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ABBREVIATIONS

MDI : Diphenylmethylene diisocyanate

HDI : Hexamethylene diisocyanate

THF : Tetrahydrofuran

PDI : Polydispersity index

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LIST of SYMBOL

- L** : Thickness of the membrane
- D** : The diffusion coefficient, (cm².s⁻¹)
- S** : Solubility
- P** : Pressure
- Da** : The difference between the value of the thermal expansion coefficient
- a** : Ideal selectivity

YARA ÖRTÜSÜ AMAÇLI POLİÜRETAN FILMLERİN ÜRETİMİ

ÖZET

Yara örtüsü amacıyla yaygın olarak kullanılan poliüretan membranlar oksijen ve karbondioksit geçişine olanak veren, buna karsın sivi geçirmeyen malzemelerdir. Günümüzde diğer birçok polimerler gibi poliüretanlar da petrol kökenli bileşenlerden üretilmektedir.

Bu çalışmanın amacı, petrol kökenli bileşenlere alternatif olabilecek yenilenebilir doğal kaynaklı bazı bileşenlerden yara örtüsü olarak kullanılacak esnek poliüretan filmlerin üretilmesidir. Çalışmada yapısal (alifatik veya aromatik) özelliklerin ve bileşen oranlarının, polimerlerin özelliklerine etkisini araştırmak amacıyla trigliserid yapıda farklı oranlarda hexametilendiizosiyanat (HMDI) ve/veya metilendifenildiizosiyanat (MDI) kullanılmıştır. Polimerlerin yapısal karakterizasyonunun yanı sıra, film özellikleri, gaz geçirgenlikleri, mekanik özellikleri belirlenmiştir. Yeni üretilcek polimerlerin biyolojik kaynaklardan üretilmesi nedeniyle, biyoyumluluklarının literatürdeki polimerlerden daha iyi olabileceği öngörülmektedir. Bu çalışmada üretilen poliüretan filmler literatürde üretilen poliüretan filmlerle uygunluk göstermektedir.

POLYURETHANE FILMS FOR WOUND DRESSING APPLICATIONS

SUMMARY

Polyurethane materials have been widely used in many areas due to the wide range of properties and processing technologies. Polyurethane membranes has a great importance in wound dressing applications. The use of advanced wound dressings helps to keep a moist environment, remove exudate and necrotic tissues, keep temperature constant, allow oxygen permeability, and impede the liquid transition. Polyurethane membranes are the reaction products of organic isocyanates, high molecular weight polyols and low molecular chain extenders. The components of the polyurethanes are mostly based on petroleum.

In this study we aimed to produce polyurethane films based on renewable sources which will be an alternative for the polyurethane films based on petroleum. In order to study the effect of structure and ratio of the isocyanate components on the polymer properties hexamethylenediisocyanate (HMDI) and diphenylmethane diisocyanate (MDI) are used in the triglyceride structure. In addition to structural properties, the film properties, gas permeability, and mechanical properties of the polymers are also investigated. The new polyurethane films were expected to have better biocompatibility properties. The polyurethane films produced in this study were in a competent agreement with the examples given in the literature.

1. INTRODUCTION

Polyurethanes (PU) have been widely used in many areas such as medical, automotive and industry fields due to the wide range of properties and processing technologies. PU's have superior strength and favorable biocompatibility. PU films have a great importance in wound dressing applications. They are thin, elastic, transparent and adhesive. PU films allow moist environment for wound and acts as a barrier for external contaminations. PU films mostly used on dry wounds or on low exudate wounds [1,2].

In this study we aimed to produce PU films based on renewable sources which will be an alternative for the PU films based on petroleum. The new PU films are expected to have better biocompatibility properties. In order to study the effect of structure and ratio of the isocyanate components on the polymer properties hexamethylenediisocyanate (HMDI) and diphenylmethane diisocyanate (MDI) are used in the structure. In addition to structural properties, the film properties, gas permeability, mechanical properties of the polymers are also investigated.

2. THEORETICAL PART

2.1. THE SKIN

Skin has a great importance in the life of human. The role of the skin is to protect the body's highly organized structure from physical, chemical, or biological insults from the environment. The skin is the largest organ of the body. Skin has an area of 2 m^2 on average in adults, and has a thickness of 1 to 2 mm. Skin is responsible for a substantial part of the thermoregulatory and communication needs of the body, including the transduction of signals from the environment such as touch, pressure, and temperature. Far from being a passive membrane that keeps the internal organs in shape, skin is a complex organ. Skin is a barrier to loss of water and electrolytes from the body, and it is a barrier to infection from airborne organisms. It has been reported that burns alone account for 2,150,000 procedures every year in the United States. Of these, 150,000 refer to individuals who are hospitalized, and as many as 10,000 die.

There are four types of tissue in skin. The epidermis, outside, is a 0.1 mm thick sheet. Epidermis has 10 layers of keratinocytes. The dermis, inside, is a 2-2.5 mm thick layer vascularized and innervated connective tissue with very few cells, mostly quiescent fibroblasts. Dermis is a massive tissue. It has a weight of 15-20% of total body. Another layer is basement membrane which is interleaved between the epidermis and dermis, the thickness of the membrane is approximately 20 nm. Fourth layer of the skin is subcutis. Subcutis is at the underneath of the dermis and has a thickness of 0.4-4 mm. Subcutis comprises of primarily fat tissue. Beside to these layers there are also several appendages, including hair follicles, sweat glands, and sebaceous glands. The latter are mostly embedded in the dermis, although they are ensheathed in layers of epidermal tissue [3,4].

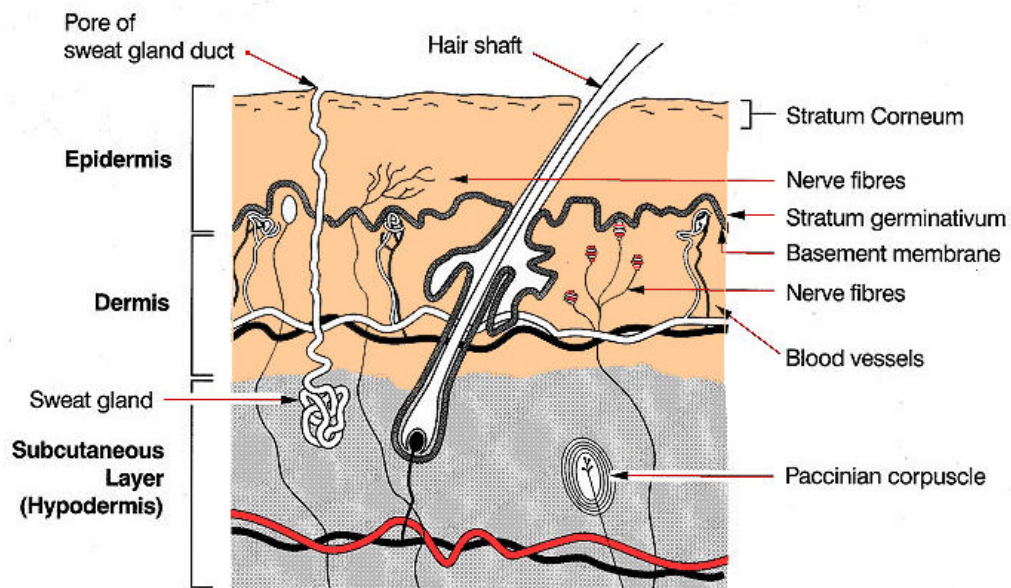


Figure 2.1 Schematic view of skin which highlights the epidermis, the basement membrane interleaved between the epidermis and the dermis, and the dermis underneath [3].

2.2. WOUND DRESSINGS

Duties of the wound dressing is to act primarily as a protective barrier, to substitute the disrupted epidermis. There is a wide range of materials which can be used for wound dressing, the selection of dressings for wound healing is changed with the type of the wound and the degree of preservation required. Type of moist wound dressings are alginates, hydrocolloids, hydrogels, foams, and films. The dressing developed in this research thesis falls under the category of transparent films [4,5,6].

2.2.1 FILM DRESSINGS

They are thin, elastic, transparent and adhesive and mostly composed of PU films. They are not absorbent. Film dressings are mostly semi-occlusive, they provide a moist environment for wound. Healing occurs more quickly under moist environment according to dry environment. Films are only considered for relatively slight wounds, they are suitable for donor sites, skin tears, shallow abrasions, burns, post operative wounds and stage 2 pressure ulcers [5]. They are also relatively inexpensive. The cost is a few dollars per package of sheets [7].

2.3 POLYURETHANS

PU's are composed of soft and hard segments. The hard segment is embedded in soft matrix. This morphology of phase distribution is the basic reason of superior mechanical and physical properties of PU's. Properties would be modified by playing with the phase distribution. The soft segment is typically a polyester or polyether and the hard segment is a diisocyanate and low molecular weight chain extender. The chain extenders is generally a diamine or diol [9,10,11,12]. PU's are thermally very stable polymers. The beginning degradation temperature of the urethane bond is related with the type of isocyanate and glycol [13].

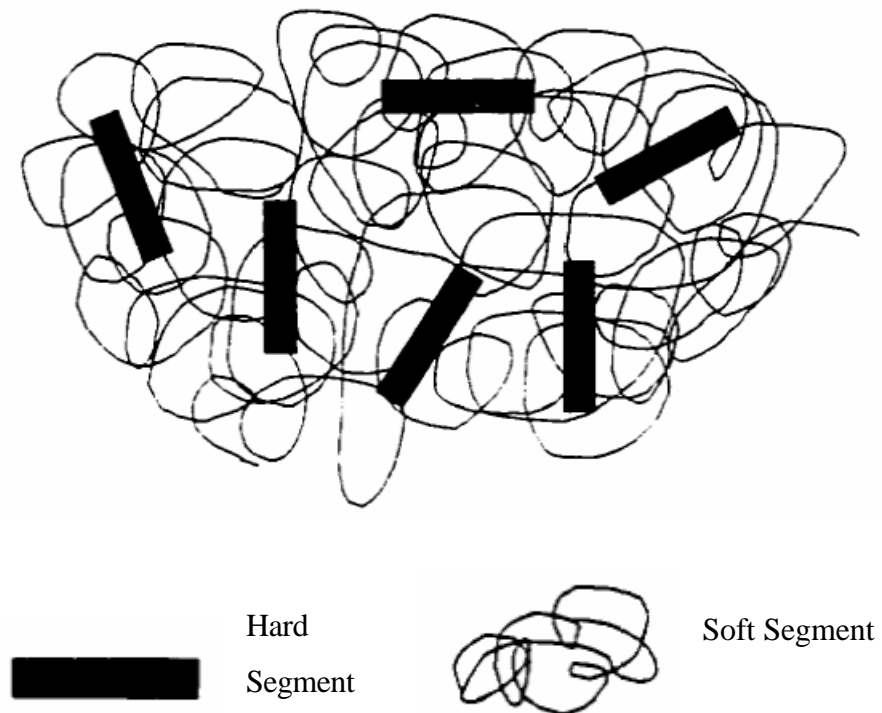
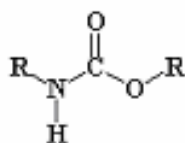


Figure 2.2 Segmented PU structure. PU is characterized by segment embedded in a matrix of segment [4].

The name PU was derived from ethyl carbamate, known as urethane. These polymers were discovered at 1937 by Otto Bayer and co-workers [14].

They are characterized

by group : [11]



The structure of a simple PU is shown in Figure 2.3.

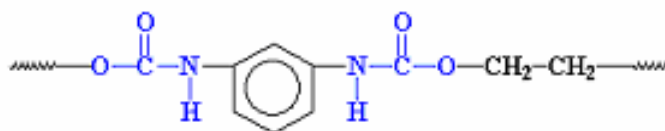


Figure 2.3 A simple PU [11].

They are generally produced by the reaction of a polyfunctional isocyanate with a polyol reaction between the isocyanates and the hydroxyl group is [12]:



The hydrogen atom of the hydroxyl group is transferred to the nitrogen atom of the isocyanates. The major advantage of the PU is that the chain is not composed exclusively of carbon atoms but rather of heteroatom, oxygen, carbon and nitrogen [14].

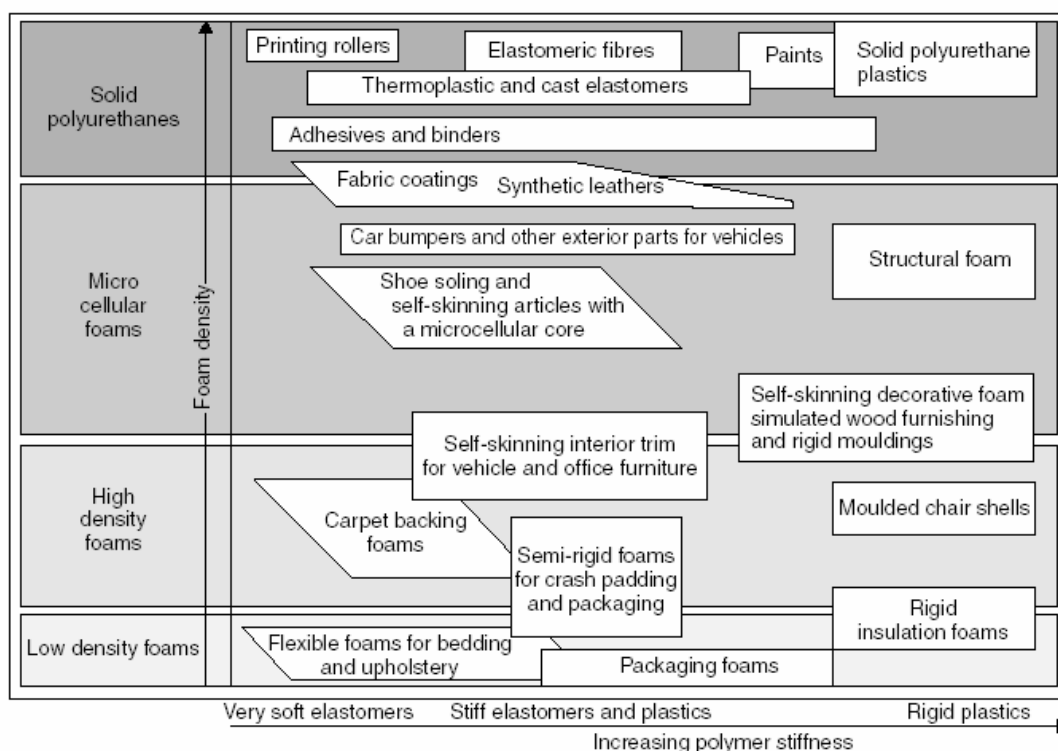


Figure 2.4 Application areas of PU's as a function of density and stiffness [15].

PU's not only contain urethane group they also including multiplicity of other groups such as urea, ester and ether as well as aromatic rings and these groups are effected the properties of the PU polymer.

Properties such as tensile strength, melting point, elongation, elasticity and glass-transitions temperature increase as the molecular weight increase. Intermolecular forces include hydrogen bonding, polarizability, dipole moment, and van der Walls forces [10].

PU are used in many different areas (Figure 2.4). They are used in biomedical applications because they have very good mechanical properties, and their biocompatability is favorable. PU's are cast, molded, and extruded into widespread of products for the medical device industry [2]. PU membranes exhibit different biocompatible properties by different fabrication processes [17]. Nonthrombogenicity and resistance to biodegradation of PU has led to its use in both commercial and experimental blood-contacting applications such as catheters, heart-assist pumps: and chambers for hearts, pacemaker wire lead insulation [18,19]. Other

biomedical applications are hospital bedding, surgical drapes, wound dressings, also in a wide applications of injection molded devices [20].

PU made from petroleum based polyols and isocyanates have widespread applications. Polyols from renewable resources such as plant oil, has attracted the attention of researchers. Cross-linking effects the mechanical properties of PU's. In the existence of high-functional reactants, such as polyol and isocyanates, forms a cross-linked network. Therefore highly cross-linked PU's useful for applications such as insulation materials or as automotive parts can be obtained [21-24]. The structure of cross-linked network is shown in Figure 2.5.

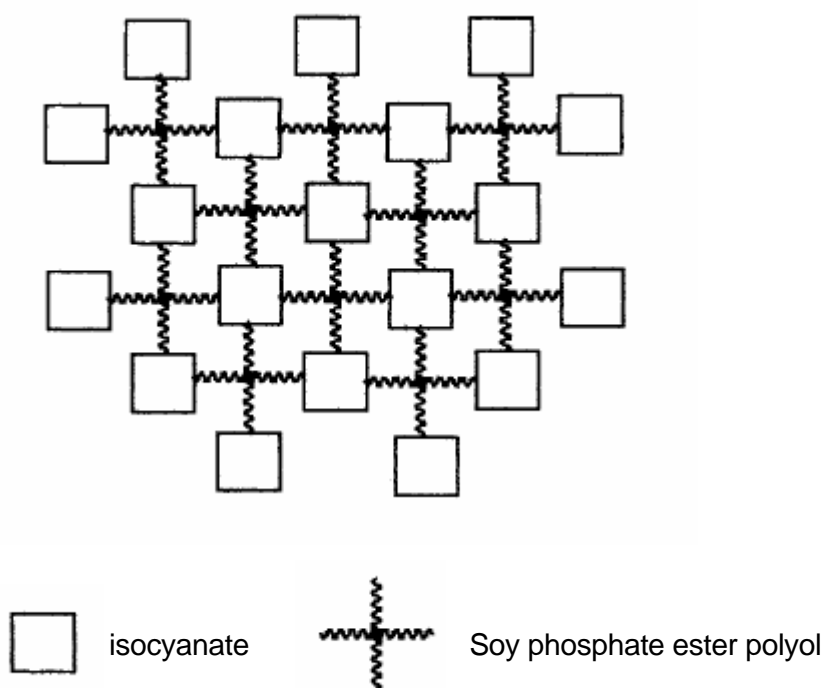
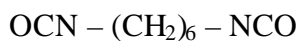


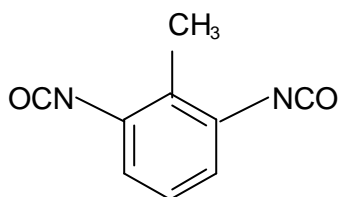
Fig 2.5 Schematic representation of a PU thermoset prepared by reaction of biobased polyol with isocyanates [21].

2.3.1 Raw Materials Using Preparation Of PU's

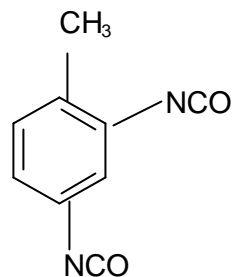
Most common raw materials using synthesis of PU's are isocyanate compounds. They are classified as aromatic and aliphatic isocyanates [1,9,10]. Some diisocyanates used in PU preparation are shown below.



(1,6 hexamethylene diisocyanate)

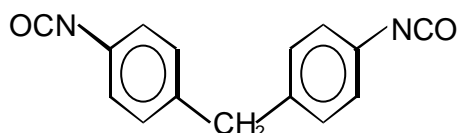


2,6 isomer



2,4 isomer

Toluene diisocyanate structure – 2,6 and 2,4 isomers



(Diphenylmethane diisocyanate)

The other raw materials are polyols, polyethers and polyesters.

2.4 DIFFUSION THROUGH POLYMERS

The transport of small molecules through a polymer membrane occurs due to random molecular motion of individual molecules. The driving force behind the transport process which involves sorption, diffusion and permeation is the concentration difference between the two phases. Molecules sorb in to the solid polymer film and diffuse across the film through a concentration gradient and desorbs from the downstream film face [25-29].

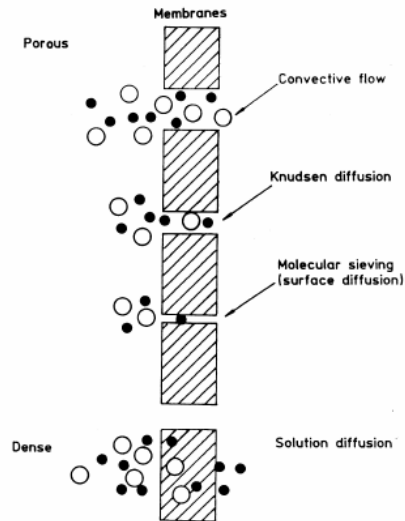


Figure 2.6 Schematic presentation of mechanisms for permeation of gases through membranes [27].

Graham proposed two mechanism for transportation of gases through a polymeric membrane:

- Solubility
- Mobility or diffusion

Diffusivity can be described by Fick's first law of diffusion states that the flux N_i is proportional to the concentration gradient in the following manner:

$$N_i = -D \frac{\partial c_i}{\partial x} \quad (2.2)$$

Solubility can be described by Henry's law.

$$C_i = S_i * p_i \quad (2.3)$$

The product of diffusivity and solubility is called the permeability coefficient.

Permeability = Solubility*Diffusivity

$$P = S * D \quad (2.4)$$

and has a unit in Barrer where $1 \text{ Barrer} = 10^{-10} \text{ cm}^3 \text{ (STP).cm.cm}^{-2}.\text{s}^{-1}.\text{cmHg}^{-1}$. The permeability coefficient, P , is defined as the amount of gas permeating per unit time, per unit membrane area, per unit pressure difference at the constant temperature at steady-state flow conditions,

$$P = \frac{N}{(p_A - p_b)/l} \quad (2.5)$$

Ideal selectivity (a_{AB}) of a membrane for component A relative to B is expressed as the ratio of the pure gas permeability's of two penetrants in the membrane material [25-28].

$$a_{AB} = \frac{P_A}{P_B} \quad (2.6)$$

or

$$a_{AB} = \frac{D_A}{D_B} * \frac{S_A}{S_B} \quad (2.7)$$

Gas selectivities of mixed soft segment polyurethane-urea (PUU) membranes are generally higher than those of single soft segment PU or PUU membranes due to little increase of diffusion selectivity [29].

Solubility and mobility factors are essential for the solution-diffusion mechanism. Solution is a physiochemical interaction between the permeate and the membrane material. Solubility is a thermodynamic parameter and gives a measure of the amount of molecules dissolved in the membrane material under equilibrium conditions. On the contrary, diffusivity is a kinetic parameter which indicates how fast a permeate is transported through the membrane. The absolute rate at which a permeate travels through a membrane is known as permeability, and the rate at which two different species permeate relative to one another is called selectivity. Diffusivity-Selectivity favors the smallest molecule. Penetrant mobility in the polymer and the sorption

magnitude can be influenced by chain segmental mobility in the polymer and the sorption magnitude can be influenced by the chain segmental mobility and interactions of different elastomers [30].

Small molecular size and high critical temperatures of permeate gases tend to produce high permeability's. Small molecular size yields high diffusion coefficients, while high high critical temperature promotes higher solubility in the membrane. The permeation rate of gases can be expected to decrease as the structural symmetry and cohesive energy of the polymer increase. The permeation of more condensable vapors and liquids through a polymer membrane usually proceeds at much greater rates than the permeation of gases [25].

The performance of permeation of gases through non-porous polymeric membranes directly related with the state of the polymer. This state is determined by the glass transition temperature (T_g) of the polymeric material. Above T_g , polymer shows rubbery behavior whereas below T_g it shows glassy behavior. Chain flexibility and chain interactions determine the glass transition. In Rubbery state segments can rotate freely along the main chain bonds. There is high degree of chain mobility. Modulus, specific volume, specific heat, refractive index, and permeability change at the glass transition temperature [25-29]. At low dissolution temperature PU molecules tended to aggregate to form a dense structure by integrity of a great number of molecular entanglements [31].

The free volume is the volume unoccupied by the macromolecules, the occupied volume contains both van der Waals volume of the atoms and excluded volume. The free volume fraction is v_f is virtually constant. When the temperature increases above the glass temperature the free volume increases linearly. The gas diffusivity increases as the fractional free-volume increases [26].

$$V_f = V_{f,T_g} + \Delta a(T - T_g) \quad (2.8)$$

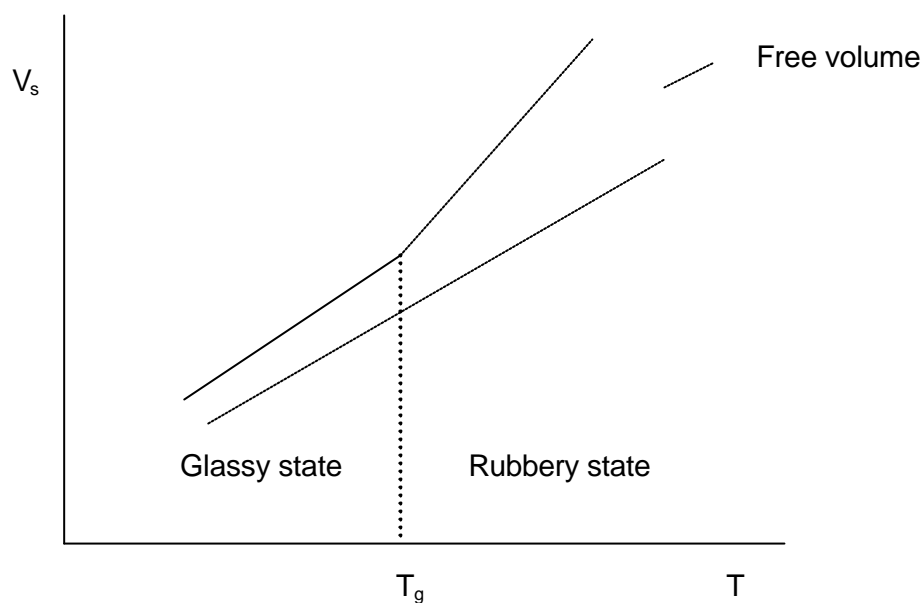


Figure 2.7 Specific volume and free volume as a function of temperature [26].

In the transport of non-interacting permeates, such as nitrogen, helium and oxygen free volume concept is very important. For interacting permeants, such as organic vapours and liquids, segmental motions are function of permeant concentration. It is possible to base the transport of penetrants through nonporous membranes on the free volume concept [25-29]. In order to increase the gas permeability, many efforts have been made to reduce the glassy polymer packing density to obtain larger specific volume [35].

For the segmented PU's, the diffusion of gas is regulated by the length of soft segment. The free volume is increases with the length and support the diffusion. The solubility is effected by the morphology. Hard block is unfavorable to the solubility [33,36]. The free volume is also related with the hydrogen bonding in the soft segment and hard segment domains, which is supported by the density of polymer.

3. EXPERIMENTAL PART

3.1 Materials And Chemicals

Oil component:

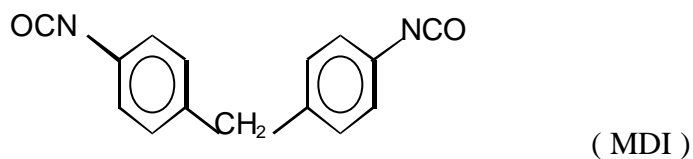
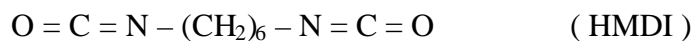
In the experimental study linseed oil is used as an oil component. Some properties of the linseed oil are given in Table 3.1.

Table 3.1. Some Properties of Linseed Oil

Refractive index, n_D^{20}	1,4812
Acid value	1,1
Saponification value	197
Iodine value	166,8
Fatty acid composition. (%)	
C _{16:0}	11
C _{16:1}	3,2
C _{18:0}	11,6
C _{18:1}	31,6
C _{18:2}	21,4
C _{18:3}	20
Other	1,2

Isocyanate component:

In the experimental study hexamethyle diisocyanate (HMDI), and diphenylmethylenediisocyanate (MDI) were analytical grade Merck (Darmstadt, Germany)



Solvents:

In the preparation of polymers and membrane solutions xylene (Merck) was used as a solvent without purification THF (Merck) was used on determination of molecular weight of polymers.

3.2 Experimental Set-Up

The polymer preparation was carried out in 250 ml three-necked flask equipped with a stirrer, a thermometer, and nitrogen inlet tube. This experimental set-up is shown in Figure 3.1.

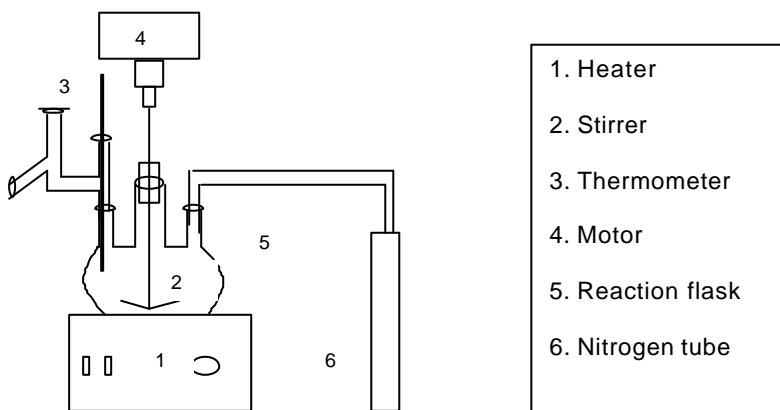


Figure 3.1 Experimental set-up

3.3 Polymer Preparation

Polymer preparation was achieved in two steps. The first step is to preparation of partial glyceride (PG) mixture which was obtained from linseed oil and glycerol and the second step is the synthesis of polymer from PG and diisocyanates.

3.3.1 Preparation of Partial Glyceride Mixture (PG)

Linseed oil and glycerol (8.5% g of the oil) were put into the reaction flask and heated. When the temperature was reached to 218°C, Ca(OH)_2 (0.1% of the oil) was added as a catalyst. After 45 min the temperature was reached at 232°C. The reaction was proceeded under the nitrogen atmosphere. After cooling the reaction mixture, it was mixed with diethyl ether and washed first with dilute hydrochloric acid and then with distilled water to remove the catalyst and free glycerol. The ethereal solution was then dried over Na_2SO_4 and the solvent was removed [38] .

3.3.2 Preparation of PU Sample

PG and dry xylene were taken into reaction flask and stirred on the atmosphere conditions for an half an hour. Then the reaction mixture was heated to 40-45°C, and an equivalent amount of isocyanate component was added slowly over a 30 min period. Lead naphthenate as a 24% solution in white spirit was added in the amount of 0.02% of the oil portion. The temperature was set at 90-95 °C and maintained. The reaction was achieved under the nitrogen atmosphere.

In the reaction of two different isocyanate component, second isocyanate component was added the reaction flask after finish the first isocyanate reaction [39]. Reaction was monitored by IR spectrometry.

3.3.3 Preparation of PU Membranes

Membranes with controlled thickness were molded on teflon coated glass into a steel ring with 55 cm diameter from xylene solution (Figure 3.2). Membranes from xylene solution was evaporated at room temperature and for 24 h [39].

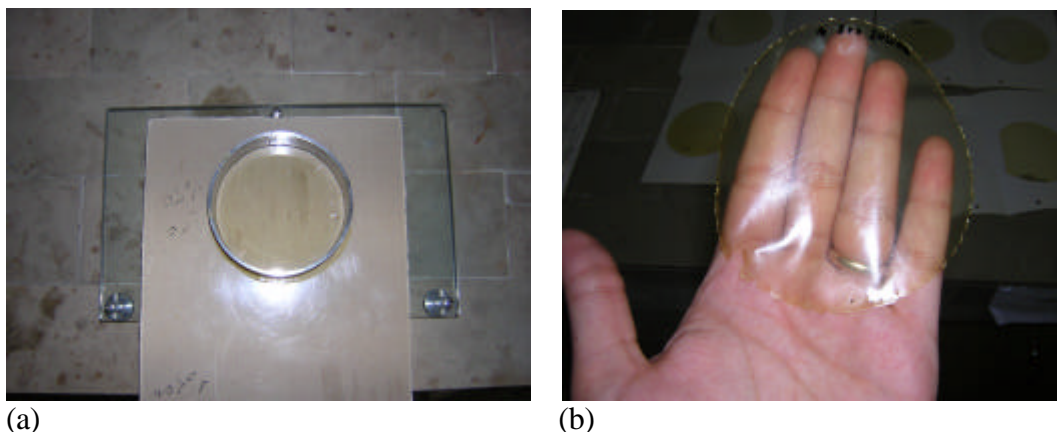


Figure 3.2 (a) Steel ring for preparation of PU membrane, (b) A view of transparent PU membrane

3.4 Characterization Methods

3.4.1 Infra Red Spectroscopy (FTIR)

Polymer reactions were monitored by IR spectra that were run on a Mattson 1000 spectrometer as films on sodium chloride discs.

3.4.2 Gel Permeation Chromatography (GPC)

GPC chromatograms were obtained by using an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran (THF) as the solvent at a flow rate 1 mL/min. Molecular weights were determined using polystyrene standards.

3.4.3 Analytical Methods

For the functional group analyses hydroxyl and, acid values, and isocyanate content were determined by using wet methods.

Acid Value:

Acid value of a PG that is the number of mg potassium hydroxide required to neutralize 1 g of PG. In the experiment approximately 1 g sample was dissolved by 30 ml toluene- alcohol solution and titrated by KOH dissolved in alcohol and calculation was made by equation 3.1

$$\text{Acid value} = \frac{56,1 * N * V}{W} \quad (3.1)$$

N: Normality of potassium solution

V: Volume of potassium hydroxide solution used (in ml)

W: Weight of PG sample (in g)

Hydroxyl Value:

Hydroxyl value is the number of mg of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylating with 1 g of sample [40].

3.5 Determination of Film Properties

Film properties such as drying time [41], water resistance [44], alkali resistance [44], and acid resistance [44], flexibility [42], adhesion [43], hardness [45] were determined.

For this purpose, samples were thinned with xylene to 0.5 Stokes. 0.5 % lead naphthenate and 0.05 % cobalt naphthenate as metal based on solid content were added as driers. Driers were added 24 hr before the film application. In drying time and hardness determinations, a Bird film applicator with 60μm aperture was used for film application on glass plate (Figure 3.3).

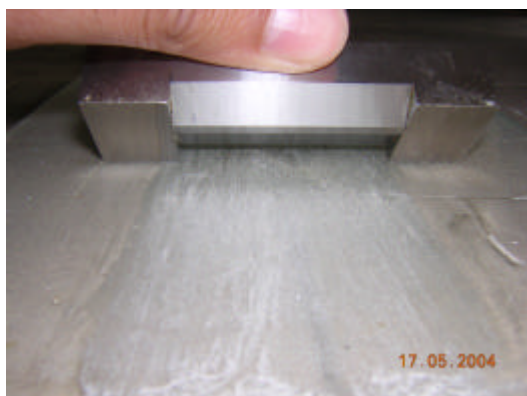


Figure 3.3 A bird film applicator

For resistance to water tin plate panels were used. They were cleaned with toluene and dried before use. Dipping method was used. Polymer films were allowed to dry for 7 days at the room temperature then panels were placed in a beaker containing distilled water at room temperature and panels were allowed to remain 18 hours in distilled water. Then panels were removed from the water, wiped carefully and time required for back to their original forms was determined.

For the resistance to alkali and acid tests glass surfaces were coated with polymer by using Bird film applicator (Figure 3.4). The chemical is spotted randomly at two or three places on the polymer film and left for 30 minutes. The spots are covered with watchglass. At the end of the exposure the chemical was removed by sponging with cotton. After drying and at the end of the recovery period, inspection made for any objectionable appearance of the coating. For alkaline resistance NaOH (3%) solution and for acid resistance sulfuric acid (9%) were used.

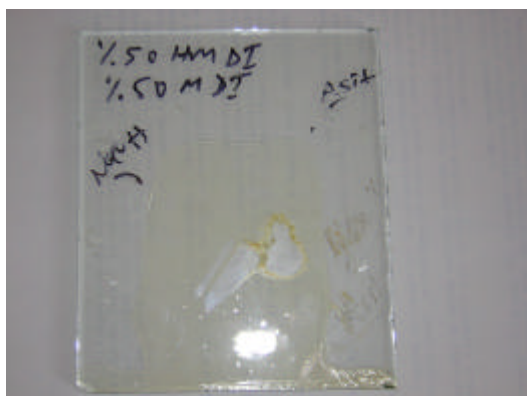
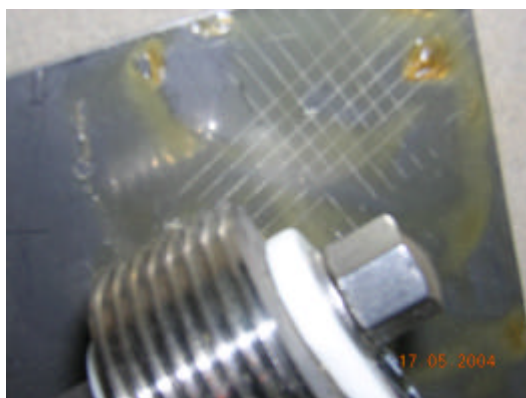


Figure 3.4 Glass Plate is used in alkaline and acid resistance.

For determination of elasticity and adhesion properties metal plates were used. First metal plates were coated with polymer, and then it was allowed to dry. An X-cut is made through the film to the substrate, pressure-sensitive tape is applied over the cut and then removed, and adhesion is assessed qualitatively on the 0 to 5 scale.



(a)

CLASSIFICATION OF ADHESION TEST RESULTS		
CLASSIFICATION	PERCENT AREA REMOVED	SURFACE OF CONTACT AREA FROM WHICH PLASTIC FILLS FORMED FOR SUBPARALLEL LINES AND ADHESION WEDGE REPERCENT
00	0%	
40	Less than 5%	
30	5 - 15%	
20	15 - 35%	
10	35 - 65%	
00	Greater than 65%	

(b)

Figure 3.5 (a) Metal plates with polymer cut by a special knife in adhesion tests. (b) Classification of adhesion test results.

For the elasticity properties metal plates were rotated on metal cylinders then deformations formed on the film surface were observed (Figure 3.6).



(a)



(b)

Figure 3.6 (a) Metal Cylinders with different diameters, (b) Bending device

For determination of drying time, set-to-touch method was used. Glass plates were covered by polymers then lightly touch the test films with the tip of a clean finger and immediately place the finger tip against a piece of clean, clear glass. Observed if any of the coating is transferred to the glass.

For the hardness tests 20 x15 glass plates were used. After the 40 hours of film formation by the help of Rocker hardness test instrument (Figure 3.7) number of oscillation made by polymer is determined.

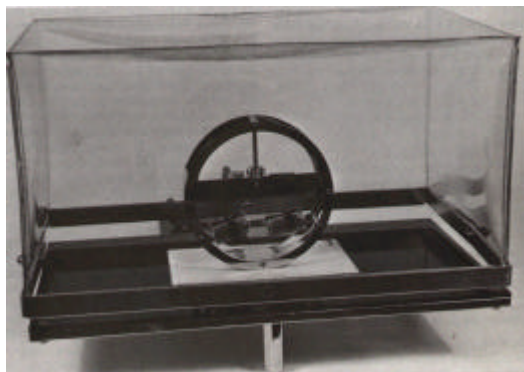


Figure 3.7 Rocker hardness test instrument

3.6 Gas Permeability Measurements

The gas permeability's of the membranes were measured in a gas permeability system based on constant volume/variable pressure technique. All measurements were carried out at 28°C and the permeation rates of O₂, N₂, and CO₂ gases were determined. Ideal selectivity's were determined by calculating the ratio of the pure gas permeability's [46].

A schematic of the gas permeation apparatus is shown in Figure 3.8

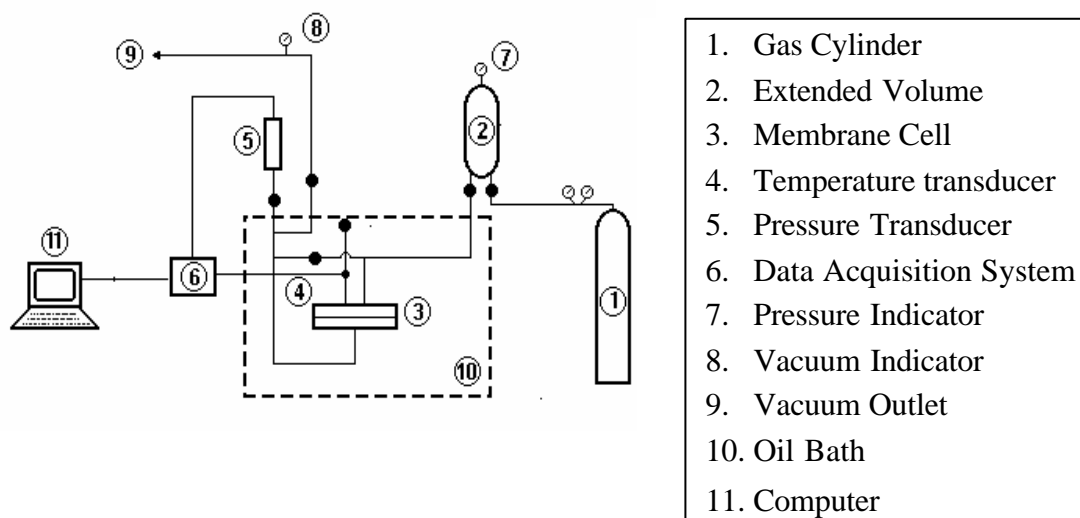


Figure 3.8 Gas permeation apparatus

3.7 Scanning Electron Microscope (SEM) Studies

The morphology of the PU membrane was observed by examining the cross sections and surfaces of the membranes in a scanning electron microscope (JEOL JSM-5410). Membrane samples were prepared for SEM by breaking it in liquid nitrogen and then coating with gold using a sputter coater [47].

3.8 Tensile Tests

Tensile strength of PU membranes were tested under dry conditions by using an Instron Universal Tester at room temperature (Figure 3.9). Films for these tests, at a thickness of 100μ , were cast onto Teflon coated glass into a ring with 55 cm diameter. A test specimen is clamped in a tensile testing machine and a force applied to the specimen until it breaks. Values for the breaking force and elongation of the test specimen were obtained from the computer interfaced with the testing machine. Operating speed was 12 in./min. Specimen type is 1R-25 mm raveled strip, which is 25 mm wide by at least 150 mm long with the long dimension accurately parallel to the direction for which the breaking force is required [48].

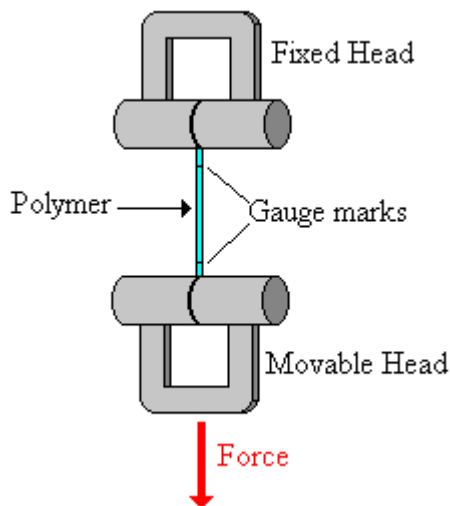


Figure 3.9 Tensile test apparatus

3.9 Water Absorbency Measurements

Absorbency is one of several factors that determines the suitability of a fabric for a particular use, as in the wound dressing, gauze, towel. A drop of a specified volume of water or another agreed upon test liquid is applied to a test specimen surface using a liquid delivery system and specified deposition parameters, observation is made on completeness and uniformity [49].

4. RESULTS AND DISCUSSION

4.1 Preparation of Polymers

Polymers were prepared by two or three successive steps. The overall reaction are described in Figure 4.1

Hydroxyl value of partial glyceride mixtures (PG) is given in Table 4.1

Table 4.1 Isocyanate ratios of the polymers

CODE	Hydroxyl value of PG	The ratio of isocyanate Components (HMDI : MDI)
PU ₁	118.2	1 : 0
PU ₂	118.2	0.50 : 0,50
PU ₃	118.2	0 : 1
PU ₄	118.2	Blend of PU1 and PU3 (1 : 1)
PU ₅	177.8	0.50 : 0.50

The equivalent amount of isocyanate component was added to PG. This means that in the reaction mixture one isocyanate group was calculated for each hydroxyl group. In the case of two isocyanate components, total isocyanate group is equivalent to hydroxyl group. But the ratio of isocyanate components to each other is given in Table 4.1.

Hydroxyl value of the partial glyceride mixture was found 118.2 mg KOH/g and acid value was found 5.36 KOH

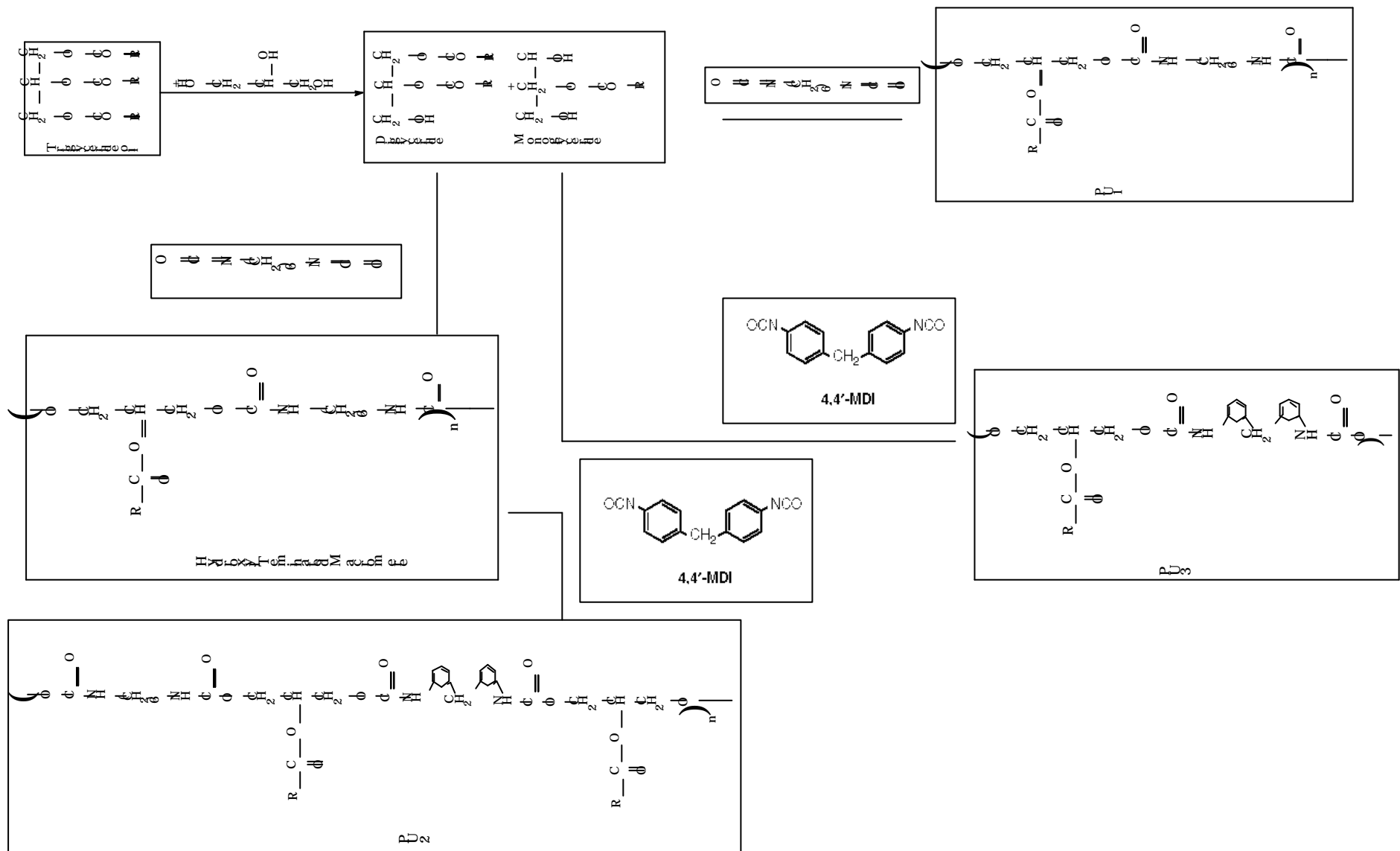


Figure 4.1 Schematically reactions equations for polymers

The reactions were controlled by IR measurements. On Figures 4.2, 4.3, 4.4 and 4.5 the IR spectra of both the initial reaction mixture and the final product are shown. The spectra of the final product does not have an absorption peak at 2250 cm^{-1} , assigned to the $\text{N}=\text{C}=\text{O}$ group.

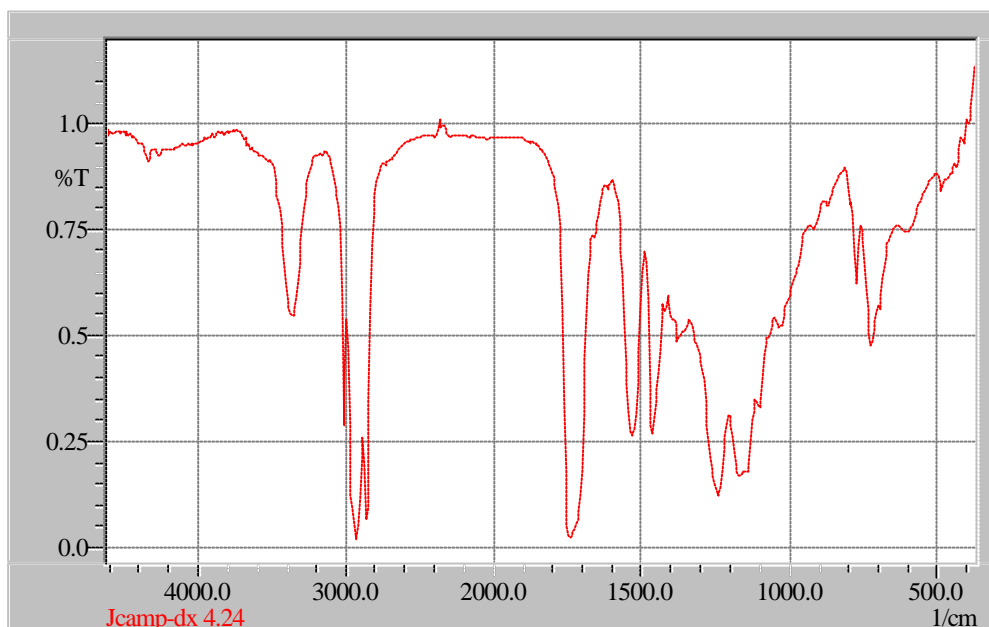


Figure 4.2 IR spectrum for PU_1

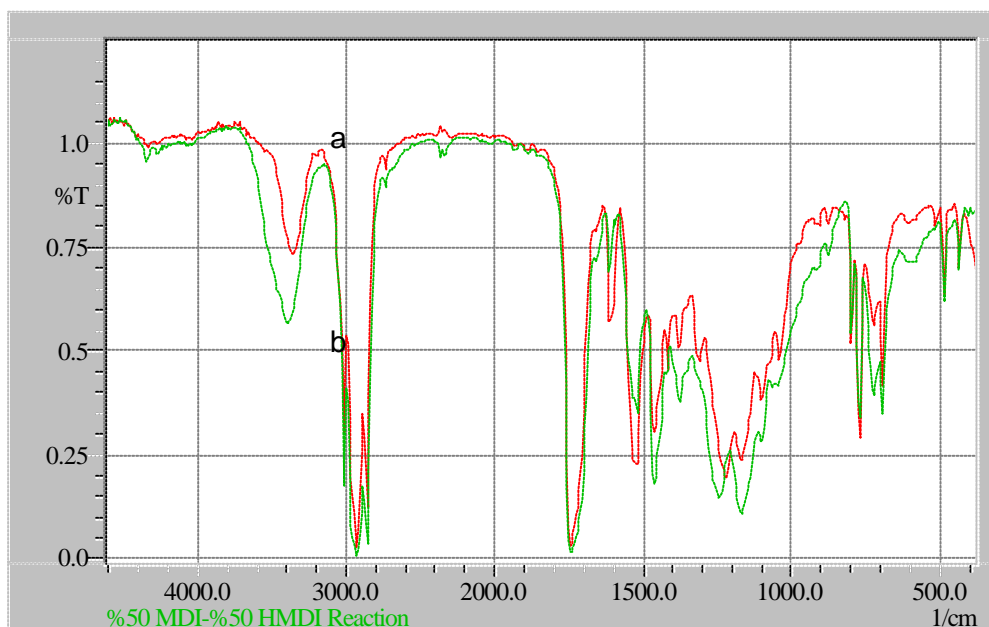


Figure 4.3 IR spectrum for PU_2 , PU_5 , (a) At the end of the reaction with HMDI
(b) At the end of the reaction Finish of reaction with MDI

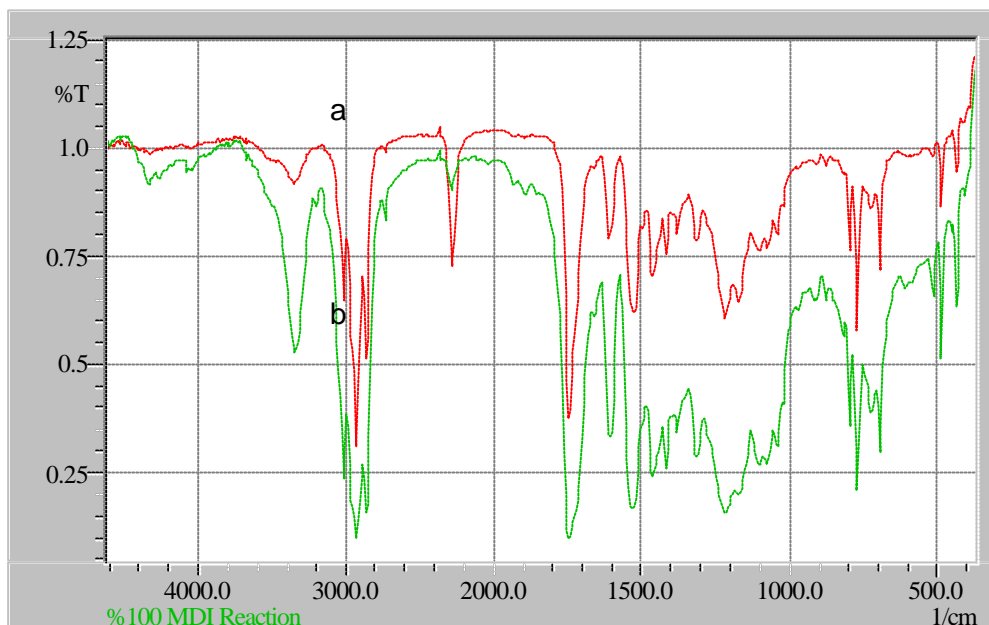


Figure 4.4 IR spectrum for PU₃ , (a) Beginning of reaction, (b) Finish of reaction

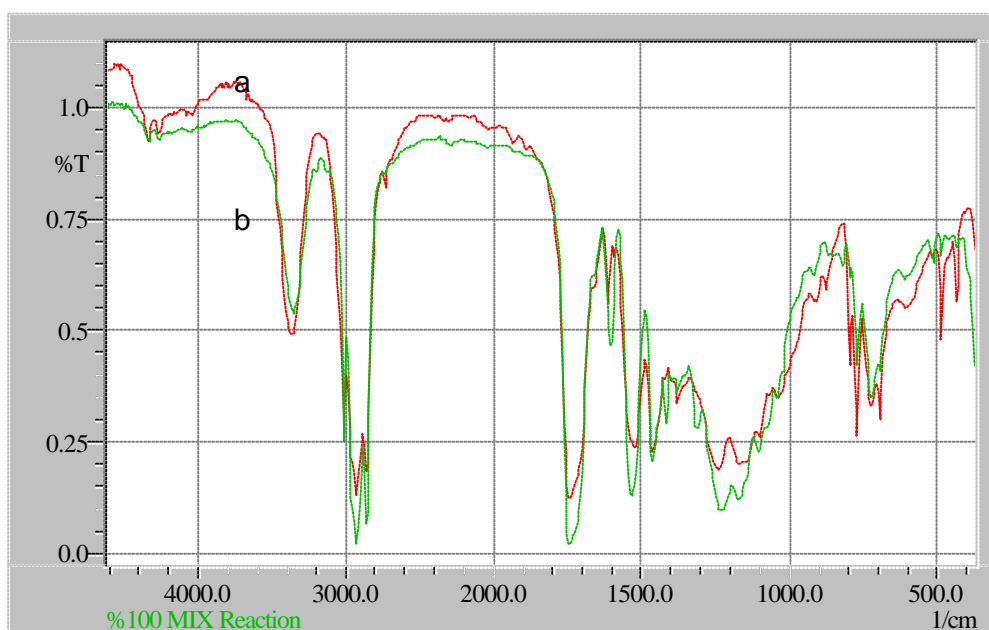
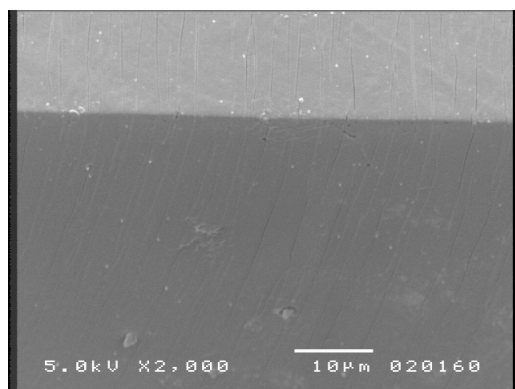


Figure 4.5 IR spectrum for PU₄, (a) At the end of reaction with HMDI, (b) At the end of reaction with MDI

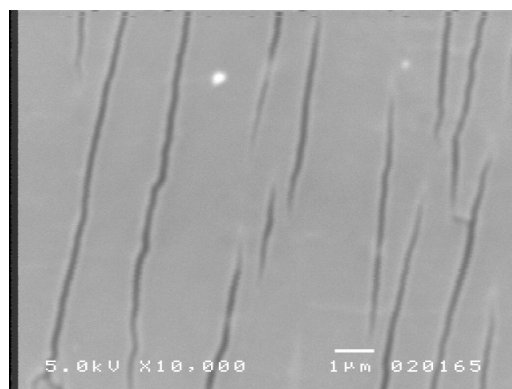
4.2 SEM Analysis

Fig shows the cross-sectional and surface views of PU membranes. In the cross-sectional photographs, upper side corresponds to the top surface. When PU2 membrane was evaporated, there were occurred a thin layer of columns (Fig.4.6(b1))

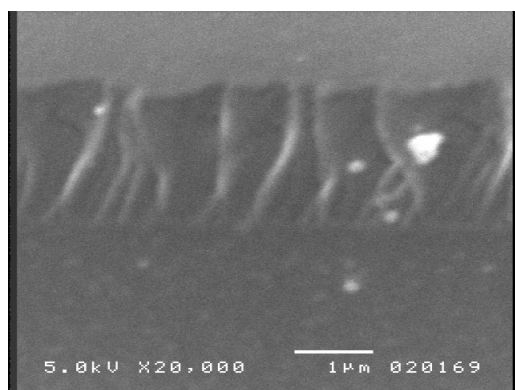
and discontinuous crack was observed at the surface. The gas permeation of PU2 weren't accomplished due to the defaults available in the membrane. On the other hand when PU1 membrane were evaporated there were formed permanent crack at the cross-sectional and at the surface of the membrane (Fig.4.6(a2)) but the gas permeation test accomplished. The structures of other PU membranes is regarded as a dense morphology. The lowest impurities and number of cracks observed in PU₃. The oriented aromatic structure formed a dense morphology.



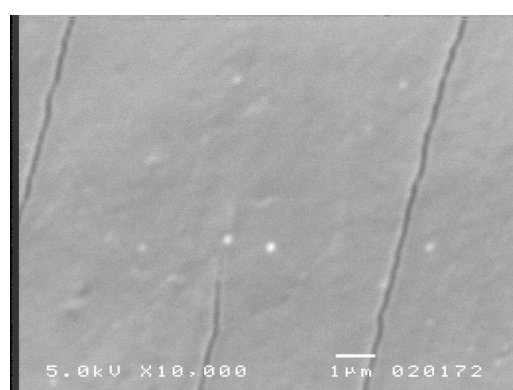
a1



a2

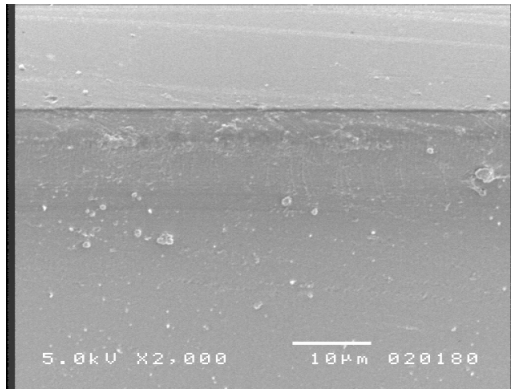


b1

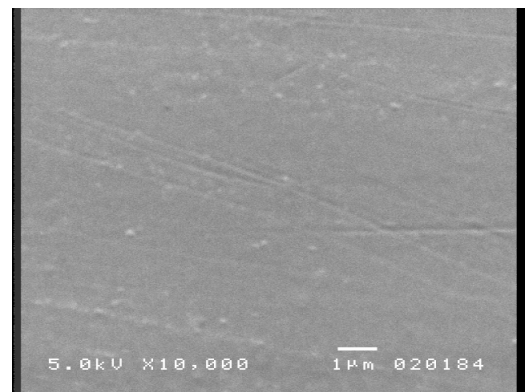


b2

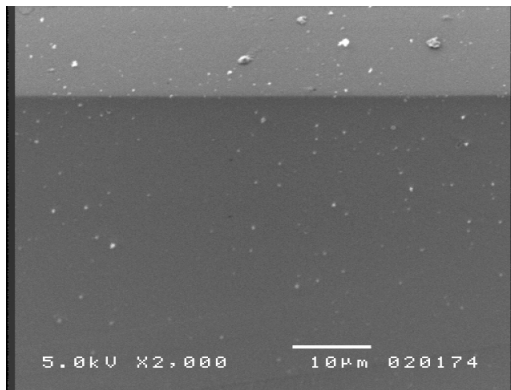
Figures 4.6 (a1), (b1), are SEM images of cross sections of PU1, PU2 membranes respectively, (a2), (b2), are SEM images of surface of PU1, PU2 membranes respectively.



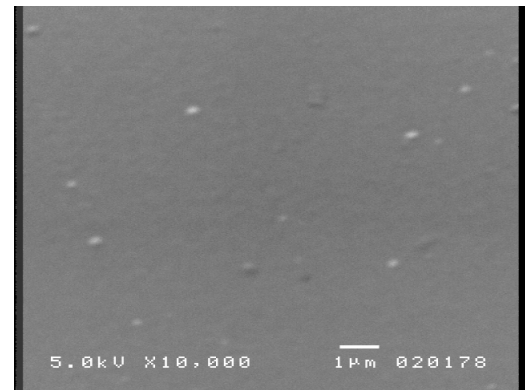
c1



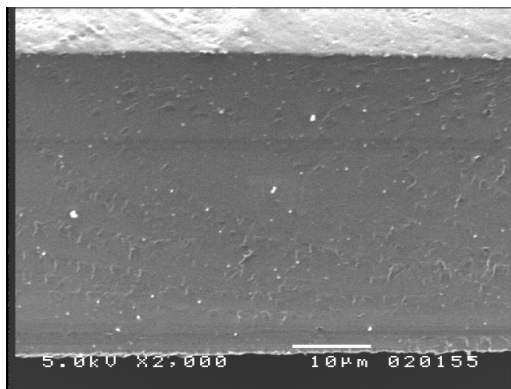
c2



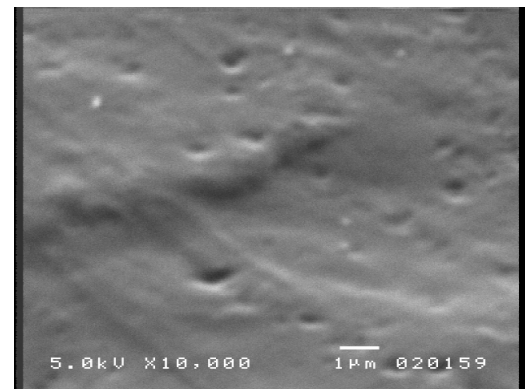
d1



d2



e1



e2

Figures 4.7 (c1) (d1), (e1) are SEM images of cross sections of PU3, PU4, PU5 membranes respectively, (c2), (d2), (e2) are SEM images of surface of PU3, PU4, PU5 membranes respectively.

4.3 Film Properties of The Polymers

Film properties such as drying time , water resistance, alkali resistance , and acid resistance, flexibility, adhesion, hardness were determined (Table 4.2).

Table 4.2 Film properties of the Polymers

Applied Test	PU ₁	PU ₂	PU ₃	PU ₄
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
Water resistance	33 min	98 min	47 min	26 min
Hardness	2	2	2	6
Alkali resistance	Removable	Removable	Partial Removable	Removable
Acid resistance	No Change	No Change	No Change	No Change

Drying times of the polymers have no particular difference. Adhesion is better in PU₁ and PU₂. However due to the increased ratio of aromatic structure, there is no adhesion in PU₃ and PU₄.

The flexibility of the PU membranes have superior properties. Cylinder with lowest diameter is used in bending tests which shows the high flexibility property of the polymers.

Hardness of polymers have no particular difference. The number of oscillations made by polymers are nearly same.

Acid resistance is superior in polymers. PU₃ has better alkali resistance compared with others due to the structure of MDI. Aromatic structure played as a barrier for NaOH .

4.4 Gas Permeabilities of The Polymers

The gas permeabilities of the membranes were measured in a gas permeability system based on constant volume/variable pressure technique. All measurements were carried out at 28°C and the permeation rates of O₂, N₂, and CO₂ gases were determined. Ideal selectivities were determined by calculating the ratio of the pure gas permeabilities. The gas permeability of the membrane was decreased as a result of increased crosslinking.

Table 4.3 Permeabilities of The Polymers

Membran	P _{O₂} (Barrer)	P _{N₂} (Barrer)	P _{CO₂} (Barrer)	α_{O_2/N_2}	α_{CO_2/N_2}	α_{CO_2/O_2}
PU1	2.76	0.42	0,09	6,57	30,67	4,67
PU3	0.67	0.17	3.86	3.94	22.71	5.76
PU4	4.38	1.538	31	2.84	20.15	7.07
PU5	0.86	0.15	4.25	5.73	28.33	4.94

4.5 Molecular Weights of The Polymers

Molecular weights of polymers obtained were given on Table 4.4 The molecular weight and polydispersity of the polymer were increased with the aromatic structure .

Table 4.4 Molecular weight of polymers

Polymer	M _w	PDI
PU1	3600	1.5
PU2	9300	3.08
PU3	2200	6.15
PU4	1200	3.8
PU5(Blend)	8500	1,49

4.6 Tensile Strengths of The Polymers

The tensile strengths of the samples were determined and the results are presented in Table 4.5. As the aromatic structure of the polymer was increased the tensile strength values increased from 1.28 to 3.80 lbf was observed. The oriented aromatic structure and due to increased molecular weight the tensile strength of PU₃ is increased.

Table 4.5 Tensile strengths of polymers

Polymer	Tensile Strength (lbf)
PU1	1.28
PU2	1.73
PU3	3.80
PU4	2.533

4.7 Water Absorbency Properties of The polymers

A drop of specified volume of water was applied on to the surface of the PU membranes, and no change on the uniformity and completeness were observed (Table 4.6).

Table 4.6 Water absorbency properties of polymers

Polymer	Absorption
PU1	>60 sec
PU2	>60 sec
PU3	>60 sec
PU4	>60 sec
PU5	>60 sec

CONCLUSION

The aim of this study is to produce the oil-based polymer and to use them in wound dressing applications. For this purpose first, partial glyceride mixtures prepared from triglyceride oils, hexamethyle diisocyanat and diphenylmethanediisosiyanat were used in the preparation of PU. The reactions of preparation were achieved in two or three steps. Then the PU membrane was prepared from the oil based PU. Gas permeability's, tensile strengths, film properties, water absorbency, structural properties were investigated.

Polyurethanes having low drying time, high acid resistance could be prepared. Additionally they were flexible, but not have good adhesion properties.

Increasing molecular weight of PU membrane decreases the permeability. The chemical composition of the PU polymers affects the strenght. Aromatic structure causes increase in molecular weight and relatively the tensile strength increase.

As a result oil- based polyurethanes could be used in wound dressing application.

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