

## Polyurethane Films for Wound Dressing Applications

Mert Umut Ozkaynak,\*<sup>1</sup> Cigdem Atalay-Oral,<sup>2</sup> S. Birgül Tantekin-Ersolmaz,<sup>2</sup>  
F. Seniha Güner<sup>2</sup>

<sup>1</sup> Istanbul Technical University, Material Science and Engineering Department  
34469 Maslak, Istanbul

E-mail: mert@be.itu.edu.tr

<sup>2</sup> Istanbul Technical University, Chemical Engineering Department 34469  
Maslak, Istanbul

E-mail: cigdemo@itu.edu.tr; ersolmaz@itu.edu.tr; guners@itu.edu.tr

**Summary:** Polyurethane films based on renewable sources were prepared as an alternative to petroleum-based polyurethane. The effects of the structure and ratio of diisocyanate components on polymer properties were investigated. Hexamethylene diisocyanate (HMDI) and diphenylmethane diisocyanate (MDI) were chosen as the diisocyanate components in polymer synthesis. Membranes were prepared by casting-evaporation technique and characterized for their gas permeability, film and mechanical properties. The oil-based membranes were found to be suitable for wound dressing applications.

**Keywords:** membrane; polyurethane; wound dressing

### Introduction

Polyurethanes (PUs) have been widely used in many areas such as medical, automotive and chemical industry fields due to their wide range of properties and processing technologies. PU copolymers are one of the most important subclasses of the family of thermoplastic elastomers. They can be prepared by the step-growth polymerization of diisocyanates with diols (Figure 1).

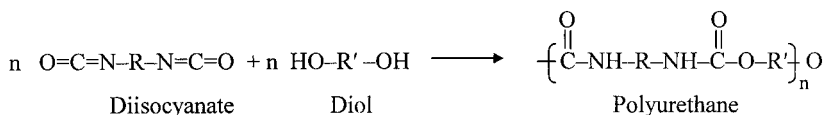


Figure 1. Polyurethane synthesis.

Depending on the chemical composition of the reactants (R and/or R' in Figure 1), the PU chain may also include ether, ester, amide or urea groups. Polyether-based polyurethanes

have better hydraulic stability and lower temperature flexibility than polyester-based PUs, which have better oxidative and thermal stability.

PU is well-known for its superior strength and favorable biocompatibility. PU films have a great importance in wound dressing applications since they are elastic, transparent, and adhesive. PU films allow a moist environment for the wound and acts as a barrier for external contamination. PU films are mostly used on dry- or low-exudate wounds<sup>[1, 2]</sup>.

A good wound dressing material is expected to act primarily as a protective barrier, and substitute the disrupted epidermis. There is a wide range of materials, which can be used for wound dressing applications. The selection of the appropriate dressing for wound healing depends on the type of the wound and the degree of preservation required. Moist wound dressings are usually made of alginates, hydrocolloids, and hydrogels, and manufactured in the form of foams and films. The dressing developed in this study falls under the category of transparent films<sup>[3-5]</sup>.

This study aims to produce polyester-based PU films based on renewable sources as an alternative to petroleum-based polyurethane films. The new PU films are expected to have better biocompatibility properties. The effect of structure and ratio of the diisocyanate components on the polymer properties are studied by using two different diisocyanates in the triglyceride structure, namely, hexamethylene diisocyanate (HMDI) and diphenylmethane diisocyanate (MDI) (Figure 2). In addition to structural properties, the film and gas permeability properties of the polymers are also investigated.

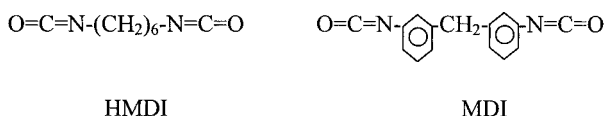


Figure 2. The structure of the diisocyanates used.

## Experimental

### Materials

Hexamethylene diisocyanate (HMDI) and diphenylmethane diisocyanate (MDI) used in polyurethane synthesis were analytical grade and purchased from Merck (Darmstadt, Germany). Polyol prepared from triglyceride oil was used in polyurethane synthesis. Hydroxyl and acid values of polyol were determined to be 118.2 and 5.4 mg/g,

respectively. Xylene (Merck) was used as a solvent both in polymer synthesis and membrane preparation. An Opsite (Smith & Nephew) brand commercial wound dressing was used to compare the properties of the polyurethane membranes prepared.

### Polymer Synthesis and Characterization

Oil-based polyurethanes were synthesized using the solvent method. The equivalent amounts of diisocyanate components were added to the polyol. Xylene was used as the solvent. Reaction was carried out at 90-95°C under inert gas atmosphere. When two diisocyanate components were used, the total diisocyanate group was equivalent to the hydroxyl group. The synthesis reaction was monitored by FTIR measurements. The spectra of the final product did not have an absorption peak at  $2250\text{ cm}^{-1}$ , assigned to the  $\text{N}=\text{C}=\text{O}$  group, indicating that all the diisocyanate were consumed in the reaction. The ratio of the diisocyanate components added to the polyol is given in Table 1.

Table 1. The ratio of diisocyanate components in the reaction mixture.

Membrane Code	Ratio of isocyanate components (HMDI : MDI)
PU1	1 : 0
PU2	0.50 : 0.50
PU3	0 : 1
PU4	Blend of PU1 and PU3 (1 : 1)

Structural characterization of the samples was made with Mattson 1000 FTIR spectrophotometer. Molecular weight of the polymers was determined by gel permeation chromatography (GPC) (Agilent 1100) equipped with a differential refractometer, using tetrahydrofuran (THF) as the solvent at a flow rate of 1 mL/min. The thermal analysis of the polymer samples was carried out by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on a Perkin Elmer Pyris1 calorimeter under nitrogen atmosphere. The heating rate was 20°C/min and 10°C/min in DSC and TGA measurements, respectively.

## Membrane Preparation and Characterization

Polyurethane membranes were prepared by casting-evaporation technique. Membranes with controlled thickness were solution cast on Teflon-coated glass plate into a steel ring of 55 mm diameter. Cast films were kept at room temperature for 24 h for evaporation of xylene.

The morphological characterization of the PU membranes was carried out by examining the cross-section and surface of the membranes by scanning electron microscopy (JEOL JSM-5410). Membrane samples were prepared for SEM analysis by breaking them in liquid nitrogen and then coating with gold using a sputter coater.

Film properties such as drying time<sup>[6]</sup>, alkali and acid resistance<sup>[7]</sup>, flexibility<sup>[8]</sup>, adhesion<sup>[9]</sup>, and hardness<sup>[10]</sup> were determined according to the ASTM standards.

The gas permeabilities of the membranes were measured in a gas permeability system based on constant volume/variable pressure technique<sup>[11]</sup>. All measurements were carried out at 28°C and the permeation rates of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> gases were determined. Ideal selectivities were also determined by calculating the ratio of the pure gas permeabilities.

The tensile strength of PU membranes were tested under dry conditions by using an Instron Universal Tester at room temperature at an operating speed of 12 in./min. Specimen type is 1R-25 mm raveled strip, which is 25 mm wide and at least 150 mm long with the longer dimension accurately parallel to the direction for which the breaking force is required<sup>[12]</sup>.

## Results and Discussion

Molecular weights and the glass transition temperatures ( $T_g$ ) of the polymers prepared are presented in Table 2. The molecular weight and polydispersity of the polymer increases with increasing aromatic structure, since the molecular weight of MDI, the diisocyanate component containing aromatic groups, is higher than that of HMDI. The molecular weight of PU<sub>4</sub>, which is a blend of PU<sub>1</sub> and PU<sub>3</sub>, is in between that of PU<sub>1</sub> and PU<sub>3</sub>, as expected.

$T_g$  is strongly influenced with the chemical structure and molecular weight of polymers. In general,  $T_g$  increases with decreasing flexibility of the polymer chain. Flexibility decreases with increasing aromatic groups in the main chain.  $T_g$  increases with increasing molecular weight at low molecular weights, however, at moderate molecular weights, it reaches to a value at which further increase in molecular weight has no important effect on the  $T_g$ . The

same trends were observed for the polymers prepared in this study (as seen in Table 2); that is, the  $T_g$  of PU<sub>1</sub> is higher than that of PU<sub>2</sub>, and PU<sub>2</sub> and PU<sub>3</sub> have the same  $T_g$ . TGA results also presented in Table 2 indicate no major difference between the temperature values at which 10 % weight loss is observed for the PU samples prepared.

Table 2. Molecular weight and thermal analysis data.

Polymer	Mw	Mw /Mn	T <sub>g</sub> (°C)	TGA (10% Weight Loss, °C)
PU1	3578	1.5	11.2	247
PU2	9268	3.1	26.5	253
PU3	21597	6.2	26.5	234
PU4	11224	3.8	-	253

Figure 3 shows the cross-sectional and surface views of the PU membranes. A thin layer of column-like structures in the cross-section close to the upper surface and discontinuous cracks at the surface were observed for PU<sub>2</sub> membrane. Cracks were also present on the surface on PU<sub>1</sub> membrane. The structures in the cross-section and the cracks on the surface may be due to fast evaporation of the solvent during membrane preparation. The structures of the other PU membranes are regarded as dense morphology.

Film properties, such as drying time, flexibility, adhesion, hardness, alkali, acid, and water resistances, and tensile strength of the membranes are summarized in Table 3. Drying times of the polymers tested showed no particular difference. Adhesion was better for PU<sub>1</sub> and PU<sub>2</sub> compared to PU<sub>3</sub> and PU<sub>4</sub>. There was no adhesion in PU<sub>3</sub> and PU<sub>4</sub> due to the increased ratio of the aromatic structure. The flexibility of all the PU membranes prepared was superior and same as the Opsite commercial wound dressing sample. Cylinder with lowest diameter was used in bending tests, which indicated the highest flexibility. The hardness tests of the polymers indicated no particular difference, because the number of oscillations made by the polymers was nearly the same. Acid resistance was superior for all samples including the Opsite. PU<sub>3</sub> showed better alkali resistance compared to others due to the structure of MDI. Aromatic structure acted as a barrier for NaOH. As the aromatic structure of the polymer was increased, the tensile strength values were also observed to increase from 1.28 to 3.80 lbf.

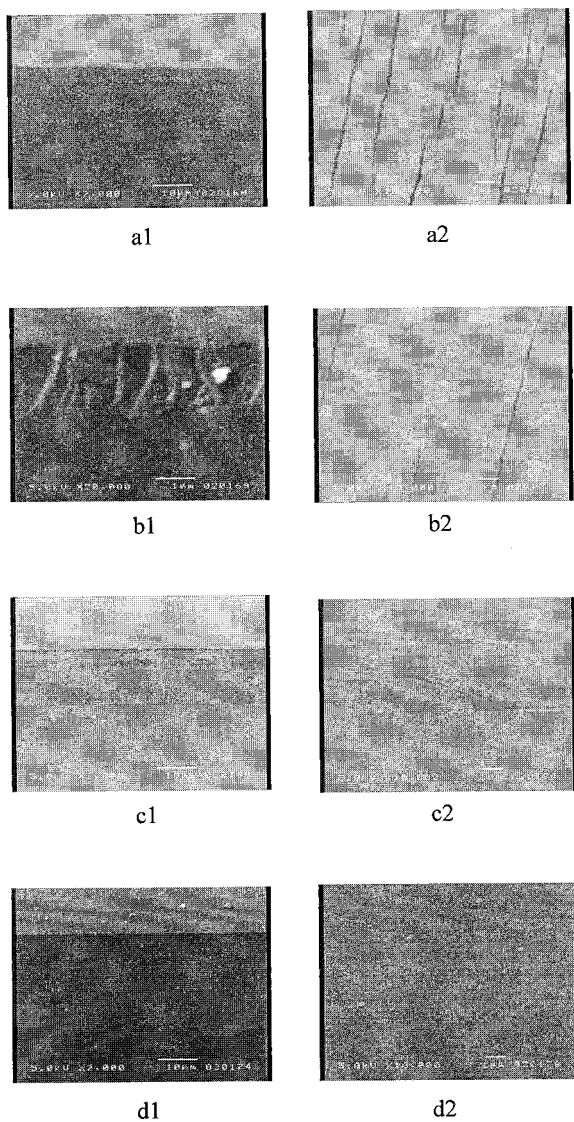


Figure 3. (a1) PU<sub>1</sub>, (b1) PU<sub>2</sub>, (c1) PU<sub>3</sub>, (d1) PU<sub>4</sub>, are SEM images of cross-sections of the polymers (a2) PU<sub>1</sub>, (b2) PU<sub>2</sub>, (c2) PU<sub>3</sub>, (d2) PU<sub>4</sub> are SEM images of surface of the polymer.

Table 3. Film properties of the polymers prepared.

Applied Test	PU <sub>1</sub>	PU <sub>2</sub>	PU <sub>3</sub>	PU <sub>4</sub>	Opsite
Drying time (set-to-touch)	6 min	9 min	7 min	9 min	-
Adhesion	2B	2B	0B	0B	-
Flexibility	2 mm	2 mm	2 mm	2 mm	2 mm
Hardness	2	2	2	6	-
Alkali resistance	Removable	Removable	Partially Removable	Removable	-
Acid resistance	No Change	No Change	No Change	No Change	No Change
Tensile Strength (lbf)	1.28	1.73	3.80	2.53	-

Table 4 presents the O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> permeabilities and the O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/O<sub>2</sub> selectivities of the PU membranes. The gas permeation measurements of PU<sub>2</sub> were not possible due to the cracks present in the membrane. Table 4 also presents the permeability and selectivity values obtained for the commercial wound dressing sample, Opsite. PU<sub>4</sub>, which is a blend of PU<sub>1</sub> and PU<sub>3</sub>, showed the highest gas permeabilities, which were closer to the values of the commercial product, compared to the other PU membranes prepared.

Table 4. Permeabilites of the polyurethane films.

Membrane	O <sub>2</sub> (Barrer)	N <sub>2</sub> (Barrer)	CO <sub>2</sub> (Barrer)	$\alpha_{O_2/N_2}$	$\alpha_{CO_2/N_2}$	$\alpha_{CO_2/O_2}$
PU <sub>1</sub>	2.76	0.42	0.09	6.57	30.67	4.67
PU <sub>3</sub>	0.67	0.17	3.86	3.94	22.71	5.76
PU <sub>4</sub>	4.38	1.54	31.00	2.84	20.15	7.07
Opsite	9.9	2.97	75.9	3.3	25.25	7.6

## Conclusions

Oil-based polyurethanes are first trialed as a membrane. They showed fairly good mechanical properties and they also have favorable acid resistance. PU<sub>4</sub>, which is a blend of PU<sub>1</sub> and PU<sub>3</sub> showed the best gas permeability and film properties. Therefore, it can be concluded that PU<sub>4</sub> can be used for wound dressing applications. However, its biodegradability and biocompatibility properties should be determined.

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