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A Novel Nano Structured Blend Membrane for Gas Separation

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Summary: This investigation involves the preparation and characterization of poly (urethane)/poly (vinyl acetate) (PU/PVAc) blend membranes. PU was synthesized by two step polymerization from toluene diisocyanate (TDI), poly (propylene glycol) (PPG) and 1, 4-butanediol (BDO).Fourier transform infrared (FTIR) spectroscopy was used to verify the chemical structure of the resulting polymer. Blend membranes with a thickness of 100 μ were prepared from the solution of PU and PVAc in chloroform by a solution-evaporation method. The amount of PVAc was varied among 10, 20 and 30 percent by weight of the membrane. Scanning Electron Microscopy (SEM) was used to investigate the morphology of the prepared membranes. The membrane containing 20% by weight of PVAc displayed a more homogenous dispersion of PVAc domains and was selected for gas permeation tests. For this purpose; oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2) and methane (CH_4) gases were used and the gas pressure was varied between 2, 4, 6, 8 and 10 bars. Comparison of the results with that of the pure PU membrane revealed that the blend membrane had a higher permeability to CO_2 and a lower permeability to the other gases and therefore had a higher value of CO_2/N_2 and CO_2/CH_4 ideal selectivity.

Keywords: blend membranes; gas permeation; poly (vinyl acetate); polyurethanes; selectivity

Introduction

Carbon dioxide separation by membranes is one the most interesting gas separation processes particularly for natural or landfill gas de-acidification and in food packaging.[1–3] Polyurethanes (PU) are typical examples of elastomers that have been reported to show good characteristics for CO_2 separation. However, the use of PU membranes for gas separation is limited by their low selectivity of separation gases.[4,5]

Compared to rubbery polymers, glassy ones offer enhanced diffusion selectivity due to the more restricted segmental motions. They are also commonly preferred as the selective layers in gas separation membranes concerning to their appropriate size and shape.[6]

Identification of new membrane materials and morphologies for industrial separations has become an important research objective in two recent decades.[7–9] Mixing different polymers to achieve a membrane material with superior properties to those of the initial constituting components has been used as an attractive method to achieve better separation characteristics in membrane materials. In most studies on blend membranes, rubbery polymers have been used as the matrix and alongside glassy polymers to combine high permeability of the former with high selectivity of the latter and achieve a better membrane material.[10]

Polyurethanes membranes have been poorly studied for gas separation.[11] Few

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researches on PU membranes have been conducted with the aim of finding a correlation between their structure and transport properties.[12–15] The main result of these works is however below the Robeson's upper bound limit for the pair of gases (O_2/N_2) and (CO_2/CH_4).[16,17] The gas permeation is considered to occur predominately through the soft phase while the hard segments acting as impermeable fillers or physical crosslinks in the rubbery soft segments.

Among the numerous factors affecting the permeability and selectivity of membranes, polymer polarity and thus the solubility factor are very important. For instance, Bhide and Stern have shown that for films of polar polymers, the permeability tends to be lower and the selectivity higher with respect to non-polar polymers.[18] PVAc as a glassy polymer seems to be one of the most interesting compounds for blending due to its polarity and CO_2 affinity among the other suggested polar structures. The interaction between the residual carbonyl groups and on the polar gases (such as CO_2) may lead to an increase of solubility associated with an increase of the Henry's contribution.[19,20]

In this study poly (urethane)/poly (vinyl acetate) (PU/PVAc) blend membranes with varying blend ratios were prepared in order to improve CO_2 selectivity of the PU membranes and membrane morphology as one of the most important parameters that affect the performance,[21] was investigated using SEM analysis.

Experimental Part

Materials

Polypropylene glycol (PPG, $\overline{M_n} = 2000$ mol g^{-1}, Fluka) and 1,4-butane diol (BDO, Merck) were dried under different conditions (in vacuum at 80 °C for 12 h and by 4 Å molecular sieves respectively). 2,4-tolylene diisocyanate (TDI, Merck), Polyvinyl acetate (PVAc, $\overline{M_n} = 40000$ mol g^{-1}, Aldrich) and chloroform (Merck) were used as received.

Synthesis of Polyurethane

Thermoplastic polyurethane was synthesized by two step polymerization using PPG and TDI. BDO was used as a chain extender. The molar ratio of the used components was as follows: PPG: TDI: BDO = 1:2:1. In order to make the prepolymer, PPG and TDI were mixed in a batch reactor at 70 °C for 2 h. For chain extension, BDO was added drop wise and reaction was carried out at the same temperature for another 2 h.

Preparation of PU-Based Blend Membranes

PU-based blend membranes were prepared by the solvent evaporation process. Solutions of PU and PVAc in chloroform were prepared separately (8 wt. % at 40 °C) with continuous stirring and then the two polymer solutions were mixed in the desired proportions: PU/PVAc = 100/0, 90/10, 80/20, 70/30 (wt. %). Obtained solutions were optically clear and showed neither visible separation into bilayers nor any precipitation on standing. The mixture solution was poured into a previously silanized glass Petri dish and left in a vacuum oven at room temperature and pressure for 24 h. The resulting membranes were dried in the vacuum oven for 2 days and thoroughly rinsed with deionized water. Thickness of the membranes was measured using a micrometer caliper and found to be around 100 μm. The average thickness of an individual membrane was calculated based on the results of five separate thickness measurements at different points on the membrane surface.

Charcterization

Fourier Transform Infrared (FTIR)

A BIO-RAD FTS-7 Fourier Transform Infrared spectrometer was used to characterize the synthesized PU using KBr method at room temperature. The scanning frequency range was 4000–400 cm^{-1}.

Scanning Electron Microscopy (SEM)

The surface and cross-section morphology of membranes were examined using Scanning Electron Microscopy (SEM). Cross-sections of membranes were obtained by fracturing in liquid nitrogen and then all the samples were coated with gold/palladium and observed with a Philips XL30 (Philips, The Netherlands) scanning electron microscope.

Measurement of Gas Permeability

O_2, N_2, CO_2 and CH_4 permeability coefficients for the membranes were determined using the constant pressure or variable volume method which has been incorporated into an ASTM standard.[22] The feed side pressure of the gases ranged from 2 to 10 bars. The permeate side was maintained at atmospheric pressure. The gas permeability was determined from the following equation:

$$P = \frac{Q \cdot L}{(p_1 - p_2) \cdot A \cdot t} \tag{1}$$

where P is the gas permeability expressed in Barrer units ($1 \text{Barrer} = 10^{-10}$ cm^3 (STP) $cm/cm^2 \cdot s \cdot cmHg$), Q is the permeation volume of gas (cm^3 (STP)) in time t (s), L is the membrane thickness (cm), p_1 and p_2 are the pressures at both sides of the membrane (Cm-Hg) and A is the effective membrane area (cm^2).The ideal selectivity of the membrane was calculated from single gas permeations as follows:

$$\alpha(O_2/N_2) = P(O_2)/P(N_2) \tag{2}$$

$$\alpha(CO_2/N_2) = P(CO_2)/P(N_2) \tag{3}$$

$$\alpha(CO_2/CH_4) = P(CO_2)/P(CH_4) \tag{4}$$

Results and Discussion

Fourier-Transform Infrared Spectra (FTIR) of PU

The FTIR spectrum of the PU samples is depicted in Figure 1. The N–H stretching vibration of urethane occurs approximately at 3313 cm^{-1} and the stretching vibration of free carbonyl groups around 1730 cm^{-1} while carbonyl group involved in hydrogen bonding is known to absorb at about 1700 cm^{-1}. In polyether polyurethane copolymers, the N–H groups form hydrogen bonds with the C=O groups of the urethane linkage as well as the oxygen atoms of the ether groups.[23,24]

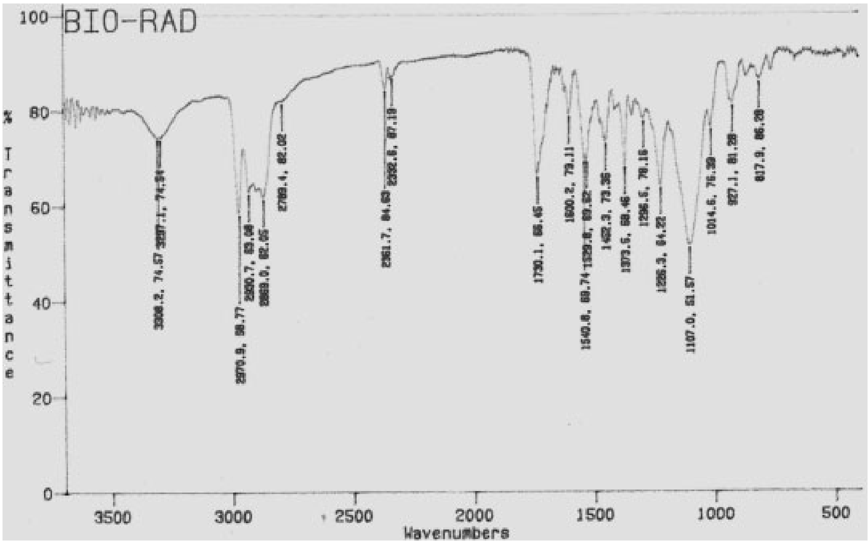

Figure 1.
FTIR spectrum of the synthesized PU.

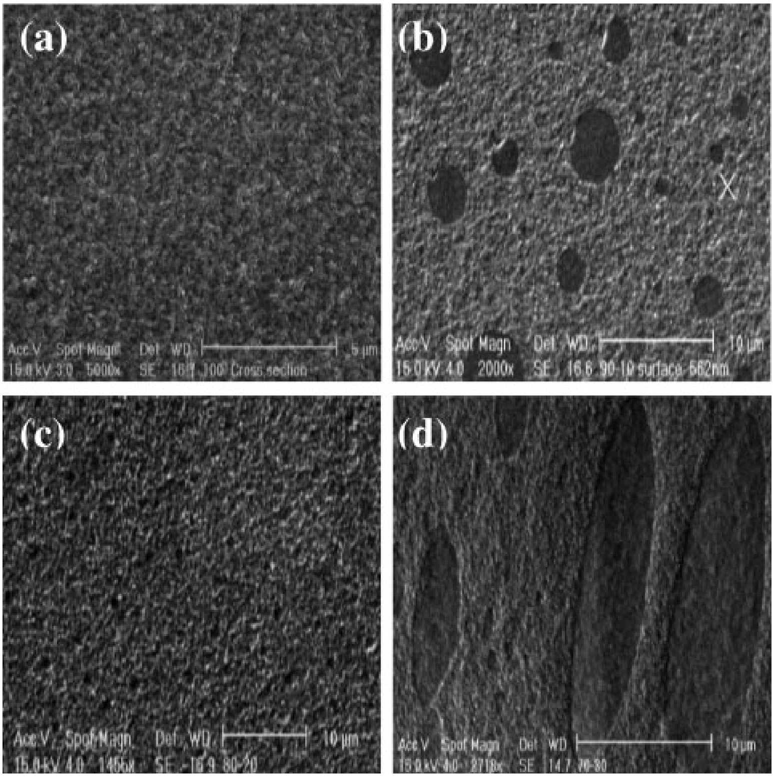

Figure 2.
SEM photographs of the cross sections of PU/PVAc blended membranes with different PVAc weight ratios: (a) PU/PVAc = 100/0 (wt/wt); (b) PU/PVAc = 90/10; (c) PU/PVAc = 80/20; (d) PU/PVAc = 70/30.

The Morphologies of PU/PVAc Blend Membranes

The SEM micrographs of the PU/PVAc blend membranes are presented in Figure 2. As can be seen, PVAc was dispersed in PU according to the mode of micro phase separation. The shape of the dispersed PVAc phase in PU changed from spherical in blends containing 10 and 20 wt.% of PVAc to ellipsoidal domains in blends containing 30 wt.% of PVAc. In 90/10 (PU/PVAc wt. %) blend membranes, the average domain size of the dispersed phase, was about 1–10 μm (Figure 2-b). In 80/20 (PU/PVAc wt. %) samples, PVAc was dispersed uniformly in the PU continuous phase and displayed a certain level of miscibility which can be inferred from the decrease in the domain size of the dispersed phase[25] to about 0.1–1 μm (Figure 2-c). It is clear from the figure that the PU component was present as the continuous phase in the blend membrane. The morphology of heterogeneous polymer blends depends on the blend composition, viscosity of the individual components and processing history. Danesi and Porter reported that for the same processing history the composition ratio and the melting viscosity differences for the components determine the morphology.[26]

Results of this work revealed that the membrane with 20 wt. % PVAc had a better mechanical stability under permeation tests. This, along with even dispersion of PVAc domains and their comparatively narrow size distribution was the reason for choosing PU/PVAc (80/20) samples for further analysis.

Table 1.
Permeation properties of PU membrane.

Pressure (Bar)	P[a] (O_2)	P[a] (N_2)	P[a] (CO_2)	P[a] (CH_4)	α[b] (O_2/N_2)	α[b] (CO_2/CH_4)	α[b] (CO_2/N_2)
2	3.71	0.88	25.15	0.91	4.22	27.63	28.55
4	3.35	0.75	24.64	0.85	4.46	28.97	32.85
6	3.08	0.63	23.51	0.74	4.88	31.77	37.31
8	3.05	0.61	23.11	0.68	5.00	33.98	37.88
10	3.11	0.60	22.98	0.64	5.19	35.91	38.31

[a] Permeability (1Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg).
[b] Selectivity.

Table 2.
Permeation properties of PU/PVAc (80/20) blend membrane.

Pressure (Bar)	P[a] (O_2)	P[a] (N_2)	P[a] (CO_2)	P[a] (CH_4)	α[b] (O_2/N_2)	α[b] (CO_2/CH_4)	α[b] (CO_2/N_2)
2	2.71	0.55	26.54	0.55	4.92	48.25	48.25
4	2.48	0.52	27.31	0.65	4.76	42.01	52.51
6	2.21	0.51	26.11	0.63	4.33	41.45	51.19
8	2.11	0.48	25.20	0.61	4.40	41.31	52.51
10	2.25	0.53	26.87	0.65	4.24	41.33	50.69

[a] Permeability (1Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg).
[b] Selectivity.

Single Gas Permeation Properties of Membranes

The O_2, N_2, CO_2 and CH_4 permselective properties of the PU and PU/PVAc (80/20) membranes are listed in Table 1 and 2. Gas permeation through a membrane can be interpreted as a solution–diffusion process that can be described in terms of solubility and diffusivity for individual polymer and gas.[27] O_2, N_2 and CH_4 permeability of PU/PVAc blend membranes decreased by adding PVAc to PU membrane. This can be attributed to the fact that PVAc is a glassy polymer at room temperature and has less permeability compared to PU and this causes a decrease in chain mobility and diffusivity of the blend membrane. The interaction between the residual carbonyl groups and on the polar gases (such as CO_2) may lead to an increase of solubility associated with an increase of the Henry's contribution.[19,20,28] The high quadrupolar moment of CO_2 allows it to interact with the polar groups in the polymer blend matrix.[29] Selectivity of various gases is listed in Table 2. $\alpha(CO_2/CH_4)$ and $\alpha(CO_2/N_2)$ increase with increasing the PVAc component. The reason might be due to the increased solubility selectivity. As the content of carbonyl group in membrane increases, the interphase and the domains available to absorb polar gases increase.[30]

Here, $\alpha(CO_2/CH_4)$ and $\alpha(CO_2/N_2)$ increase by addition of 20%.wt of PVAc, resulting mainly from the increase of solubility selectivity, while $\alpha(O_2/N_2)$ does not change much because solubility selectivity of O_2/N_2 is almost the same[30,31].

Conclusion

Polyurethane (PU)-based blend membranes were prepared by the solvent evaporation process. PVAc has been chosen as a blend component for improving carbon dioxide selectivity of PU membrane. The gas separation properties of PU-based blend membranes have been studied. The morphologies of PU-based blend membranes were investigated by SEM. SEM micrographs showed that the membranes are immiscible polymer blends.

The permeability of O_2, N_2 and CH_4 decreased by addition of 20%.wt PVAc but the permeability of CO_2 increased. Therefore, CO_2/N_2 and CO_2/CH_4 selectivity of PU-based blend membranes were improved. It was found that the phase morphology of PU-based blend membranes could significantly influence the permeation properties of the membranes.

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