Theses of doctoral (Ph.D.) dissertation

PREPARATION AND CHARACTERIZATION OF SHAPE MEMORY POLYURETHANES

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1. Introduction

Nowadays, one of the most intensively researched areas is the production and characterization of smart materials. Smart materials are those materials that perceive changes in their environment (e.g.: temperature, light, pH, redox potential, magnetic field, etc.) to which a reversible "response" is given by changing their properties. One of the great class of smart materials is the shape memory polymers that "respond" to the external effects by changing their shape. One of the most commonly used type of shape memory polymers is the segmented polyurethanes, which are made up of hard and soft segments.

In linear polyurethane chains, aromatic / aliphatic diisocyanates (hard segments) create urethane bonds by polyaddition reaction with polyols (soft segment). In order to improve shape memory and mechanical properties, crosslinked structure can be achieved by chemical cross-linking (allophanate bonds). In order to enhance the property of shape memory, a thermoreversible crosslink can be formed using a Diels-Alder (DA) reaction, too. Polyester-based polyol is often used in the synthesis of polyurethanes (e.g. PCL), which ensures the biodegradability of the polymer produced. The biodegradability, low glass transition and melting temperature of PCL allows for the widespread use of shape memory polymers from medical applications (e.g. stents, sutures etc.) to space technology (e.g. solar cells, antennas). Accordingly, our aim was to produce and characterize linear and cross-linked polyurethanes containing Diels-Alder (DA) adducts.

Nowadays, polyurethane derivatives and co-networks (e.g. epoxy-polyurethanes) are playing an increasingly important role. The great advantage of such polymer systems is that it is possible to combine the properties of the individual building blocks to meet the needs. Another aim of my work was the synthesis and characterization of epoxy-polyurethane systems containing Diels-Alder adducts, in which the beneficial properties of epoxy and polyurethane can be combined.

2. Experimental methods

The linear polyurethane samples and the epoxy-polyurethane co-networks was characterized by size-exclusion chromatography (SEC), attenuated total reflectance Fourier-transform infrared spectroscopy (FTIR-ATR) and nuclear magnetic resonance spectroscopy (1H-NMR). The mechanical properties of PU samples of different compositions were analyzed by tensile test, thermal properties by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The shape memory properties of the selected PU samples were also investigated. The crosslinking densities of the polymers were determined by swelling tests. Morphology of the PU samples was characterized by scanning electron microscopy (SEM).
3. New scientific results

3.1. Linear polyurethanes containing Diels-Alder adduct

3.1.1. Linear polyurethanes containing Diels-Alder adduct were prepared using poly(ε-caprolactone) and different diisocyanates.

For the synthesis of linear polyurethanes (Figure 1.) poly(ε-caprolactone) of various molecular weights (PCL, Mn = 10, 25, 50 kg/mol), as well as various types and amounts of diisocyanates (4,4'-methylene diphenyl diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI), 2,4-toluene diisocyanate (TDI)) and Diels-Alder adducts were used, which resulted in the formation of linear polymers containing thermoreversible bonds (Table 1.). The Diels-Alder adduct was prepared by the reaction of furfureylamine (FA) with bismaleimide (BMI).

![Synthetic route for the preparation of linear polyurethanes containing DA-adducts](image)

Figure 1. Synthetic route for the preparation of linear polyurethanes containing DA-adducts.

3.1.2. Definite relationships were found between the composition, mechanical, thermal, and shape memory properties of linear polyurethanes containing Diels-Alder adducts.

Size-exclusion chromatography was used to determine the number- and mass average molecular weight and polydispersity of the starting materials and each linear PU sample.
Table 1. Composition of initial reaction mixtures and average molecular weights of the resulting polymers (M_n)

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition / monomer ratio</th>
<th>M_n (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU 1</td>
<td>PCL (10)-MDI-FA-BMI / 1:3:2:1</td>
<td>76,0</td>
</tr>
<tr>
<td>PU 2</td>
<td>PCL (10)-MDI-FA-BMI / 1:3:2:2</td>
<td>66,4</td>
</tr>
<tr>
<td>PU 3</td>
<td>PCL (10)-HDI-FA-BMI / 1:3:2:2</td>
<td>53,6</td>
</tr>
<tr>
<td>PU 4</td>
<td>PCL (10)-TDI-FA-BMI / 1:3:2:2</td>
<td>57,0</td>
</tr>
<tr>
<td>PU 5</td>
<td>PCL (25)-MDI-FA-BMI / 1:3:2:2</td>
<td>67,3</td>
</tr>
<tr>
<td>PU 6</td>
<td>PCL (25)-HDI-FA-BMI / 1:3:2:2</td>
<td>67,2</td>
</tr>
<tr>
<td>PU 7</td>
<td>PCL (25)-TDI-FA-BMI / 1:3:2:2</td>
<td>61,6</td>
</tr>
<tr>
<td>PU 8</td>
<td>PCL (50)-MDI-FA-BMI / 1:3:2:2</td>
<td>116,7</td>
</tr>
<tr>
<td>PU 9</td>
<td>PCL (50)-HDI-FA-BMI / 1:3:2:2</td>
<td>95,9</td>
</tr>
<tr>
<td>PU10</td>
<td>PCL (50)-TDI-FA-BMI / 1:3:2:2</td>
<td>85,8</td>
</tr>
</tbody>
</table>

* The number in parentheses indicates the average number of molecular weights (M_n) of the PCL expressed in kg/mol.

It was found that by increasing the molecular weight of the PCL, the number of PCL units was reduced (Table 1.).

The formation of the Diels-Alder adduct was modeled and the protons belonging to the adduct in the PU samples were identified on the basis of 1H-NMR spectra.

Based on the results of the tensile tests, it was found that the polyurethanes containing MDI and HDI have more favorable mechanical properties than those containing TDI, independently of the molecular weight of the PCL. The "rigid" molecular structure of MDI is advantageous for the mechanical properties of samples containing 10 kg/mol molecular weight PCL, while aliphatic HDI has worked well for samples containing 50 kg/mol molecular weight PCL. It was found that the most favorable mechanical properties have the polyurethanes containing MDI (PU 2, 5, 8).

It can be concluded that the degree of crystallinity of PCL segments incorporated into PU samples is essentially determined by the type of the diisocyanate and the molecular weight of the PCL segment. The crystallization study (DSC) showed that the samples had a degree of crystallinity of 41-68 %.

The shape memory property of each PU sample was characterized by DMA (Table 2.).

Table 2. Circumstances of the shape memory cycle and typical R_f and R_r values

<table>
<thead>
<tr>
<th>Code</th>
<th>Temperature (°C)</th>
<th>Strain (%)</th>
<th>R_f (%)</th>
<th>R_r (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU 2</td>
<td>80</td>
<td>80</td>
<td>99</td>
<td>43</td>
</tr>
<tr>
<td>PU 5</td>
<td>80</td>
<td>80</td>
<td>100</td>
<td>56</td>
</tr>
</tbody>
</table>
The \( R_f \) value for both samples was nearly 100\%, and the \( R_f \) values were 43\% and 56\%, respectively. It was found that the combination of 10 and 25 kg/mol PCL and MDI is necessary to obtain the shape memory behavior.

3.2. Crosslinked polyurethanes containing Diels-Alder adduct

3.2.1. Crosslinked polyurethanes containing Diels-Alder adduct were prepared using poly (\( \varepsilon \)-caprolactone) and different diisocyanates.

For the preparation of crosslinked polyurethanes, the type (MDI, HDI) and the amount of diisocyanate, and the molecular weight of polyol (PCL, \( M_n = 10, 25, 50 \) kg/mol) were modified. In order to increase the crosslinking density and to improve the shape memory performance, DA adducts were used as thermoreversible coupling units. The synthesis of crosslinked polyurethanes is illustrated in Figure 2.

![Synthetic route for the preparation of crosslinked polyurethanes containing DA-adducts](image)

**Figure 2.** Synthetic route for the preparation of crosslinked polyurethanes containing DA-adducts

3.2.2. Definite relationships were found between the composition, mechanical, thermal, and shape memory properties of crosslinked polyurethanes containing Diels-Alder adducts.

The composition of crosslinked polyurethanes containing Diels-Alder adduct is summarized in Table 3.
Table 3. Composition of the starting reaction mixtures for crosslinked polyurethane samples

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition / monomer ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU 1</td>
<td>PCL (10)–MDI–FA–BMI-MDI / 1:3:2:1:1</td>
</tr>
<tr>
<td>TPU 2</td>
<td>PCL (10)–MDI–FA–BMI-MDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 3</td>
<td>PCL (10)–MDI–FA–BMI-MDI / 1:3:2:2:2</td>
</tr>
<tr>
<td>TPU 4</td>
<td>PCL (10)–MDI–FA–BMI-MDI / 1:3:2:2:3</td>
</tr>
<tr>
<td>TPU 5</td>
<td>PCL (10)–MDI–FA–BMI-HDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 6</td>
<td>PCL (10)–HDI–FA–BMI-HDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 7</td>
<td>PCL (25)–MDI–FA–BMI-MDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 8</td>
<td>PCL (25)–MDI–FA–BMI-HDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 9</td>
<td>PCL (25)–HDI–FA–BMI-HDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 10</td>
<td>PCL (50)–MDI–FA–BMI-MDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 11</td>
<td>PCL (50)–MDI–FA–BMI-HDI / 1:3:2:2:1</td>
</tr>
<tr>
<td>TPU 12</td>
<td>PCL (50)–HDI–FA–BMI-HDI / 1:3:2:2:1</td>
</tr>
</tbody>
</table>

* The number in parentheses indicates the average number of molecular weights (Mn) of the PCL expressed in kg/mol

The complete transformation of the NCO groups and the presence of the DA adduct were confirmed by FTIR spectroscopy.

Swelling tests were carried out to verify the formations of crosslinks. The gel content varied between 12.5 and 89.5 % depending on the composition, while the crosslinking density was between 10^{-3} and 10^{-6} mol/cm^{3} (TPU 1-12). It was found that the crosslinking density of TPU 2-4 samples increases with the increase in the amount of crosslinking diisocyanate.

It was observed that increasing the amount of crosslinking component and the molecular weight of the PCL do not result in significant differences in the mechanical properties, but variations the type of the crosslinking and crosslinking diisocyanate causes significant changes. The highest tensile strength values (σ = 36 and 34 MPa) are those TPU’s (TPU 8, 11), where Mn-s of PCL segment were 25 or 50 kg/mol, the coupling element was MDI and the crosslinker was HDI.

DSC studies revealed that the degree of crystallinity of each sample varied between 45 and 68 %. It was observed that the highest melting temperature (T_m = 61.9, 63.7 and 64.8 °C) have polyurethanes that contain MDI as the coupling element and HDI as the crosslinker (TPU 5, 8, 11).

DMA analysis was carried out to characterize the thermal properties. Figure 3. shows a sharp decrease in storage modulus for all TPU samples at 60 °C caused by the melting crystalline PCL phase followed by a plateau above the melting point of the PCL (70 °C). In the case of TPU 7, the formation of two "rubbery" plateaus (between 90 and 110 °C and between 120 and 140 °C) can be observed due to the presence of physical and chemical crosslinking including the DA adduct (rDA).
Shape memory tests showed that TPU 7 can achieve 100 % $R_f$ and 80 % $R_r$ at 80 °C at 80 % strain.

3.3. Epoxy-polyurethane co-networks containing Diels-Alder adduct

3.3.1. Epoxy-polyurethane co-networks (EP-PU) containing Diels-Alder adducts with IPN structure were synthesized using bisphenol-A based epoxy resin and poly($\varepsilon$-caprolactone) / poly($\varepsilon$-caprolactone-diol) (PCD).

In our work, poly($\varepsilon$-caprolactone) based epoxy-polyurethane co-networks with Diels-Alder adducts were synthesized by two methods.

The novelty of our work is that PCL / PCD based linear prepolymer were reacted with bisphenol-A based epoxy resin (DGEBA) and DA adduct. As a result, epoxy-polyurethane co-networks with reversible DA-bonds were obtained. Crosslinkings were carried out with different amine-type crosslinking agents (Jeffamine, JA) added to EP-PU 10-15 samples.

Two synthetic approaches were developed. According to using the first synthetic approach, the isocyanate-terminated prepolymer was reacted with an OH-terminated DA adduct and a DGEBA oligomer (EP-PU 1-15, Table 4). The molecular weight of PCD/PCL ($M_n = 2$, 10, 25 and 50 kg/mol), the ratio of DA adduct, DGEBA, and crosslinker JA were systematically varied (Figure 4).

Table 4. Composition of the starting reaction mixtures of EP-PU 1-15 samples

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition / mól ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-PU 1</td>
<td>PCD(2)-HDI-DA adduct-DGEBA / 1:2:0.5:0.5</td>
</tr>
<tr>
<td>EP-PU 2</td>
<td>PCD(2)-HDI-DA adduct-DGEBA / 1:2:1:1</td>
</tr>
<tr>
<td>EP-PU 3</td>
<td>PCL(10)-HDI-DA adduct-DGEBA / 1:2:1:1</td>
</tr>
<tr>
<td>EP-PU 4</td>
<td>PCL(25)-HDI-DA adduct-DGEBA / 1:2:1:1</td>
</tr>
<tr>
<td>EP-PU 5</td>
<td>PCL(50)-HDI-DA adduct-DGEBA / 1:2:1:1</td>
</tr>
<tr>
<td>EP-PU 6</td>
<td>PCD(2)-HDI-DA adduct-DGEBA / 1:2:2:2</td>
</tr>
<tr>
<td>EP-PU 7</td>
<td>PCL(10)-HDI-DA adduct-DGEBA / 1:2:2:2</td>
</tr>
<tr>
<td>EP-PU 8</td>
<td>PCL(25)-HDI-DA adduct-DGEBA / 1:2:2:2</td>
</tr>
<tr>
<td>EP-PU 9</td>
<td>PCL(50)-HDI-DA adduct-DGEBA / 1:2:2:2</td>
</tr>
<tr>
<td>EP-PU 10</td>
<td>PCL(10)-HDI-DA adduct DGEBA-JA / 1:2:1:1:1</td>
</tr>
</tbody>
</table>
In the second synthesis method, DGEBA was reacted with FA and then the compound prepared (FA_DGEBA oligomer) was added to the furan-terminated prepolymer (EP-PU 16-24, Table 5) in the presence of BMI. In the synthesis of EP-PU 16-24 co-networks, the molecular weight ($M_n = 10$ and $50$ kg/mol) of the PCL and the oligomer ratio of FA_DGEBA were changed (Figure 5).

![Synthetic pathway for the preparation of samples EP-PU 16–24 containing DA-adducts](image)

**Figure 5.** Synthetic pathway for the preparation of samples EP-PU 16–24 containing DA-adducts

**Table 5.** Composition of the starting reaction mixtures of EP-PU 16-24 samples

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition / mól ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-PU 16</td>
<td>PCL(10)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:1:1</td>
</tr>
<tr>
<td>EP-PU 17</td>
<td>PCL(10)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:1:2</td>
</tr>
<tr>
<td>EP-PU 18</td>
<td>PCL(10)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:2:1</td>
</tr>
<tr>
<td>EP-PU 19</td>
<td>PCL(10)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:5:1</td>
</tr>
<tr>
<td>EP-PU 20</td>
<td>PCL(10)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:3:1</td>
</tr>
<tr>
<td>EP-PU 21</td>
<td>PCL(50)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:5:1</td>
</tr>
<tr>
<td>EP-PU 22</td>
<td>PCL(50)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:10:1</td>
</tr>
<tr>
<td>EP-PU 23</td>
<td>PCL(50)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:12.5:1</td>
</tr>
<tr>
<td>EP-PU 24</td>
<td>PCL(50)-HDI-FA-FA_DGEBA oligomer-BMI / 1:2:2:15:1</td>
</tr>
</tbody>
</table>
3.3.2. Relationships between the composition and mechanical, thermal, and shape memory properties of epoxy-polyurethane co-networks with IPN structure, containing Diels-Alder adducts.

In the case of EP-PU samples, the presence of the DA adduct was confirmed by infrared spectroscopy (FTIR-ATR) and DSC measurements.

Based on tensile test results of EP-PU samples, it was found that EP-PU s with PCD have low E-modulus values (EP-PU 2 and 6, respectively 4 and 6 MPa). Furthermore, it was also observed that varying the molecular weight of PCL significantly influences the E-modulus values of EP-PU 1-15 samples.


The EP-PU samples obtained by the second synthetic approach have higher E-modulus values, but smaller elongations than those produced by the first synthetic method.

The glass transition (-55 and -40 °C) and melting temperature (20 °C) of the samples containing PCD were determined by DSC measurements. The melting temperature of the PCL is about 60 °C. As the epoxy content increases, the degree of crystallinity decreases (EP-PU 2 and 6), which can be attributed to the fact that crosslinking reduces the flexibility of the PCL segments (EP-PU 3 and 10; EP-PU 7 and 13; PU 4 and 11). DSC studies further confirmed the presence of DA adduct. The peak in temperature-heat curves (110-145 °C) is the result of the rDA reaction (Figure 6.).

![DSC curves of the samples EP-PU 2, 3, 7 and 16](image)

**Figure 6.** DSC curves of the samples EP-PU 2, 3, 7 and 16.
For the samples EP-PU 3, 10, and 13 the shape fixity ratio ($R_f$) were nearly 100% at 60 °C with a 30% elongation. The highest shape recovery ratio ($R_r = 85\%$) was obtained for the cross-linked EP-PU 13 sample.

4. Applications of results

The linear and crosslinked polyurethanes containing Diels-Alder adduct consist of poly($\varepsilon$-caprolactone) and different types and amounts (MDI, HDI, TDI) diisocyanate. Using different building blocks, the mechanical properties of polyurethanes can be varied over a wide range. More rigid materials can be produced using the aromatic MDI, while more flexible materials can be synthesized using HDI. The Diels-Alder adduct built into polyurethane chains serves as a coupling element that allows thermoreversible coupling and decoupling of polyurethane chains, and enhances the ability of polyurethanes to obtain good shape memory property. Shape memory polymers are important also in the production of textiles and membranes, but there is a wide range of development facilities in space technology and automotive applications. The biodegradable polymers can be synthesized by incorporating poly($\varepsilon$-caprolactone), allowing such systems to be used for biomedical purposes.

The synthesis of interpenetrating (IPN) epoxy-polyurethane co-networks provides an opportunity to combine the favorable properties of different building blocks. Epoxy-urethane co-networks have advantages such as good storage stability, curing at room temperature, or mixing with epoxy resins. Because of these properties, they are suitable as adhesives or as epoxy reinforcing agents. Using Diels-Alder adduct as a reversible linking element, it is also possible to modulate the shape memory property.

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List of publications related to the dissertation

Foreign language scientific articles in Hungarian journals (1)
DOI: http://dx.doi.org/10.3144/expresspolymlett.2016.30
IF: 2.983

Foreign language scientific articles in international journals (2)
DOI: http://dx.doi.org/10.3390/polym1005004
IF: 2.935 (2017)

DOI: http://dx.doi.org/10.1002/app.44145
IF: 1.86

Hungarian abstracts (5)


List of other publications

Hungarian scientific articles in Hungarian journals (3)


Foreign language scientific articles in international journals (1)

   DOI: http://dx.doi.org/10.1002/slct.201702251
   IF: 1.505

Hungarian abstracts (4)

   In: XXIV. Nemzetközi Végyszkonferencia. Szerk.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság (EMT), Kolozsvár, 61, 2018, (ISSN 1843-6293)

   In: 24th International Conference on Chemistry = XXIV. Nemzetközi Végyszkonferencia. Szerk.: Majdik Kornélia, Erdélyi Magyar Műszaki Tudományos Társaság (EMT), Kolozsvár, 53, 2018, (ISSN 1843-6293)


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Total IF of journals (publications related to the dissertation): 7,778

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02 January, 2019
Conference participation

Presentations related to the dissertation


Other presentations, posters


2. Csilla Lakatos, László Miló, Andrea Keczánne-Üveges: Környezetbarát nanokompozitok előállítása és vizsgálata, „Víz a házban és a ház körül” Környezetmérnöki konferencia, Debrecen. poszter (2013. október 11.)

3. László Miló, Csilla Lakatos, Andrea Keczánne-Üveges: Nanotitanát alkalmazása aktiv és passzív módon a környezetvédelemben, „Víz a házban és a ház körül” Környezetmérnöki konferencia, Debrecen. poszter (2013. október 11.)

