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Environment friendly rubbery polyurethane membranes; preparation and fabrication of gas emission control for green textile industry

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Key words: Polyurethane, Permselectivity, Solution diffusion, Molecular sieve property, Chain length

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Abstract

Diisocyants (-Isocyanato-1-(isocyanatomethyl)-1, 3,3-trimethylcyclohexane (IPDI)), polyols (Polycaprolactone) and chain extender (1-4butanodiol) were incorporated in preparation of polyurethane based membranes. The prepared membranes were characterized by Fourier Transform Infrared spectroscopy (FTIR), permeability and selectivity of prepared membranes was measured by gas permeation cell. The effect of Mw content of polycaprolactone (750, 1000, 1250, 1600 and 2000), feed pressure (0.1-0.4MPa), operating temperature (20-50°C), and hard segment combination of (diiosocyante +chain extender) effect on transport property of CO_2/CH_4 and CO_2/N_2 selectivity were investigated. CO_2/CH_4 gas mixture selectivity enhanced 46% in PUM15 (2000Mw) as compared to membrane sample PUM1 (750Mw) is 2.4% and CO_2/N_2 selectivity is 51% in PUM15 (2000Mw) as compared to membrane sample PUM1 (750Mw) is 2.6%.The results revealed that PUM15 (Mw2000) display CO_2 permeability of 39.7 Barrer, higher than the PUM1 (750) is 4.3 Barrer. As the operating temperature increased from 20to 50°C CH_4 permeability increased about.9 to 8.6 Barrer for 750Mw (PUM11) and 2000Mw (PUM15) membranes samples. The correspondence decrease in the CO_2/CH_4 selectivity as compared to CO_2/N_2 is 46% and 51%. This is supported that high molecular weight polyurethane membrane are good CO_2 selective as compared to lower molecular weight polyurethane membranes. Because the heat trapping capabilities of this gas molecule into Environment may cause global warming.

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Introduction

The control of exuding Greenhouse gases such as NO_x, CO_2, CFCs and ozone into the atmosphere is the most challenging issue of global warming (Scholes *et al.,* 2010; Hamad and Matsuura, 2005). Among these gases CO_2 emissions from the textile industry have considered the greatest pollution problem in natural gas (Amooghin *et al.,* 2015). Air pollution is the presence of chemicals, organic material or substance that cause poisonous or harmful effects to mankind or other living creatures and damage the natural environment. Textile mills usually generate nitrogen and carbon dioxide from boiler house and sizing units in the energy production process (Lau *et al.,* 2009; Seo *et al.,* 2006). More important origin of air ejection in textile processes is resin finishing, drying processes, printing, tinting, fabric production, and wastewater management plants. Drying ovens and mineral oils ejected Hydrocarbons at high-temperature in curing. There is several CO_2 separation technology including absorption, distillation, adsorption and membrane separation.

In current ages, membrane separation (Lipnizki *et al.,* 999) is the most vital method of separation due to less energy expenditure, high performance, low operating rate requirements and space operations have become a significant point of research and attracted the industrial interest as new technical knowledge, eco-friendly, high energy efficient, proficient in money-making and easy operation as compared to other mention methods. (Vinoba *et al.,* 2017; Howard, 2002).

Polymeric membranes with permeation property and glowing selectivity are mostly used for gas separation operations, such as CO_2 capture, biogas upgrading, natural gas sweetening (Ghosh *et al.,* 2010; Bley *et al.,* 2009) and hydrogen production and can probably contest with some old separation mean in terms of energy needs and cost effective (Ghosh *et al.,* 2006; Shih-Li and Juin-Yih, 996). Some efforts are made to improve the interaction with polymer chain and solubility of CO_2 the polymeric membranes namely used in past decade for the separation of mixtures are polydimethylsiloxane (PDMS), polybutadiene (PBD), polypropylene (PP), polytetrafluoroethylene (PTFE), polyether (PE) block polyimide (PI) (Wolińska-Grabczyk and Jankowski, 2007; Wang *et al.,* 2003) cellulose acetate (CA) (Jiang *et al.,* 2003), silicon imide(SI), polyvinyl alcohol (PVA) (Khosravi *et al.,* 2014), asymmetric nylon4 (ASN4) (Sadeghi *et al.,* 2015), chitosan (CN) (Saedi *et al.,* 2014) and PI (Plyamides) (Kara *et al.,* 2014), and polyurethane urea (PUU) (Scholes, *et al.,* 2012; Wang *et al.,* 2003) have been utilized. However poor compatibility introduce in between organic and inorganic phases and lack of adhesion between polymer chain and free volume spaces which leads to decrease permeability and selectivity. In glassy polymers, the diffusion coefficient decreases very rapidly with increasing the permeation size (Saedi *et al.,* 2014). In addition, the glassy polymers are not suitable for the separation of organic fumes from gas streams because they preferentially permeate non-considerable gases over considerable ones (Scholes *et al.,* 2010). The glassy polymers are commercially used for the separation of small gas molecules (Jiang *et al.,* 2008).

Out of these membranes, polyurethane possesses excellent mechanical properties and good chemical resistance against gases mixtures. However, good computability between organic and inorganic phases achieved during membrane fabrication. Polyurethane (PU), a rubbery polymer is widely used in gas separation techniques (Khosravi *et al.,* 2014). Polyurethanes are massive copolymers with soft and hard sections alternatively. Soft sections mostly come from a polyether or polyester polyols, while the hard sections from diisocyanates with the chain extender in conversion to urethane linkages. The hard sections provide dimensional stability and integrity while the soft sections provide flexibility to chains which increase chain mobility. The surface of polyurethane contain a lot of polar OH groups provided by soft segment (polycaprolactone diol) which are good source of polar active sites for CO_2 absorption and increase the polymer chain interaction. Due to the different polarity of these two sections, microphase separation regulates the mechanical effects of Polyurethanes (Sadeghi *et al.,* 2015; Saedi *et al.,* 2014). This polymer has outstanding properties such as good mechanical strength and desirable permeation (Kara *et al.,* 2014). The solution diffusion model provides foundation to transport mechanism (Semsarzadeh *et al.,* 2013). The aforementioned model consisted of three steps) adsorption of liquids at the feed sided membrane, 2) Distribution of the sorbed particles across the membrane, 3) Removal of the sorbed particles at the permeate side. The separation of a gas mixture by the non-pours membrane is due to solubility and diffusivity difference. The sorption and desorption of permeant are usually very fast and the sorption equilibrium is thus assumed to be established rapidly between the permeate membrane interfaces (Semsarzadeh *et al.,* 2013; Scholes *et al.,* 2010). On the other hand, the slowest molecular diffusion is considered to be the rate-determining step in permeation (Semsarzadeh *et al.,* 2013; Sadeghi *et al.,* 2009; Fu *et al.,* 2007).

Recently the polytetramethylene (PTMG) polyurethane urea based membranes with diamine chain extenders were reported for gas separation (Pournaghshband *et al.,* 2016). The plybutadiene based chain extenders enhanced the gas separation performance in plyethylene glycol (PEG) based membranes (Semsarzadeh *et al.,* 2013. There are few reports for the polycaprolactone based plyurethane membrane for pervaopration process but there is no report for polycaprolactone based membranes discussed with introduction of low or higher weight polycaprolactone for gas separation experiments. Crosslink based polyurethane membranes also reported in previous study (Scholes *et al.,* 2010).

In this project isophrane diisocyante based defect free polyurethane membranes with different molecular weight of polyols were studied. We study the high molecular weight polyols in different membranes increases the extend of hydrogen bonding and promotes active sites for CO_2 absorption due to presence of NH groups and increase selectivity and permeability. The high phase separation between hard segments enhances free volume and the transport for large gas molecules to easily diffuse through membrane. Membranes were synthesized by solution casting method, gas permeation test of pure O_2, N_2, CH_4 and CO_2 gases were conducted to evaluate gas separation behavior. In this study, the variability of polyurethane for CO_2/CH_4, CO_2/N_2, CH_4/N_2, O_2/N_2 gas mixtures separation is studied.

Materials and methods

Required Material

In this project all laboratory grade chemicals are used like Isophoronediisocyanate (IPDI), tetrahydrofuran (THF) dimethyl formamide (DMF) as solvents, dibutyltindilaurate (DBTDL) as catalyst, Butane-1,4 diol (1,4-BD) as chain extender and Poly (caprolactone) diol CAPA of different molecular weight were bought from Sigma Aldrich.

Synthesis of Polyurethane membranes

The polyols were drying at 80°C in vacuum for 24h to remove water vapours and air bubbles before membrane preparation otherwise that may interfere with the isocyanate reactions. To obtain isocyanate (NCO) terminated polyurethane prepolymer 5-Isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethylcyclohexane (IPDI) was reacted firstly; with Poly (caprolactone) diol to synthesized PU prepolymer. As follow, Poly (caprolactone) was placed into a spherical bottom glass flask having 4 necks, fitted with temperature-controlled oil bath, dropping funnel, condenser for reflux, electrical stirrer, and inner-outer attachment pipes for argon atmosphere. To start reaction the oil bath temperature at 60°C was increased. The final membrane product was obtained with the addition of chain extender at 100°C with constant stirring for 20 min. The overall reaction was performed below the argon atmosphere. The samples were stored in a desiccator to avoid the ensnared air bubbles for farther testing. The polymer viscous solution was cast on spotless Teflon plates furthermore, dried at 90°C for 24 h to remove excess solvent. The chemical scheme of prepared membranes is shown in fig.1.

Molecular characterization

The configuration of the prepared PU membranes by using lower and higher molecular weight of Polycaprolactonediol, affirmed by utilizing FT-IR spectroscopy in the scope of 500–4000cm^{-1}. A Shimadzu 80900 Fourier Transform Infra-red (FT-IR) spectrometer was used to record the samples in transmission mode.

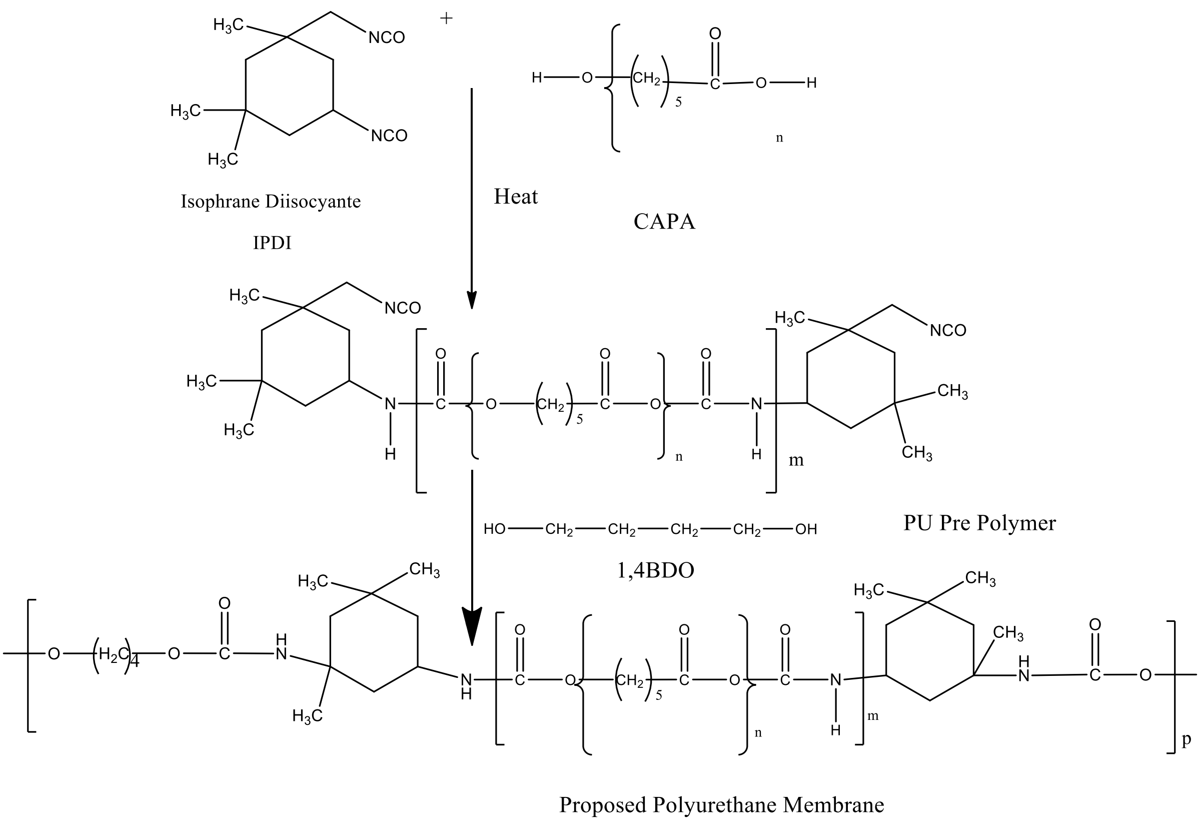

Fig. 1. Chemical scheme of polyurethane membrane.

Membrane performance in gas permeability

Gas permeation

The polymeric membrane sample with an operative infusion area of $1.3 cm^2$ was mounted into the permeation cell. Pure gas (N_2, O_2, CO_2 and CH_4, research grade) at given pressure flowed through a water vapour saturator before admission to infusion cell. The given gas pressure varied from 0.1to 0.4 MPa, However, permeate side was under pressure of atmosphere. Humidified gas was used to prevent the membrane from drying during gas permeation measurement. The permeation value was noted with help of bubble flow meter. The permeability of different molecular weight of polyurethane membranes was tested at a pressure from 0. to 0.4MPa at room temperature. Between measurements at different pressures, h of stabilization was allowed when varying the temperature the water vapour saturator and the permeation cell were immersed in a water bath. The temperatures tested were: 20, 30, 40, 50°C, because the gas for permeation is inside the saturator and permeation cell, more time (1.5h) was allowed to stabilize the membrane conditions between changing temperatures. The following equation was used for gas permeability calculation.

$$J = \frac{V}{At\Delta p} \cdot \frac{273.15}{T0} \cdot \frac{Po}{76}$$

Where membrane permeance [cm^3(STP)/(cmHg)] stands for by means of J, V is the volume (cm^3) of the permeate collected at ambient surroundings (temperature on the way to (K) pressure p^o(cmHg) finished a time period (s) The effectual area A (cm^2) of the membrane, Δp the cross-membrane pressure difference (cm Hg). Permeance is customarily expresses in the unit of GPU, and GPU= 10^{-6} (1GPU=10^{-6cm3} (STP)/cm^2. s.cmHg).

Results and discussion

Characterization

To characterize the structure of polyols, diisocyanates, chain extenders, Prepolymers and final polymers were recorded in 4000–500cm^{-} range. FTIR spectra of, 5-Isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (IPDI) hydroxyl terminated Polycaprolactonediol (PCL), prepolymer, 4-butanediol (BDO) and cured polyurethane are jointly recorded in Fig. 1. The FT-IR spectrum of isophoronediisocyanate (IPDI) (Fig. 1a) the very strong peak located at 2259.5cm^{-} is attributed to the isocyanate (NCO) group linked to the IPDI. It is significance monitoring to hydrocarbons show IR absorption peaks between 2926.8cm^{-} and 2853.5cm^{-} due to CH stretching vibrations (Semsarzadeh *et al.,* 2013). Assigned the region of isocyanate group, –N= C= O stretching band appearance at 2273cm^{-} as well as C–H symmetric then antisymmetric stretching band on both sides of on or after 2950 near 2850cm^{-1}. The peak at 366.5cm^{-} is for $C(CH_3)_2$ present on the carbonylic ring of IPDI.

In (Fig. 1.1b) the peaks of Polycaprolactonediol assigned by FTIR spectrum were assigned as 1727.1cm^{-} (stretching of C=O) 167.7cm^{-} (stretching of C-O); (OH stretching vibrations) 3521.1cm^{-1}; 2865.6cm^{-} (symmetric CH_2 stretching); 2942.8cm^{-} (asymmetric CH_2 stretching) (Hassanajili *et al.,* 2013). Experimental peaks by the side of 3442.15cm^{-} (OH stretching vibration); 2940.50cm^{-} (asymmetric CH_2 stretching); 2868.15cm^{-} (symmetric of CH_2 stretching); 730.58cm^{-} (C=O of stretching); 193.34cm^{-} (C-O stretching). After hour by the reaction of NCO group of IPDI with OH group of PCL the NCO terminated polyurethane polymer was created in Fig. (1.1.c). It can be clearly seen from FTIR spectrum that signal of OH group completely disappeared and the intensity of NCO groups was reduced to some extent. Indicating that the reaction is not yet completed or that the proportions are not adjust. The exterior of highest peak at 3372.3cm^{-} was assigned on the way to the amine proton of the urethane by way of NH moiety suggesting that polyurethane prepolymer had been formed (Fig. 1c). The PU prepolymer has moreover publicized the absorption peaks (Fig. 1c) as: 531.4cm^{-1}, 461.0cm^{-1}N-H) after that (C-N), bending furthermore stretching respectively.

(Liu *et al.*, (2011) pragmatic (N-H out of plane bending as well as C-N stretching next to 535cm^{-} and 537cm^{-1}). The PUs had a characteristic broad amide –NH– peak at 3325cm^{-} with strong carbonyl stretching absorption bands of an amide at 743cm^{-} and 697cm^{-} reported in the literature by (Ameri *et al.,* 2015; Hassanajili *et al.,* 2013). The peak at 3325cm^{-} indicating that probably all the PCL diol hydroxyl groups have reacted in the company of isocyanate groups voguish prepolymer. The presence of H-bonds among soft and hard section is a hint of phase mixing, in prepolymer polyurethane. The other peaks observed in the NCO terminated prepolymer were assigned as: 2949.0cm^{-} (CH symmetric stretching of CH_2); 2866.0cm^{-} (CH asymmetric stretching of CH_2) 2265.2cm^{-} (NCO group); at 732.9cm^{-} (C=O stretching) a large intense peak of soft segment of Polycaprolactonediol; and other peaks with medium intensity which appears 732.9cm^{-} (CNH stretching). The same results reported in previous literature (Ameri *et al.,* 2015). To obtain final PU membrane product the prepolymer samples was further reacted with, 4-butane diol.

In (Fig. 1d) has two prominent peaks at 2779.72cm^{-} and 2833.7cm^{-} assigned just before asymmetric with symmetric stretching of the CH_2 groups, respectively. The broad peak appeared on 3300.0cm^{-} is exactly en route to intra and intermolecular hydrogen bonding with corresponds in the direction of hydroxyl group Hassanajili *et al.,* 2013). The reaction of isocyanate terminated PU prepolymer with that of, 4-butanediol (BDO) used as chain extender produced polyurethane membrane. FT-IR spectra obtained from the cured film are illustrated in (Fig. 1e). The spectra showed that the urethane groups appear at 3372.3cm^{-} (NH stretching). It is estimated that valence vibrations of the band corresponding to methyl (antisymmetric C–H stretching) antisymmetric and methylene (symmetric C–H stretching vibration) groups, with two peaks at 2948.0cm^{-} and 2866.0cm^{-1}. The polyurethane membrane has specific groups: CH_2, NH in the hard segment and soft segments characterized by C–O–C groups which are observed by ATR FTIR spectra. In polyurethane membrane that has higher degree of phase separation presents in the surface which improves the mechanical strength of membrane (Saedi *et al.,* 2013).

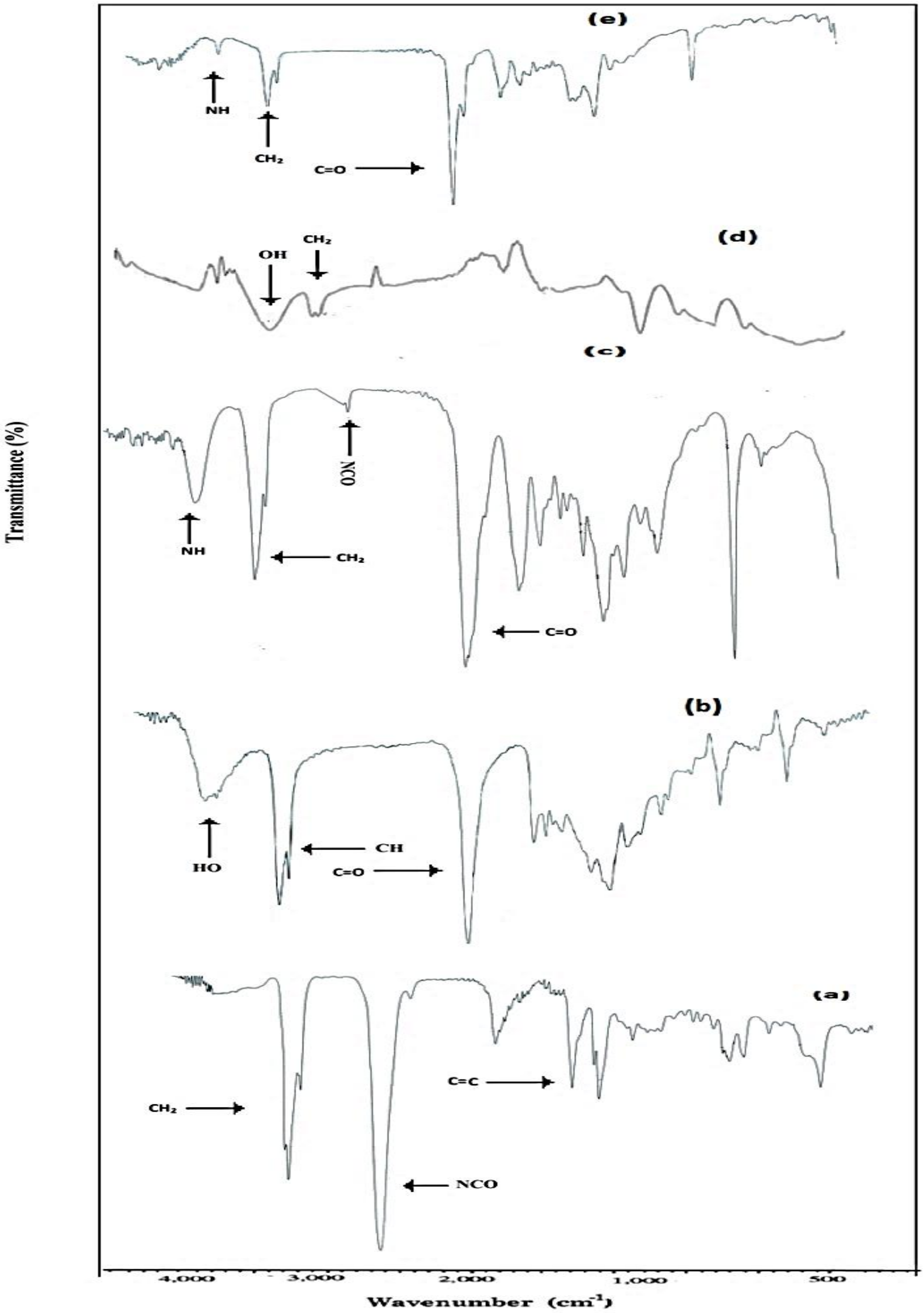

Fig. 2. FT-IR Spectra (a) 5-Isocyanato-1-(isocyanatomethyl)-1,3,3 trimethylcyclohexane (IPDI) (b); Polyols Polycaprolactone; (c) Polyurethane NCO terminated Prepolymer (d) chain extender,4-Butane diol; (e) Cured polyurethane membrane.

Table 1. Formulation and Sampling Code of polyurethane membrane.

Sample code	aCAPA (MW)	CAPA Trade name	b IPDI (Mole ratio)	c CAPA (Mole ratio)	d1,4-BDO (Mole ratio)
PUM-11	750	2077A	2	1	1
PUM-12	1000	2100A	2	1	1
PUM-13	1250	2125A	2	1	1
PUM-14	1600	2161A	2	1	1
PUM-15	2000	2200A	2	1	1

[a]Different molecular weights of polycaorplactonediol.

[b]5-Isocyanato-1-(isocyanatomethyl)-1, 3, 3-trimethy lcyclohexane (IPDI)

[c]Polycaorplactonediol.

[d]1, 4-Butane diol

Performance of Isophranediisocyanate based polyurethane membranes

In these study, molecular weights of PCL 750, 1000, 1250, 1600 and 2000 are shown in Fig. 3. These five kinds of polyol were used as soft segment IPDI and, 4- Butanediolis used as a hard segment to prepare the non-porous PU membranes. The solution casting method was used to prepare the membranes. The main reason of CO_2 has higher permeability in comparisons of other gases is due to high condensability and more interaction of this gas with polar groups in the polymer membrane. Therefore CO_2 act as diametric (polar) gas and can associate with the polar ethereal groups in the soft region more easily, synthesized PCL based PUs. Such as presented in Fig 3 CH_4 is lesser permeable extent as compared to N_2 and O_2 molecules. This deed exposure the dominance of a solution-diffusion mechanism used for the gas permeation in the PU membranes. The fact solution mechanism indicates that the higher weight molecules of PCL membranes exhibited higher rubber properties in the membrane. Increase hydrophilicity, which increases interaction between water vapour molecules and the polymer chain. The non-condensable gases like N_2 and O_2has high permeability with soft segment related to higher chain mobility with high Mw polyols in long membrane chain. The polymer membrane thickness transported small molecules more easily as compared to large size molecules in comparison of gas molecules (Saedi *et al.,* 2013).

The greater decrease in permeability of CH_4 in contrast with N_2, O_2 and CO_2 is due to its superior molecular size and the existence of IPDI (isophranediisocyamtes) as hard segment, a significant decrease in the amount of free volume of the polymer matrix. In Fig. 3 CO_2/N_2, CH_4/N_2, CO_2/CH_4, and O_2/N_2 gas pair selectivities of the PU membranes presented. It is evident that the selectivities of every one of couple gases increase by increasing the high molecular weight PCL content in the membranes. As shown, the CO_2/CH_4 and O_2/N_2 pair gases present higher selectivities than CO_2/N_2, CH_4/N_2 pair of gases. Diffusivity plus solubility is the product of total selectivity. By the addition of higher weight PCL content into the membranes, the permeation of bigger molecular size gases is more limited than small ones, the –OH groups in the soft segment make the best contact within the polymer chains. The phase separation among hard and soft has been improved by hydrophilic content in the PU backbone (Fu *et al.,* 2007).

High permeability of O_2 is related to high critical temperature, solubility and small molecular size are the main reason as compared to methane and nitrogen. The phase separation between soft and hard segment increases, as free volume and gas solubility increases (Sadeghi *et al.,* 2009). Transport property of gases mainly depends upon free volume and chain mobility within the membrane. Subsequently, the gases pair of CO_2/CH_4 and O_2/N_2 has high selectivity; due to a CO_2 high affinity with ester groups of the soft segments enhances the solubility of this gas pairs in the membranes. Finally, the better CO_2/CH_4 selectivity in contrast with the CH_4/N_2 selectivity is attributed to methane's much decrease condensability than nitrogen's. Although CH_4 larger molecular length may want to offer decrease selectivity for the CH_4/N_2 gasoline pair (Sadeghi *et al.,* 2009; Fu *et al.,* 2009).

Effect of temperature

To evaluate the temperature dependence of the permeability, the gas permeation through the various PCL membranes (PUM1 to PUM15) were tested at a different operating temperature ranging from 20 to 50°C. The gas permeabilities of O_2, N_2, CH_4, and CO_2

all increased with an increase in temperature and follow the Arrhenius relationship, from which the activation energy was calculated. The activation energy defines the energy barrier that needed to be overcome for molecules to permeate through the membrane. In standard, an increase in temperature will result in an increase in diffusion and a lower insolubility. The driving force enhanced mass transfer and vapour pressure of components at permeate side which easily permeating through the membrane by increasing feed temperature.

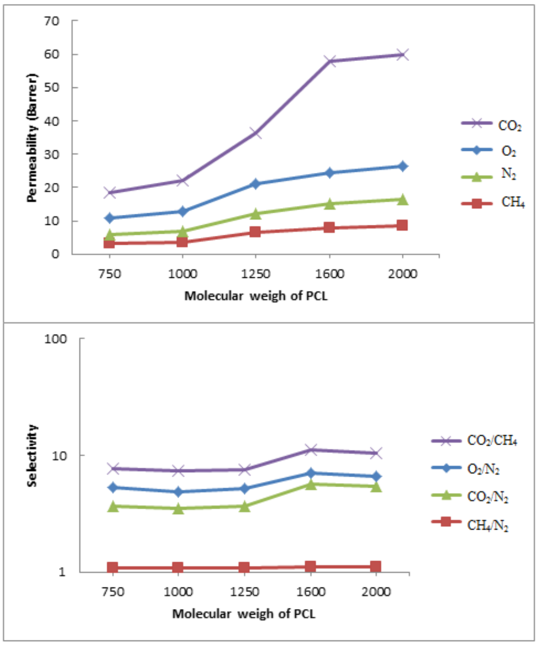

Fig. 3. Effect of molecular weight of polyol on permeability and selectivity.

The influence of temperature on the gas permeability in the polyurethane membrane is shown in Figs 4 and 5. The activation energy of permeation was calculated by using equation E.3.13. Selectivity, CO_2/N_2, CO_2/CH_4, gas pair is enhanced in higher (PUM15, 2000Mw) molecular weight polyol with the increase of temperature.

At higher temperature, the polymer membrane segments became more flexible as compared to when high pressure is applied the membrane might be more comparable. The following factors affect the increase in selectivity) Plasticization effect (Hassanajili *et al.,* 2013; Sadeghi *et al.,* 2009) 2) saturation of carrier efficiency 3) swelling of membrane 4) frequency diffusional jump 5) chain mobility in the membrane (Lipnizki *et al.,* 1999). Especially the effect of the feed temperature at the selectivity of CO_2/CH_4 pair is shown in Fig 5. The activation energies determine the rate of the increase of permeability through the polymer membrane. The activation energy of the gasoline permeation depends on the scale of the penetrant, polymer kind and membrane structure (Ameri *et al.,* 2015). Incorporation of high molecular weight content of PCL inside the polymer membrane increases the density of polar OH groups inside the matrix, forming polar sites polymer interface and also the morphological adjustments passed off which aids the solution of the condensable gases within the membrane (Sadeghi *et al.*, 2017).

(Sadeghi *et al.,* 2017) suggested that permeability of the condensable gases CO_2 and CH_4 were enhanced in comparison with the permeability of non-condensable N_2 gas significantly decreased is due to the change into a polymer matrix structure (Semsarzade *et al.*, 2017). The O_2 permeability is higher as compared to the CH_4 and N_2 permeability. Polyurethane possesses the amino carriers that can specifically interact with CO_2 to facilitate gas transport through membranes. Comparison of the permeability of CO_2, CH_4 and N_2 gases in polyurethane membranes leads to the following order $CO_2 > CH_4 > N_2$. The small molecular size and excessive critical temperature tend to produce high permeability because the high diffusion coefficient promotes solubility in the membrane. The higher CO_2 permeability is due to interplay of CO_2 with the polar groups in the polymer chain in contrast with other gases; CO_2 has a small molecular size and has smaller kinetic diameter like CH_4 (3.8°A), N_2 (3.64°A), O_2 (3.46 °A) and CO_2 (3.3 °A) (Ameri *et al.*, 2017).

Thus, the higher condensation temperature of CH_4 promotes its solubility inside polymer and results in a higher permeability of this gas in polyurethanes as compared to N_2. The molecule sieving property helpful in the transportation of methane as compared to nitrogen as solubility, of gases in polymer, relies upon on condensability of the gas and energetic functional groups present in the polymer backbone.

The chain mobility in different polyurethane membrane is different and this difference is due to the presence of aromatic and aliphatic diisocyanates which act as hard segment in the polymer. The selectivity typically occurs by way of converting the solubility behavior of the polymer by using adding a special functional group to the polymer structure. Polar, acidic or other active gases are separated by this way. The other one diffusivity, which in occurs by changing the molecular motion and size of the trapped free volume in the polymer structure.

The solution-diffusion mechanism enhances the molecular sieve property of polymer and is used for separation of great numbers of gases with different molecular sizes. This is the primary reason molecular sieve property of polymer that increases the selectivity gases in polymer membranes.

We have compared the permeability and selectivity of polyurethanes membranes in higher molecular weight (PUM 5 with Mw 2000) PCL bases membranes as shown in in Figs 6. The obtained result suggest that gas permeability of polymer increases while the selectivity will also increases, these effects are because of increasing of the polyol content material in the polyurethane structure. As temperature increases, contrary outcomes have been come about CO_2 solubility decreases even as its diffusivity enhances considerable. This is because of the reality that the temperature impact is more distinct for gas diffusivity in comparison to solubility, therefore penetrability is more increased. The penetrants molecular sizes and their interaction with the polymer matrix impact on the activation energy of the gases.

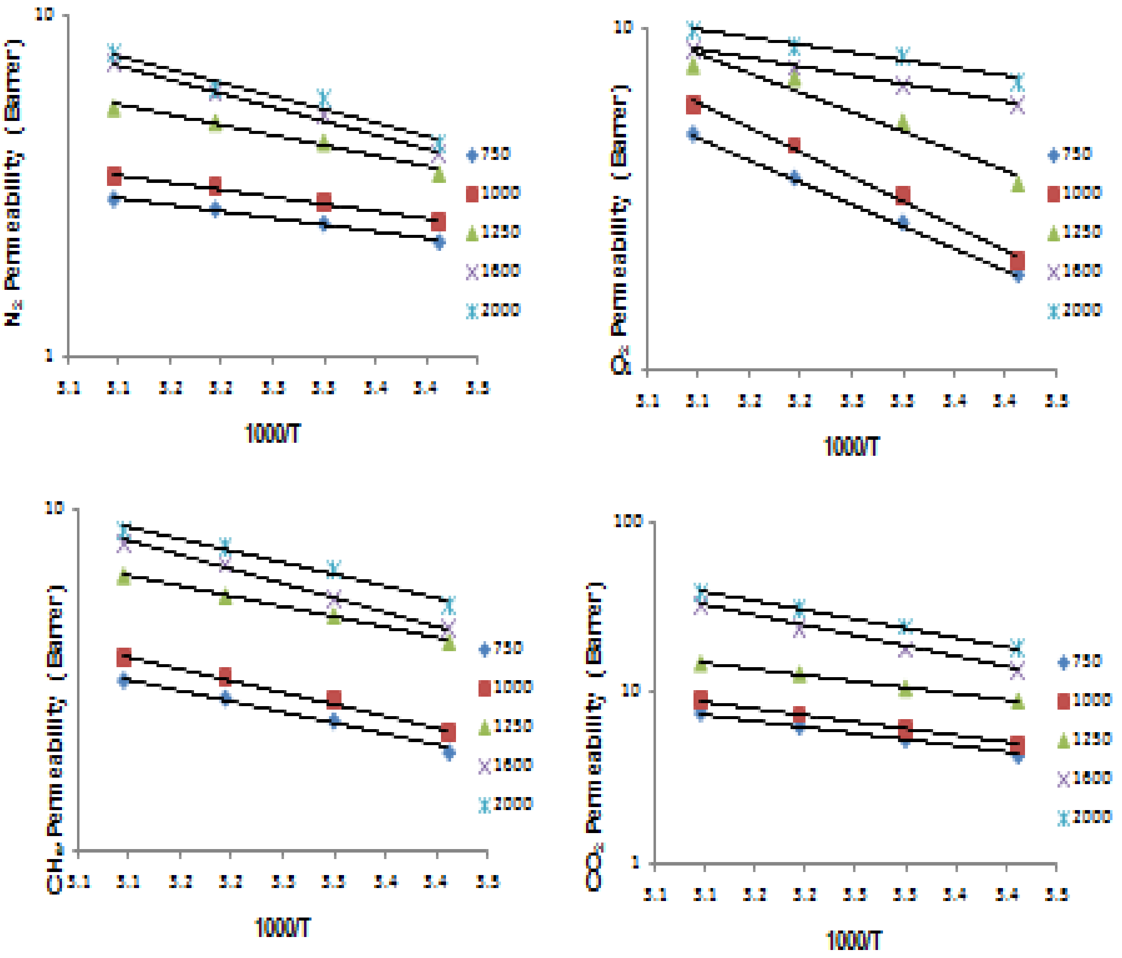

Fig. 4. Operating temperature effect on the permeance of IPDI based polyurethane membranes.

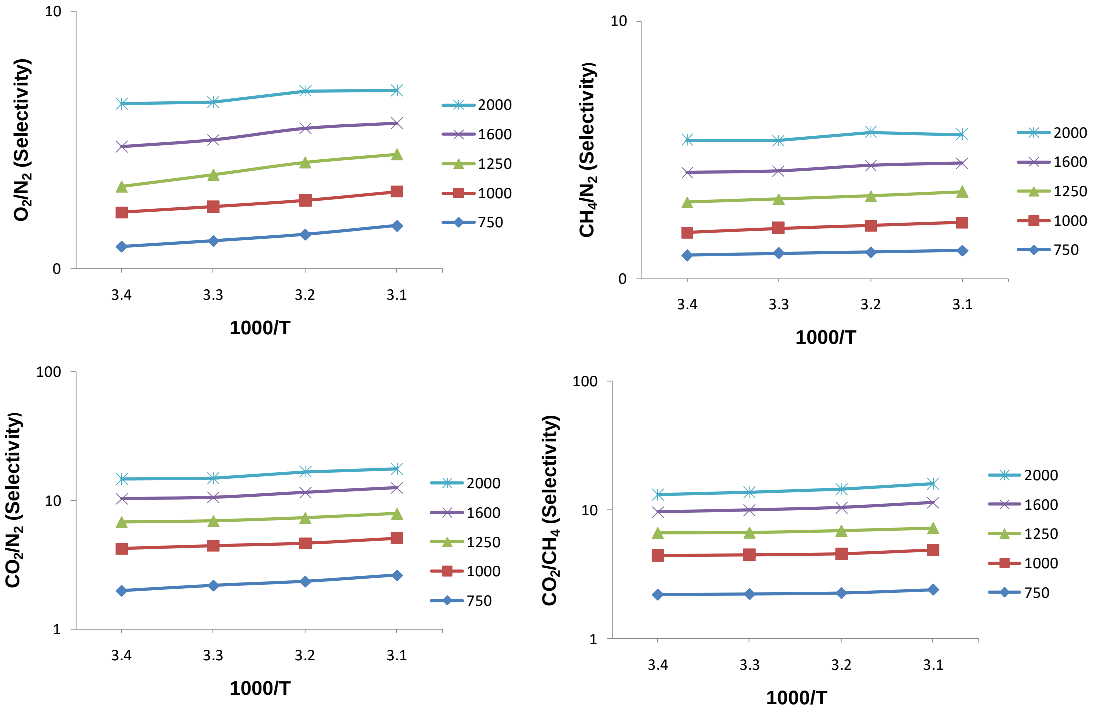

Fig. 5. Operating temperature effect on the selectivity of IPDI based polyurethane membranes.

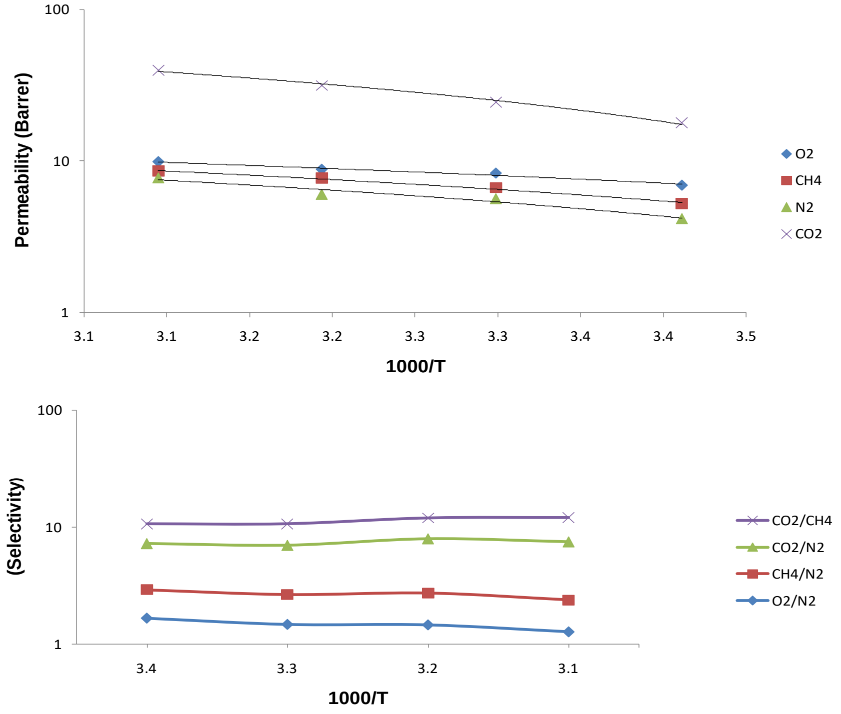

Fig. 6. Permeability and selectivity comparison in PUM15with 2000Mw of Polycaprolactone based membrane sample with respect to temperature range.

It should be pointed out that the activation energy dependent on the permeation flux. The permeation flux increases with the increase of temperature. Because of the thermal motion of the polymer chains, the diffusivity of permeant and free volume inside the membrane increases, with the temperature increase. In order to evaluate the influence of temperature, the activation energy was calculated from the slope of Arrhenius plots. The activation energy for O_2, N_2, CH_4, and CO_2 at different concentration of Polycaprolactone was shown in Table 2. The data in the table shows that a CO_2 has lower activation energy as compared to oxygen, nitrogen and methane in the higher molecular weight polyurethane membrane. The temperature dependence of permeation flux appears to fallow an Arrhenius relationship.

$P=P_0 \exp(-Ep/RT)$..................................... Eqn 3.13

Where R is gas constant, pre-exponential factor is indicated by Po, the activation energy of permeation Ep expressed in (kJ) and P is permeability coefficient is temperature (k). The higher activation energy of permeation indicates that temperature has a larger effect on the gas permeation results presented in Table. 2. CO_2 has lower activation energy than O_2, CH_4, N_2 and the lower activation energy indicated that CO_2 diffuses through the membrane more easily as compared to others. The same results in the study of Novel poly (arylene ether) membranes for gas separation reported by (Lipnizki *et al.*, 1999). As is clear, by means of increasing the amount of PCL inside the polymer structure, activation energy will increases which indicate the greater dependency of polymer to a temperature in high Mw PCL-based polymer as shown in table 2. The results imply that the temperature dependence of pure gases permeabilities in polyurethane membranes is through by diffusion. Gases inclusive of CO_2 that present low E_P values have a greater permeability. The large size gas molecules N_2 and CH_4 have high E_P values were calculated from the permeability graphs. Two foremost reasons govern the behaviour of E_P of different gases are the size of molecules and interplay with the polymer (solubility). The cause why N_2 is much less permeable than CH_4 regardless of its being a smaller molecule is its low solubility within the polyurethane. Hydrogen bonding can also may vicinity among CO_2 and N–H groups. N_2 has the maximum E_P value because of its small solubility.

Table 2. The activation energy based on permeation flux (Ej) and membrane permeance (Ep) for different gases at different contents of polycaprolactone diol.

PUM	CO_2KJ/mol	CH_4KJ/mol	O_2 KJ/mol	N_2 KJ/mol
PUM1	4.0	20.71	18.69	22.81
PUM2	8.81	24.29	21.00	25.53
PUM3	5.87	25.25	23.17	26.97
PUM4	12.81	37.04	34.98	35.85
PUM5	75.31	124.29	113.65	119.56

$S=S_o \exp(-\Delta H_s/RT)$.................................... Eqn 3.2

The penetrate with a high solubility has low activation energy for permeation. Permeation activation energy (Ep) is the sum of diffusion (Ed) and heat of solution (ΔHs). The literature indicates that, CH_4possess a small (ΔHs) heat of sorption that brings about lower in solubility with increase in the temperature. While, CO_2 has a large ΔHs which causes an increase in solubility at higher temperatures as shown in table3 by using 3.2 Equation. However contrary to this, increase in the temperature caus to increase in mobility of the penetrant molecules and polymer segmental chain mobility as well. The high permeation rate of CO_2 in contrast with CH_4 is due to its higher condensability, low kinetic diameter and greater interaction of this gas with polar groups within the polymer membrane (Ameri *et al.*, 2015).

Table 3. The heat of solution for different gases in different membrane samples.

PUM	CO_2KJ/mol	CH_4KJ/mol	O_2 KJ/mol	N_2 KJ/mol
PUM1	4.0	20.71	18.69	22.81
PUM2	8.81	24.29	21.00	25.53
PUM3	5.87	25.25	23.17	26.97
PUM4	12.81	37.04	34.98	35.85
PUM5	75.31	124.29	113.65	119.56

Effect of pressure

Various cross pressure (0.1, 0.2, 0.3, 0.4) MPa applied on membranes samples include Mw 750, 1000, 1250, 1600, 2000 molecular weight of PCL as a soft segment and IPDI used as hard segment were studied to investigate the effect of pressure. It can be understood that with will increases in pressure the permeability of CH_4 drops while the permeability of CO_2 increases. The selectivity of, CO_2/CH_4, O_2/N_2, CH_4/N_2 and CO_2/N_2 increased in 2000 molecular weight polyol with an increase in pressure. The above results may be due to the difference in the molecular structure of the polyurethane membrane. The high penetrate pressure applied to the flexible polymer membrane could slightly compress the polymer matrix, thereby reduction in the amount of free volume available for penetrating transport, leading to a decrease in selectivity in 750PUM1 sample. The high CO_2/CH_4 permselectivity in the PCL (polycaprolactone) membrane can be used to separate the CO_2 from flue gas. The effect of cross-membrane pressure on the permeation of O_2 is similar to that of N_2. The permeability of lower molecular weight polyurethane membranes was lower than the permeability of higher molecular weight membrane as shown in Figs 7 and 8. It indicates that all samples of polyurethane membrane follow the basic principle of solution diffusion interactions with N_2 and O_2 the same statement reported in previous literature by (Ameri *et al*., 2015; Sadeghi *et al*., 2015).

A linear descent happening in the case of the CH_4 system$_1$infers that the rise in the pressure would lower the free volume of the polymer chain. Whereas, a permeability arise for the CO_2 shows that the rise in absorption of the$_1$dissolved penetrant of condensable CO_2 gas overcomes the pressure effect and cause an increase in the free volume. The selectivities of CO_2/CH_4 and O_2/N_2 gas pairs increased with the increase of molecular weight of (2000Mw) of polyol in the polyurethane membranesas presented in fig. 9. The CH_4/N_2 selectivity drops down with pressure due to disruption of chain packing density and lower sorption of penetrants into excess free volume of polymer. Therefore, the CO_2/CH_4 selectivity increase with the rise in feed pressure. This is due to the plasticization effect of CO_2 that will increases chain mobility and gas diffusion of the polymer with pressure. At high-pressure carrier separation lowered because of the interaction of CO_2 gas$_{11}$with a polymer, hurries up the diffusivity of penetrants because of the swelling of the polymer matrix$_1$ (Scholes *et al*., 2012).

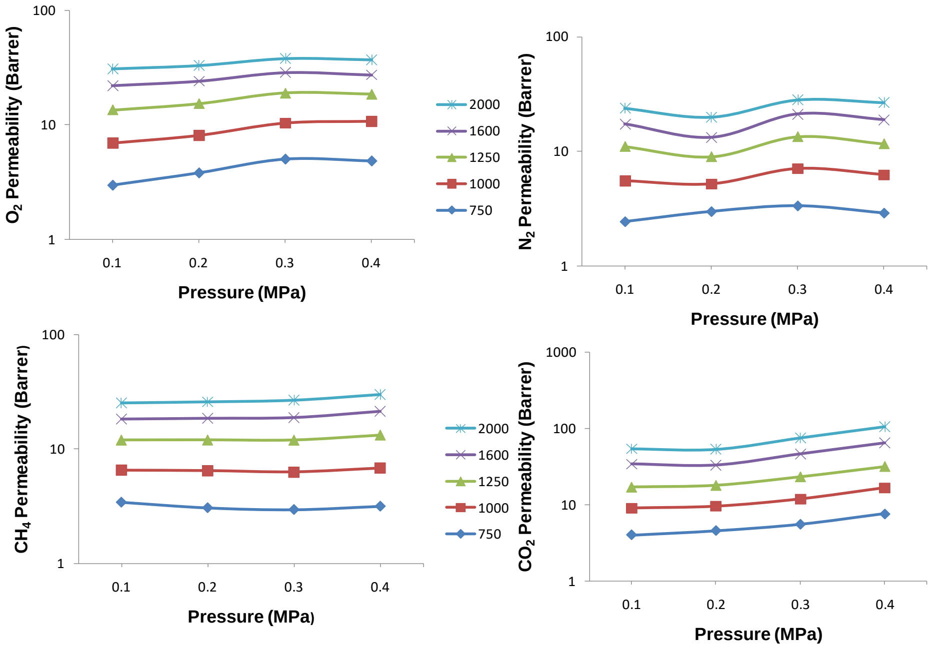

Fig. 7. Feed pressure effect on the permeability of IPDI based polyurethane membranes sample.

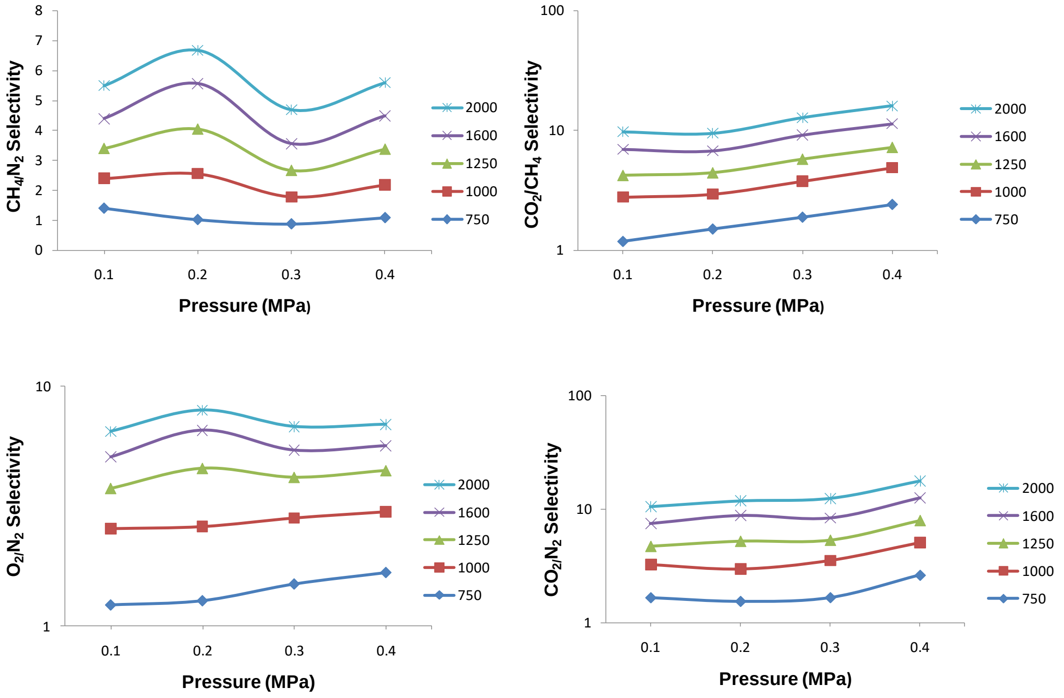

Fig. 8. Feed pressure effect on the selectivity of IPDI based diisocyante polyurethane membranes sample.

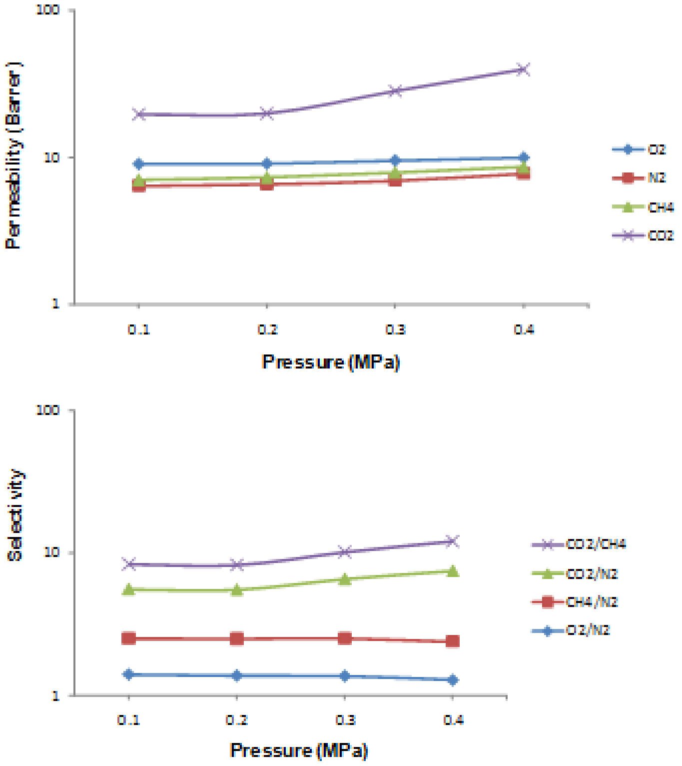

Fig. 9. Permeability and selectivity comparison in PUM15with 2000Mw of Polycaprolactone based membrane sample with respect to pressure change.

Hydrophilic membranes improved interactions among amino groups and CO_2 molecules. With an increase of pressure, the selectivity was enhanced and permeation flux decreased. The free volume has a stronger impact on the reduction of O_2/N_2 selectivity. The high molecular weight membrane showed the good selection for the gas pair CO_2/CH_4, which is related to CO_2 capture from flue gas for greenhouse gas emission control. The increase in selectivity is mainly due to the chain packing density while the decrease in selectivity is due to relative depression like structures that is induced by low viscosity (Jiang *et al.*, 2008). Relatively higher CO_2 solubility and selectivity for CO_2/CH_4 and CO_2/N_2 and were observed for the 2000 PU membranes in fig. 9.1

Conclusions

From the observed results, it can be concluded that the membrane prepared from high (2000Mw) polyols have high permeability and improve selectivity properties. The permeance of gases will increase with the rise of temperature ensuring in the reduction of CH_4/N_2 selectivity. But, the CO_2/CH_4, CO_2/N_2 gas mixture selectivity increased with the increase of high molecular weight polyol. The high molecular weight membrane is good for textile industry for the separation of CO_2 and N_2 oxide from boiler system because these membranes have high thermal stability and good mechanical strength. Polyether polar groups are essential to increase or facilitate interactions between acidic gases or condensable higher hydrocarbon molecules.

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