Thermal, mechanical and wettability properties of some branched polyetherurethane elastomers

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Abstract: In this study three series of polyetherurethanes (PEU) based on Terathane ® (polytetramethyleneetherglycol - PTMEG, Mₙ 1400) as polyol; isophorone diisocyanate (IPDI), 4,4’-methylene-bis-(cyclohexyl-isocyanate) (HMDI) and hexamethylene diisocyanate (HDI) as aliphatic diisocyanate components; 1,4-butanediol (BD) and glycerin (Gly) as chain extenders were synthesized. The glycerin as triol is responsible for the crosslinking structures. All polyether urethanes were synthesized by prepolymer method. The PTMEG was reacted with diisocyanate to realize a diisocyanate-terminated prepolymer, which in next step was extended with blend of the 1,4-butanediol (BD) and glycerin (Gly) in different proportion. The influence of the diisocyanate structure and chain extender functionality on the thermal, mechanical and wettability properties were the aim of this study. The physical, mechanical and wettability properties of these polymers were measured according to standard methods. All polymers were characterized by conventional characterization methods. Different methods of thermal analysis (TGA and DSC) were used for characterization. Wettability was estimated by determination of the dynamic contact angle. The structures were confirmed by FT-IR and H-NMR analysis. The results show that the thermal stability, mechanical and wettability properties of the final products are influenced by the diisocyanate and chain extenders nature.

Keywords: polyetherurethane, diisocyanate, mechanical properties, dynamic contact angle, surface tension

Introduction

Polyurethanes chemistry is considered one of the most versatile chemistries for polymer materials. They can be easily prepared by a simple polyaddition reaction of polyl, isocyanate and chain extender. Due to the ability to adapt polyurethanes' molecular structures to specific property requirements, different types of polyurethane can be synthesized and used in a variety of applications including elastomers [1-3], flexible and rigid foams [4-7], medical devices [8-10], adhesives and coatings [11-14]. Segmented polyurethanes (PU) are generally composed of polyether or polyester soft segments and urethane based hard segments along the polymer backbone giving rise to a microphase-separated morphology caused by the usual poor compatibility between both segments. The unique properties of these polymers are directly related to their two phase microstructure, in which the hard domains act as reinforcing filler and as a thermally reversible cross-link [15]. Polyurethanes are produced by the exothermic reaction of molecules containing two or more isocyanate groups with polyl molecules containing two or more hydroxyl groups. Relatively few basic isocyanates and a far broader range of polyols of
different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials. Additionally, several other chemical reactions of isocyanates are used to modify or extend the range of isocyanate-based polymeric materials. Chain extenders are chemical species of low molecular weight like ethylene glycol, diethylene glycol, butanediol, propanediol, hexanediol etc. The amount and the type of chain extender influence the properties and the processing behaviour of the polyurethane rubber substantially [16]. Branched or crosslinked structures can be prepared using a chain extender a compound with more functionality than two, ex: trimethylol propane, glycerin, etc [17]. In this way the mechanical and/or thermal properties can be improved.

**Results and discussion**

The polyurethanes structures based on PTMEG/DI/BD+Gly were confirmed by conventional spectroscopic methods. The H-NMR spectra of the polymer samples (Fig. 1) present suitable signal of -NH from urethane group between 6.95-7.05 ppm. Other important signals are –OH at 4.41-4.44, -CH from glycerine at 2.5 and CH$_2$ from diols at 3.95-3.99, from polyether at 3.20 and respectively from disiocyanates at 1.50-1.55 ppm. From ratio of integrals at number of protons (182.0/145=1.25 for polyether, 31.2/12=2.6 for HDI, 44.0/18=2.44 for IPDI and respectively 53/22=2.41 for HMDI) result in that the composition of obtained polymers was in agreement with composition of the mixture used for synthesis (good correlation, aproximately 1:2, PTMEG:Dl).

*Fig. 1.* HRMN spectra of polyurethane samples based on PTMEG/DI/BD+Gly.
FTIR spectra of the polymer samples (Fig. 2) showed characteristic vibrational absorption bands at 3322-3330 cm\(^{-1}\) (N-H stretching, combined with hydrogen bond) for urethane groups, at 2739-2940 cm\(^{-1}\) for CH\(_2\) from isocyanate component, at 1717-1720 cm\(^{-1}\) (NHCOC stretching, urethane groups combined with ester carbonyl groups of PTMEG), and 1527-1536 cm\(^{-1}\) (C-N stretching, combined with N-H out of plane bending).

![FTIR spectra of polyurethane samples based on PTMEG/DI/BD+Gly](image)

**Fig. 2.** FT-IR spectra of polyurethane samples based on PTMEG/DI/BD+Gly.

**Wettability of polyurethanes based on PTMEG/DI/BD+Gly**

Wettability could be estimated by determination of the dynamic contact angle. For that the samples were immersed and withdrawn into and out from a liquid simultaneously measuring the force acting on the samples. The advancing and receding contact angles were determined from the obtained force curve. The difference between the maximum (advancing) and minimum (receding) contact angle values is called the contact angle hysteresis.

The measured force \(F_1\) was related to the dynamic contact angle through the general equation:

\[
F_1 = \text{weight probe} + \text{wetting force} - F \text{ (buoyancy)} \tag{1}
\]

Sigma 700 tensiometer tared the weight of the probe and the effects of the buoyancy force were removed by extrapolating the graph back to zero depth of immersion. The remaining component force was the wetting force \((F_w)\) which was defined as:

\[
F_w = \gamma_v P \cos \theta \tag{2}
\]

where \(\gamma_v\) represented the surface tension of the fluid, \(P\) the perimeter of the plate and \(\theta\) is the contact angle. Both advancing and receding contact angles could be obtained from Eq. (2).
Advancing and receding contact angle measurements of the films casted from polyurethanes based on PTMEG/DI/BD+Gly could provide more information on the hydrophilicity of films and hence the wettability. A better understanding of the hydrophobicity of the cast films was achieved from dynamic contact angle studies. Fig. 3 showed the results of the dynamic advancing contact angle study. The decreasing values for the advancing contact angles might be connected with the increasing values of the aliphatic diisocyanate molecular mass. Tab. 1 shows the advancing, receding and hysteresis contact angle of the samples.

**Tab. 1.** Water contact angle of polyurethanes based on PTMEG/DI.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio of PTMEG/DI/BD+Gly</th>
<th>$\theta_{\text{adv}}$ (deg)</th>
<th>$\theta_{\text{rec}}$ (deg)</th>
<th>Hysteresis (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI-1400</td>
<td>1:2:1</td>
<td>90.82 ± 1.08</td>
<td>58.40 ± 0.55</td>
<td>32.42 ± 0.38</td>
</tr>
<tr>
<td>IPDI-1400</td>
<td>1:2:1</td>
<td>88.68 ± 1.02</td>
<td>59.69 ± 0.51</td>
<td>28.99 ± 0.36</td>
</tr>
<tr>
<td>HMDI-1400</td>
<td>1:2:1</td>
<td>85.64 ± 1.06</td>
<td>56.85 ± 0.45</td>
<td>28.79 ± 0.21</td>
</tr>
</tbody>
</table>

Surface wettability is a relative criterion to define biodegradability and/or biocompatibility of synthetic polymers. The obtained results of contact angle measurements revealed that the wettability depends on the diisocyanate nature: an aliphatic diisocyanate with small molecular weight has a hydrophilic behaviour. Wettability decreases as follows: HDI>IPDI>HMDI. Additionally, the polyurethane films were found to have the hysteresis values between 28.79 and 32.42 degrees. This signifies that the film polymers surface presented some chemically or physically heterogeneous domains. For the case of chemical heterogeneity these domains represent areas with different contact angles than the surrounding surface. For situation in which surface roughness generates hysteresis the microscopic variations of angle in the surface create barriers which attach the motion of the contact line and change the macroscopic contact angles. In general, it is claimed that the contact angles are greater on rough surfaces than on smooth surfaces and that the wetting hysteresis increases with the surface roughness [18].

**Fig. 3.** Advanced contact angle and hysteresis of polyurethanes based on PTMEG/DI/BD+Gly.
The effect of the diisocyanate and chain extender nature on the surface tensions of the polyurethane based on PTMEG/DI/BD+Gly is presented in Tab. 2. The surface tensions of the polyurethane solutions in DMF increased with diisocyanate molecular weight enrichment. The aliphatic structure of diisocyanates influenced the surface tensions in the order: HDI>IPDI>HMDI.

**Tab. 2.** Surface tension of polyurethane based on PTMEG/DI/BD+Gly.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio of PTMEG/DI/BD+Gly</th>
<th>Solution concentration % wt</th>
<th>Molar ratio of chain extender mixture</th>
<th>Surface tension mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI 1400</td>
<td>1:2:1</td>
<td>0.40</td>
<td>3/5 BD + 2/5 Gly</td>
<td>30.86</td>
</tr>
<tr>
<td>IPDI 1400</td>
<td>1:2:1</td>
<td>0.40</td>
<td>3/5 BD + 2/5 Gly</td>
<td>27.12</td>
</tr>
<tr>
<td>HMDI 1400</td>
<td>1:2:1</td>
<td>0.40</td>
<td>3/5 BD + 2/5 Gly</td>
<td>25.78</td>
</tr>
</tbody>
</table>

**Thermal stability**

The influence of temperature on the decomposition reaction was investigated by TGA and the trace amounts of material left were used for evaluation of thermal stability of polyurethanes based on PTMEG/DI/BD+Gly (Fig. 4).

![Thermograms of polyetherurethane samples based on PTMEG/DI/BD+Gly.](image)

Fig. 4. Thermograms of polyetherurethane samples based on PTMEG/DI/BD+Gly.

The polyurethane samples analyzed by TGA decomposed in two steps and maximum weight loss was between 388 and 451 °C (step II). The glycerin from chain extender mixture caused an increase in the thermal stability due to the branched structures that were formed. The onset temperature of degradation for each tested
polyurethane based on PTMEG/DI/BD+Gly was approximately 280 °C (weight losses up to 1 %), making it possible to maintain stable conditions during processing (Tab. 3).

**Tab. 3.** Thermal stability of the polymers based on PTMEG/DI/BD+Gly.

<table>
<thead>
<tr>
<th>Code</th>
<th>Decomposition</th>
<th>Reaction order*</th>
<th>Temperature range</th>
<th>Weight loss, %</th>
<th>Residue %</th>
<th>Activation Energy* KJ/mol</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI</td>
<td>Step I</td>
<td>0.0</td>
<td>278.73-388.68</td>
<td>19.99</td>
<td></td>
<td>53.42</td>
<td>-73.1</td>
</tr>
<tr>
<td></td>
<td>Step II</td>
<td>0.6</td>
<td>388.68-443.73</td>
<td>78.70</td>
<td>1.31</td>
<td>140.64</td>
<td>-64.5</td>
</tr>
<tr>
<td></td>
<td>Global</td>
<td>1.0</td>
<td>278.73-443.73</td>
<td>98.69</td>
<td></td>
<td>105.33</td>
<td></td>
</tr>
<tr>
<td>IPDI</td>
<td>Step I</td>
<td>0.0</td>
<td>285.91-390.55</td>
<td>22.32</td>
<td></td>
<td>54.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Step II</td>
<td>0.5</td>
<td>390.55-445.77</td>
<td>76.33</td>
<td>1.35</td>
<td>123.51</td>
<td>-64.5</td>
</tr>
<tr>
<td></td>
<td>Global</td>
<td>1.0</td>
<td>285.91-445.77</td>
<td>98.65</td>
<td></td>
<td>98.48</td>
<td></td>
</tr>
<tr>
<td>HMDI</td>
<td>Step I</td>
<td>0.1</td>
<td>291.24-391.45</td>
<td>26.81</td>
<td></td>
<td>55.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Step II</td>
<td>0.5</td>
<td>391.45-451.14</td>
<td>72.62</td>
<td>0.57</td>
<td>107.76</td>
<td>-61.2</td>
</tr>
<tr>
<td></td>
<td>Global</td>
<td>1.0</td>
<td>291.24-451.14</td>
<td>99.43</td>
<td></td>
<td>87.69</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated through Reich-Levi method.  
** Determined by DSC

The thermal properties of the samples were studied too, by means of Differential Scanning Calorimetry. DSC is a thermal analytical technique which measures the amount of energy absorbed or released by a material as it is heated, cooled or held at constant temperature. This method was appropriate for the evaluation of the glass transition temperature. The polyurethane based on PTMEG/HDI/BD+Gly exhibit $T_g$ equal to -73.1 °C, a crystallization peak at -43.1 °C (probable a reorganization of the polyurethane structures) and $T_{melt}$ at +6.5 °C, while the next two polymers only $T_g$, first based on PTMEG/IPDI/BD+Gly presented $T_g$ at -64.5 °C, and second based on PTMEG/HMDI/BD+Gly $T_g$ at -61.2 °C, these values were obtained on the samples with 1:2:1 molar ratio (Fig. 5).

**Fig. 5.** DSC curves of polyurethanes based on PTMEG/DI/BD+Gly.
The dependence of the activation energy (Reich-Levi method) versus conversion degree is presented in Fig. 6. The energy of activation presented a steep decrease until a conversion of $\alpha=0.15-0.2$, after that increased slightly till a conversion of $\alpha=0.6-0.7$, and in the end activation energy slightly decreased again. An important depression in activation energy values versus conversion could be observed for $\alpha<0.2$. This behaviour was also characteristic of an autocatalytic reaction. In connection with this, one should note that the oxygen traces in the polymer ran as a catalyst for the decomposition process.

**Fig. 6.** Activation energy vs. conversion of the polyurethanes based on PTMEG/DI/BD+Gly.

**Mechanical properties**

The mechanical properties were discussed in relationship with aliphatic diisocyanate natures and influence of the glycerin amount in the chain extender mixture. Their mechanical properties were comparable with those of good quality general purpose rubber materials. The molecular weight decreasing in the polyurethane structure generated a corresponding increase of tensile strength, hardness and elongation. By using a convenient structure of diisocyanate for same chain extender mixtures, it was possible to prepare polyurethanes with hardness between 59-72 °ShA.

The number-average molecular weight, $M_n$, and the polydispersity of studied samples were determined by GPC. The values resulted have only a qualitative meaning and were used for comparison of the samples. The numerical values of the important mechanical properties, molecular weight and polydispersity are shown in Tab.4.

The tensile strength values of polyurethane samples based on PTMEG/DI/BD+Gly are in the range of 9.16 and 10.18 MPa. The structure of diisocyanate has a small influence on the tensile strength and hardness of polyurethane samples. This behaviour was sustained also, by the molecular weight distributions, see Tab. 4. The Young’s modulus is influenced by the structure of polyurethanes too; the cyclic structure of aliphatic diisocyanate influences the Young modulus in order: HMDI>IPDI>HDI.
Fig. 7. Stress – strain measurements of PTMEG/DI/BD+Gly.

Tab. 4. Mechanical and physical properties of polyurethanes based on PTMEG/DI/BD+Gly.

<table>
<thead>
<tr>
<th>Code</th>
<th>PTMEG/DI/BD+Gly</th>
<th>Tensile strength (MPa)</th>
<th>Young Modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Hardness oShA</th>
<th>M_w</th>
<th>M_n</th>
<th>M_w/M_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI 1400</td>
<td>1:2:1</td>
<td>10.18±0.09</td>
<td>2.1±0.1</td>
<td>654±13</td>
<td>71±1</td>
<td>106000</td>
<td>65000</td>
<td>1.63</td>
</tr>
<tr>
<td>IPDI 1400</td>
<td>1:2:1</td>
<td>10.01±0.07</td>
<td>2.5±0.2</td>
<td>614±14</td>
<td>68±1</td>
<td>91000</td>
<td>55000</td>
<td>1.65</td>
</tr>
<tr>
<td>HMDI 1400</td>
<td>1:2:1</td>
<td>9.16±0.09</td>
<td>2.8±0.2</td>
<td>468±20</td>
<td>59±1</td>
<td>89000</td>
<td>54000</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Conclusions

The intend of this work was to investigate the influence of the chain extender functionality and diisocyanate structures on the thermal, mechanical and wettability properties of some polyetherurethanes. Diisocyanate structures used in this study, aliphatic linear or cyclic, produce an increase of hydrophilic behaviour with decreasing diisocyanate molecular mass. By using as chain extender, a compound with functionality greater than two, in this case glycerine, the mechanical and thermal properties can be improved. The results showed that the thermal, mechanical and wettability properties of the final products might be controlled by fine control of the amount of glycerine as chain extenders and the aliphatic diisocyanate structures.

Experimental

Materials

The materials used in this research were Terathane (polytetramethyleneetherglycol-PTMEG - generous gift from INVISTA BV, Nederland), M_w 1374 g/mol, mp 35-40 °C,
water 115 ppm, hydroxyl number 81.7 mgKOH/g; hexamethylene diisocyanate (HDI - Fluka), M_w 168.20, bp 82-85 °C, d_20^0 1.05, n_D^20 1.453; isophorone diisocyanate (IPDI - Fluka), M_w 222.29, bp 153 °C, d_20^0 1.061, n_D^20 1.484; 4,4'- methylenebis(cyclohexyl isocyanate) (HMDI – Aldrich) M_w 262.35, bp 113 °C, mp 19-23 °C, d_20^0 1.066; 1,4-butanediol (Fluka, purum), M_w 90.12; mp 18-20; bp 120-122 °C/10 mm; d_20^0 1.014; n_D^20 1.474; glycerine (Gly-Fluka), M_w 92.09, bp (20 mmHg) 182 °C, d 1,231 g/cm³, n_D^20 1,4740; PTMEG and chain extenders were tested for the moisture content and, in some cases, dried under vacuum until a content of water of less than 0.03% was reached. All the chemicals were used as received, without further purification.

**Measurements**

The HNMR measurements were performed on a **Bruker** Avance DRX-400 NMR spectrometer using deuterated DMSO as the solvent with TMS as the internal standard.

Infrared Spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range 600-4000 cm⁻¹.

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer under a flow of nitrogen (20 mL/min) with a heating rate of 10 °C/min from room temperature to 700 °C and 4-6 mg of sample mass. The operational parameters were kept constant to all probes for obtaining comparable data.

A Perkin Elmer DSC-7 was used for thermal analysis and was operated under a nitrogen atmosphere with a heating rate of 10 °C/min.

Stress-strain measurements were performed at room temperature on dumbbell-shaped samples cut from thin films on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5kN load cell and activated grips which prevented slippage of the sample before break. The used cross-head speed was 50 mm/min. All samples were measured three times and the averages were obtained.

Gel permeation chromatography (GPC) measurements were carried out on a PL-EMD 950 Evaporative Mass Detector instrument using THF as eluent after calibration with polystyrene standards.

Dynamic contact angles were performed by the Wilhelmy plate technique, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were 50x8 mm and rate of immersion-emersion was 5 mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were the average of 3 contact angle measurements of samples.

Hardness was measured on Instron Shore Durometer instruments, using scale A.

**Polyurethanes synthesis**

Polyurethanes were synthesized by bulk polymerization using the prepolymer method, under an inert atmosphere of nitrogen. Aliphatic polyurethanes were synthesized using hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and dicyclohexane diisocyanate (HMDI). Terathane ® (polytetramethyleneetherglycol - PTMEG) with molecular mass M 1400 as soft segment and a mixture of 1,4-
butanediol (BD) and glycerine (Gly) as short-chain extender were used. Polyol PTMPEG was carefully dried (4 h, 70 °C in vacuum) in order to decrease the water content. BD and Gly were dried under vacuum at 0.5-1 mmHg for 2 h. Isocyanates were used as received. The synthetic route for the polyurethane samples preparation is described in Scheme 1.

\[
\begin{align*}
\text{HO-R-OH} + 2 \text{OCN-I-NCO} & \rightarrow \text{OCN-I-NH-CO-O-R-O-CO-NH-I-NCO} \\
\text{OCN-I-NH-CO-O-R-O-CO-NH-I-NCO} + 3/5 \text{HO-R}_1\text{-OH} + 2/5\text{HO-R}_2\text{-OH} & \rightarrow \text{...-I-NH-CO-O-R-O-CO-NH-I-NH-CO-O-R}_1\text{-O-OC-HN-I-NH-CO-O-R-O-CO-NH-I-...} \\
\text{...-I-NH-CO-O-R-O-CO-NH-I-NH-CO-O-R}_2\text{-O-OC-HN-I-NH-CO-O-R-O-CO-NH-I-...} & \rightarrow \text{Branched polyetherurethane} \\
\text{Prepolymer} & \rightarrow \text{Linear polyetherurethane}
\end{align*}
\]

Scheme 1. Synthetic route for preparation of the polyurethane samples based on PTMPEG/DI/BD+Gly.

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References