Polyurethane elastomers from cycloaliphatic diisocyanate and polyols with participation of castor oil

In order to obtain the elastomers useful for medicine, the polyurethanes (PURs) with 4,4'-methylenedicyclohexyl diisocyanate and castor oil participation were obtained in the presence of different catalysts. These PURs are of good mechanical properties and good chemical resistance to hot water and hexane. In sorption of water and contact angle with water the obtained PURs are close to some typical "biomedical" polyurethanes but there was found greater sorption of natural oil in these elastomers. The thermomechanical and thermochemical properties of PURs were described.

Key words: polyurethanes, castor oil, physical and chemical properties

Elastomery uretanowe z cykloalifatycznego diizocyjanianu i polioli z udzialem oleju rycynowego

W celu uzyskania elastomerów przydatnych dla medycyny dokonano syntezy poliuretanów (PUR) z udziałem 4,4'-diizocyjanianu dicykloheksylometanu i oleju rycynowego, w obecności różnych katalizatorów. Otrzymane PUR charakteryzowały się dobrymi właściwościami mechanicznymi i dobrą odpornością chemiczną na działanie gorącej wody i heksanu. Pod względem sorpcji wody i kąta zwilżania otrzymane elastomery są podobne do typowych poliuretanów "biomedycznych", natomiast wykazują zwiększona sorpcję oleju naturalnego. Opisano stabilność termomechaniczną i termochemiczną otrzymanych elastomerów uretanowych.

Słowa kluczowe: poliuretany, olej rycynowy, właściwości fizyczne i chemiczne

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We expected that use of the castor oil in PUR synthesis would allow hemocompatibility because of the expected greater affinity to albumins, countering the deposition of thrombogenic fibrinogen. The PUR with incorporated natural lipid substance would be more close to the natural cell membrane, built from proteins and fats. The partial crosslinking of PURs and their intrinsic plasticization connected with the I structure should have an advantageous effect on the flexibility of the PURs. It was interesting if such obtained elastomers fulfil requirements of materials for medicine with regard to physical and chemical properties.

**Experimental**

**Materials**

The substrates used in PUR synthesis:
- Poly(oxytetramethylene) glycols (PTMG): Terathane 2000, (Du Pont, Aldrich), M=2040 g/mol, and PTMG M= 1000 g/mol, (Du Pont); before synthesis the melts of PTMG were filtrated and dehydrated by heating at mixing at 90°C under reduced pressure (1.4 hPa) through 3 h.
- 4,4'-Methylene dicyclohexyl diisocyanate (SMDI), (Aldrich), mixture of isomers; distilled under reduced pressure at temp. 200°C.
- 1,4-Butanediol (1,4-BD) (BASF), dehydrated and purified by azeotropic distillation.
- Castor oil (C.O.), (Aldrich), dehydrated by heating in vacuum rotatory (1.4 hPa) at 60°C/3 h; the estimated L<sub>OH</sub>=177 mg KOH/g, L<sub>COOH</sub>=5.48 mgKOH/g.
- Catalysts;
  - Dibutyltindioctoate (DBTDO), (Air Chemicals);
  - Stannous 2-ethylhexanoate (stannous octoate, SnOc), (Sigma);
  - Diazabicyclooctane (tri-ethylendiamine) (DABCO), (Houdry-Hüls).
- Solvent - dimethylformamide (DMF) (POCh Poland), dehydrated over P<sub>2</sub>O<sub>5</sub> and distilled under reduced pressure.

**Synthesis of PURs**

PUR-I based on PTMG 1000 and PUR II-V based on PTMG 2040 were obtained by two step method with the equivalent ratio of NCO to OH groups with different contents of the substrates and catalysts (Table 1). In the first step the prepolymer from PTMG,
C.O. and diisocyanate was obtained at temp. 90-95°C under reduced pressure (1,4 hPa) in a presence of the catalyst with mass % shown in Table 1. After cooling the prepolymer to 60°C the DMF was added (to solid mass concentration of 30-50%), and in the second step the reaction with 1,4-BD was followed under normal pressure through 2 h at temp. 60°C. The reaction was controlled by IR spectroscopy, after evaporation of the solvent from the polymer films on NaCl.

Table 1. Ratio of poliol hydroxyl groups and catalysts in synthesis of PUR-I from PTMG 1000 and PUR II-V from PTMG 2040

<table>
<thead>
<tr>
<th>PUR</th>
<th>Stoichiometric ratio of OH groups</th>
<th>Catalysts, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PTMG Castor oil 1,4-BD</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1 0.2 2</td>
<td>DBTDO (0.04)</td>
</tr>
<tr>
<td>II</td>
<td>1 0.3 3.5</td>
<td>DBTDO (0.04)</td>
</tr>
<tr>
<td>III</td>
<td>1 0.3 3.5</td>
<td>SnOc (0.09)</td>
</tr>
<tr>
<td>IV</td>
<td>1 0.73 4.72</td>
<td>SnOc (0.09)</td>
</tr>
<tr>
<td>V</td>
<td>1 0.73 4.72</td>
<td>DABC0 (2.5)</td>
</tr>
</tbody>
</table>

PURs were processed into foils by pouring the polymer solution into a centrifuge aluminium drum, covered by silicon antiadhesion layer, and evaporation of the solvent at temp. up to 60-70°C. Polymer layer was gradually heated in vacuum dryer (1,4 hPa) to temp. 80°C/1 h and next to temp.110°C/5 h. PUR foils were finally heated in vacuum dryer for 3 h at 140°C.

Before the investigations of properties the PUR foils were seasoned for 7 days at room temperature.

Methods of investigation

Mechanical properties

The stress-strain properties of PURs were tested at room temperature with the tensile tester FPZ 100 (Rauenstein, Germany), using samples of 50 mm x 10 mm in dimensions and thickness of 0.1 to 0.2 mm, at the extension rate of 4.5 mm/s.

The hardness was determined with Shore’s A apparatus on samples consisting of several layers of PUR foils (approximate value).

The flexibility of PURs was measured with use of de Mattia apparatus, according to PN-69/C-94170 with a frequency of 300±10 cycles/min; the samples of foils of 140x25 mm in dimensions and 0.1-0.3 mm in thickness were used.

Thermomechanical and thermochemical analyses

The dynamic mechanical thermal analysis (DMTA) in the temperature range from -100°C to 200°C was carried out on Polymer Laboratory DMTA Mk III analyser (England), at a heating rate of 4 deg/min and at a frequency of 1 Hz.

The thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed in air by means of the OD 104 MOM Derivatograph (Hungary), at the heating rate of 6 deg/min and sensitivity of TG-200, DTG-1/5 and DTA-1/3.

Stability of PURs in contact with water, hexane and natural oil

The properties of PURs in contact with water and oil were performed on samples of foils washed before with water containing detergent, water from mains and distilled water. After drying foils were extracted by hexane in Soxhlet apparatus for 5 h. Foils were next dried for five or more days at room temperature.

The changes of surface view were investigated after this cleaning process with use of the optic reflected microscope of PZO, Warsaw, with the objective 20/0.6 and the camera of Videotronic International GmbH; the magnification - 300x.

The samples of PUR foils with both sides surfaces of 120 cm² were treated by 20 cm³ of redistilled water at temp. 70°C/24 h. pH of the water extracts was measured at room temperature with the CP-215 pH-meter (Elmetron, Poland). Such obtained water extracts from PURs were evaporated and their dry residues were compared with a dry residue of the same volume redistilled water. This investigation was made according to USP XXII, Physicochemical Tests-Plastics.

According to procedure outlined in Code of Federal Regulation,Title 21, Ch. 1, Subchapter B, part 177.2600 [12], the extracts from PURs in boiling water and in boiling hexane were obtained (at refluxing) for 7 h and additionaly 2 h. Dry residues of the extracts were determined and investigated by IR spectroscopy, by means of the Specord 71 IR (Carl Zeiss, Jena) - films on NaCI or by means of Bruker IR spectrophotometer - in KBr.

Sessile drop contact angles with water in air were
measured using a goniometer, at room temperature.

Water sorption and sunflower oil sorption were determined with an accuracy of 0.0001g by measuring the increase of weight of dried PUR samples after keeping them in distilled water or in oil at temp. 38°C/24 h. Samples of foils were after sorption pressed between filter paper and immediately weighed.

Results and discussion

In the Table 1 the polyol components and catalysts used in PURs synthesis is presented and on the Fig. 1 the scheme of their chemical structure is shown. The IR spectrum of PUR - II on the Fig. 2 measured after synthesis and drying the film on NaCl (0.5 h/50°/1.4 hPa) shows the bands: NH at 3200 cm⁻¹, CH₂ at 2860 cm⁻¹, 2795 cm⁻¹ and 1450 cm⁻¹ (in cyclohexane ring), C=O at 1703 cm⁻¹ in urethane group and 1690 cm⁻¹ in ester group, N-H + C-N at 1530 cm⁻¹, C-O-C in ester group at 1250 cm⁻¹, CH₂-O-CH₂ in polyether chain at 1110 cm⁻¹; the bands at 1675 cm⁻¹ and 980 cm⁻¹ are due to C=C band.

Besides of typical substrates e.g. polyetherdiol - PTMG and 1,4-BD as a chain extender of PUR macromolecules, we used in syntheses the castor oil and SMDI. The means of the cycloaliphatic diisocyanate allow to eliminate the possibility of occurrence of the toxic, carcinogenic aromatic p,p'-diamine, which may occur through hydrolysis in PUR obtained from 4,4'-methylene diphenylmethane diisocyanate (MDI). SMDI is now used in producing of some commercial polyurethane elastomers for medical applications [1-5].

The advantageous feature of such elastomers is also the low temperature of processability and the lack of yellowing in comparison to polyurethanes from the aromatic MDI, in which the quinoid structure is formed on the light [13].

Mechanical properties of PURs

PURs I-IV obtained in our work are similar in hardness and tensile strength (Table 2) to such commercial "biomedical" polyurethanes as Pellethane 2363 - 80A (Dow Chemical)[12] or ChronoThane P-
75A (CardioTech International)[14] (Table 3) produced from MDI, PTMG and 1,4-BD and also to elastomers manufactured from SMDI as Tecoflex - 80A (Thermedics Inc.)[3,5] and ChronoFlex AL - 80A (CardioTech International), the last one manufactured from polycarbonatediol[14] (Table 3).

The PUR - V synthesised with use of tert-amine catalyst DABCO is characterized by lower tensile strength than remaining PURs, obtained with organic tin compounds presence. From these last catalysts, the DBTDO was more active in syntheses than SnOc, which concentration necessary to obtain elastomers of

Table 2. Mechanical properties of obtained PURs
Tabela 2. Właściwości mechaniczne otrzymanych

<table>
<thead>
<tr>
<th>PUR</th>
<th>Hardness, °ShA</th>
<th>Stress at 100% elongation, ( \sigma_{100%} ), MPa</th>
<th>Stress at 300% elongation, ( \sigma_{300%} ), MPa</th>
<th>Tensile strength ( \sigma_s ), MPa</th>
<th>Ultimate elongation ( \varepsilon_s ), %</th>
<th>Tension set, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>82</td>
<td>7.1</td>
<td>27.5</td>
<td>41.4</td>
<td>370</td>
<td>4</td>
</tr>
<tr>
<td>II</td>
<td>82</td>
<td>8.2</td>
<td>17.2</td>
<td>49.5</td>
<td>550</td>
<td>10</td>
</tr>
<tr>
<td>III</td>
<td>82</td>
<td>6.8</td>
<td>14.5</td>
<td>34.8</td>
<td>530</td>
<td>13</td>
</tr>
<tr>
<td>IV</td>
<td>83</td>
<td>8.8</td>
<td>17.1</td>
<td>31.0</td>
<td>500</td>
<td>18</td>
</tr>
<tr>
<td>V</td>
<td>81</td>
<td>6.8</td>
<td>13.5</td>
<td>18.6</td>
<td>430</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 3. Mechanical properties of some commercial "biomedical" polyurethanes
Tabela 3. Właściwości mechaniczne wybranych handlowych poliuretanów "biomedycznych"

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>Hardness, °ShA</th>
<th>Stress at 100% elongation, ( \sigma_{100} ), MPa</th>
<th>Stress at 300% elongation, ( \sigma_{300} ), MPa</th>
<th>Tensile strength ( \sigma_t ), MPa</th>
<th>Ultimate elongation ( \varepsilon_t ), %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellethane 2363-80A</td>
<td>83</td>
<td>5.86</td>
<td>10.0</td>
<td>41.4</td>
<td>550</td>
<td>12</td>
</tr>
<tr>
<td>ChronoThane P-75A</td>
<td>75</td>
<td>5.80</td>
<td>11.4</td>
<td>35.2</td>
<td>800</td>
<td>14</td>
</tr>
<tr>
<td>Tecoflex 80A</td>
<td>85</td>
<td>2.8*</td>
<td>6.7</td>
<td>42.0</td>
<td>580</td>
<td>2,3</td>
</tr>
<tr>
<td>ChronoFlex AL</td>
<td>80</td>
<td>4.5</td>
<td>-</td>
<td>36.5</td>
<td>585</td>
<td>14</td>
</tr>
</tbody>
</table>

* Initial modulus

good mechanical properties had to be more than twice greater. The advantageous property of SnOc catalyst is its low toxicity [15]; according to the producers (f.e. Akzo Chemie) this catalyst is harmless.

In comparison to commercial "biomedical" polyurethanes the PURs obtained in our work with C.O. participation are characterized by greater stress at 100% and 300% of elongation \( (\sigma_{100}, \sigma_{300}) \) measured at room temperature. It may be changed to lower values by decrease of the 1,4-BD and SMDI ratio in polymer synthesis.

PUR - I from PTMG 1000 is more stiff than elastomers obtained from PTMG 2040, as indicate the much higher \( \sigma_{300} \) and lower \( \varepsilon_t \) (Table 2).

We compared also the PURs II - IV with polyurethanes described by Saxena and coworkers[16] and with PUR obtained in another way in our laboratory[17] from poly(oxypropylene)glycol, MDI, 1,4-BD and C.O. The elastomers presented in this paper are of distinctly higher tensile strength.

Investigation of resistance to multiple bending on de Mattia flexometer showed that the PUR - II, III and IV withstand without fatigue failure over 23 912 000 cycles. For the Tecoflex 80A the fatigue cycles of 2x10^6 and for Pellethane 2363 - 80A the fatigue cycles of 23x10^6 was mentioned [3].

**Thermomechanical and thermochemical stability of obtained PURs**

On the Fig. 3 the dynamic mechanical thermal analysis diagram is shown for PUR-IV. The average glass temperatures \( (T_g) \), the softening temperatures \( (T_{m1}, T_{m2}) \) and the storage moduli of elasticity \( (E') \) in three temperatures are described in the Table 4 for PUR I-IV.

The glass temperatures assigned from the maximum of the loss moduli \( (E'') \) were shown for all PURs near temp. -57°C (Table 4). On the \( \tan \delta = E''/E' \) temperature dependence, beside of the maximum responsible for \( T_g \), a second maximum was visible for all PURs at temp. 36-50°C connected probably with the change in the hard segments of small range of arrangement. This conversion in physical structure of obtained PUR and their partial softening at body temperature, was noted also on decrease of the \( E' \) moduli with increasing the temperature to 40°C, particularly great for PUR-I from PTMG 1000 (Table 4). The PURs from PTMG 2040 even at temp. 100°C exhibit the elastic moduli at bending of significant value.

Table 4. Thermomechanical properties of PURs (from DMTA with bending)
Tabela 4. Właściwości termomechaniczne PUR (na podstawie DMTA przy zginaniu)

<table>
<thead>
<tr>
<th>PUR</th>
<th>( T_g ), °C</th>
<th>Storage moduli of elasticity, ( E' ), MPa</th>
<th>( T_{m1} ), °C</th>
<th>( T_{m2} ), °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-57</td>
<td>156.4</td>
<td>37.2</td>
<td>4.9</td>
</tr>
<tr>
<td>II</td>
<td>-57</td>
<td>120.0</td>
<td>103.0</td>
<td>29.8</td>
</tr>
<tr>
<td>III</td>
<td>-56</td>
<td>267.0</td>
<td>182.0</td>
<td>42.0</td>
</tr>
<tr>
<td>IV</td>
<td>-57</td>
<td>316.0</td>
<td>214.0</td>
<td>29.0</td>
</tr>
</tbody>
</table>

The very strong deflections of \( \tan \delta \) temperature dependence up to 126-150°C for PUR II-IV and up to 160°C for PUR-I corresponds to full softening and flow of these elastomers \( (T_{m2}) \) (Table 4).

On the DTA plots for PUR I-IV we observed an endothermic pick in the range of 170°C - 177°C (Table 5), which may be connected with melting temperature of the segments from SMDI and 1,4-BD.

From the thermogravimetric analysis (TG, DTG) the temperatures of the decomposition start responsible for 10% weight loss \( (T_{10}) \) of PURs were determined at 322-336°C. Next two steps of the
maximal thermal decomposition were visible ($T_{1\text{max}}$, $T_{2\text{max}}$); at temp. 400°C the mass residue of obtained PURs was in the range of 65-68% (Table 5).

Table 5. Thermal stability of PURs (from DTA and TG)

<table>
<thead>
<tr>
<th>PUR</th>
<th>$T_{\text{melt}}$ °C</th>
<th>$T_{1\text{max}}$ °C</th>
<th>$T_{2\text{max}}$ °C</th>
<th>Mass residue at 400°C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>174</td>
<td>336</td>
<td>354</td>
<td>420</td>
</tr>
<tr>
<td>II</td>
<td>177</td>
<td>336</td>
<td>347</td>
<td>428</td>
</tr>
<tr>
<td>III</td>
<td>170</td>
<td>327</td>
<td>332</td>
<td>428</td>
</tr>
<tr>
<td>IV</td>
<td>174</td>
<td>322</td>
<td>333</td>
<td>434</td>
</tr>
</tbody>
</table>

Investigation of the interaction PUR with water, hexane and natural oil

The microscopic observations of the PURs surfaces showed that the cleaning of these polymers by water with detergent did not cause greater changes on the foil surfaces, but after the extractions by hexane in Soxhlet apparatus the view of the foils surface was more extended (Fig. 4).

The sessile drop contact angles with water were measured from 72° for PUR-II to 81° for PUR-I (Table 6). The lower hydrophilicity of PURs obtained with C.O. participation caused lower water sorption in these polymers (Table 6) than was found for such “biomedical” polyurethanes as polyurethane-polysiloxane Cardiothane 51 or poly(urethaneurea) Biomer Sol G, to which sorption of water was given 1.6% and 1.2% responsible [3].

Table 6. Properties of PURs in contact with water

<table>
<thead>
<tr>
<th>PUR</th>
<th>Sessile contact angles, °</th>
<th>Sorption of water Δm/m, %</th>
<th>Extracts in water past 24 h/70°C</th>
<th>pH</th>
<th>pH displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>81</td>
<td>0.1</td>
<td>4.95</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>72</td>
<td>0.7</td>
<td>5.15</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>79</td>
<td>0.8</td>
<td>5.76</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>80</td>
<td>0.86</td>
<td>5.55</td>
<td>1.24</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4. The microscopic image of the PUR-II surface: a) raw, b) after washing by water with detergent, c) after extraction with hexane in Soxhlet apparatus; magnification 300x

Rys. 4. Obraz mikroskopowy powierzchni PUR-II: a) folia surowa, b) po myciu wodą z detergentem, c) po ekstrakcji heksanem w aparacie Soxhleta; powiększenie 300x

Treating of PUR I-IV by redistilled water at temp. 70°C through 24 h caused a small acidification of water, what probably was the result of partial hydrolysis of the ester bonds of fatty glycerides. The differences between pH of water and pH of the extracts from PUR I-IV, were measured in the range of 1.03 - 1.84 after such heating (Table 6) and were lower than it was found for Pellethane 80 AE (pH displacement 2.14) [18]. Differences between mass of dry residues of such obtained water extracts from PUR I, II, III and dry residues of equal water volume (0.25 mg) were respectively 0.25, 1 and 0.50 mg e.g. were much lower than difference maximal allowed in USP XXII (15mg).

We investigated also the stability of PUR II and IV on extraction by water and hexane at reflux temperatures, according to Code of Federal Regulation[12]. The dry extractibles estimated after 7 hours were lower than maximal allowed for both boiling water and boiling hexane extraction, but dry extractibles from next 2 hours refluxing were greater than allowed (Table 7).

<table>
<thead>
<tr>
<th>Boiling water</th>
<th>Boiling hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>first 7h</td>
<td>next 2h</td>
</tr>
<tr>
<td>PUR-II</td>
<td>0.17</td>
</tr>
<tr>
<td>PUR-IV</td>
<td>0.12</td>
</tr>
<tr>
<td>Max. allow.</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* after converting the milligrams/inch² into mg/cm²

The IR spectrum of the dry residue of PUR-IV extract in boiling water (Fig. 5) exhibits the absorption band of the ether C-O-C groups (1096 cm⁻¹) and a broad absorption band 3700 cm⁻¹ - 3000cm⁻¹, which may be described to OH or/and COOH groups and, possibly to N-H groups (3485 cm⁻¹). The band at 1606 cm⁻¹ indicate the presence of the NH, groups connected with cyclohexyl ring in the extractibles obtained from PUR in such drastic conditions of hydrolysis.
Fig. 5. IR spectrum of the extractibles from PUR-IV in boiling water (in KBr)
Rys. 5. Widmo absorpcyjne w podczerwieni suchej pozostałości ekstraktu z PUR-IV we wrzącej wodzie (w KBr)

Fig. 6. IR spectrum of the extractibles from PUR-IV in boiling hexane (on NaCl)
Rys. 6. Widmo absorpcyjne w podczerwieni suchej pozostałości ekstraktu z PUR-IV we wrzącym heksanie (film na NaCl)
The dry residue of PUR-IV extract's in boiling hexane shows on IR spectrum (Fig.6) small absorption bands at 3400-3500 cm⁻¹, at 1720-1700 cm⁻¹ (C=O) and at 1250 cm⁻¹ for C-O-C bands from ester groups, what may suggest the extraction of some glycerides.

The sorption of natural (sunflower) oil in PUR foil was much greater than oil sorption measured for Pellethane 2363-80A and poly(carbonateurethane)(Aldrich)(Table 8). It arises from a certain affinity of fat to the PURs containing incorporated structure of the natural fat acids glycerides and also from the lower density of obtained PURs, connected with the structure of castor oil and the structure of isomeric, cycloaliphatic diisocyanate (SMDI).

The data Table 8 indicate that oil sorption in described in this paper PURs was however lower than measured for poly(urethaneurea) with long side aliphatic (C₁₆) group, obtained earlier in our laboratory[10]. In the polymers obtained from PTMG 2040 the oil sorption was several times greater than in PUR-1 from PTMG 1000.

Conclusions

PURs obtained in this work from cycloaliphatic diisocyanate and polyols with castor oil participation in regard to physical properties fulfil the requirements for polymeric materials used in medicine. The stability with treatment by hot water is for these PURs satisfied. In comparison to typical polyurethanes the obtained PURs are characterized by lower water sorption but greater sorption of natural fat.

It is necessary to investigate in future researches how the modification of PUR by the structure of castor oil will improve albumins binding and induce better hemo- and biocompatibility in comparison to typical PUR. It is also purposeful to verify if such chemical structure PUR would not enlarge a tendency to calcification on polymer surface in living tissues.

References