Polyurethanes: effect of chemical composition on mechanical properties and oxygen permeability

Kezban Ulubayram and Nesrin Hasırcı*
Department of Chemistry, Middle East Technical University, Ankara 06531, Turkey

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A series of polyether urethane films with varying hard/soft segment ratio were synthesized using toluene-2,4-diisocyanate (TDI) and polypropylene glycol (PPG) in order to evaluate them as biomaterials. In order to obtain medical purity the polymerization reactions were carried out in bulk without using any other ingredients such as solvent, catalyst, u.v. absorber, etc. The effects of chemical composition and the presence of the chain extender on some properties were examined. For the samples with higher TDI to PPG ratio, a decrease in ultimate elongation and an increase in tensile strength were observed. Addition of chain extender caused an increase in both. On the other hand, the ultimate elongation increased and tensile strength decreased with an increase in molecular weight of the PPG used. As the chemical compositions are changed by increasing the polyol content, an increase in oxygen permeability is also observed.

(Keywords: polyether polyurethane; mechanical properties; oxygen permeability; biomaterial)

INTRODUCTION

During the past two decades there have been many successful attempts to prolong human life. Among these studies, the development of artificial organs has an important place. Devices manufactured from synthetic polymers have become an integral section of health care programmes and created a medium for extensive cooperation between the material suppliers, designers, manufacturers and physicians. The polymers used most often in biomedical applications are acrylate elastomers, butyl rubber, chloro sulphonated polyethylene, silicone rubber and heat vulcanizing silicone rubber[1].

As a new family of polymers, bio- and haemocompatible polyurethane elastomers with their unique physical and mechanical properties resulting from hard segment/soft segment microphase segregation, are materials of choice for a number of biomedical applications[2]. These polymers were originally developed for commercial applications unrelated to the medical field and exhibit high flexure endurance, high strength and inherent non-thrombogenic characteristics[3].

Polyurethane elastomers are the reaction products of organic isocyanates, high molecular weight polyols and low molecular weight chain extenders. Chemical factors such as composition, molecular weight of soft segment, length of hard segment, addition of chain extender and physical factors such as the fabrication method are used to alter the structure and morphology of phase separation in bulk or on the surfaces of the polymer. These factors, in turn, determine the performance in biomedical applications[4,5].

In the synthesis of polyurethanes several di- and polyfunctional, active hydrogen reactants have been used as chain extenders or crosslinkers. The selection of chain extender affects the elastomeric properties. The most important in this group are aliphatic and aromatic diols and diamines. When a diamine is employed as an extender a higher level of physical properties results than if a diol were used[2,6]. Many diamines are too reactive for use as chain extenders in the preparation of bulk elastomers because the time available is insufficient for adequate mixing and pouring before gelation occurs.

In this study, a series of polyurethane membranes was prepared in order to test them as biomaterials. Mechanical and oxygen permeability tests were performed on the prepared samples. The effects of chemical composition and the presence of chain extender on these properties were examined.

EXPERIMENTAL

Materials. Toluene-2,4-diisocyanate (TDI, EGA Chemie, Germany) was purified by vacuum distillation. Polypropylene glycol (PPG, BDH Chemicals, UK) of two different molecular weights (PPG-1025, PPG-2025) was used without further purification. 1,3-Propanediol (PD, Eastman, USA) was used as received.

Preparation of membranes. The polymerizations were carried out in bulk (under vacuum) without any additions such as solvent or catalyst. In some samples PD was used as chain extender. Polymerization reactions were performed at ~80°C and the duration for the preparation of prepolymer was 3 h. The samples containing chain extender were prepared by adding the chain

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* To whom correspondence should be addressed

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Table 1 Mol and volume ratio of monomers

Sample	Mol ratio PPG/TDI	Volume ratio PPG/TDI	Mol ratio C/TDI
PU1.5	0.67	4.806	–
PU1.5C[a]	0.67	4.806	0.67
PU2	0.50	3.605	–
PU2C	0.50	3.605	0.50
PU2.5	0.40	2.884	–
PU2.5C	0.40	2.884	0.40
PU3	0.33	2.403	–
PU3C	0.33	2.403	0.33
PU4	0.25	1.802	–
PU2(2)[b]	0.50	7.122	–
PU2C(2)	0.50	7.122	0.50
PU3(2)	0.33	4.748	–
PU3C(2)	0.33	4.748	0.33
PU4(2)	0.25	3.561	–
PU4C(2)	0.25	3.561	0.25

[a] C defines the presence of chain extender

[b] The molecular weight of PPG is 2025 g mol^{-1} in the sample notations suffixed by (2). For the nine other samples the molecular weight of PPG is 1025 g mol^{-1}

extender (in the same mol ratio as PPG) after the preparation of prepolymer. A detailed procedure has been given previously[7]. The viscous prepolymer solutions were poured into moulds and kept under vacuum. After the solidification of samples, the moulds were placed in a boiling water bath in order to eliminate the small amount of isocyanate present in the structure and to peel off the membrane easily from the moulds. The mol and volume ratio of the components used in the preparation are listed in *Table 1*.

The progress of the polymerization was followed using a Philips i.r. spectrophotometer (model PU 9716). For this purpose, the viscous prepolymer solution was smeared on NaCl crystals and i.r. spectra were taken at regular intervals. Both the crystals and the moulds were kept under the same conditions.

Mechanical properties. The stress–strain properties of the samples were determined with an Instron tensile tester. The crosshead speed was 1.25 cm min^{-1} and the measurements were made at 37°C until the sample broke. For each membrane, several runs (at least five) were carried out and the average value of these runs was used.

Oxygen permeability. An Otto Brugger gas permeability tester was used for the oxygen permeability measurements of four membranes [PU1.5, PU2.5, PU2.5C, PU3C(2)]. The tester is shown in *Figure 1*.

The following equation was used to calculate the gas permeability of the samples:

$$D^x = \frac{qXP_u}{F(1 + t/273)(P_b - P_u)} \qquad (1)$$

where D^x is the oxygen permeability of the sample (ml m^{-2} day^{-1} bar^{-1}) (ml at 1013 mbar and 0°C), q is the cross-sectional area of the capillary (cm^2), X is the sink rate of the mercury thread (cm day^{-1}), P_u is the pressure in the space between the membrane and the mercury thread (mbar), P_b is the atmospheric pressure (mbar), P_m is the pressure gauge reading (mbar), l is the length of the mercury thread (35 mm) in $P_u = P_b - P_m - l$, t is the test temperature (°C), F is the surface area (m^2) of the sample and $q/F = 1.63$.

RESULTS AND DISCUSSION

As mentioned previously, during synthesis no ingredients (e.g. solvent, catalyst, initiator, etc.) were used in order to attain medical purity, because their leaching from the crosslinked structure decreases biocompatibility[8]. In earlier studies, even chain extenders were not used for that reason[7,9,10]. However, as summarized in the Introduction, chain extenders significantly improve the mechanical properties of the polymers. Hence, in this study, chain extenders were used in the preparation of some samples in order to observe their effect on the properties of the product.

The reaction between isocyanate and alcohol groups takes place even at very low temperatures but the reactivity of the second isocyanate group after the first one has reacted is very low. In the literature it is given that these two reactivities get closer with an increase in temperature. At ~90°C they have almost equal values and therefore the formation of polyurethane takes place easily[11]. It is also known that at >150°C decomposition of the urethane bonds becomes significant. For these reasons, in this study polymerization reactions were achieved at ~80°C.

The progress of the polymerization reactions was followed from the i.r. spectra taken for each sample. As the reactions proceed and the samples solidify with the

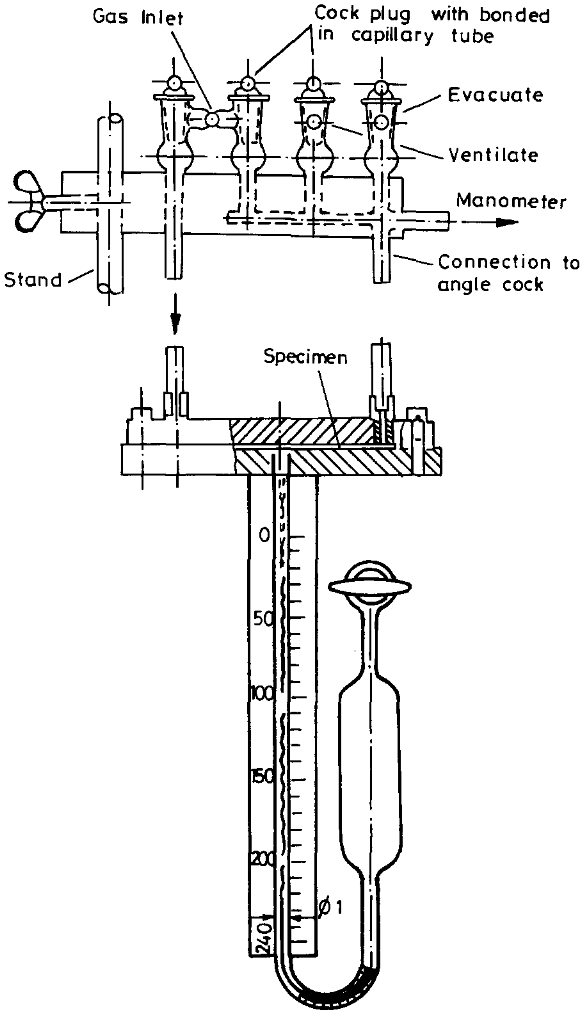

Figure 1 Otto Brugger gas tester

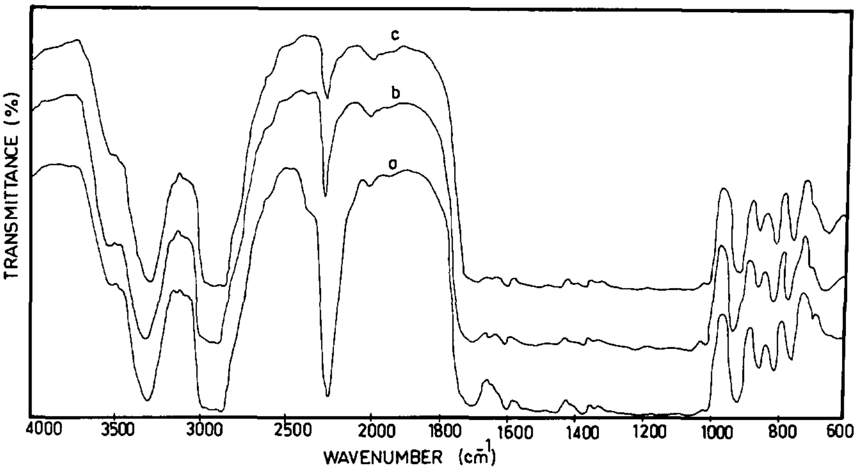

Figure 2 I.r. spectrum of PU2: (a) day 7; (b) day 30; (c) day 50

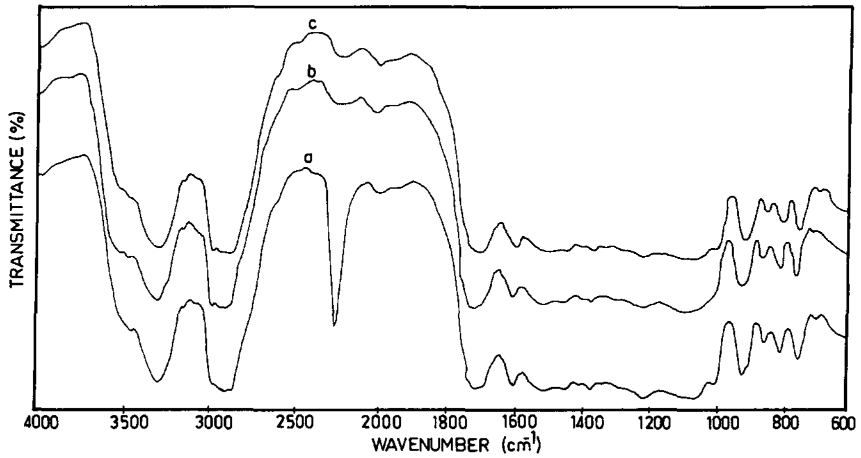

Figure 3 I.r. spectrum of PU2C: (a) day 7; (b) day 30; (c) day 50

formation of crosslinks, a decrease in the absorption peak of the isocyanate group at 2270 cm^{-1} occurs. A decrease of ~90% occurs in ~3–7 weeks depending on the presence of chain extender. Presence of chain extender in the reaction medium causes an increase in the reaction of the isocyanate group as shown in *Figures 2* and *3*. Lower amounts of free isocyanate were observed for PU2C samples compared to PU2 samples.

The stress–strain properties of the samples were determined and the results are presented in *Table 2*. As the molar ratio of glycol to TDI was decreased from 0.67 to 0.25 (respectively for PU1.5 and PU4 samples) an increase in the tensile strength values from 1.9 to 5.4 MPa and a decrease in the ultimate elongation from 95 to 71% was observed (*Figure 4*). Similar behaviour was also observed for samples with PPG-2025 (*Figure 5*).

This expected increase in the tensile strength with a decrease in polyol content is due to an increase in the number of crosslinks between the chains providing more resistance to the applied forces. On the other hand, a decrease in the amount of flexible soft segment (polyols) causes a decrease in the ultimate elongation[7,10,12].

As mentioned previously, chain extenders play an important role in the mechanical properties. Addition of chain extender causes a general increase of both tensile strength and ultimate elongation as shown in *Figures 6* and *7*. Tensile strength values of the samples PU1.5, PU2 and PU3 were 1.9, 3.1 and 4.6 MPa, respectively. However, similar samples prepared with the same composition plus chain extenders (PU1.5C, PU2C and PU3C) have higher tensile strength values, 2.7, 3.8 and 7.4 MPa, respectively. The ultimate elongation values demonstrated a substantial increase (three or four times)

Table 2 Mechanical properties of polyurethane films

Sample	Tensile strength (MPa)	Ultimate elongation (%)	Elastic modulus (MPa)
PU1.5	1.9 ± 0.1	95	3.5
PU2	3.1 ± 0.3	87	4.9
PU3	4.6 ± 0.7	84	9.3
PU4	5.4 ± 0.4	71	13.1
PU1.5C	2.7 ± 0.2	430	1.6
PU2C	3.8 ± 0.1	381	2.3
PU3C	7.4 ± 0.2	244	3.6
PU2(2)	1.9 ± 0.3	105	2.8
PU3(2)	2.9 ± 0.1	96	8.6
PU4(2)	1.5 ± 0.4	33	13.6
PU2C(2)	2.0 ± 0.1	209	1.9
PU3C(2)	6.1 ± 0.1	310	3.6
PU4C(2)	6.4 ± 0.1	239	5.6

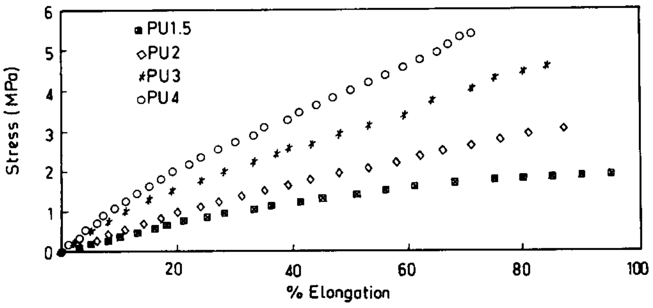

Figure 4 Stress *versus* percentage elongation for PU samples

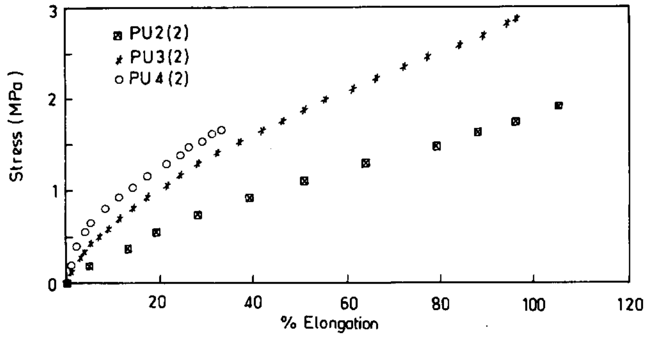

Figure 5 Stress *versus* percentage elongation for PU(2) samples

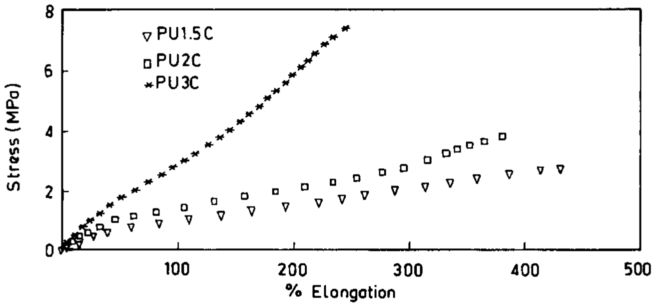

Figure 6 Stress *versus* percentage elongation for PUC samples

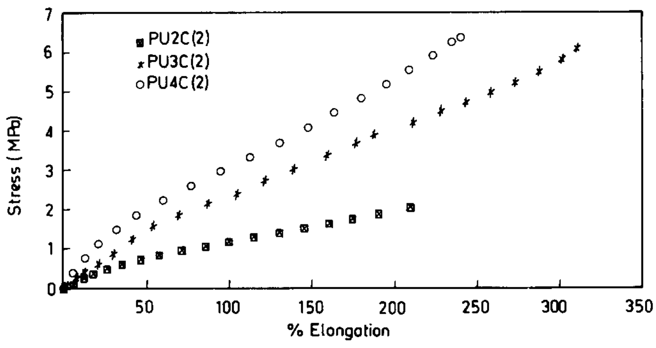

Figure 7 Stress *versus* percentage elongation for PUC(2) samples

with addition of chain extender. An increase from 95 to 430% for PU1.5 and PU1.5C, respectively, and from 84 to 244% for PU3 and PU3C, respectively was observed. A similar trend was observed for the samples prepared with PPG-2025. This increase in ultimate elongation values with addition of chain extender can be explained as follows: During the preparation of samples, the presence of excess TDI leads to isocyanate-tipped macrochains and chain extenders connect these groups leading to longer macrochains. That, of course, causes an increase in the flexibility leading to higher ultimate elongation values while decreasing the hardness of the products.

The chemical composition of the polyurethane polymers also affects their modulus values as shown in *Table 2*. An increase in the molar ratio of TDI to PPG-1025 causes an increase in modulus values. Addition of chain extender caused a drop in modulus values from 3.4 to 1.6 MPa and from 9.3 to 3.6 MPa for PU1.5 and PU3 samples, respectively. The same trend was also observed for samples prepared from PPG-2025.

As it can be seen from *Table 2*, an improvement in the mechanical properties was observed upon reducing the glycol molecular weight at constant hard segment content. The decrease of molecular weight of PPG from 2025 to 1025 causes an observed increase in tensile strength and elastic modulus for all samples and leads to a decrease in ultimate elongation. As the molecular weight of the glycol was increased from 1025 to 2025 for the same type of samples, more flexible chains were obtained. Thus one can conclude that the flexibility leads to softness and elasticity[13,14].

In this work, the mechanical test values were found to be lower than the results for conventional polyurethanes[13] which are generally produced by solution polymerization using solvent, catalyst, chain extenders and other ingredients. It was mentioned previously, however, that these additives decrease biocompatibility.

Polyurethanes are commonly used as skin graft materials. In these types of applications an important factor is the oxygen allowance of the graft. Since human beings obtain oxygen through their skin (at a rate of $0.5\ \mu\text{mol cm}^{-2}\ \text{h}^{-1}$)[15], oxygen permeability tests were performed on the samples and the results are presented in *Table 3*. According to these values, oxygen permeability increases with an increase in the amount of flexible soft segment. It was also found that oxygen permeability drops from 2.14×10^{-8} to $8.47 \times 10^{-9}\ \text{cm}^2\ \text{s}^{-1}$ when a chain extender is added to samples with the same composition. Addition of chain extender causes longer flexible chains and therefore an increase in oxygen permeability was expected. An almost three-fold decrease obtained in the permeability values could be the result of the regular arrangement of the macrochains of polyglycols. For the PU3C(2) sample, although the molar TDI to polyol ratio was twice that of PU1.5, the oxygen permeability values were found to be similar. The presence of chain extender affects this permeability like the increase of the molecular weight of the polyol. The values obtained are almost one order lower than the human skin values. Use of higher molecular weight polyols or non-aromatic isocyanates could be suggested in order to increase the oxygen permeability values.

Table 3 Oxygen permeability of polyurethane films

Sample	Thickness (m)	D^x (ml m^{-2} day^{-1} bar^{-1})	Oxygen permeability (cm^2 s^{-1})
PU1.5	1.306×10^{-3}	325.1	4.93×10^{-8}
PU2.5	1.345×10^{-3}	162.4	2.14×10^{-8}
PU2.5C	1.086×10^{-3}	67.3	8.47×10^{-9}
PU3C(2)	1.485×10^{-3}	274.2	4.72×10^{-8}

CONCLUSIONS

The properties of the polyurethane membranes prepared from TDI and PPG vary depending on the composition, presence of chain extender or molecular weight of PPG.

The samples with higher TDI to PPG ratios had higher tensile strength, lower ultimate elongation and lower oxygen permeability. Incorporation of a chain extender or increasing the PPG molecular weight had a similar effect on these properties.

In conclusion, it is possible to synthesize polyether urethanes with the desired properties by varying the initial composition, the type of ingredients and their molecular weights.

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