

Synthesis of polyimide membrane for the separation of CO₂/CH₄ gases

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Abstract

Separation of CO₂/CH₄ is one of the most important separations in oil and gas industries. Polyimide membranes are remarkable material for this purpose. Robson's curve considers our claim about polyimide. One of the famous commercial polyimide membranes is Kapton. The structure of Kapton comprised from pyromellitic dianhydride (PMDA) and 4,4'-Oxydianiline (ODA). The permeability of Kapton is low so it's necessary to reclaim structure to promote their properties. In this study we tried to enhance the gas permeability in this polymer by adding the aliphatic diamine to the polymer structure. The copolyimide synthesized base on PMDA as anhydride and also ODA and 4,9-dioxo-1,12-dodecane diamine as diamines. Polymer synthesis was performed via thermal imidization based on two-step procedure. The physical properties of the copolyimide were characterized by FT-IR and XRD analyses. The gas separation studies showed higher permeation of gases at the aliphatic based polyimides in comparison to the fully aromatic ones. Also the permselectivity of gases has not changed significantly. The order of the increment in gas permeation of gases was in the reverse order of the size of the gas molecules.

Keywords: Polyimide, gas separation membrane, CO₂/CH₄ separation

Introduction

Over the past decades, investigation on polymer membranes for gas separation has focused on aromatic, glassy polymers, and particularly on rigid, high glass transition temperature (T_g) polymers, such as polyimides [1,2]. Aromatic polyimides have achieved growing importance as high performance materials, thanks to their excellent balance of mechanical and thermal properties; however, despite their undeniable favourable characteristics they did not deserve special attention as membrane-forming materials until the boost of thermoplastic and soluble polyimides, which took place in the eighties of the last century [3,4]. Regarding gas permeability, penetration of small molecules is severely restricted through polymer matrixes with strong interchain attraction forces and high degree of molecular packing, as it is the case of wholly aromatic classical polyimides. This is especially true for commercial polyimides as Kapton® and Upilex®. The permeability of these materials to gases is rather low in comparison with other glassy polymers such as spolycarbonates or polysulfones [5,6].

Experimental

1. Material

The dianhydride monomer used in this study was pyromellitic dianhydride (PMDA) which purchased from Merck (GERMANY). The aliphatic diamine monomer used was 4,9-dioxo-1,12-dodecane diamine and aromatic diamine monomer used was 4,4'-Oxydianiline (ODA) which both obtained from Merck (GERMANY). Also dimethylacetamide (DMAc) as solvent was obtained from Merck (GERMANY).

2. Polymer synthesis

For synthesis random polyimide, into a three-necked flask ODA and aliphatic diamine dissolved at DMAc then all of the anhydride added to mixture until poly (amic acid) (PAA) synthesis. Finally, Thermal imidization carried out for convert polyamic acid to polyimide. The PAA solution casted on a glass plate and left at 80°C over night. Film was imidized by sequential heating at 100, 125, 150, 175, and 200 °C for each 1 hr, respectively. Then film heated for 30 min at 220 °C. Structure of polyimide show at Fig.1. Also PMDA-ODA (Kapton) was synthesis in our laboratory.

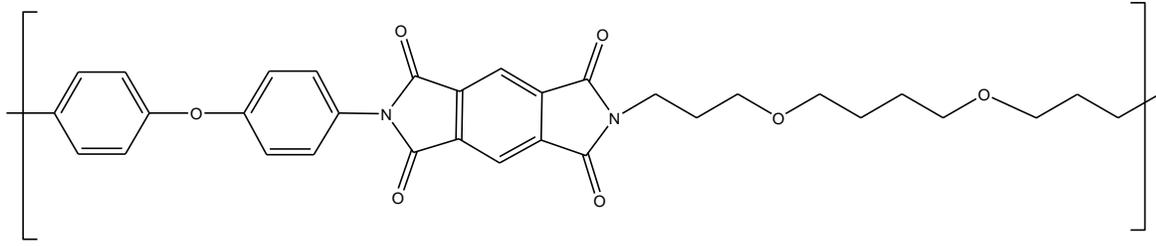


Fig.1- polyimide structure

Results and Discussion

1. FTIR spectra

The FTIR analysis of poly (amic acid) showed wide peak at around 3200-3700 cm^{-1} that determined PAA synthesis. Fig.2 shows FTIR spectra of PAA.

2. X- ray diffraction

The analyses of X-ray diffraction in a range of 2θ between 0° and 60° were carried out using a Rigaku model D-Max III C device, lamp of CuK α and filter of Nickel. The d-spacings (dsp) of each synthesized membrane were determined by Bragg's equation (Eq. (1)). Figure 3 show X-ray of polyimide.

$$n\lambda = 2d\sin \theta \quad \text{Eq.(1)}$$

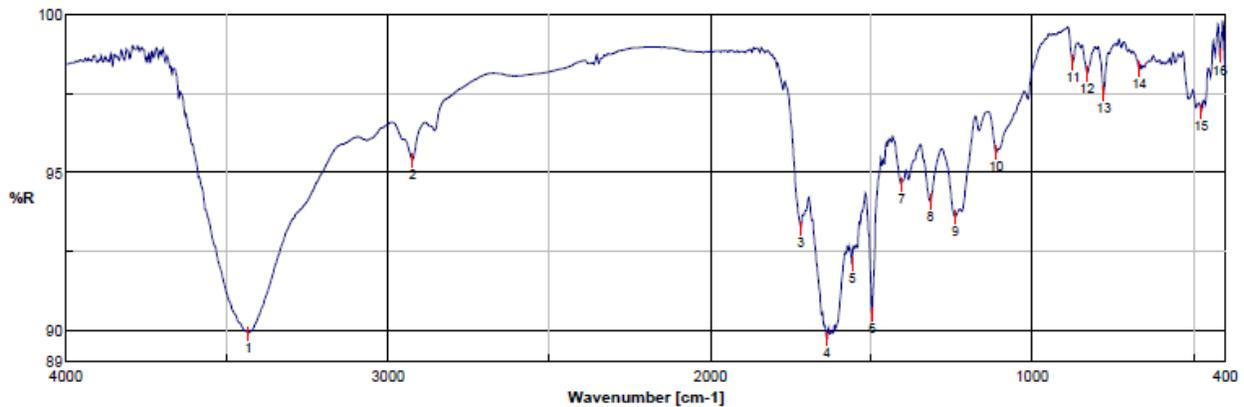


Fig.2- FTIR spectra of PMDA-ODA-4,9 poly(amic acid)

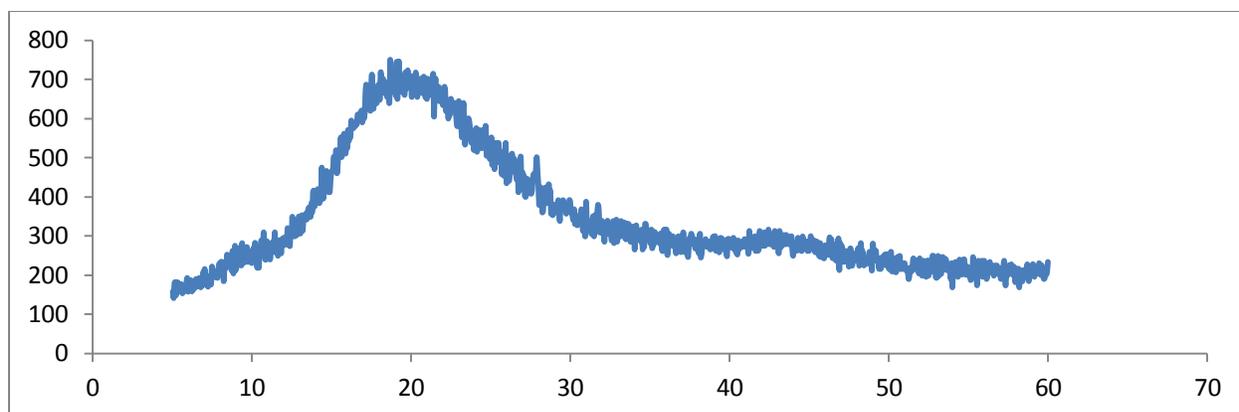


Fig.3 X-ray diffraction of PMDA-ODA-4,9 polyimide

3. Gas separation properties

Gas permeability of synthesized membranes at $T = 35\text{ }^{\circ}\text{C}$ and $P = 10\text{ atm}$ was measured. The permeation of polymeric dense membrane by a penetrant gas is generally considered to be a solution-diffusion process. According to this mechanism, gas permeation is a complex process that involves first, the sorption of the penetrant in the polymeric material, followed by a diffusion of gas molecule across the membrane matrix due to a concentration gradient.

The permeability coefficients are summarized in Table1. The results show an increase on gas permeability values of the copolyimide membrane compared with kapton. The main factor which affects the gas permeation rate is the chain packaging. In PMDA-ODA-4,9 membrane, the packaging decreases with enter aliphatic diamine, which leads to both higher fractional free volume (FFV) and gas permeation rate. The kinetic diameter, which corresponds more closely to the minimum diameter of the molecule, will have a strong effect on the penetrant mobility. The smaller the penetrant kinetic diameter, the higher should be the penetrant mobility through the polymer gaps should be, to reach a new site. The results show an adequate correlation between the permeation coefficients $P_{\text{CO}_2} > P_{\text{O}_2} > P_{\text{N}_2} > P_{\text{CH}_4}$ and their kinetic diameters $\sigma_{\text{KCO}_2} < \sigma_{\text{KO}_2} < \sigma_{\text{KN}_2} < \sigma_{\text{KCH}_4}$.

Table 2 compares the apparent diffusion coefficients of various gases in these films and shows their overall magnitude following the same order as that of permeability: PMDA-ODA-4,9 > kapton. The apparent diffusion coefficient for each individual gas obeys the order: CH_4 (kinetic diameter: $3.80\text{ }^{\circ}\text{A}$) < N_2 ($3.64\text{ }^{\circ}\text{A}$) < CO_2 ($3.30\text{ }^{\circ}\text{A}$) < O_2 ($3.46\text{ }^{\circ}\text{A}$). The increasing order corresponds well with the increase of gas kinetic diameter except for CO_2 . Clearly the temporary gaps created by thermal motion of polymeric chains control the diffusion process, but the diffusion rate is strongly dependent on gas molecule diameter. For the CO_2 gas, it may arise from the possibility of different orientations of its anisometric molecule.

Table1. Permeability coefficients and permselectivities at $P = 10\text{ bar}$ and $T = 35\text{ }^{\circ}\text{C}$

Structure	permeability coefficient (barrer) ^a		permselectivity
	CH_4	CO_2	
PMDA-ODA-4,9	0.04	1.262	CO_2/CH_4 31.55
Kapton	0.026	0.866	33.3

^a 1 Barrer = $1 \times 10^{-10}\text{ cm}^3(\text{STP})/\text{cm}^2\text{ s cmHg}$

Table2. Diffusion coefficient and selectivity at P = 10 bar and T = 35 °C

Structure	diffusion coefficient (*10 ¹⁰)		selectivity
	CH ₄	CO ₂	CO ₂ /CH ₄
PMDA-ODA-4,9	12.15	50.31	4.14
Kapton	6.59	32.86	4.96

Conclusion

The gas separation studies showed higher permeation of gases at the aliphatic based polyimides in comparison to the fully aromatic ones. Also the permselectivity of gases has not changed significantly. The order of the increment in gas permeation of gases was in the reverse order of the size of the gas molecules. The main factor which affects the gas permeation rate is the chain packaging. In PMDA-ODA-4,9 membrane, the packaging decreases with enter aliphatic diamine, which leads to both higher fractional free volume (FFV) and gas permeation rate.

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