

Membranes of Polyurethanes Containing Crystalline Soft Segments: Oxygen Permeability and Morphology

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In order to look for polymeric materials applicable to the oxygen electrode membranes of biosensors, polyurethanes (PUs) were synthesized from poly(butylene succinate) diol (M_n 1150), poly(ethylene glycol) (M_n 200), and 4,4'-methylenebis(cyclohexyl isocyanate). The PUs (M_n 15000-100000) underwent the crystallization and melting transitions in the temperature range of 20-30 °C and 90-110 °C, respectively. The oxygen permeability for the PU membranes prepared by the solution casting method could not be measured since oxygen simply leaked through the membranes with an audible noise. However, when the PUs were blended with carboxylated poly(vinyl chloride) (CPVC), the permeability could be measured. The oxygen permeability coefficient (P_{O_2}) of the PU/CPVC (96/4) membranes (6.4 Barrer) was high enough for the application as the electrode membranes. The P_{O_2} decreased dramatically when the CPVC content increased from 4 to 5 wt%, but decreased very slowly and approached to that of CPVC (~0.26 Barrer) when the CPVC content increased further. The scanning electron micrographs of the membranes revealed that the PU membranes were composed of large crystal grains with many pores, but the size of the PU crystal grains and pores decreased progressively with increasing the CPVC content.

Keywords : Membranes, PU, CPVC, PEG, PBS, Oxygen permeability.

Introduction

Three different layers such as a gas-permeable membrane, an enzyme-immobilized layer, and a dialysis membrane are usually employed for construction of an enzyme sensor based upon the Clark-type oxygen sensor.¹⁻⁴ If a gas-permeable and enzyme-immobilized membrane can substitute for the first two layers, it may give some advantages such as easier fabrication, rapid response, and higher sensitivity.^{5,6} Immobilization methods of enzymes may include adsorption, microencapsulation, entrapment, cross-linking, and covalent bonding.⁷ In general, the lifetime of the biosensor is greatly enhanced by proper immobilization, and the covalent bonding is most effective among the immobilization methods.⁸

Various types of polymers, for example, Teflon, polypropylene, polystyrene, polysulfone, and polyethylene, have been employed in preparing the oxygen electrode membranes. Among these polymers, Teflon is the most frequently used since it has less shortcomings than the other polymers.^{9,10} However, enzymes cannot be covalently immobilized on the membranes of Teflon or its derivatives without chemical modifications which seem to be complicated.⁶

A polyurethane (PU) was synthesized from polycaprolactone diol and 4,4'-methylenebis(phenyl isocyanate) in the presence of 2,2-bis(hydroxymethyl)propionic acid as a chain extender in this laboratory.¹¹ The PU did not form a free-standing film because of its high elasticity and cohesion. The PU membranes could be prepared when the PU was blended

with at least 20 wt% carboxylated poly(vinyl chloride) (CPVC), but their oxygen permeability was not satisfactory for the use as an oxygen electrode membrane. Furthermore, the melting transition of the polymer occurred at about 25 °C, which is too low for the application.

Recently, the hydrolytically degradable PUs were synthesized from poly(butylene succinate) diol (PBS), poly(ethylene glycol) (PEG), and 4,4'-methylenebis(cyclohexyl isocyanate) (H_{12} MDI).^{12,13} Some of the PUs showed the relatively high melting temperatures, good film-forming properties and tensile strengths. Thin films of the PUs were not cohesive. This result led us to study the gas permeability of the membranes prepared from the type of PUs for an application in biosensors. For the synthesis of the PUs, PEG with M_n 200 was chosen among other PEGs of higher M_n s in order to minimize the water absorption by the resulting PUs.¹⁴ This paper describes the oxygen permeability and morphology of their membranes.

Experimental Section

Materials. Succinic acid, 1,4-butanediol, CPVC (M_w 220,000, carboxyl content 1.8 wt%), titanium(IV) isopropoxide (99.999%), and PEG (M_n 200) were purchased from Aldrich. Succinic acid, 1,4-butanediol, and PEG were dried in an oven at 65 °C for 1 day before their use in polymerization. H_{12} MDI, N,N-dimethylformamide (DMF), chloroform, and dibutyltin dilaurate (T-12) were obtained from Bayer, Oriental Chemical Industries, and Air Product, respectively.

Instruments. The chemical structures of PUs were con-

firmed by analyzing the spectra obtained from a JEOL-JMN 400 (400 MHz) ^1H NMR spectrometer and a JASCO (300E) FT-IR spectrophotometer. The thermal transitions of PUs were observed using a DuPont 2910 differential scanning calorimeter. The average molecular weights of PUs were estimated with gel permeation chromatography (PL GPC 110) using polystyrene solutions in chloroform as the calibration standard. The morphology of the PU membranes was studied with scanning electron microscopy (SEM, Hitachi X-650) after the samples were washed with methanol, dried in a vacuum oven at 70 °C and 40 psi for 24 h, and coated with Pt-Pd. A wide angle X-ray diffraction was studied with a X-ray diffractometer (Rigaku Co., Cu target) at 40 kV and 20 mA.

Synthesis. A mixture of 1,4-butanediol and succinic acid in a 1.2 : 1 molar ratio was reacted at 180 °C for 3 h under a nitrogen atmosphere. The mixture was further heated in the presence of titanium(IV) isopropoxide (0.02 wt%) at 210–220 °C for 5 h under a nitrogen flow for deglycol reaction. The number-average molecular weight (M_n) of PBS was calculated to be about 1150, using the hydroxy and acid values which were determined on the basis of ASTM D 1957-63 and ASTM D 1980-67, respectively.

The PBS was dried at 70 °C and 50 torr for 24 h, and melt at 130 °C in a reaction flask, followed by the addition of an appropriate amount of PEG. The H_{12} MDI was added at 120 °C. The mixture was heated in the presence of T-12 (0.1 wt%) until the isocyanate peak in the FR-IR spectrum disappeared. The molar ratios of PBS/PEG/ H_{12} MDI were 2/1/2, 1.5/1.5/2, and 1/2/2, and the corresponding PUs were designated as PU-1, PU-2, and PU-3, respectively.

Preparation of Polymeric Membranes. The polymer solutions in DMF (4 wt%) were cast on the flat glass plates. DMF was evaporated slowly at room temperature for 2 h and the membranes were completely dried at 70 °C for 24 h, and further dried in a vacuum oven at 70 °C and 50 psi for 24 h. The PUs readily formed the membranes (~40–60 μm in thickness). The pure PU membranes were also prepared using a hot press at 160 °C.

Measurement of Gas Permeability Coefficient. The permeability of oxygen in the PU membranes was determined using the same apparatus as reported previously.¹¹ The oxygen permeability coefficient (P_{O_2}) was calculated employing the equation derived from the Fick's first law, and expressed in Barrer, corresponding to $10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm/cm}^2 \cdot \text{sec} \cdot \text{cmHg}$.

Results and Discussion

The FT-IR spectrum of PU-1 showed that the NCO peak (~2260 cm^{-1}) of H_{12} MDI disappeared completely, but the peaks for NH and C=O groups of the urethane bonds appeared (~3328 and 1730 cm^{-1}). The observation indicates that the polymerization reaction was almost completed. The molar feed ratio of PBS, PEG, and H_{12} MDI for PU-1 was 2 : 1 : 2. The NMR resonance peaks in the range of 4.2–4.0, 3.8–3.6, 2.7–2.5, and 2.0–0.8 ppm were assigned as shown in

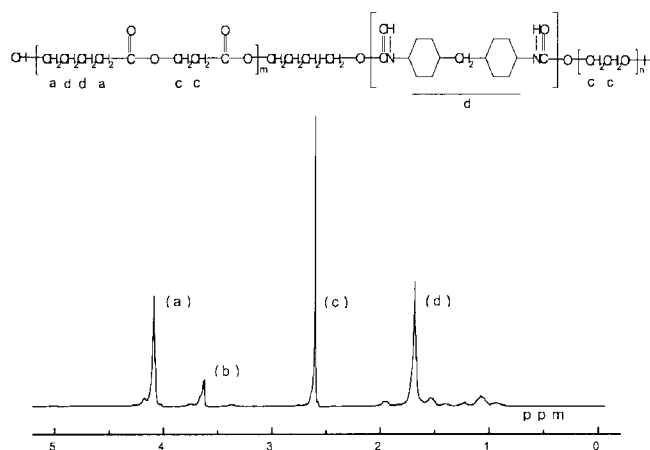


Figure 1. ^1H -NMR spectrum of PU-1 in CDCl_3 .

Figure 1. The corresponding peak integral ratio was predicted to be 3.5 : 1.0 : 3.0 : 6.4, and the actual integral ratio was 3.6 : 1.0 : 3.1 : 6.9. This result indicates that the molar component ratio of PU-1 is in good agreement with the feed ratio of the comonomers within the experimental error. The number- and weight-average molecular weights (M_n/M_w) of PU-1, PU-2, and PU-3 were 51000/113000, 100000/228000, and 15000/38000, respectively.

The glass transitions of PU-1, PU-2, and PU-3 occur below -30 °C (Figure 2). The T_m of PU-1, PU-2, and PU-3 at the maximum heat flow are in the range of 90–110 °C, which are somewhat lower than that of PBS (~120 °C). The PUs are crystallized in the temperature range of 20–30 °C, while PBS begins to be crystallized at the temperature just below the T_m of PBS. This result suggests that the melting transitions of the PUs arise from the PBS soft segments and can be affected by the polymer chains.^{12,13,15} Thus the PU membranes were dried at 70 °C and cooled to room temperature

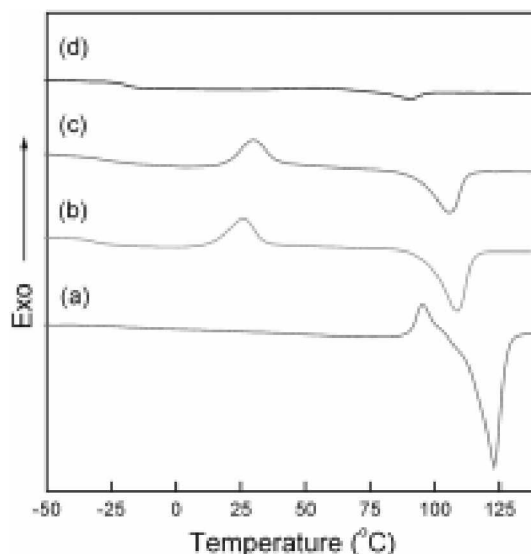


Figure 2. DSC thermograms of (a) PBS, (b) PU-1, (c) PU-2, and (d) PU-3. All of the thermograms were obtained from the second heating scans and the scan rate was 10 °C/min.

in order to maintain the physical state of the membranes in the temperature range employed for characterizations.

The oxygen permeability for the PU membranes prepared from chloroform or DMF solutions could not be measured since oxygen leaked through them from one side to the other with an audible noise as soon as a pressure of oxygen was applied. This suggests that the membranes may be highly porous. The PUs were blended with CPVC in the DMF in order to obtain a measurable oxygen permeability from the resulting membranes. The CPVC was chosen as a blend material since it contains -COOH groups which can link enzymes via covalent bonds, and has a good film-forming ability.^{11,16}

Fortunately, the oxygen permeability was able to be measured for the PU/CPVC membranes. For example, the oxygen permeability coefficient (P_{O_2}) of the PU-1/CPVC (96/4) membranes was 6.4 Barrer. This value is high enough for an application as the oxygen electrode membranes whose P_{O_2} values are usually in the range of 4-5 Barrer. However, the P_{O_2} decreased dramatically as the CPVC content in the PU-1 membranes increased from 4 to 5 wt%, and then decreased slowly as the CPVC content increased further as shown in Figure 3. A similar dependency of the P_{O_2} on the CPVC content was observed for the PU-2/CPVC and PU-3/CPVC membranes whose P_{O_2} values were also very close to those of the PU-1/CPVC membranes. The P_{O_2} of the pure CPVC membranes was measured to be 0.26 Barrer under the identical conditions. The permeability behavior suggests that oxygen molecules permeate mainly through the pores at low contents of CPVC, but do through the CPVC domains at high contents of CPVC in the blend membranes. This is understandable if the blend membranes become less porous with increasing the CPVC content and the oxygen permeability of PU membranes is much lower than that of CPVC membranes.

Actually, the pure PU membranes were prepared by a hot press method, but the oxygen permeability of the membranes was too low to be measured with the present apparatus. A SEM micrograph revealed the surface of the membrane was pretty smooth without any appreciable crystal grains or pores. This result indicates that the crystalline PU membranes do not have enough free volumes and solubilities to show a measurable permeability of oxygen.

The morphology of the PU membranes prepared from the solution casting method was examined with SEM, and the micrographs are shown in Figure 4. As expected, the surface of the PU-1 membrane is composed of large crystal grains of several tens of micrometers in diameter with large pores. The SEM micrograph for the cryo-fractured PU-1 membrane indicates that the membrane appears to be a two-dimensional arrangement of the large crystal grains. The surfaces of the PU-1/CPVC membranes are also composed of many crystal grains, but the size of the crystal grains and pores decreased as the CPVC content increased. This result clearly supports the oxygen permeability behavior of the membranes.

The DSC thermograms of PU-1, PU-1/CPVC, and CPVC

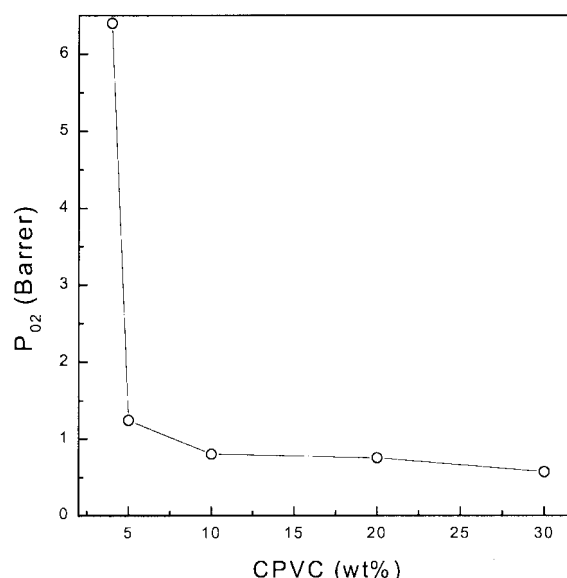


Figure 3. The P_{O_2} for the PU-1 membranes containing the various contents of CPVC at 25 °C and 80 psi.

membranes are shown in Figure 5. The T_g and T_m of the PU-1 component in the blends were not changed appreciably, but the T_c was shifted to higher temperatures. This suggests that the two different polymers are not compatible and the crystallization of the PU-1 may be inhibited by the CPVC in the blends. The X-ray diffraction data also revealed that the crystal structure of PU-1 was not changed by the presence of CPVC.

It can be speculated that the PU may be crystallized slowly as the solvent evaporates from the polymer solutions since the crystallization begins to occur at room temperature. This results in the formation of the two-dimensional arrangement of the large crystal grains with pores. The PU crystal growth in the blends, however, may be prohibited by the near CPVC molecules which are more rigid ($T_g \sim 63$ °C). In the crystallization process, the size of the PU crystal grains should be dependent on the CPVC content in the solutions, and decreased with increasing the CPVC content. Then, the pores between the crystal grains can be filled partially or completely by the CPVC molecules, depending on the CPVC content.

In summary, the PUs were synthesized from PBS, PEG, and H_{12} MDI. The PU membranes prepared from the solution casting method are the two-dimensional arrangements of the PU crystal grains with too large pores, and their oxygen permeability could not be measured. However, the oxygen permeability was measurable when the PU was blended with CPVC. Especially, the P_{O_2} of the PU-1/CPVC (96/4) membranes was so high (6.4 Barrer). The oxygen permeability decreased significantly when the CPVC content was greater than 4 wt% and approached to that of the CPVC membrane. The SEM micrographs showed that the size of the crystal grains and pores in the PU/CPVC membranes decreased with increasing the CPVC content. This result suggests that the PU membranes containing appropriate amounts of CPVC may be applicable as oxygen electrode membranes of

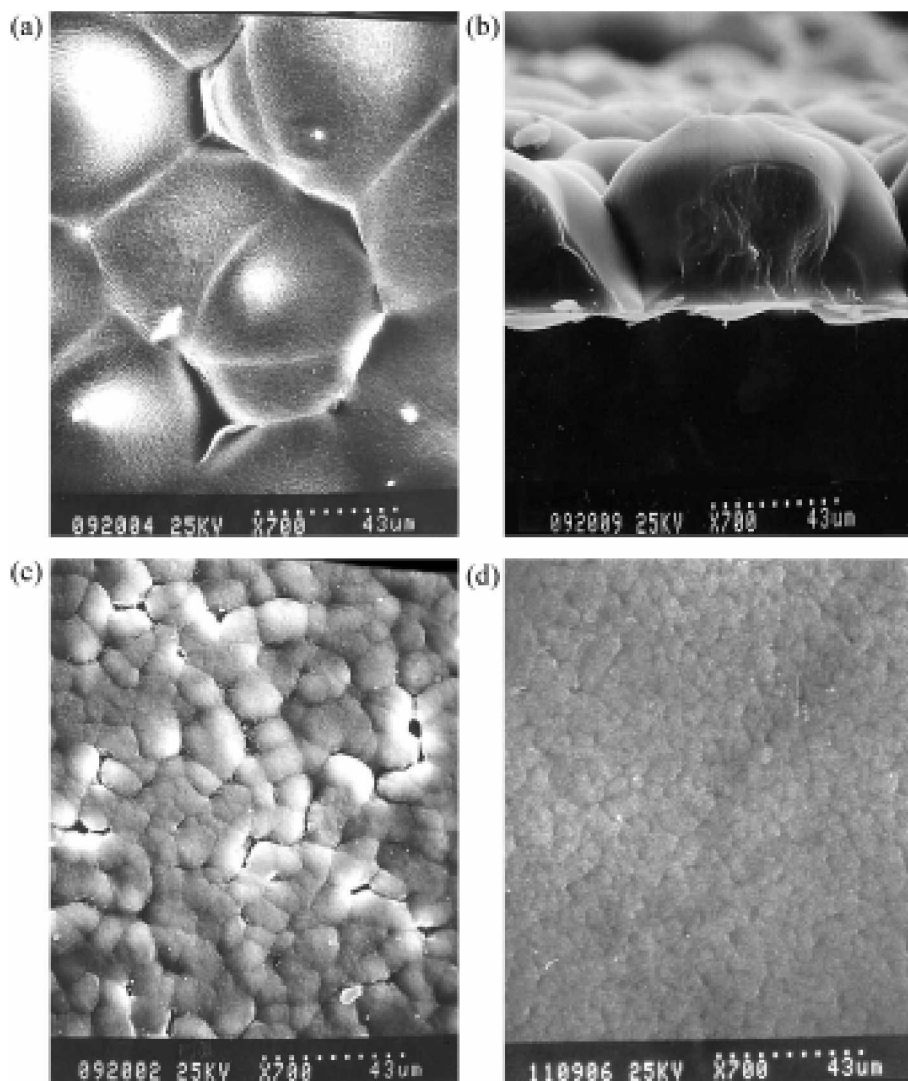


Figure 4. SEM micrographs of the membrane surfaces of (a) PU-1, (b) the cryo-fractured membrane of PU-1, (c) PU-1/CPVC (96/4), and (d) PU-1/CPVC (80/20).

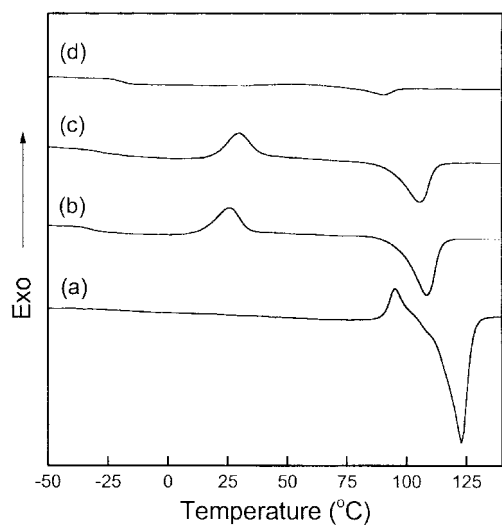


Figure 5. DSC thermograms of membranes: (a) PU-1, (b) PU-1/CPVC (96/4), (c) PU-1/CPVC (95/5), and (d) PU-1/CPVC (80/20). All of the thermograms were obtained from the second heating scans and the scan rate was 10 °C/min.

biosensors as long as other requirements are fulfilled.

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