Castor oil and PEG-based shape memory polyurethane films: effect of chain extender amount on some polymer properties and performance

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Abstract: A series of polyurethane (PU) films were synthesized via one-shot bulk polymerization with polyethylene glycol, castor oil, hexamethylene diisocyanate, and 1,4-butanediol (BD) at three different chain extender ratios. Since it was found in our previous study that hard segment content is more effective on shape memory property than soft segment length (Bonfil, M., Sirkecioglu, A., Bingol-Ozakpinar, O., Uras, F., Güner, F. S. J. Appl. Polym. Sci. 2014, 131, 1–12), in this study the effects of BD amount on some physical properties, thermal properties, and shape memory performance of the films were investigated. Shape fixity and shape recovery were achieved under two different cooling/heating regimes. The amount of BD is an important parameter affecting the physical properties, chemical structure, and thus shape memory performance. Decreasing the BD amount increased the crystallinity and the films, being of relatively high crystallinity, showed the highest shape recovery ratio. Increasing BD amount in PU films increases the hydrogen-bonded structure and the films having a relatively high degree of hydrogen-bonded structure showed the highest shape fixity ratio. The samples showed higher shape memory performance at high cooling and heating rates.

Key words: Polyurethane, shape memory, chain extender

1. Introduction

Since the first shape memory polyurethanes were discovered in 1988 by Mitsubishi Heavy Industry, the research area has developed rapidly. In recent years, smart textile and biomedical applications have become the most promising fields for shape memory polyurethanes.

Polyurethane (PU) is a special polymer composed of soft and hard segments in its structure. Hard segments consist of diisocyanate and chain extender. Soft segments are formed by long chain polyether or polyester glycols. Urethane groups have an ability to self-associate via hydrogen bonds between interurethane and urethane–ester or urethane–ether groups.¹ Due to the aggregation of hard segments via hydrogen bonds to form hard segment domains, which disperse in the soft segment matrix, a segmented structure and thus, microphase separation occur.²,³ Interactions between the molecules of hard segments increase the phase separation between soft and hard segments and enhance the shape memory properties of polyurethanes.⁴ Since soft segments show a thermal transition at transition temperature and they work like a reversible molecular switch point, the molecular weight and the amount of polyol in the polymer are important parameters. The type and the amount of chain extender, which is an indispensable component of the hard segments, are also important parameters, since hard segments are responsible for the original shape.

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There are two main categories that directly affect the shape memory performances of a polymer: the polymer properties and the applied processing and programming conditions. By controlling the chemical structure and morphology of a polymer or optimizing conditions in the deformation step, its shape memory performances can be optimized.

In the literature, studies have focused on the effect of molecular weight, type, and amount of soft segment; type and content of hard segment; and type and ratio of chain extender on the shape memory performance.\textsuperscript{5,6} For instance, Chen et al. investigated the relationship between the structure of soft/hard segments and shape memory properties.\textsuperscript{7} Shape fixity performance increased and shape recovery performance decreased with increasing molecular weight of the soft segment. In the same study, increasing the ratio of the hard segment negatively affected both shape fixity and shape recovery properties. Mondal et al. applied polyethylene glycol (PEG) 3400 to the polyurethane structure as a polyol.\textsuperscript{8} As a result, the mechanical properties of polyurethane were enhanced and the shape memory properties were developed. Chun et al. developed shape memory performance by changing the chain extender ratio.\textsuperscript{4}

There are a few studies investigating the effects of applied conditions, such as heating and cooling rate, on shape memory performance.\textsuperscript{9,10} Tobushi et al. reported that shape fixity and shape recovery are failures for foams, and if the holding temperature is above $T_g$, secondary shape forming is avoided.\textsuperscript{9} Bonfil et al. found that improved shape memory performance could be obtained at relatively high cooling rates.\textsuperscript{10}

As mentioned above, one of the critical reactants for a polyurethane structure is the chain extender. Its type and ratio directly affect the morphology and thermal, mechanical, and other physical properties, and thus also the shape memory performance of polyurethanes.\textsuperscript{4,11-14} 1,4-Butanediol is widely used as a chain extender and its amount is optimized depending on the polyurethane performance.

In our previous works, some noncytotoxic polyurethane films were prepared with polyethylene glycol, castor oil (CO), 1,6-hexamethylene diisocyanate (HDI), and 1,4-butanediol (BD) for the first time, and the effects of soft segment length and hard segment content on shape memory properties for the films were investigated.\textsuperscript{10,15,16} After evaluating data using a nonlinear equation,\textsuperscript{10} it was determined that hard segment content has more of an effect on shape memory performance than soft segment length. This result led to further works in understanding the relationship between the hard segment content and the shape memory performance for polyurethane films prepared for biomedical applications. The aim of this study is to investigate the effect of amount of chain extender on the shape memory performance of polyurethane films and obtain a process parameters that can benefit shape memory polyurethane synthesis with the requested manageable properties for suitable biomedical applications. The phenomenon was investigated for polyurethanes prepared with relatively high and low molecular weights of polyethylene glycol. Two different temperature programs were applied in deformation and shape recovery steps.

The novelty of this work is that the synergistic effects of three important parameters, two of them polymer properties/structure and one of them programming condition, have been investigated for the bio-based polyurethanes synthesized in our labs. Our results indicate that the amount of chain extender is an important factor together with programming conditions. Additionally, a very similar result obtained earlier.\textsuperscript{10} is that soft segment length is less important than hard segment content. One of the polyurethane films, synthesized at a 60/40 BD/(PEG + CO) ratio, has great potential for biomedical applications such as ureteral stents, tissue engineering scaffolds, and wound healing materials, since its shape memory properties yielded an $R_f$ and $R_r$ of more than 90% with a switching temperature around body temperature.
2. Results and discussion
2.1. Polymer synthesis and characterization

The Fourier transform infrared (FTIR) spectra of final samples with different BD/(PEG + CO) molar ratios are shown in Figure 1. All samples exhibit characteristic polyurethane peaks in their FTIR spectra. There are two regions that were focused on, the C = O stretching vibration amide I region between 1680 and 1730 cm\(^{-1}\) and the N–H stretching vibration between 3200 and 3500 cm\(^{-1}\), in Figures 2a and 2b, respectively. There are two C = O stretching vibration amide I regions: the first H-bonded urethane C = O, referred to as crystalline hard domains (1695–1715 cm\(^{-1}\)), and the second non H-bonded urethane C = O, referred to as the free C = O (1731–1733 cm\(^{-1}\)). As shown in Figure 2a, a non-H-bonded carbonyl peak was not observed, whereas a strongly hydrogen-bonded carbonyl peak at about 1682 cm\(^{-1}\), indicating the presence of H-bonded urethane C=O groups for the ester structure,\(^{10}\) was observed for all samples and poorly hydrogen-bonded carbonyl was observed at about 1715 cm\(^{-1}\) for PU-3000-60 and PU-3000-70 samples. The correlation between the intensity of the C = O peak, hard segment content, and effective phase separation is reported in the literature.\(^{17,18}\) This correlation was also investigated for the samples prepared in this study, since hard segment content and H-bonding affect shape memory polyurethane. The intensity of the peak at about 1682 cm\(^{-1}\) increased with decreasing hard segment content. It can be concluded from this result that H-bonding increases with decreasing hard segment content. The effect of H-bonding on shape recovery behavior is also discussed in the next sections.

The absorption band at around 3330 cm\(^{-1}\) (Figure 2b) displays N–H stretching vibration regions for PUs, which indicates the impact of the hard segments on the hydrogen-bonded urethane carbonyl regions.\(^{12,19}\) The narrow and relatively symmetric N–H peak at around 3330 cm\(^{-1}\) indicates that there is not a significant number of free amines on the structure of polyurethane. In fact, if the mixing phase is available, a shoulder on the high frequency side of the 3330 cm\(^{-1}\) band would appear, related to free N–H between 3445 and 3450 cm\(^{-1}\).\(^{2,10,20}\)

The structure of the polymers was further investigated by XRD and the calculated crystallinity percentage (\(X_c\)) is presented in Table 1. Figure 3 represents the X-ray diffraction patterns of all samples. The sharp peaks at around 2\(\theta = 20^\circ - 25^\circ\) are characteristic of PEG crystallinity.\(^{21}\) The crystallinity of PEG-3000-based samples
is higher than that of PEG-1500-based samples. This result can be explained by the structure of polyethylene glycol. PEG is a semicrystalline material, and its crystallinity increases with molecular weight. That is why PU series that are synthesized with PEG-3000 have higher $X_c$ values. Crystallinity of the samples decreases conversely with increasing BD concentration. This may be due to the hard segment content of the polymers. The amounts of soft segments (which are PEG-1500 or PEG-3000 chains) decreased with increasing hard segment content, and thus the crystallinity in the polymers decreased.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>MW of PEG</th>
<th>Amount of BD : (PEG + CO) (mol percent of the hydroxyl groups)</th>
<th>$X_c$ (%) by:</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C) by:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>XRD</td>
<td>DSC</td>
<td>DSC</td>
</tr>
<tr>
<td>PU-1500-40</td>
<td>1500</td>
<td>40 : 60</td>
<td>5.7</td>
<td>17.9</td>
<td>25.4</td>
</tr>
<tr>
<td>PU-1500-60</td>
<td></td>
<td>60 : 40</td>
<td>5.3</td>
<td>11.9</td>
<td>23.4</td>
</tr>
<tr>
<td>PU-1500-70</td>
<td></td>
<td>70 : 30</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PU-3000-40</td>
<td>3000</td>
<td>40 : 60</td>
<td>7.1</td>
<td>19.3</td>
<td>35.7</td>
</tr>
<tr>
<td>PU-3000-60</td>
<td></td>
<td>60 : 40</td>
<td>6.7</td>
<td>16.5</td>
<td>38.8</td>
</tr>
<tr>
<td>PU-3000-70</td>
<td></td>
<td>70 : 30</td>
<td>5.8</td>
<td>15.7</td>
<td>38.1</td>
</tr>
</tbody>
</table>
2.2. Thermal and viscoelastic properties

Thermal properties of polyurethanes were studied by DSC analysis. The DSC curves and calculated $T_g$ and $T_m$ values for all samples are given in Figures 4a and 4b and Table 1. $T_g$ and $T_m$ values of PEG-1500-based PU series are lower than those of PEG-3000-based PU series. This result can also be explained by the crystalline structure of PEG. PEG-3000-based polyurethane samples have relatively high crystallinity compared to PEG-1500-based polyurethanes. Increasing crystallinity decreases chain mobility and increases $T_g$ and $T_m$ values.

![Figure 3. X-ray diffraction patterns of PU samples.](image)

![Figure 4. DSC curves of PU-3000 coded samples and PU-1500 coded samples.](image)

In this study, crystalline melting temperature-based shape memory polyurethanes were synthesized. In view of biomedical applications, PEG-3000-based samples have an absolute advantage for body-based applications since their crystalline melting temperatures are close to human body temperature.

Crystallinity of the polyurethanes was calculated from the ratio of the enthalpy of the samples ($\Delta H_m$) and the enthalpy of melting of 100% crystalline PEG ($\Delta H_m^{(PEG)} = 202.41$ J g$^{-1}$). The calculated values are given in Table 1. The crystallinity of a sample depends on the molecular weight and amount of PEG in the polymer structure. Crystallinity increases with increasing molecular weight and amount of PEG. Compared with XRD results, the difference of crystallinity percentage for each sample can be explained by different measurement principles of DSC and XRD. DSC is a more sensitive method for determining polymer crystallization.

Viscoelastic properties of polyurethanes were investigated by dynamic mechanical analysis (DMA). Figures 5 and 6 represent the data obtained from the DMA study. All samples have two transition temperatures: a glass transition temperature as a low temperature and a melting temperature as a relatively high temperature. When the molecular weight of the soft segment increased, $T_g$ shifted to high temperatures. Glass transition temperatures of all polyurethanes are below room temperature and thus all samples are rubbery at human body temperature. This result indicates that the polymers are suitable for use as a biomaterial. The intensity (height) of the maximum tan delta peak reflected the extent of mobility of polyurethane chain segments. PU-3000-70 has the lowest chain mobility since it has the highest chain extender and a crystalline domain in its structure.
2.3. Crosslink density and average molecular weight between two crosslinks

Table 2 presents the crosslink density \( (v_c) \) and average molecular weight between two crosslinks \( (M_c) \) calculated by the Flory–Rehner equation and DMA data. The calculated values for each sample are not the same. As mentioned in the literature,\(^{10,23}\) crosslink density calculated by the Flory–Rehner equation was lower than those calculated by DMA data. The difference between the two results can be explained by the fact that both chemical and physical crosslinks are calculated from DMA results, whereas only chemical crosslinks are calculated from the equilibrium swelling method according to the Flory–Rehner equation.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( v_c \times 10^3 ) (mol/cm(^3))</th>
<th>( M_c \times 10^{-3} ) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMA</td>
<td>Flory–Rehner</td>
</tr>
<tr>
<td>PU-1500-40</td>
<td>7.26</td>
<td>2.61</td>
</tr>
<tr>
<td>PU-1500-60</td>
<td>14.93</td>
<td>2.93</td>
</tr>
<tr>
<td>PU-1500-70</td>
<td>9.36</td>
<td>3.13</td>
</tr>
<tr>
<td>PU-3000-40</td>
<td>16.05</td>
<td>2.36</td>
</tr>
<tr>
<td>PU-3000-60</td>
<td>21.48</td>
<td>2.79</td>
</tr>
<tr>
<td>PU-3000-70</td>
<td>22.14</td>
<td>2.91</td>
</tr>
</tbody>
</table>

The crosslink density calculated by the Flory–Rehner equation increased and consequently \( M_c \) decreased with increased BD due to the increasing ratio of short-chain molecules in the polymer structure. For the same reason, PEG-1500-based polyurethanes had a higher crosslink density than PEG-3000-based ones.

Systematic results could not be obtained from DMA data for PEG-1500-based polyurethanes. On the other hand, \( v_c \) increased with increasing amounts of chain extender for PEG-3000-based samples.

2.4. Shape memory properties

Among polymer properties, the most important factors affecting the shape memory properties are soft segment lengths, hard segment contents, degree of crystallinity, and crosslink density.\(^{24–26}\) In our previous study, the
effects of soft segment length and hard segment content on shape memory behavior were investigated at constant chain extender ratios for PEG- and CO-based polyurethanes, and hard segment content was more important. In this study, we focused on the effect of chain extender ratio on shape memory performance for polyurethane films prepared from PEG and CO, since the chain extender directly affects hard segment content. As explained in the Section 3, shape memory studies were carried out with two different temperature programs, which were low (ΔT = 35 °C) and high (ΔT = 60 °C) temperature differences in cooling and heating steps. In Table 3, experimental shape fixity rate (Rf) and shape recovery rate (Rr) of the PU samples are given for the two temperature programs. Tests were repeated 6 times for each sample. The arithmetic average of these values is given in the table together with the standard deviation.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Hard segment content (%)</th>
<th>Shape fixity rate (Rf) at:</th>
<th>Shape recovery rate (Rr) at:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ΔT = 60 °C</td>
<td>ΔT = 35 °C</td>
</tr>
<tr>
<td>PU-1500-40</td>
<td>26.3</td>
<td>57.5 ± 1.3</td>
<td>48.9 ± 1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0 ± 0</td>
<td>98.1 ± 0.7</td>
</tr>
<tr>
<td>PU-1500-50a</td>
<td>30.9</td>
<td>89.8 ± 1.5</td>
<td>-b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96.7 ± 0.8</td>
<td>-b</td>
</tr>
<tr>
<td>PU-1500-60</td>
<td>36.8</td>
<td>75.2 ± 3.0</td>
<td>63.8 ± 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88.3 ± 1.2</td>
<td>81.0 ± 1.9</td>
</tr>
<tr>
<td>PU-1500-70</td>
<td>44.7</td>
<td>59.4 ± 1.1</td>
<td>47.8 ± 2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88.6 ± 1.2</td>
<td>83.1 ± 1.6</td>
</tr>
<tr>
<td>PU-3000-40</td>
<td>23.1</td>
<td>66.5 ± 0.7</td>
<td>64.4 ± 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100.0 ± 0</td>
<td>98.4 ± 0.7</td>
</tr>
<tr>
<td>PU-3000-50a</td>
<td>27.4</td>
<td>92.3 ± 1.1</td>
<td>-b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96.3 ± 0.8</td>
<td>-b</td>
</tr>
<tr>
<td>PU-3000-60</td>
<td>33.0</td>
<td>90.7 ± 0.6</td>
<td>87.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90.1 ± 0.8</td>
<td>88.5 ± 1.0</td>
</tr>
<tr>
<td>PU-3000-70</td>
<td>40.5</td>
<td>85.6 ± 3.2</td>
<td>72.2 ± 1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>91.7 ± 0.9</td>
<td>88.8 ± 0.3</td>
</tr>
</tbody>
</table>

a From ref. [10].
b No available data.

Rr values are higher than Rf values due to the existence of hard domains (obtained from FTIR data) in the polymer structure for all samples. There is a correlation between Rr values and hard segment content. Rr decreases with increasing hard segment content, but the correlation is not linear (R² is 0.7073 for PU-3000 series and 0.8187 for PU-1500 series in Figure 7). This is because of the H-bonding in the polymer structure. Decreasing hard segment content increased H-bonding and thus increased Rr values. H-bonding controls the morphology of polyurethanes and it determines stronger interaction between hard segments due to the additional driving force for more complete phase segregation. PU-1500-40 and PU-3000-40 coded samples, which were prepared with relatively low hard segment content, had the highest Rr values. On the other hand, both samples had low Rf values. The results reveal that increasing hard segment content decreased shape fixity. In the literature, polyurethanes were synthesized by using methylene diphenyl diisocyanate (MDI), poly(tetramethylene glycol), and BD with different hard segment contents. PUs with 20 and 25 wt.% of hard segment content had weak interactions due to the low percentage of hard segment, resulting in the loss of shape memory effect. On the other hand, the PU prepared with relatively high hard segment content (50 wt.%) showed the worst shape recovery due to the more rigid polyurethane structure. In another study, Ahmad et al. prepared some polyurethane-based shape memory polymers from different polyols. In that study, isophorone diisocyanate (IPDI) and MDI were used as hard segment sources. Similarly, the Rr value decreased for all systems as the hard segment content increased. On the other hand, shape fixity increased from 78% to 90% when IPDI content increased from 0% to 70% for polycaprolactone-based samples.
In our study, a correlation was not determined between $R_f$ values and hard segment content. $R_f$ increases first with increasing hard segment content, and then it decreases for both series of polyurethane. The lowest and the highest hard segment contents of PU-1500 series films (PU-1500-40 and PU-1500-70, respectively) showed almost the same $R_f$ values. For PU-3000 series films, on the other hand, $R_f$ values of the films prepared with the highest and lowest hard segment contents are not the same. This may be because of the higher crystalline structure of the PU-3000 series compared to the PU-1500 series. It is reported in the literature that morphological features and crystallinity contribute to improvement in the shape memory properties of polyurethanes.\(^{5,27,28}\)

Cooling and heating rates also affect the shape memory property of the materials.\(^6,11,26\) The shape fixity and shape recovery performances of the PU films are better at high temperature differences ($\Delta T = 60 \degree C$) in cooling and heating steps. This may be because of the higher orientation of polymer chains in the crystalline region at high temperature differences. However, the results of the shape recovery rate are favorable for applications at $\Delta T = 35 \degree C$. In view of biomedical applications, transition temperature (melting temperature in our case) should be between 37 and 40 \degree C, which is the human body temperature. Thus, the results at $\Delta T = 35 \degree C$ for the heating step (heating from 5 \degree C to 40 \degree C) should be considered for shape recovery tests. There is no temperature limitation for shape fixity in the cooling step, since this step is performed before body applications. In this step, limitation significantly depends on the thermal stability of the polymer. After evaluating all $R_f$ and $R_r$ results, the polyurethane films prepared in this study should be programmed at a high cooling rate (cooling from 65 \degree C to 5 \degree C in the shape fixity step) and they recovered their original shape at a low heating rate (heating from 5 \degree C to 40 \degree C in the shape memory step).

Since melting temperatures are close to human body temperature, PU-3000 series polymers are good candidates for biomedical applications. Among the PU-3000 series polymers, the PU-3000-60 coded sample gave acceptable $R_f$ and $R_r$ values. The PU-3000-70 coded sample also showed acceptable $R_f$ value at $\Delta T = 60 \degree C$.

Figure 7. Shape recovery rate versus hard segment content.
2.5. Some physical properties

Densities of the samples are given in Table 4. Increasing BD amount decreased polymer density ($\rho$). Increasing PEG molecular weight also decreased the density of the polymers that had the same hard segment content. All these results can be explained by the density differences and structure of the monomers that are used for polyurethane synthesis ($\rho_{CO} = 0.96$ g/cm$^3$, $\rho_{PEG1500} = 1.23$ g/cm$^3$, $\rho_{PEG3000} = 1.21$ g/cm$^3$, and $\rho_{BD} = 1.015$ g/cm$^3$).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Density (kg/m$^3$)</th>
<th>Swelling ratio (%)</th>
<th>Gel content (%)</th>
<th>Contact angle (°)</th>
<th>Surface free energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-1500-40</td>
<td>1.1141</td>
<td>33.5</td>
<td>77.4</td>
<td>59.9 ± 1.8</td>
<td>48.5 ± 0.8</td>
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<tr>
<td>PU-1500-60</td>
<td>1.1065</td>
<td>28.4</td>
<td>83.0</td>
<td>61.9 ± 1.1</td>
<td>47.5 ± 1.0</td>
</tr>
<tr>
<td>PU-1500-70</td>
<td>1.1033</td>
<td>26.9</td>
<td>90.2</td>
<td>70.3 ± 1.2</td>
<td>44.6 ± 1.9</td>
</tr>
<tr>
<td>PU-3000-40</td>
<td>1.1165</td>
<td>37.1</td>
<td>73.8</td>
<td>48.7 ± 1.9</td>
<td>49.5 ± 1.5</td>
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<tr>
<td>PU-3000-60</td>
<td>1.1147</td>
<td>33.4</td>
<td>80.0</td>
<td>47.2 ± 0.9</td>
<td>49.1 ± 1.8</td>
</tr>
<tr>
<td>PU-3000-70</td>
<td>1.1115</td>
<td>29.5</td>
<td>84.3</td>
<td>59.8 ± 1.4</td>
<td>44.3 ± 1.4</td>
</tr>
</tbody>
</table>

Table 4. Contact angle and surface free energy measurements for PU samples.

Gel content and swelling ratio of the polymers are shown in Table 4. Gel content is directly proportional to the chemical crosslink density of PU films, which is calculated from the Flory–Rehner equation. Increasing crosslink density increases gel content. Swelling ratio is inversely proportional to chemical crosslink density. As expected, polyurethanes having more crosslinked structure showed lower swelling ratios.

Contact angle and surface free energy of PU films are also given in Table 4. Increasing the BD amount in the polymer formulation decreased the hydrophilicity of the samples, and consequently the contact angle increased with decreasing surface free energy. On the other hand, increasing molecular weight of PEG increased surface hydrophilicity. As a general trend, samples with a contact angle smaller than 65° are good candidates for biomedical applications due to the expectation for their low protein adsorption. In view of the hydrophilicity, all polyurethane films except the PU-1500-70-coded sample can be suggested as biomaterials.

2.6. Conclusion

A series of polyurethane with various chain extender contents and with two different molecular weights of PEG were synthesized. They were characterized in view of shape memory performance in two cooling and heating regimes for deformation and shape recovery steps. It was determined that the amount of chain extender is a very important parameter either for shape memory performance or some physical properties affecting usage area and performance of the polyurethane film, such as melting temperature, density, swelling behavior, and surface hydrophilicity. One important parameter for shape memory performance is the temperature program in the deformation and shape recovery steps. Polymer films synthesized in this study showed better shape memory performance at high temperature differences. After evaluating all data, it is suggested that the PU-3000-60 coded sample synthesized at a 60/40 BD/(PEG + CO) ratio is the optimal choice among the polyurethane films in view of its shape memory performance and transition temperature. The PU-3000-50 coded sample prepared in our previous study (its shape memory performance is given in Table 3) is also a good candidate for biomedical applications such as ureteral stents, tissue engineering scaffolds, and wound healing materials.
3. Experimental

3.1. Materials

Castor oil (CO) with hydroxyl number of 160 mg KOH/g sample and acid number ≥1 mg KOH/g was supplied by Sigma-Aldrich (St. Louis, MO, USA). PEG with number-average molecular weights of 1500 g/mol and 3000 g/mol from Fluka (Morris Plains, NJ, USA) and HDI from Sigma-Aldrich were used. BD from Fluka was used as the chain extender.

3.2. Synthesis of PUs

PU synthesis was explained in our previous study. In brief, PEG was dried on a rotary evaporator under vacuum for 6 h at 90 °C. BD and CO were dried in a vacuum oven before use for 24 h at 80 and 50 °C, respectively. HDI was used as received. The PU films were synthesized with a one-step bulk polymerization procedure. All PU films were prepared at an equimolar amount of diisocyanate relative to hydroxyl groups and a constant weight ratio of CO:PEG (50/50). PEG and CO were placed in a flask in connection with a rotary evaporator and heated in a thermos-regulated oil bath for 30 min at 90 °C. Then the chain extender was added to the mixture at the same conditions with rapid spinning in a rotary evaporator to homogenize the mixture and evacuate the air trapped within. PU films were synthesized at three different chain extender ratios (BD/(CO + PEG): 40/60, 50/50, 60/40) as mole percent of the hydroxyl groups. The resulting mixture was quickly poured into a three-necked round-bottom reaction flask fitted with a dry nitrogen inlet, dropping funnel, and mechanical stirrer and heated in a thermos-regulated oil bath. HDI was added to the mixture from a dropping funnel for 5 min at 50 °C with stirring rate of 400 rpm. The resulting viscous liquid was quickly poured into glass petri dishes to form 1-mm-thick films and left to cure for 20 h at 80 °C. The reaction was monitored by FTIR spectroscopy. The disappearance of the absorption peak at 2250 cm \(^{-1}\), assigned to the N = C = O group, confirmed that all the diisocyanate was consumed in the reaction.

PU films are designated using the abbreviation PU-a-b, where a refers to the number-average molecular weight of PEG and b indicates the percentage of BD in the mixture of BD, PEG, and CO.

3.3. Polymer characterization

FTIR spectra, obtained with a PerkinElmer (Waltham, MA, USA) Spectrum One Instrument in the range from 650 to 4000 cm \(^{-1}\), were used to characterize the functional groups of the synthesized PU films and also to investigate hydrogen bonding in the hard segment.

PU films were investigated with a PerkinElmer Diamond differential scanning calorimeter between –65 and 150 °C, under dry nitrogen atmosphere at a scan rate of 20 °C/min. The glass transition temperature \((T_g)\) refers to the midpoint of the heat capacity change and the melting point \((T_m)\) refers to the maximum point of the endotherm peak.

Dynamic mechanical properties of the PU films were determined with a PerkinElmer Diamond dynamic mechanic thermal analyzer (DMA), using a straining mode under dry nitrogen atmosphere at a heating rate of 3 °C/min and 1 Hz, between –70 and 170 °C. Specimens with dimensions of 4 × 1 cm were cut from the film. The thickness of each sample was measured with a caliper.

A Panalytical X’Pert Diffractometer (Almelo, the Netherlands) was used for XRD measurements in the range of Bragg’s angle \(2\theta = 5°–55°\). Crystallinity of the polyurethanes was determined according to the method previously described by Komiya and Nara.
Two methods were used for determination of crosslink density \((v_c)\) and average molecular weight between two crosslinks \((M_c)\). The first method was the swelling method according to the Flory–Rehner equation, which depends on the chemical structure of the polymer, based on the idea of polymers showing different swelling behaviors with different solvents. The specimen \((1 \times 1 \text{ cm})\) was swollen in toluene, acetone, dioxane, N-methyl 2-pyrrolidone, and methanol. The solubility parameters for these solvents are 8.9, 9.9, 10, 11.3, and 14.5 \((\text{cal/cm}^3)^{1/2}\), respectively.\(^3\) \(M_c\) was calculated from Eq. (1):

\[
M_c = \frac{\nu_s d_p (V_p^{1/3} - V_p/2)}{\ln(1V_p) + V_p + \chi_{12}V_p^2},
\]

where \(\nu_s\) is the molar volume of the solvent, \(d_p\) is the density of the polymer, \(V_p\) is the volume fraction of the polymer in the swollen state, and \(\chi_{12}\) is the polymer–solvent interaction parameter of the solvent, which can be calculated by Eq. (2):

\[
\chi_{12} = 0.34 + \frac{\nu_s(\gamma_P\gamma_S)^2}{RT},
\]

where \(\gamma_P\) is the solubility parameters of the polymer, \(\gamma_S\) is the solubility parameters of the solvent, \(R\) is the gas constant, and \(T\) is the absolute temperature. The solubility parameter of the polymers was determined by swelling measurements of the polymer samples with different solvents at 25 °C, as mentioned above. The equilibrium swelling degree was calculated according to Eq. (3):

\[
Q = \frac{W_p/d_p + W_s/d_s}{W_p/d_p},
\]

where \(W_P\) is the dry weight of the polymer, \(W_S\) is the weight of the solvent, and \(d_S\) is the density of the solvent.

Crosslink density is calculated using Eq. (4):

\[
v_c = \frac{d_p}{M_c}.
\]

The second method for determination of \(v_c\) and \(M_c\) was the rubber elasticity method according to DMA. Via this method, the effects of both chemical and physical crosslinking were determined. The crosslink density from DMA was calculated using Eq. (5):

\[
v_c = \frac{E'}{3RT},
\]

where \(E'\) is the storage modulus at 25 °C and \(T\) is 298 K.

The swelling behavior of the polyurethane films was determined according to ISO D570 standards. The polymer films were dried in an oven and then desiccator for 24 h. They were immersed in a beaker with water at 37 °C until equilibrium. The surfaces of the films were dried with filter paper softly and they were weighed. Swelling ratio was calculated using Eq. (6):

\[
\text{Swelling ratio (\%) } = \frac{W_sW_d}{W_d} \times 100,
\]

where \(W_s\) and \(W_d\) are the weights of the swollen and dry samples, respectively.
Contact angle and surface energy measurements were carried out with a KSV CAM 200 contact angle meter to evaluate the surface hydrophilic properties. Five measurements for each PU film were carried out with different solutions (water, ethylene glycol, diiodomethane, and formamide) at room temperature. Surface energy was calculated by the Fowkes equation.

Density measurements were carried out with a density gradient column (Ray-Ran Test Equipment, Warwickshire, UK) at 23 °C.

Hard segment content was calculated as in the study of Sivakumar and Nasar,

\[ \text{Hard segment content (weight \%) = } \frac{W_{HDI} + W_{BD}}{W_{HDI} + W_{BD} + W_{CO} + W_{PEG}} \times 100 \]  

(7)

3.4. Shape memory performance

The test samples were cut to 50 × 15 mm. The thickness of each sample was 1 mm. A bending test was applied and transition temperature was chosen as 40 °C in order to determine the shape memory performance in body conditions. The tests were also applied at 65 °C to compare the results with the previous studies. The steps of the bending test are as follows:

(i) Heat the sample to 40 or 65 °C,

(ii) Apply deformation (bending) to the sample under a constant load (\( \theta_{\text{max}} \)),

(iii) Cool the sample to 5 °C at the same load,

(iv) Maintain the sample at this temperature for 5 min without the removal of the load,

(v) Remove the load and measure the angle (\( \theta_{\text{fixed}} \)),

(vi) Raise the temperature to 40 or 65 °C and keep it at this state for 5 min,

(vii) Measure the angle (\( \theta_{\text{final}} \)).

Under these conditions, shape fixity (\( R_f \)) and shape recovery (\( R_r \)) rates are defined via Eqs. (8) and (9):

\[ R_f = \frac{\theta_{\text{fixed}}}{\theta_{\text{max}}} \times 100 \]  

(8)

\[ R_r = \frac{\theta_{\text{fixed}}}{\theta_{\text{final}}} \times 100 \]  

(9)

References