_1 - p_2)} \qquad (1)$$

where P is permeation in barrer (1 barrer = 10^{-10} cm^3 (STP) cm^{-1} s^{-1} cm Hg^{-1}), q is the flow rate of gas passing the membrane (cm^3/s), l is the thickness of membrane (cm), A is the area of membrane, and p_1 and p_2 are absolute pressures of inlet and permeate side of the membrane, respectively. For dense and non-porous polyurethane membrane, a solution-diffusion model is supposed, and therefore, permeation can be determined as follows:

$$P = S \times D \qquad (2)$$

where D is diffusion coefficient, and S is solubility parameter of the membrane. The ideal selectivity of the membrane can be calculated as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \qquad (3)$$

where D_A/D_B is the diffusivity selectivity, and S_A/S_B is the solubility selectivity of A/B gas pair [13].

(2a)   (2b)
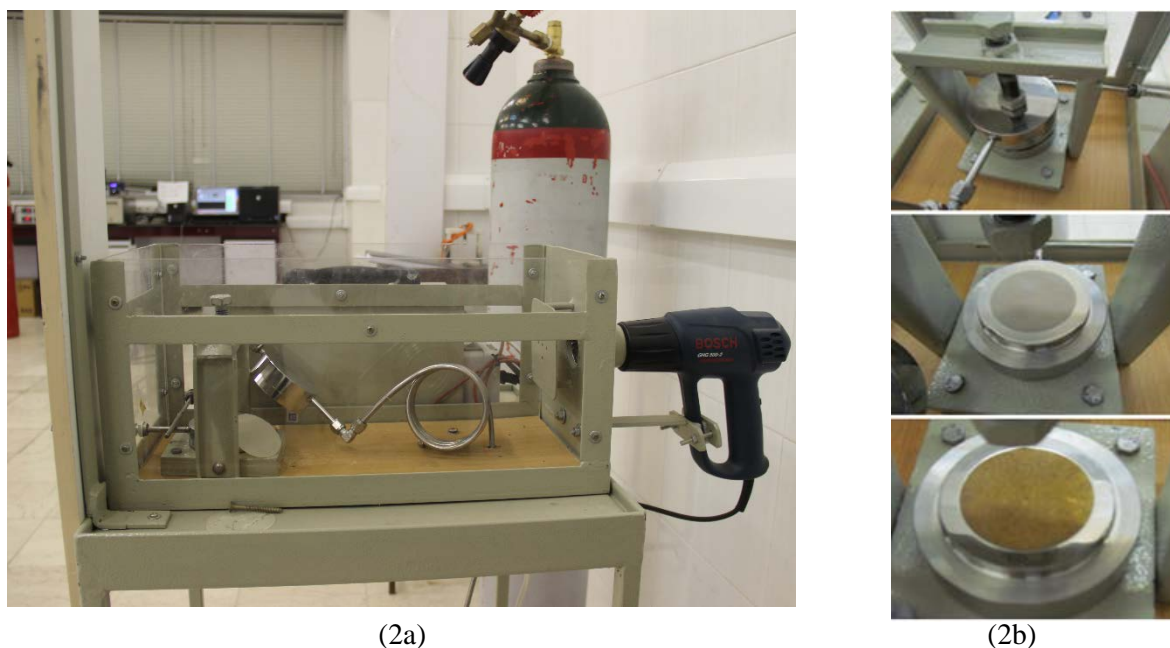
Figure 2. Setup for measuring permeation of gases.

3. Results and discussion

### 3.1. Contact angle measurement analysis

Figs 3a, b and c show water drop shape for pure PU, MAA grafted, and AA grafted membranes, respectively. Although average contact angle measurements illustrate that, generally, functional groups are grafted on membrane surface, but drop shapes may not change uniformly all over the surface due to uncontrollable active site creation during plasma irradiation.

For the grafted membranes, the nature of functional groups on the surface highly affects hydrophilicity of membrane. The used

PU membrane has weak hydrophilicity and its average contact angle is about 88°. This value has been decreased to 79° and 75° for MAA and AA grafted surfaces, respectively, due to polar-polar interaction between water and functional groups on the surface of modified PU membranes.
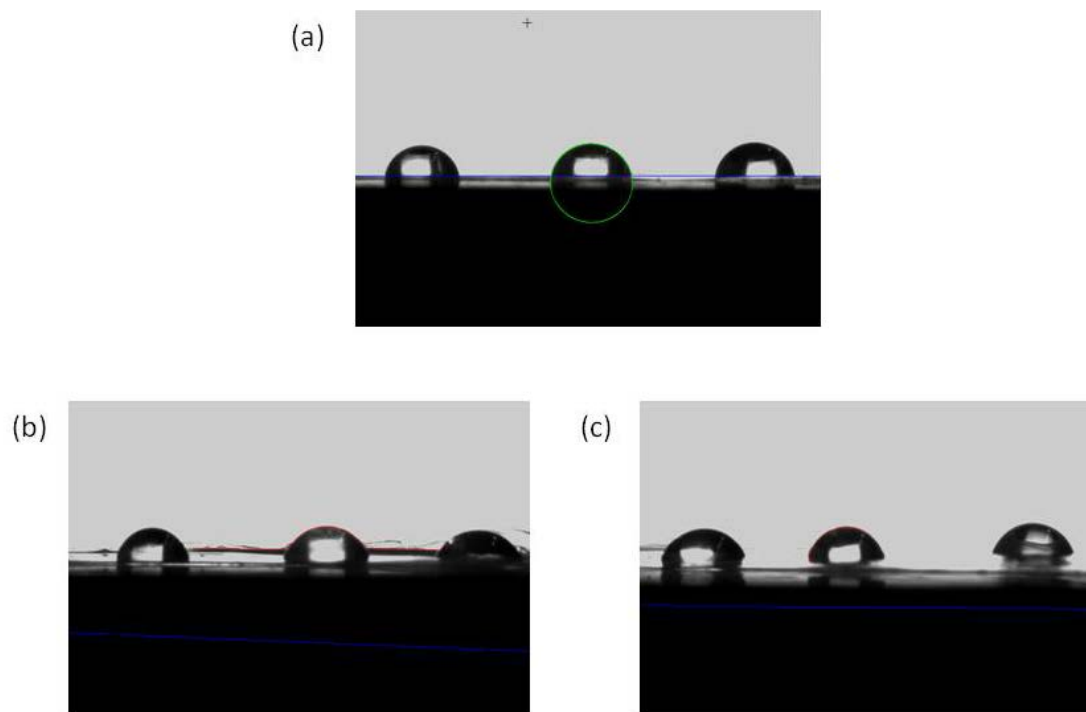
Figure 3. Contact angle drop shape for (a) Pure PU, (b) MAA grafted polyurethane, and (c) AA grafted polyurethane.

Table 2
Contact angle results.

Sample	PU	Acid graft	Amide graft
1st Location	92.6°-91.2° -90.4°	91.4° -91.4° 88.9° -88.3°	77.1° -77° -77.2°
2nd Location	85.9° -82.8° 86.2° -82.8°	77.7° -76.3° 79.1° -77.8°	78.6° -78.7° -78.1°
3rd Location	90.1° -85.9° 91.7° -92.2°	65.7° -65.3° -65.3°	70° -70° -70.4°
Average	**88.3°**	**78.8°**	**75.5°**

3.2. AFM analysis

Grafting affects membrane surface morphology and roughness by adding branches to polymer chains. Added branches fill surface voids, showing smoother topography and lower roughness (Fig. 4).

Figs 5a, b, and c show surface topography for pure PU, MAA grafted, and AA grafted membranes, respectively. It is clearly seen that MAA and AA branches are added to PU chains on the surface, causing smooth surface for grafted membranes.
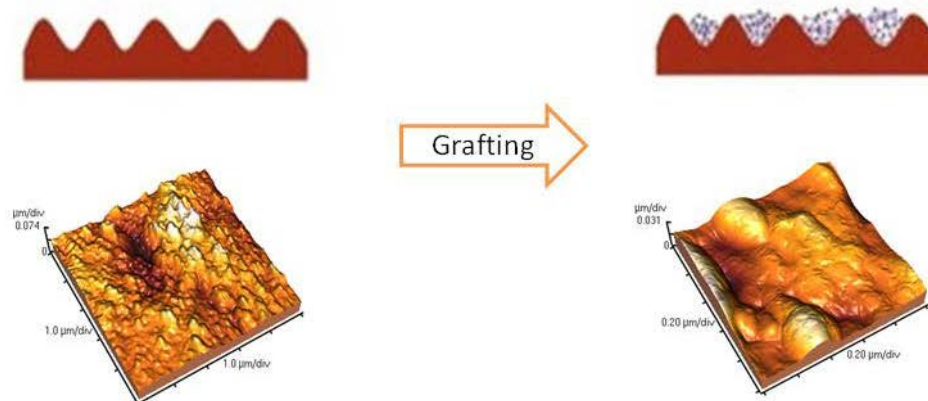
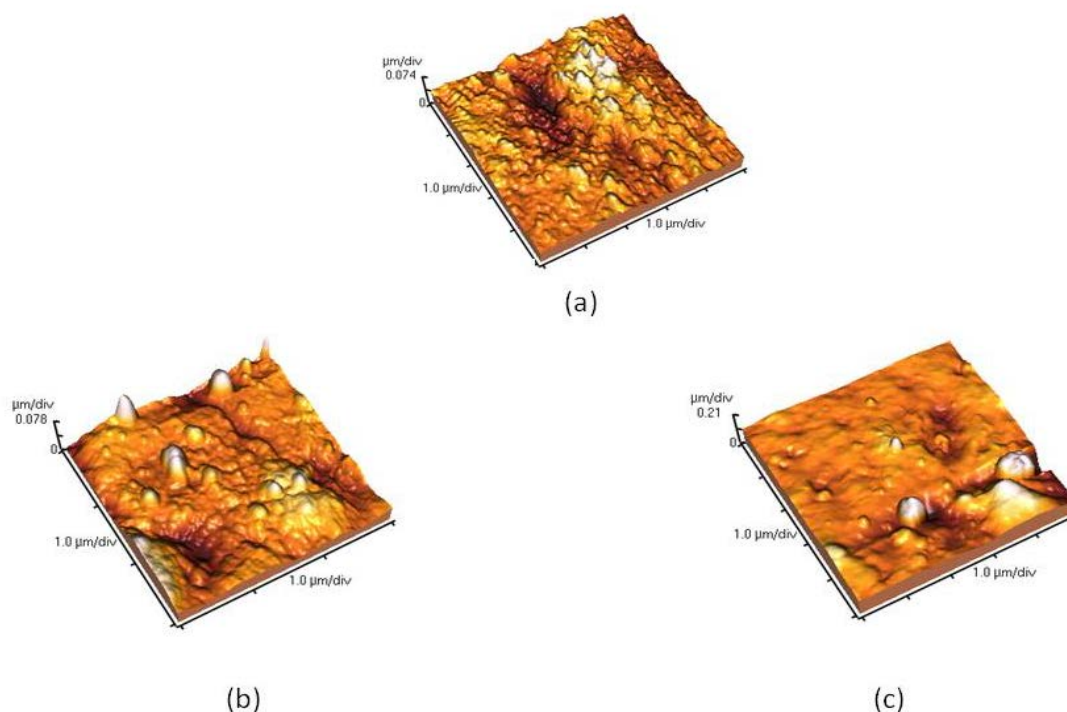**Figure 4.** Grafted branches fill surface voids.

Figure 5. AFM photographs for a) Pure PU, b) MAA grafted PU, and c) AA grafted PU.

3.3. Gas permeation properties

Table 3 shows permeability test results of CO_2 and CH_4 gases for pure PU, MAA grafted, and AA grafted membranes carried out at different pressures. As shown, the permeability of CO_2 is significantly higher than that of CH_4 in all pure and grafted membranes. The higher permeation rate of CO_2 in comparison with CH_4 is due to its greater condensability and more interaction with polar groups in the polymer structure [11]. Data were then fed to Minitab 16 statistical software, and effects of pressure, power, and monomer were studied, separately.

Table 4 shows CO_2/CH_4 selectivity calculated based on permeation results from Table 3.

Table 3
Permeability of CO_2 and CH_4 at different pressures.

Membrane Sample	Permeation (barrer)					
	CH$_4$			CO$_2$		
	6 (bar)	9 (bar)	12 (bar)	6 (bar)	9 (bar)	12 (bar)
250-2-MAA	2.76E-05	2.82E-05	3.04E-05	2.46E-04	2.35E-04	2.49E-04
250-2-AA	3.36E-05	3.78E-05	3.81E-05	3.30E-04	2.82E-04	3.36E-04
250-5-MAA	3.21E-05	3.47E-05	3.70E-05	2.81E-04	2.60E-04	3.09E-04
250-5-AA	3.72E-05	3.78E-05	4.33E-05	-	-	-
500-2-MAA	3.24E-05	3.78E-05	3.81E-05	2.16E-04	2.10E-04	2.59E-04
500-2-AA	3.44E-05	4.02E-05	4.60E-05	2.36E-04	2.32E-04	2.75E-04
500-5-MAA	2.93E-05	3.23E-05	3.39E-05	2.42E-04	2.36E-04	2.49E-04
500-5-AA	3.32E-05	3.35E-05	3.46E-05	2.53E-04	2.40E-04	2.61E-04
750-2-MAA	4.50E-05	4.73E-05	4.85E-05	1.55E-04	1.58E-04	1.70E-04
750-2-AA	3.36E-05	3.75E-05	4.02E-05	2.42E-04	2.76E-04	3.22E-04
750-5-MAA	3.78E-05	4.07E-05	4.36E-05	2.43E-04	2.74E-04	3.27E-04
750-5-AA	3.65E-05	4.16E-05	4.22E-05	2.63E-04	2.84E-04	3.42E-04
Pure PU	3.51E-05	3.85E-05	3.98E-05	2.61E-04	2.96E-04	3.01E-04

Table 4
CO_2/CH_4 Selectivity.

| Membrane Sample	Selectivity		
	6 (bar)	9 (bar)	12 (bar)
250-2-MAA	8.91	8.36	8.19
250-2-AA	9.82	7.44	8.81
250-5-MAA	8.77	7.50	8.36
250-5-AA	-	-	-
500-2-MAA	6.67	5.56	6.78
500-2-AA	6.85	5.78	5.97
500-5-MAA	8.27	7.32	7.32
500-5-AA	7.63	7.18	7.54
750-2-MAA	3.45	3.33	3.50
750-2-AA	7.19	7.35	8.03
750-5-MAA	6.43	6.74	7.50
750-5-AA	7.22	6.82	8.10
Pure	7.44	7.70	7.56

3.3.1. Effect of pressure

Figs. 6a and b show permeability of CO_2 versus pressure and its selectivity to CH_4. As expected, increasing pressure will increase CH_4 permeation through membranes. But, because of the strong interaction between CO_2 and membrane structure, this increase in permeation is not significant for lower

pressure changes and selectivity decreases. Similar behavior was reported by Kapantaidakis et al. [9] and Maeda and Paul [12] for CO_2 permeation through the membranes, where the presence of hydrophilic polymer in the matrix, i.e., poly (phenylene oxide) and polyimide, causes matrix densification and consolidation at high gas pressures. But, higher pressures up to 12 bars cause polar interaction and increase CO_2 permeation.
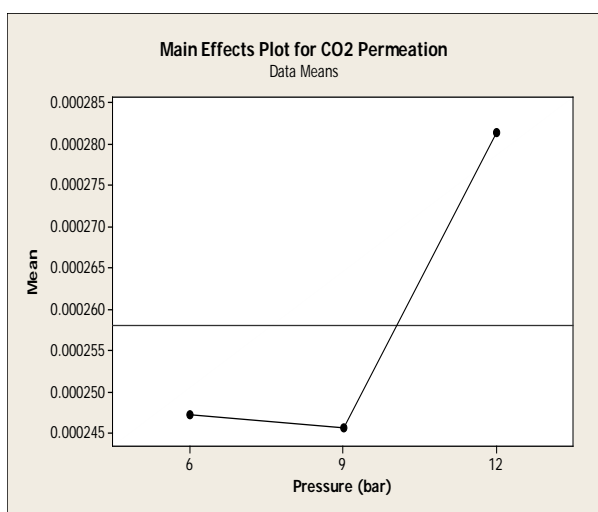

(a)
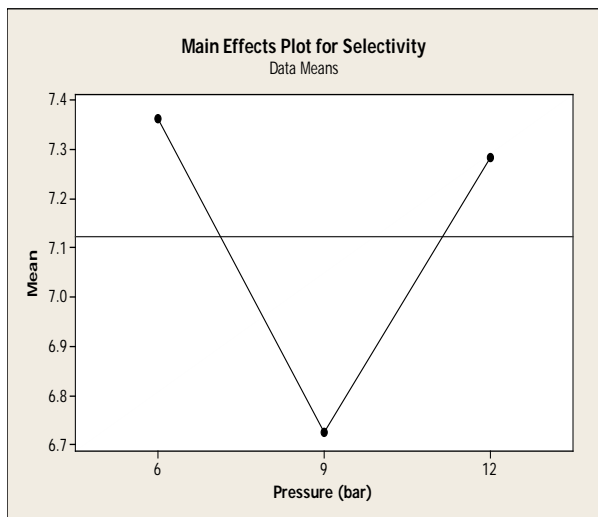
(b)

Figure 6. Effects of (a) pressure on CO_2 permeation (barrer) and (b) pressure on CO_2/CH_4.
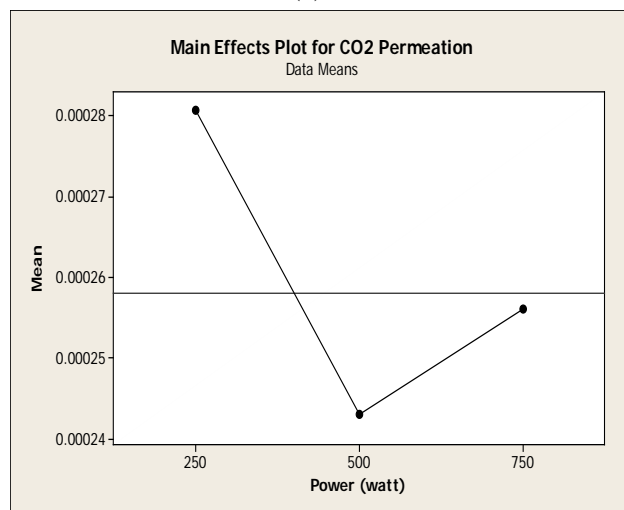
3.3.2. Effect of plasma power

Increasing plasma power causes CO_2 permeation to decrease, but has little effect on

CH_4 permeation (Fig. 7a and b). Using higher powers increases the number of active sites on surface. When a high density of active site exists on a surface, they may tend to bond with nearby active sites and crosslink than to create peroxide and promote grafting [20].

Membrane cross-linking has little effect on CH_4 permeation due to the absence of polar interactions with substrate and its small molecular size. But, CO_2 permeation decreases as the possible cross-linking makes an intertwined structure with polar interactions against molecule passage. Using very high power may also cause chain scission in polymeric membrane which increases the permeation of both gases and so lower selectivities.
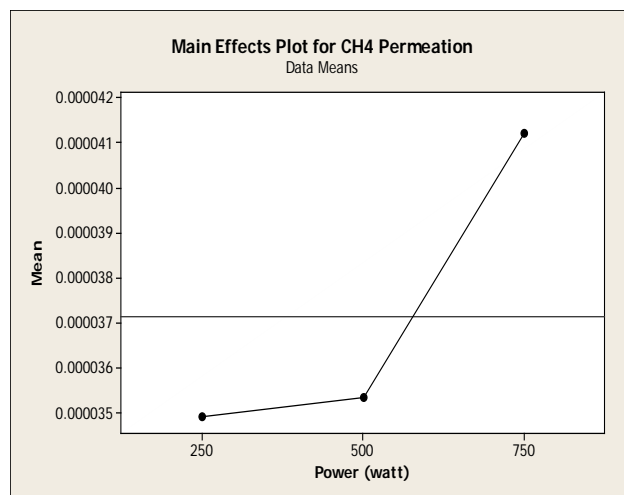

(a)

(b)
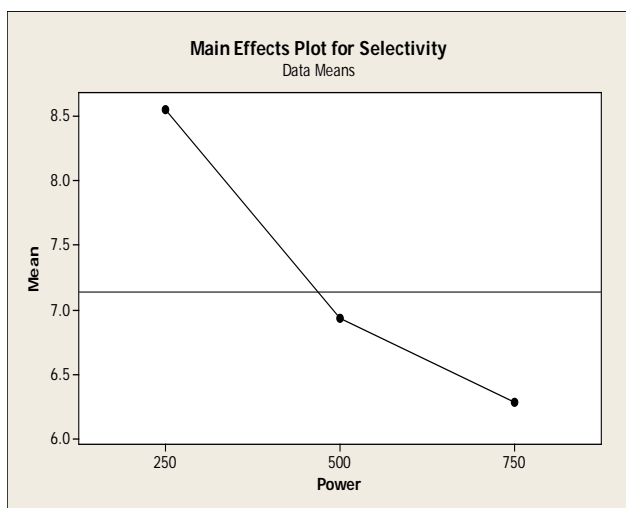
(c)

Figure 7. Effect of plasma power on (a) CH_4 permeation*, (b) CO_2 permeation*, and (c) selectivity.

3.3.3. Effect of monomer

According to Tables 2 and 3, higher permeations and selectivities are achieved with AA grafted membranes (Fig. 8). Studying the chemical nature and structure of applied monomers shows that interaction between acidic CO_2 and amide graft with a base nature might cause more permeation, and therefore, a higher selectivity is compared to acrylic acid. Similar results were reported by Suzuki F. et al. [23] and Yang. Y [24].
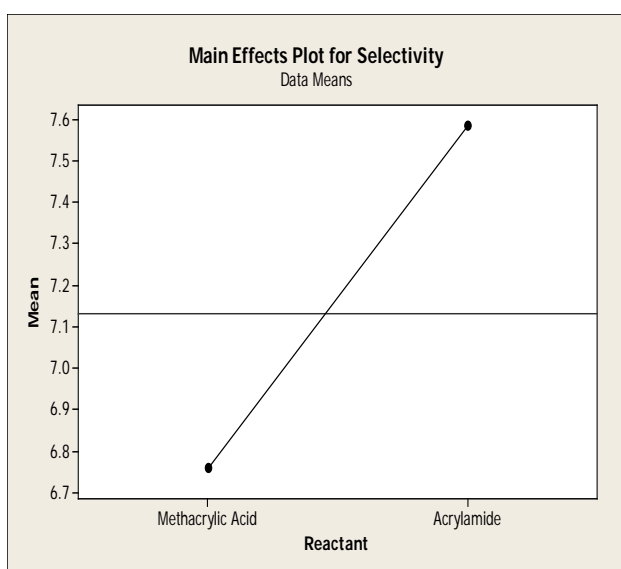
Figure 8. Effect of monomer type on CO_2/CH_4 selectivity.

4. Conclusions

In the present study, the effect of plasma grafting on gas separating properties of polyurethane membrane was studied. Contact angle and AFM tests showed that monomers were successfully grafted on polymer surface, although some non-uniformities were observed due to uncontrollable active site creation of plasma on substrate surface. Results show the increase in selectivity of CO_2 over CH_4 by grafting. For pure polyurethane, selectivity of CO_2 to CH_4 is controlled by solubility-diffusivity mechanism. But, for grafted membrane, solubility mechanism enhances and higher selectivities are reachable. Low powers of plasma and acrylamide monomer can increase CO_2 permeation up to 15 percent (P_{CO2}=3.36e-4), and a selectivity of 9.82 was achieved, which is 32 percent higher than pure polyurethane membrane with selectivity of 7.32.

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