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# Shape Memory Polyurethanes Based on Polyols Derived From Renewable Resources

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**Summary:** Segmented polyurethanes have been synthesized employing polyols derived from renewable resources, semicrystalline or amorphous in nature, as soft segment, and an aliphatic (1,6-hexamethylene diisocyanate, HDI) or aromatic (4,4′-diphenylmethane diisocyanate, MDI) diisocyanate and 1,4-butanediol (BD) as hard segment using two-step bulk polymerization procedure. The effect of soft and hard segment structure and hard segment content on thermal, mechanical and shape memory properties has been studied by means of differential scanning calorimetry, tensile tests and tensile tests performed using a thermal chamber.

**Keywords:** polyols; polyurethanes; renewable resources; shape memory

## Introduction

In the last years, shape memory polymers have attracted a great deal of attention because they are able to remember their original shape after being deformed and recover their original shape as a response to an external stimulus.[1,2] They may find applications in textiles, automotive parts, intelligent packing, implantable medical devices, minimally sensors and actuators in the forms of polyurethane such as solution, emulsion, film, fiber, bulk and foam.[3–5]

Shape memory polymers can be categorized into covalently crosslinked glassy thermosets, covalently crosslinked semicrystalline rubbers, physically crosslinked amorphous thermoplastics and physically crosslinked semicrystalline block copolymers.[6,7] A class of these block copolymers are the segmented polyurethanes comprising of soft segments (SS), usually formed by a polyether or polyester macrodiol, and hard segments (HS) formed from the reaction of a diisocyanate with a low molecular weight diol. The shape memory effect is largely dependent on the morphology and degree of microphase separation of the copolymer, which in turn are determined by the molecular characteristics such as the molecular weight and the composition of the two segments.

Shape memory polyurethanes have two classes of segments, hard segment as the net points that determine the permanent shape imparting a level of rigidity, dimensional stability and thermal resistance and soft segment or amorphous hard segment as the switching segments that are associated with the temporary shape. The permanent shape is stored in the system while the polymers assume different temporary shapes, and by heating the polymers above the switch transition temperature, the permanent shape can be recovered sharply.[8–10] The molecular switch to freeze temporary shapes may be a melting[8,11] or glass transition of soft segment phase or a mixed glass transition temperature of soft segment and hard segment phase.[12–14]

The aim of this work was to analyze the shape memory properties of segmented polyurethanes (SPU) synthesized with both amorphous and crystalline soft segments derived from renewable resources by thermo-mechanical cyclic tensile testing. The effect of hard segment content and nature on the shape memory properties was also studied.

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## Experimental Part

SPU were synthesized using semicrystalline CO1 and amorphous CO2 polyols derived from castor oil with a functionality of 2 and 2.7 respectively, 1,6-hexamethylene diisocyanate (HDI) and 4,4′-diphenylmethane diisocyanate (MDI), kindly supplied by Bayer and 1,4-butanediol (BD) from Sigma-Aldrich as chain extender. The molecular weight of CO1 and CO2 (3505 and 3366 g/mol) was evaluated from the hydroxyl number determined by the standard procedure ASTM D4275–05 test method A. Prior to be used, polyols and BD were dried at 60 °C during 6 h.

Polyurethanes with different HS content ranging from 21 wt % to 39 wt %, maintaining a NCO/OH molar ratio equal to 1 for all the compositions, were prepared using two-step bulk polymerization procedure. Firstly, the isocyanate-terminated prepolymers were prepared by the reaction between the polyol with the diisocyanate at 90 °C for 5 h in nitrogen atmosphere. Then, BD was added at the same temperature during 10 min with vigorous stirring. Finally, the viscous liquid was quickly poured between two Teflon coated metal plaques separated by 1.5 mm and left to cure under pressure for 10 h at 100 °C. The synthesized SPU were designated as PU followed by the abbreviation of the first letter of the diisocyanate and followed by polyol-x where x is the diisocyanate equivalents number in the SPU, i.e PUHCO1–3 corresponding to HDI:-CO1:BD with molar ratio 3:1:2 and PUMCO2–5 is MDI:CO2:BD with molar ratio 5:1:4.

Thermal properties of synthesized polyurethanes were investigated using a Mettler Toledo 822e differential scanning calorimeter (DSC) provided with an electronic intracooler and nitrogen as the purge gas. The samples were heated from - 60 to 200 °C at rate of 20 °C/min.

Mechanical properties were carried out at room temperature on an Instron 4206 tensile machine according to ASTM D 1708–93 standard procedure. The sample gauge length was 22 mm and load cell of 250 N was used. Tensile modulus (E), tensile strength at maximum elongation ($\sigma_{max}$) and percentage elongation at break ($\varepsilon_b$) were measured. Tests were performed at 10 mm/min and the results were averaged out from five tested specimen data.

Shore D hardness measurements were performed at room temperature with a MD-202 Durotech digital hardness durometer, following ASTM D 2240 standard procedure. Results were averaged from a minimum of five tests realised in several zones of the sample.

The shape memory properties were evaluated with thermomechanical cyclic tensile tests using an Instron 4206 tensile machine equipped with a temperature controlled chamber. Samples were heated above the switching temperature, 70 °C, according to the values obtained by DSC, and stretched to 100% strain to get the desired temporary shape at a speed of 10 mm/min. In the next step, the deformed materials were cooled down to room temperature to fix the temporary shape and the external force was removed. The deformation was recovered by heating the sample above the switching temperature. Five thermomechanical cyclic tensile tests were consecutively performed.

The shape fixity ($R_f$) and the shape recovery ratio ($R_r$) can been calculated with eq. 1 and 2 respectively.

$$R_f = \varepsilon_U / \varepsilon_M X100 \tag{1}$$

$$R_r = (\varepsilon_M - \varepsilon_P) X 100 \tag{2}$$

where $\varepsilon_M$ is the maximum strain in the tensile test, $\varepsilon_U$ is the residual strain after unloading to room temperature and $\varepsilon_P$ is the residual strain after the shape recovery.

## Results and Discussion

The differential scanning calorimetry curves of synthesized polyurethanes are shown in Figure 1. The polyurethanes based on CO1 polyol show a melting temperature around 56 and 65 °C for PUHCO1–3 and

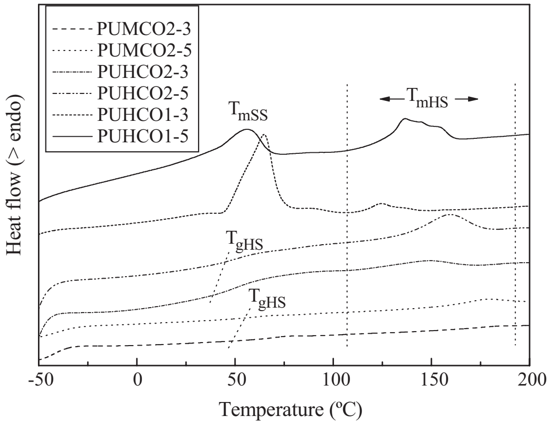

***Figure 1.***
DSC thermograms of synthesized polyurethanes.

PUHCO1–5 respectively, this transition is associated to crystalline soft segment. Polyurethanes based on CO2 polyols don't show melting temperature related with soft segment indicating that this soft segment is amorphous. However, they showed a glass transition temperature ($T_g$) related with amorphous phase of hard segment.

The results obtained for the thermomechanical cyclic tensile tests were taken at temperature above soft segment melting temperature for crystalline soft segment and hard segment glass transition temperature for amorphous soft segment, 70 °C, as switch transition temperature.

Other transition at higher temperature associated to multiple melting endotherms resulting from different crystal structures, domain sizes or different degrees of order and reorganization in the crystalline structure of hard segment,[15,16] $T_{mHS}$, which shifts to higher with the increase of hard segment content, can be observed. Hard segment based on HDI showed higher $T_{mHS}$ than their homologous based on MDI and it is related with the ability of HDI units to be packaged.

Table 1 displays the results of tensile properties derived from stress-strain curves and shore D hardness of synthesized polyurethanes. As can be observed, the Young modulus, shore D hardness and tensile strength increase but elongation at break decreases with the increase of hard segment content for all synthesized polyurethanes. This is related to the formation of more ordered hard segment domains as observed by DSC which provide higher stiffness to the polyurethane. Polyurethanes based on crystalline polyol, CO1, show higher Young modulus, hardness, tensile strength and elongation at break.

The strain-stress curves of synthesized polyurethanes obtained by thermomechanical cyclic tensile test are shown in Figure 2. The significant difference between

***Table 1.***
Mechanical properties of synthesized polyurethanes.

| Polyurethane Code | E (MPa) | $\sigma_{max}$ (MPa) | $\varepsilon_b$ (%) | Hardness (Shore D) |
|---|---|---|---|---|
| PUMCO2–3 | 2.9 ± 0.2 | 3.2 ± 0.1 | 305.0 ± 23.7 | 17.6 ± 0.2 |
| PUMCO2–5 | 15.1 ± 3.8 | 12.5 ± 0.3 | 265.0 ± 29.8 | 33.7 ± 1.6 |
| PUHCO2–3 | 11.0 ± 0.7 | 2.9 ± 0.4 | 260.7 ± 52.4 | 18.2 ± 0.6 |
| PUHCO2–5 | 36.5 ± 7.6 | 5.3 ± 0.1 | 194.4 ± 8.4 | 22.4 ± 0.8 |
| PUHCO1–3 | 129.0 ± 6.1 | 16.4 ± 0.8 | 410.0 ± 22.0 | 35.2 ± 0.6 |
| PUHCO1–5 | 169.0 ± 1.6 | 19.5 ± 1.6 | 375.0 ± 27.0 | 41.0 ± 0.6 |

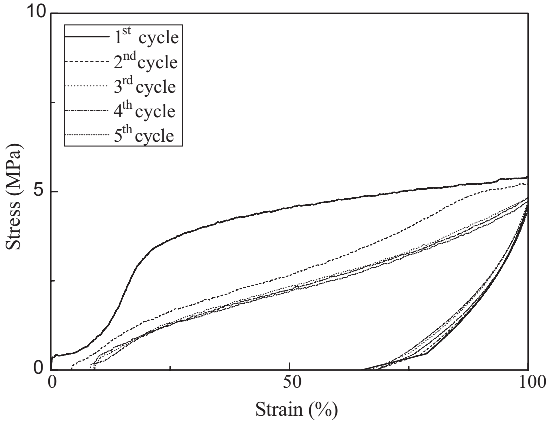

**Figure 2.**
Thermomechanical cyclic tensile testing curves of the PUHCO2-5 polyurethane.

the first thermal cycle and the remaining cycles is related to the reorganization of SPU molecules, involving molecule orientation, crystallization and weak point breakage during elongation.

After several cycles, the material thermomechanical properties become very similar. This suggests that the SPU has stable thermomechanical cyclic properties.

In the shape memory polyurethane, the hydrogen bonded hard segment phase is responsible for shape recovery, while the soft segment phase or amorphous hard segment plays the mayor role in shape fixity.[17] The polyurethane fixes the temporary deformation by freezing the deformed hard or soft segment phase using the crystallized soft segment or glassy hard segment when cooled down below the switch transition temperature. When heated above the switch transition temperature, it recovers the original shape by releasing the internal stress stored among the physical crosslinked hard segments during the deformation.

The shape memory properties of polyurethanes based on CO1 and CO2 polyols, varying hard segment content and nature, are showed in Table 2. It can be observed that for SPU based on CO1 polyols, semicrystalline, $R_f$ increases with increasing crystallinity of soft segment, thereby decreasing the hard segment content. Crystallinity of soft segment is an effective parameter to fix temporary shape due to crystallinity leds to more shape fixity. The retention strain ($\varepsilon_U$) depends on the immediate shrinkage after unloading,[18] therefore as soft segment crystallinity increases, lower shrinkage, higher $\varepsilon_U$ and higher shape fixity ratio is observed. For SPU based on CO2 polyol, amorphous, $R_f$ increases with the increase of hard segment content showing values lower than SPU based con CO1 polyol. Another parameter that affects $R_f$ is the phase separation

**Table 2.**
Shape memory properties of synthesized polyurethanes.

| | PUMCO2–3 | | PUMCO2–5 | | PUHCO2–3 | | PUHCO2–5 | | PUHCO1–3 | | PUHCO1–5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R_f$ (%) | $R_r$ (%) | $R_f$ (%) | $R_r$ (%) | $R_f$ (%) | $R_r$ (%) | $R_f$ (%) | $R_r$ (%) | $R_f$ (%) | $R_r$ (%) | $R_f$ (%) | $R_r$ (%) |
| 1st cycle | 54.5 | 99.1 | 59.5 | 98.3 | 62.2 | 97.9 | 65.1 | 95.7 | 82.4 | 95.7 | 79.7 | 86.9 |
| 2nd cycle | 54.9 | 98.5 | 60.1 | 98.1 | 61.5 | 97.3 | 68.2 | 92.4 | 87.6 | 93.9 | 83.1 | 84.8 |
| 3rd cycle | 55.3 | 98.9 | 60.1 | 97.4 | 62.4 | 96.9 | 66.9 | 91.8 | 85.4 | 93.9 | 83.4 | 84.2 |
| 4th cycle | 54.3 | 98.5 | 60.1 | 97.1 | 62.4 | 96.3 | 68.2 | 91.4 | 86.1 | 93.1 | 83.8 | 83.4 |
| 5th cycle | 54.3 | 98.2 | 60.4 | 96.7 | 61.8 | 94.9 | 68.2 | 91.1 | 87.3 | 92.6 | 82.7 | 84.8 |

between hard and soft segments. In this way, the SPUCO2 based on MDI shows lower shape fixity and higher shape recovery that SPUCO2 based on HDI. It is related to HDI based polyurethanes to give higher phase separation degree and form hard segment domains with higher crystallinity at the same components ratio.[19]

One of the most important features of shape memory materials is their ability to recover their original dimensions after being deformed and when a triggering signal is applied. To have effective shape memory behavior, the hard segment domains must remain mostly unperturbed, inter- or intrapolymer chain attractions, such as hydrogen bonding or dipole-dipole interactions, must retain the physical crosslinking. For all synthesized polyurethanes, $R_r$ shows values in the range 99.1 at 83.4, behaving like a shape memory material. As can be observed in Table 2, $R_r$ decreases with the increase of hard segment content in both SPU based on CO1 and CO2 polyols.

## Conclusion

Shape memory properties of SPU based on polyols derived from castor oil have been analyzed varying hard and soft segment nature and hard segment content by means of thermomechanical cyclic tensile tests. As hard segment content increases, the crystallinity increases and $R_f$ ratio increases in all synthesized polyurethanes. Polyurethanes based on amorphous soft segment showed lower $R_f$ ratio than those based on crystalline. For all synthesized polyurethanes, $R_r$ ratio showed values in the range 99.1 at 83.4, behaving like shape memory materials.

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