

Research note

Relationship Between the Microstructure and Gas Transport Properties of Polyurethane/Polycaprolactone Blends

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ABSTRACT

In this study, the relation between the permeation properties and structural characteristics of thermoplastic polyurethane based on polycaprolactone diol, TPU(PCL), and polycaprolactone (PCL) blends is investigated. For the purposes of this study, PU, PCL, and TPU/PCL blends containing 20 wt% and 40 wt% PCL were prepared via a solution blending method. The miscibility and good distribution of PCL in the soft segment of PU were represented by the reduced intensity of the band attributed to the NH band at 3400 cm⁻¹ in the Fourier transform infrared (FTIR) spectra. X-ray diffraction (XRD) results indicated that the amorphous structure of TPU changed to a crystalline one when PCL was added. These results were further confirmed by FTIR and differential scanning calorimetry (DSC) analyses. The permeability of CO₂, O₂, N₂, and CH₄ gases at different feed pressures ranging from 12 to 16 bar was determined. A reduction in gas permeability due to the increase in PCL content was observed in the blends. However, gas selectivity did not change with addition of PCL.

1. Introduction

Polymeric blends can be used as gas separation membranes to make gas transport management possible through morphological control of the material's cross-section, which mainly depends on blend components, phases, and interface characteristics [1-3]

The interactions and compatibility of blend components affect the transport properties of materials. Incompatible polymer blends show

microphase and macrophase separation. In these heterogeneous systems, the transport process depends not only on the composition, size, shape, and distribution of the constituent phases but also on the morphology of the samples [4,5]. So far, efforts have been made to induce changes in the separation properties of polyurethanes by blending them with other polymers [6]. The properties of segmented PUs are greatly influenced by the degree of micro-

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phase separation. PUs are particularly suitable for generating polymers with a wide variety of chemical natures and very different (partially crystalline, glassy amorphous, or elastomeric) structures [7,8].

Ajili *et al.* first studied the blend of polycaprolactone-diol-based polyurethane [TPU(PCL)] and polycaprolactone (PCL). They prepared the blend via the melt blending method and studied its rheological behavior to demonstrate its useful biomedical applications due to its biocompatibility and shape memory behavior [9-11]. In a previous work [12], this same blend had been prepared by solution blending and its rheological behavior examined. However, no published report is so far available on the influence of morphology on the transport properties of PU/PCL blends.

In the present study, an amorphous thermoplastic elastomeric polymer, PU, is mixed with PCL using a solution method. The PU used is based on polycaprolactone diol with no crystalline behavior because of the low molecular weight of its soft segment (PCL). It is the objective of the study to investigate the gas transport properties of PU/PCL blends and to correlate these properties with the chemical structure, composition, and morphology of the blend. Moreover, gas permeation is used as a useful technique to study the morphology and the interactions of the multi-component system. The permeability of oxygen, nitrogen, methane, and carbon dioxide gases through membranes of the blends with different PCL contents are tested and the effects of PCL content are investigated using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and Differential Scanning Calorimetry

(DSC).

2. Experimental

2.1. Materials

The polyesterpolyurethane, Laripur® LPR2102-85AE from Coim Co. (Italy), was used in this study. The hard segment is composed of 4,4'-methylenediphenyl diisocyanate (MDI) chain extended with 1,4-butanediol (BDO), while polycaprolactone (PCL) ($M_n=2000$ g/mol) was used as a soft segment. The weight percent of hard segment was 30 wt%. Polycaprolactone (PCL) was supplied by Aldrich Co. (Germany) with a M_n of 42,500 g/mol. Dimethylacetamide (DMAc) solvent used for membrane preparation was purchased from Merck Co. The CO₂, N₂ and O₂ (purity 99%) gases used for gas permeation tests were purchased from Roham Gas Co. (Iran) and CH₄ (purity 99.5%) was purchased from Air Products Co., USA.

2.2. Membrane preparation

The samples were prepared by a solution blending method. The polymers were dissolved in DMAc at 50°C (0.05 g/mL) and cast in Petri dishes at 60°C for 24 h. The films were further dried in a vacuum oven at the same temperature until a constant weight was achieved. Different blends were prepared with 20 and 40 wt% of PCL, hereafter called TPU-80 and TPU-60, respectively.

2.3. Gas permeation

The permeability of oxygen, nitrogen, methane and carbon dioxide was determined using constant pressures and at 25°C as described in refs [5,13,14]. Fig. 1 shows the schematic representation of the gas permeation equipment. The gas permeability

of membranes was determined using the following equation:

$$P = \frac{ql}{A(P_1 - P_2)} \quad (1)$$

Where P is permeability expressed in Barrer (1 Barrer = 10^{-10} cm³ (STP) cm/cm² s cmHg), q is flow rate of the permeate gas passing through the membrane (cm³/s), l is membrane thickness (cm), P_1 and P_2 are the absolute pressures of feed side and permeate side, respectively (cmHg) and A is the effective membrane area (cm²). The permselectivity α_A/α_B (the ratio of pair gas permeabilities) of membrane was calculated from pure gas permeation experiments.

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2)$$

2.4. Characterization

In order to investigate the functional groups of the prepared samples, PCL together with polyurethane containing various amount of PCL were analyzed by Fourier transform infrared (FTIR), Bio-Rad FTS7, spectrometer

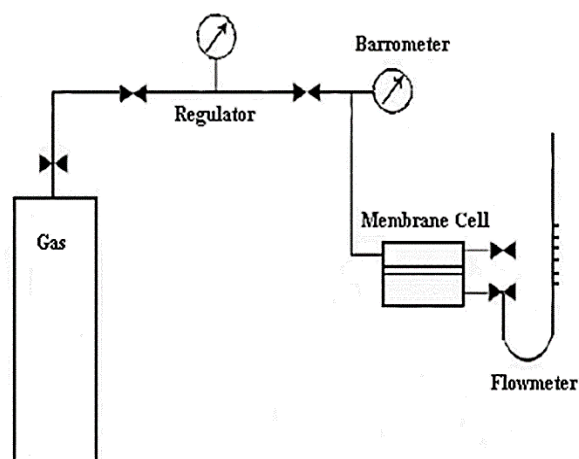


Figure 1. Schematic design of the gas permeation apparatus.

in the range of 500-4000 cm⁻¹. All spectra were recorded at room temperature. The films used in this study were sufficiently thin to obey the Beer Lambert law. To evaluate the results correctly the thickness of prepared samples was kept constant.

X-ray diffraction patterns were recorded in reflection by monitoring the diffraction angle 2θ from 10-40°C on a Philips PW/840 using nickel-filtered CuK α radiation ($\lambda=0.154$ nm) under a voltage of 40Kv and a current of 25mA. The scanning speed and the step size were 5 steps per min and 0.05, respectively.

The thermal behavior of polyurethanes was investigated by a differential scanning calorimeter, Mettler-Toledo DSC-822 (Switzerland) from 100-250°C at a heating rate of 10°C/min.

3. Results and discussion

3.1. Characterization

3.1.1. X-ray diffraction (XRD)

The morphological changes in the polymer matrix due to the presence of PCL (a crystalline polymer) were investigated using the wide angle X-ray diffraction (WAXD) technique. Fig. 5 shows a comparison of XRD patterns of PU and PCL with those of their blends containing 20 and 40 wt% PCL.

When a polymer contains numerous large crystalline regions, the peaks observed in the X-ray diffraction patterns of the polymer are usually sharp and the intensity is strong whereas broad halos may be due to either the amorphous structure, the presence of small crystalline structures, or the diffraction from large crystals [13,14]. Pure PCL shows an X-ray pattern with two strong crystalline peaks at

$2\theta=21.3$ and 23.7 attributed to the (110) and (200) planes in the PCL [15,16] resulting from its crystalline regions. In spite of containing PCL soft segments, polyurethane showed a broad peak, indicating that these segments in PU based on polycaprolactone would not be crystallized. This might be due to the low molecular weight of the PCL segments and the connection of the PCL soft segments to the hard segments which reduced PCL segment mobility and prevented PCL chains from organizing in crystalline regions. On the other hand, as also confirmed by the DSC results reported below, the broad halo might be due to the presence of small crystallites of the hard segments probably scattered in the polymer matrix that failed to be detected by XRD [13,14]. In the hard segment regions, the chains were immobilized in the crystal regions because of the high interaction and hydrogen bonding of urethane NH and carbonyl groups [17].

Thus, the results reveal that the crystalline regions were enhanced as the PCL content increased in polyurethane. Incorporation of PCL as a semi-crystalline polymer in polyurethane increased the crystalline regions in the blend membranes and PCL chains therefore formed crystalline structures due to their long order structure [13,14].

3.1.2. Fourier transform infrared (FTIR) spectroscopy

The results of FTIR analyses of polycaprolactone, polyurethane, and blends containing 20 and 40 wt% PCL are presented in Fig. 2. Clearly, the N-H bending of urethane, the C=O stretching, and the CH₂ signal of polycaprolactone appear at 3300 cm^{-1}

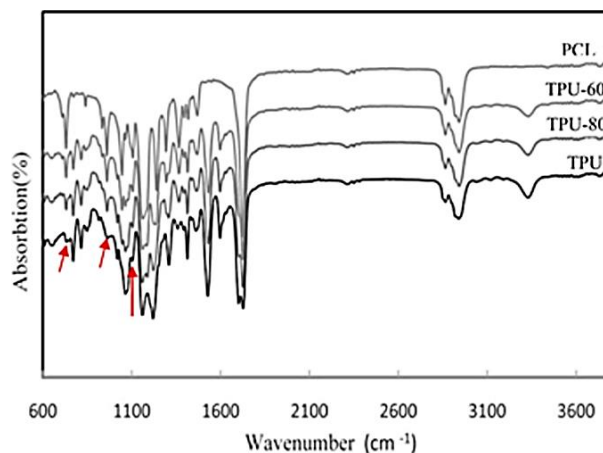


Figure 2. FTIR spectra for the prepared samples: TPU, TPU-80, TPU-60, and PCL.

, $1600\text{-}1730\text{ cm}^{-1}$, and about 2900 cm^{-1} , respectively. Moreover, hydrogen bonding is seen to occur between the O-(CO-) group from the soft segment and the -(CO-)NH group from the hard segment. Fig. 3 presents the associated N-H bending group in the hard segments of the samples in the range $3200\text{-}3400\text{ cm}^{-1}$. The decrease observed in peak intensity with PCL addition is due to the reduction of PU in the sample when PCL is added.

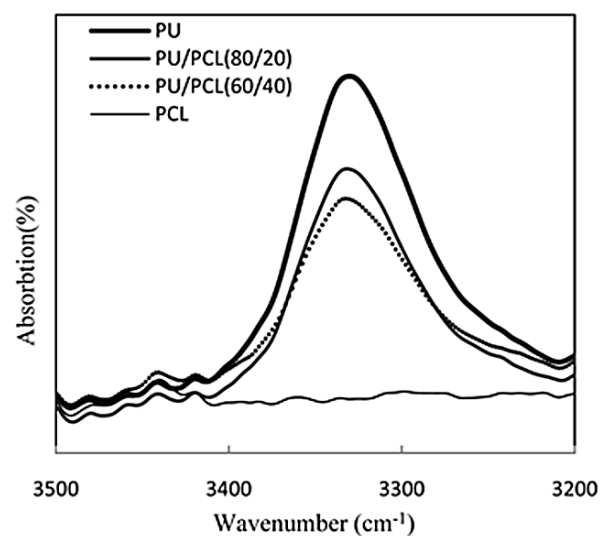


Figure 3. FTIR spectra in the range $3200\text{-}3500\text{ cm}^{-1}$.

The amount and variation of hydrogen bonding can be represented by the hydrogen bonding index which characterizes the effect of PCL on PU [6,18]. The index is expressed as the ratio of the associated absorbance (A_{NH}), NH band to CH_2 band as a base peak. Because the amount of TPU was variable in the blend, an additional normalization was applied to account for the TPU quantity in the hydrogen bonding index. As can be seen in Fig. 4, the results indicate that the value for the index decreased from 0.95 to 0.6 with increasing PCL content. Addition of PCL disrupts the hydrogen bonds between the hard and soft segments, yielding bonded NH groups in the hard segment domains [19] to give rise to a higher phase separation. Changes in this intensity suggest the miscibility and good distribution of PCL in the soft segment domains of TPU.

Upon blending with PCL, some of the absorption band intensities changed in the blends, which correspond to a crystalline band. As known, crystalline absorption peaks are those whose intensities change greatly

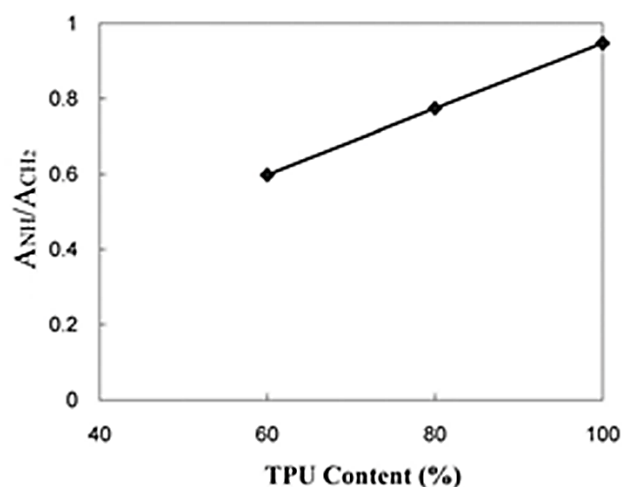


Figure 4. Hydrogen bonding index vs. TPU content.

when an amorphous polymer changes to a crystalline one. These effects occurred in the peaks at 1105, 965, and 730 cm^{-1} . Thus, addition of PCL to polyurethane gave rise to crystallinity in these blends [20]. These peaks are shown in Fig. 2.

3.1.3. Differential scanning calorimetry (DSC)

The thermal properties of PU, PCL, and their blends were investigated by differential scanning calorimetry. The DSC data in Table 1, also shown in Fig. 6, indicate that polyurethane does not show any melting point for the crystalline regions of its soft segments, rather it shows a transition in the temperature range of 150 to 170°C, which may refer to the melting point, T_g , or H-bond breaking of the hard segments. This indicates that the amount of phase mixing in polyurethane is high so that the crystallization of soft segments did not occur due to the high interaction of hard and soft segments. Formation of hard segment domains and its effect via hydrogen bonding to the soft segments prevents the soft segment

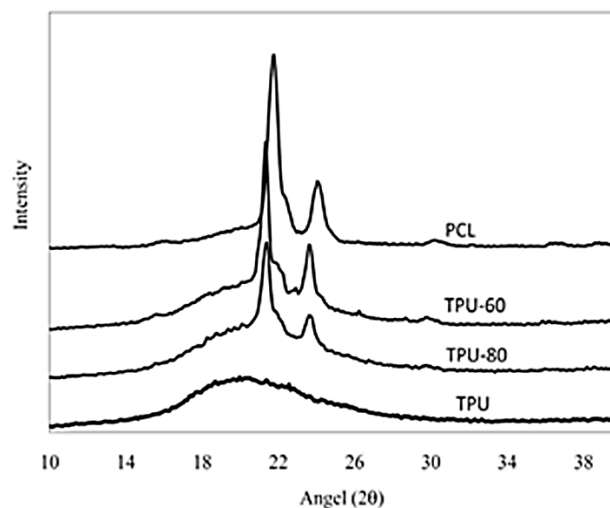


Figure 5. WAXD patterns obtained for pure TPU, PCL, and TPU containing 20 and 40 wt% PCL.

Table 1.
Thermal property of the prepared samples.

Code	TPU/PCL	T_{gs}^1	T_{ms}^2	T_{mh}^3	ΔH_{fs} (J/g soft segment)	ΔH_{fh} (J/g hard segment)
TPU	100/0	-37.96	-----	164.58	-----	32.44
TPU-80	80/20	-48.08	37.62	161.24	1.77	24.99
TPU-60	60/40	-56.06	45.59	155.44	29.94	10.4
PCL	0/100	-60.00	56.85	-----	81.65	-----

1) Glass transition temperature of soft segment

2) Melting temperature for soft segment

3) Melting temperature related to hard segment

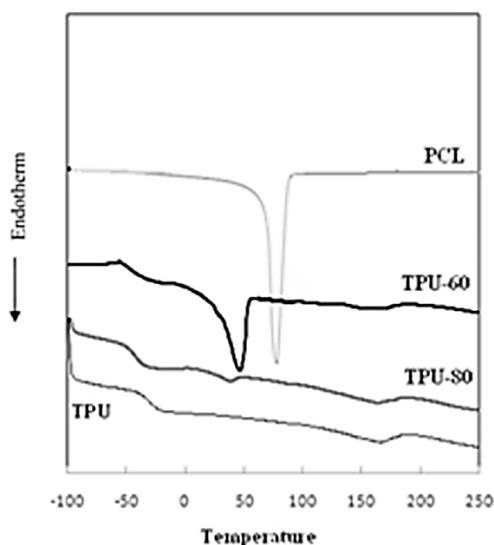


Figure 6. DSC thermograms for pure TPU, PCL, and TPU containing 20 and 40 wt% PCL.

chains from organizing in crystal lattices. The existence of a broad halo for pure PU in the XRD study and the small transition at high temperatures in the DSC diagrams might be attributed to the small hard segment crystalline regions [13,14]. As already mentioned, the hydrogen bonding of urethane NH and carbonyl groups led to high interactions in the hard segments. These interactions enhanced the capability of small hard segments to organize in the crystalline lattice [17].

Upon incorporation of PCL in TPU, the PCL melting peak appeared at a lower

temperature attributed to the smaller crystallites in PCL domains. This also confirms that addition of PCL led to the formation of PCL crystalline regions in PU/PCL blends.

Formation of a single T_g at low temperatures characterizes two polymers as a miscible blend. As reported in Table 1, the glass transition temperature of the samples decreased with increasing PCL content. The gradual decrease of T_g with the addition of PCL is due to the similarity of PCL to the PCL soft segments of PU. These results clearly indicate some degree of miscibility in the blend between PCL and PCL based PU [18,21], which may also be due to the increase in PCL domain size as a result of being less mixed in the PU hard segment.

3.2. Gas permeation

The effects of polycaprolactone (PCL) content on gas permeation of the TPU/PCL blends were studied. The Permeabilities of N_2 , O_2 , CH_4 , and CO_2 gases through the prepared membranes were determined at different feed pressures from 12 to 16 bar at room temperature ($25^\circ C$). The results are shown in Fig. 7 and summarized in Table 2. As

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expected, the permeability of CO₂ was much higher than those of the other gases while N₂ exhibited a slightly lower permeability than CH₄ and O₂ gases. As already stated elsewhere [22-24], these observations may be justified

by the higher diffusivity (D) and solubility (S) of CO₂ than those of the other gases. The kinetic diameter and condensability of gases influence their diffusion and solubility coefficients, respectively. Table 3 shows the

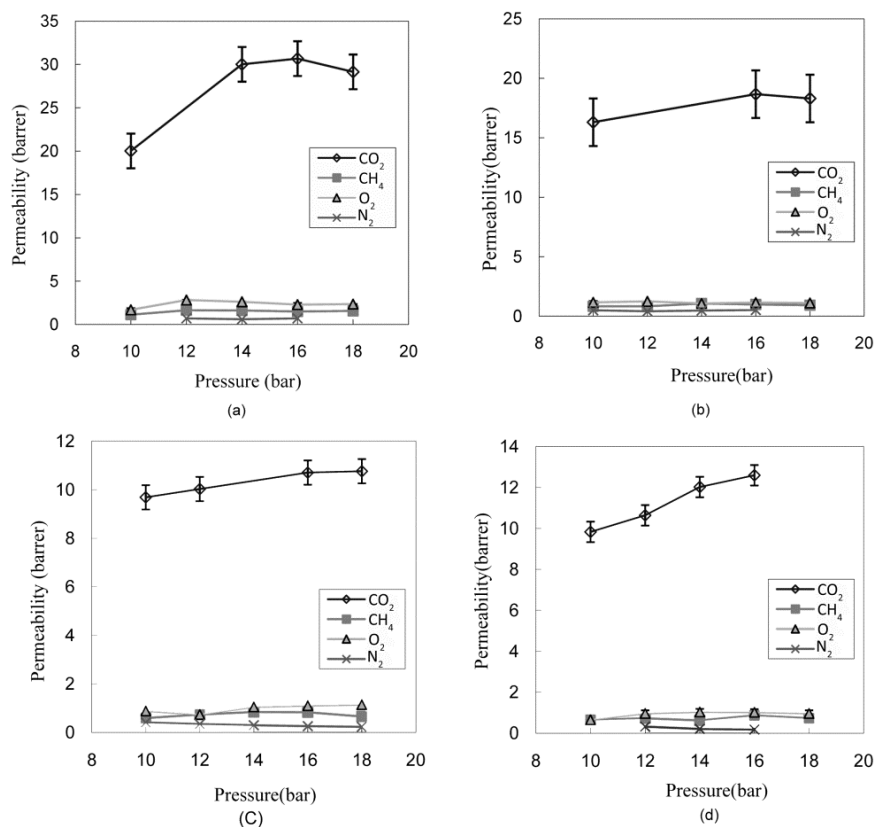


Figure 7. Gas permeability of TPU(a), TPU-80(b), TPU-60 (c), and PCL (d) vs. feed pressure of CO₂ (◆), CH₄ (■), O₂ (▲), N₂ (×) gases.

Table 2.

Gas permeability and permselectivity of the prepared samples at 12 bar pressure.

Polymer	Permeability				Permselectivity		
	O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
TPU	2.82	0.71	1.65	20.92	4.00	12.71	29.67
TPU-80	1.25	0.42	0.83	12.48	3.00	15.00	30.00
TPU-60	0.73	0.34	0.73	10.03	2.16	13.67	29.51
PCL	0.97	0.32	0.66	10.65	3.05	14.67	33.56

Table 3.

Condensability and kinetic diameter of studied gases.

Gas	Kinetic diameter (Å)	Condensability (K)
Carbon dioxide	3.3	195
Methane	3.8	149
Oxygen	3.46	107
Nitrogen	3.64	71

kinetic diameter and the condensability of the gases investigated. CO₂, having the lowest kinetic diameter and the highest condensability, exhibited the highest permeability. Moreover, the solubility of CO₂ increases with the number of polar and electronegative groups in the main chain of a polymer. In light of the well-known solution-diffusion mechanism of gas transport through polymeric membranes (P=DS), the permeability of gases is determined by their solubility and diffusivity. Thus, permeability increases with increasing solubility of gases in a polymer. Therefore, the presence of polar carbonyl groups in the main chain of TPU may be claimed as another important parameter involved in the permeability of CO₂. On the other hand, CO₂ exhibits a higher permeability than N₂ (Table 2) because of its higher condensability and in spite of the larger molecular size of CH₄ (Table 3). This indicates the domination of the solubility mechanism in the permeation of gases in PU and PU/PCL blend membranes.

Fig. 7 shows the effects of feed pressure on the permeability of TPU, TPU-80, TPU-60, and PCL. As shown, pressure had no significant effect on the permeability of O₂, N₂, and CH₄ gases. However, due to the high polarity, lowest size, and highest condensability of CO₂, the interaction of CO₂ with the polymer chains increased and led to a plasticizing effect on the polymer when its concentration increased in the membranes with increasing feed pressure. The higher plasticizing effects of CO₂ at higher pressures also led to its enhanced permeability with pressure [1,25].

PCL is a crystalline polymer of highly

ordered and amorphous chains with a high segmental motion at room temperature because of its low glass transition temperature. The crystalline regions are impermeable to gas transport in the membranes because of the packing of the chains in the crystal lattice [1,25]. This led to the low gas permeability of this polymer due to the high PCL crystallinity. On the other hand, TPU has soft and flexible segments based on the polycaprolactone-diol while PCL has a low molecular weight and, thereby, a low crystallinity because of the restricted ordering by the hard segment. Thus, PCL introduces flexible molecular chains that enhance the diffusion of gases through the blend membrane. As can be seen in Fig. 8, blending the crystalizable PCL with TPU reduced the gas permeability of TPU membranes, especially for CO₂ and the permeabilities of the gases investigated reduced with increasing PCL.

The permselectivity values of the prepared membranes for O₂/N₂, CO₂/CH₄, and CO₂/N₂ are reported in Table 2 for a feed pressure of 12 bar. Clearly, the selectivities of CO₂/N₂ and CO₂/CH₄ increased by adding PCL into the blend membrane. More interestingly, addition of polar PCL domains in the membranes increased the interaction between the CO₂ polar gas and the membrane; hence, the greater increase in the selectivity of this gas compared with other non-polar ones.

The effects of feed pressure on O₂/N₂, CO₂/CH₄, and CO₂/N₂ permselectivities of the TPU membrane samples are shown in Fig. 9. It can be clearly seen that the CO₂/N₂ permselectivity increased significantly when

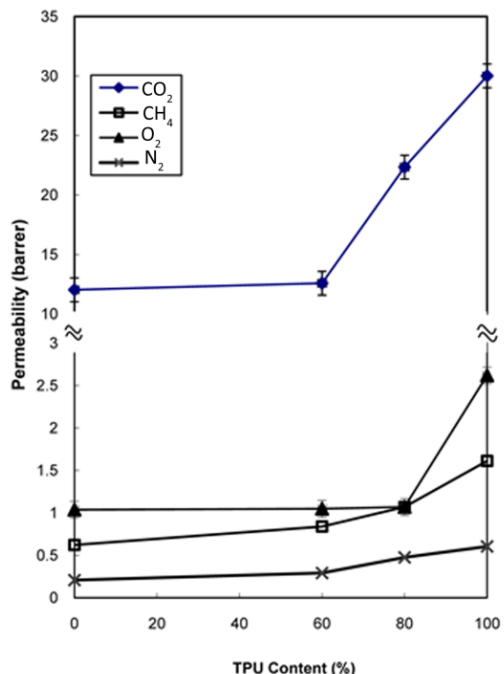


Figure 8. Gas permeability of CO₂ (♦), CH₄ (■), O₂ (▲), and N₂ (×) for the various samples prepared.

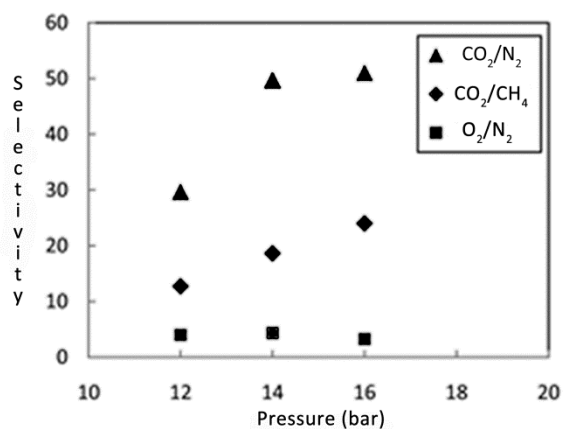


Figure 9. O₂/N₂ (▲), CO₂/CH₄ (♦), and CO₂/N₂ (■) permselectivities of TPU vs. feed pressure.

the feed pressure was increased from 12 to 14 bar followed by a further but slight increase at 16 bar. On the other hand, CO₂/CH₄ permselectivity increased while that of O₂/N₂ did not exhibit any significant changes with increasing feed pressure from 12 to 16 bar. The lower effect of pressure on the selectivity

of CO₂/CH₄ compared to that of CO₂/N₂ paired gases is due to the plasticizing effect of CH₄ at high pressures in the blends, while nitrogen is not capable of plasticizing the membranes. The lower CO₂/CH₄ selectivity compared to that of CO₂/N₂ could be attributed to the greater condensability of CH₄ than that of N₂ [1,21,25]. Finally, it should be noted that pressure had no significant effects on the permeability of either O₂ or N₂.

4. Conclusions

In this study, the effects of PCL content on the gas separation of TPU, PCL, and TPU/PCL blends were investigated. The prepared membranes were characterized using FTIR, DSC, and XRD techniques, all of which qualitatively confirmed an increase in the crystalline regions of the blend membranes as a result of adding PCL to TPU. As expected, the appearance of crystalline regions in the blends led to their reduced permeability with increasing PCL content.

Gas permeation of PU, PCL, and TPU/PCL blends with PCL contents of 20 and 40 wt% was also studied for CO₂, O₂, N₂, and CH₄ at feed pressures from 12 to 16 bar. It was observed that the permeability of all the gases decreased with increasing PCL content, with CO₂ exhibiting the greatest decrease despite its higher permeability compared to the other gases.

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