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Thermoplastic shape-memory polyurethanes based on natural oils

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Abstract

A new family of segmented thermoplastic polyurethanes with thermally activated shape-memory properties was synthesized and characterized. Polyols derived from castor oil with different molecular weights but similar chemical structures and a corn-sugar-based chain extender (propanediol) were used as starting materials in order to maximize the content of carbon from renewable resources in the new materials. The composition was systematically varied to establish a structure–property map and identify compositions with desirable shape-memory properties. The thermal characterization of the new polyurethanes revealed a microphase separated structure, where both the soft (by convention the high molecular weight diol) and the hard phases were highly crystalline. Cyclic thermo-mechanical tensile tests showed that these polymers are excellent candidates for use as thermally activated shape-memory polymers, in which the crystallites ensure high shape recovery values (80–100%) depending on the hard segment content). The high proportion of components from renewable resources used in the polyurethane formulation leads to the synthesis of bio-based polyurethanes with shape-memory properties.

Keywords: shape-memory, polyurethane, crystallinity, hard domain network

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last decade, the interest in stimulus responsive or 'smart' materials has increased enormously, owing to the possibility that their properties can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH and electric or magnetic fields [1-4]. Shape-memory polymers represent a subset of smart polymeric materials that have the ability to be manipulated to retain or 'fix' a temporary shape, and later recover to their 'memorized' original (permanent) shape upon exposure to an external stimulus [5, 6]. This functionality is useful for application in smart fabrics [7], films for packaging [8], intelligent medical devices [9], minimally invasive surgery [10], and many other technologies.

Polymers that exhibit shape-memory properties require two molecular components or segments: crosslinks or net points that define the permanent shape, by means of either physical interactions or chemical bonds, and switching segments that permit fixing of the temporary shape by forming a switchable second network, for example by forming a glass or semicrystalline phase that can be softened upon heating to the respective transition temperature [11, 12]. The elasticity of the crosslinks formed by physical interactions or chemical bonds strongly affects the behaviour of shape-memory polymers, being the main driving force for shape recovery.



Figure 1. The chemical structures of the polyurethanes synthesized with (a) polyol CO1, (b) polyol CO2 and (c) polyol CO3, leading to different soft segments (SSs). In all cases 1,6-hexamethylene diisocyanate (HDI)–1,3-propanediol (PD) was used as the hard segment (HS).

Therefore, the shape-memory effects are largely dependent on the microphase separation of the segments or blocks, which in turn is determined by molecular characteristics such as the molecular weight and composition of the two segments [13]. Furthermore, the transition temperature must be matched to the intended application, so that programming and release can be performed at a convenient temperature. Taking these aspects into account, polyurethanes have emerged as ideal candidates for use in shape-memory applications, due to their easily tunable mechanical properties and transition temperature by manipulating their composition [14–16].

Despite increasing efforts to explore polymers from renewable resources [17–20], in particular also polyurethanes [21-24], examples of shape-memory polymers based on renewable monomers are still rare. Thus, we study here a new family of thermally activated shape-memory polymers based on segmented thermoplastic polyurethanes (STPUs), synthesized with different hard segment contents and also polyols with different molecular weights. The use of components derived from renewable resources for the synthesis makes these polyurethanes interesting from the viewpoint of environmental impact. The temporary shape was fixed by the soft phase melting point (T_{mSS}) , which acts as the switching segment. Above this temperature, the soft segment chains can change their conformation, and polyurethane can undergo large deformation. In contrast, below T_{mSS} , the soft segment chains crystallize and prevent spontaneous recovery of the permanent shape, which is defined by the hard segment crystallites. Therefore, the crystallinities of both the soft and the hard phases, and consequently the phase separation, are important factors for the thermally activated shape-memory properties. Thus, the thermal and shape-memory properties were studied by differential scanning calorimetry, dynamic mechanical analysis and thermo-mechanical cycles.

2. Experimental details

2.1. Materials

Highly crystalline castor-oil-derived polyols with similar chemical structures but different molecular weights were used as soft segments (SSs) for bio-based segmented thermoplastic polyurethane (STPU) synthesis. These polyurethanes have already been used and characterized in a previous study [25]. where it was observed that the polyol crystallinity increased with increasing polyol molecular weight. Figure 1 presents the chemical structures of the synthesized polyurethanes prepared with three different castor-oil-derived polyols, named as CO1, CO2 and CO3. CO1 ($T_{\rm g} = -60 \,^{\circ}\text{C}$, $T_{\rm m} = 59 \,^{\circ}\text{C}$ and $\Delta H_{\rm m} =$ 103.0 J g⁻¹) consists of sebacic acid copolymerized with 2,2-dimethylpropane-1,3-diol and is the one with the lowest molecular weight, $M_n = 1320 \text{ g mol}^{-1}$ (figure 1(a)). CO2 $(T_{\rm g} = -54 \,^{\circ}{\rm C}, T_{\rm m} = 67 \,^{\circ}{\rm C} \text{ and } \Delta H_{\rm m} = 138.3 \,\,{\rm J g^{-1}}) \text{ and CO3}$ $(T_{\rm g} = -52 \,^{\circ}{\rm C}, T_{\rm m} = 70 \,^{\circ}{\rm C}$ and $\Delta H_{\rm m} = 142.0 \,^{\circ}{\rm J} \,^{\circ}{\rm g}^{-1}$) have the same general chemical structure (sebacic acid copolymerized with 1,4-butanediol) but higher molecular weights (CO2 $M_{\rm n} = 1900 \text{ g mol}^{-1}$ and CO3 $M_{\rm n} = 3500 \text{ g mol}^{-1}$) (figures 1(b) and (c)), polyol CO3 being the one with the highest molecular weight, which translates into higher $T_{\rm m}$ and $\Delta H_{\rm m}$ values. The hydroxyl content of the polyols was determined using a standard procedure (ASTM D 4274-05 test method A). Moreover, the quantity of carbon from renewable resources was determined by ASTM D 6855, giving values of around 70% for the three polyols. On the other hand, a corn-sugar-based chain extender, 1,3-propanediol (PD), and 1,6-hexamethylene diisocyanate (HDI) were used as the hard segment (HS) (figure 1). A polymer consisting of the hard segment only (HDI-PD) was also synthesized and characterized ($T_g = 53 \degree C$, $T_m = 164 \degree C$, $\Delta H_m = 114.0 \text{ J g}^{-1}$

Table 1. Designation, chemical composition, molar ratio of polyol, 1,6-hexamethylene diisocyanate (HDI) and 1,3-propanediol (PD), and hard segment (HS) content of the synthesized STPUs.

Polyurethane	Chemical composition	Molar ratio polyol:HDI:PD	HS content (wt%)
STPU CO1-17	CO1:HDI:1,3-PD	1:1.5:0.5	17
STPU CO1-25		1:2:1	25
STPU CO1-32		1:3:2	32
STPU CO1-39		1:4:3	39
STPU CO1-46		1:5:4	46
STPU CO2-17	CO2:HDI:1,3-PD	1:2:1	17
STPU CO2-25		1:3:2	25
STPU CO2-32		1:4:3	32
STPU CO2-39		1:5:4	39
STPU CO2-46		1:7:6	46
STPU CO3-17	CO3:HDI:1,3-PD	1:3:2	17
STPU CO3-25		1:5:4	25
STPU CO3-32		1:7:6	32
STPU CO3-39		1:9:8	39
STPU CO3-46		1:13:12	46
HDI-PD	HDI:1,3-PD	0:1:1	100

and $M_n = 52\,100 \text{ g mol}^{-1}$) in a previous study [25]. The polyols and PD were dried under vacuum at 80 °C for 12 h prior to synthesis to remove traces of moisture.

2.2. Synthesis of STPUs

STPUs with a high content of carbon from renewable resources were synthesized by a two-step bulk polymerization process. The prepolymer was prepared by reacting HDI with polyol for 5 h at 90 °C in a three-necked round bottom flask, with a dry nitrogen inlet, condenser and mechanical stirrer. The temperature was maintained using an oil bath. The 5 h reaction time for the first step was sufficient for complete conversion of OH groups, as determined by kinetic measurements [25]. Once the first step was completed, the chain extender was added in a stoichiometric ratio, mixing for 15 min with vigorous stirring. The resulting viscous liquid was quickly poured between two Teflon-coated metal plates and compression moulded at 50 bar and 100 °C for 10 h. The cooling procedure was kept uniform for all materials by controlling the air flow rate. Table 1 shows the composition and HS content of the synthesized polyurethanes.

2.3. Characterization techniques

Differential scanning calorimetry (DSC) experiments were performed on a Mettler Toledo 822^e instrument, equipped with a robotic arm and with an electric intracooler as refrigeration unit. During the first heating run, samples were heated from -60 to 220 °C at a scanning rate of 20 °C min⁻¹. Subsequently, a cooling and a second heating run were also performed, but as the data did not provide any extra information, they are not reported here. Taking into account the melting enthalpy values determined by DSC for the STPUs and the constituent phases, and based on equations (1) and (2), the relative crystallinities of the polyurethane soft (χ_{cSS}) and hard (χ_{cHS}) phases (relative crystallinities to the



Figure 2. Typical stress–strain–temperature diagram for an STPU with a thermally induced shape-memory effect, showing the different steps applied in the thermo-mechanical cycle: force ramp to achieve the desired strain at the programming temperature (1), cooling step (2), stress release (3) and, finally, temperature increase and recovery of the permanent shape (4). ε_m , ε_u and ε_f indicate the strain before releasing the stress, the fixed strain of the unloaded sample and stabilized at 15 °C and the final strain of the sample at 60 °C, respectively.

crystallinity of the neat phase alone) were measured for each of the polyurethanes synthesized [26]:

$$\chi_{\rm c} = \frac{100 \cdot \Delta H_{\rm e}}{\Delta H_{\rm t}} \tag{1}$$

$$\Delta H_{\rm t} = \frac{\Delta H_{\rm p} \cdot \omega}{100} \tag{2}$$

where ΔH_e is the experimental melting enthalpy value and ΔH_t is the theoretical value calculated by equation (2), where ΔH_p is the melting enthalpy value of the corresponding neat phase and ω is the weight fraction of that phase.

The dynamic mechanical analysis (DMA) and thermally activated shape-memory properties of the synthesized STPUs were measured in tensile mode on an Eplexor 100 N analyser from Gabo and a DMA Q-800 from TA Instruments, respectively, using in both cases a strain amplitude of 15 μ m. Samples were prepared by cutting strips (22.25 mm in length, 5 mm in width and 0.5 mm in thickness) from compression-moulded samples. For DMA, the temperature was varied from -100 to 175 °C at a heating rate of $2 \,^{\circ}$ C min⁻¹ and at a fixed frequency of 10 Hz. To establish the shape-memory properties, as described in figure 2, the following steps were taken. The sample was equilibrated at 60 °C and a force ramp of 0.1 N min⁻¹ was applied until a pre-determined strain of 50% (all the synthesized polyurethanes presented yield strain values well below 50%) was reached (step 1). Maintaining the stress applied, the sample was cooled to $15 \,^{\circ}$ C at a rate of $5 \,^{\circ}$ C min⁻¹ (step 2). The stress was subsequently released and the temperature was maintained at 15 °C for 5 min (step 3). Finally, the temperature was increased at a rate of $5 \,^{\circ}$ C min⁻¹ to $60 \,^{\circ}$ C (step 4) [5, 13]. Six cycles were applied to each sample. In all the applied thermo-mechanical cycles samples were deformed by 50%, regardless of their initial length. Strain fixity (R_f) and strain recovery (R_r) ratios were measured for the different cycles using the following equations [5, 10, 11]:

$$R_{\rm f}(N) = \frac{\varepsilon_{\rm u}(N)}{\varepsilon_{\rm m}(N)} \times 100 \tag{3}$$

$$R_{\rm r}(N) = \frac{\varepsilon_{\rm m}(N) - \varepsilon_{\rm f}(N)}{\varepsilon_{\rm m}(N) - \varepsilon_{\rm f}(N-1)} \times 100 \tag{4}$$

where $\varepsilon_{\rm m}$ is the strain before releasing the stress, $\varepsilon_{\rm u}$ is the fixed strain of the unloaded sample and stabilized at 15 °C, $\varepsilon_{\rm f}$ is the final strain of the sample at 60 °C, and *N* is the number of cycles.

3. Results and discussion

Castor-oil-derived polyols and corn-sugar-based chain extender were used as components from renewable resources for bio-based segmented thermoplastic polyurethane (STPU) synthesis. The synthesis was carried out in bulk without catalyst by a two-step polymerization process and samples were processed by compression-moulding. As explained in the introduction, the phase separation between the hard and soft segments has an important influence on the properties of segmented polyurethanes, and therefore study of the morphology and thermal transitions is essential to understand the behaviour observed for the synthesized STPUs in thermo-mechanical cycles.

Figure 3 presents the thermo-mechanical data for the STPUs synthesized with different hard segment (HS) contents and soft segment (SS) molecular weights, obtained by DSC and DMA.

The DSC measurements reveal two distinct endothermic transitions around 60 and 150 °C. The first one is associated with the melting of soft phase crystallites (T_{mSS}) ; as determined in a previous study [25], the glass transition temperature of the hard phase (T_{gHS}) is also around 60 °C and therefore the signals associated with the melting of the soft phase and the glass transition of the hard phase could be overlapping. However, the contribution of T_{gHS} to the DSC signal is much smaller than that of T_{mSS} and therefore does not influence the determination of the crystallinity in a significant manner. The endotherms observed around 150 °C can be assigned to the melting of hard phase crystallites $(T_{\rm mHS})$. In some cases, more than one peak could be observed in that region, related to different crystal structures, domain sizes or degrees of order and reorganization in the crystalline structure of the hard phase [27–29].

As detailed in the experimental section, the relative crystallinity values of the three polymer series based on CO1, CO2 or CO3 were determined taking into account the data obtained by DSC and applying equations (1) and (2). By this means, the effect of the SS chemical structure and molecular weight, as well as the HS content, on the relative crystallinity values was studied. As can be seen from the data in figure 4(a), the relative crystallinity of the soft phase decreased with increasing HS content, due to the formation of



Figure 3. DSC (top) and DMA (bottom) curves obtained for thermal characterization of (a) the STPU CO1 series, (b) the STPU CO2 series and (c) the STPU CO3 series.

a higher fraction of ordered hard domains, which restricts soft segment mobility and therefore lowers the crystallinity of the soft phase [25, 30]. Moreover, the least pronounced decrease was observed for the polyurethanes based on the highest molecular weight polyol (the STPU CO3 series), giving crystallinity values ranging from 62% for STPU CO3-17 (17 wt% HS content) to 53% for STPU CO3-46 (46 wt% HS content), owing to the larger degree of phase separation and the higher molecular weight of polyol CO3; in this series, crystalline ordered soft domains were formed even with high HS contents [31]. By contrast, polyurethanes based on polyol CO1 exhibit the lowest crystallinity values for



Figure 4. Relative crystallinity of (a) the soft phase and (b) the hard phase of the STPU series as function of hard segment content.

the soft phase, 45% for STPU CO1-17 and 25% for STPU CO1-46, due to the lower molecular weight and therefore lower crystallinity of polyol CO1. The STPU CO2 series exhibit relative crystallinity values between the ones given by the STPU CO1 and STPU CO3 series, ranging from 48% for STPU CO2-17 to 34% for STPU CO2-46.

The crystallinity of the hard phase increased significantly with increasing HS content and also SS molecular weight, as can be seen from the data presented in figure 4(b). The increase of the HS content implies a higher molar amount of chain extender, and therefore longer HS units, thus easing microphase separation and formation of ordered hard domains [32, 33]. As polyurethanes based on the longest polyol (CO3) feature the highest molar amount of chain extender, more ordered hard domains are more likely to be formed, and therefore higher crystallinity values result for the STPU CO3 series, ranging from 43% for STPU CO3-17 to 88% for STPU CO3-46. The STPU CO1 and STPU CO2 series exhibit lower hard phase crystallinity values, ranging from 13% for STPU CO1-17 to 77% for STPU CO1-46 and from 26% for STPU CO2-17 to 84% for STPU CO2-46.

Figure 3 shows also the storage moduli (E') and tan δ values of STPUs with different HS contents and SS molecular

A Saralegi et al

Table 2. Storage modulus (E') values for the three STPU series at different temperatures: below the soft phase glass transition temperature (at -75 °C), before the soft phase melting temperature (at 45 °C) and after the soft phase melting temperature (at 75 °C).

Polyurethane	<i>E</i> ′ (MPa) at -75 °C	<i>E</i> ′ (MPa) at 45 °C	<i>E</i> ′ (MPa) at 75 °C
STPU CO1-17	2000	50	15
STPU CO1-32	2155	90	60
STPU CO1-46	2270	115	75
STPU CO2-17	2080	175	40
STPU CO2-32	2185	135	70
STPU CO2-46	2410	215	165
STPU CO3-17	2280	240	30
STPU CO3-32	2375	235	85
STPU CO3-46	2800	385	105

weights, and table 2 summarizes the E' values below T_{gSS} (at $-75 \,^{\circ}$ C), before T_{mSS} (at $45 \,^{\circ}$ C) and after T_{mSS} (at $75 \,^{\circ}$ C). Below the T_g of the soft phase, which appeared around $-25 \,^{\circ}$ C, all materials display E' values of 2000–2800 MPa. E' values increased with HS content in all the series, which is associated with the formation of ordered hard domains and, therefore, increase in crystallinity [34].

The highest E' values were observed for the STPU CO3 series (2280–2800 MPa). This series exhibits the highest crystallinity values for both the soft and the hard phases (figure 4) and the materials are thus the stiffest [25]. Around the T_g of the soft phase (around -25 °C), a decrease in E' and a maximum in tan δ could be observed (figure 3). While the position of the tan δ peak remained nearly constant with increasing HS content and SS molecular weight, its intensity decreased considerably, and a broadening of the peak was observed. This is consistent with the formation of more ordered soft and hard domains, as HS content and SS molecular weight increase, which restricts amorphous SS molecular mobility and flexibility [30].

Above T_{gSS} , the storage modulus decreased slightly with temperature, and dropped markedly around 50 °C, i.e., at the soft phase melting temperature, in the case of compositions with low HS content. Due to the higher crystallinity of polyols CO2 and CO3 compared with polyol CO1, the E'values before the sharp decrease of STPU CO2-17 and STPU CO3-17 are slightly higher than the ones observed for STPU CO2-32 and STPU CO3-32. In the case of the STPU CO3 series, all samples present a sharp decrease in E', and the transition is also clearly observable by DSC. This indicates that the polyurethanes based on polyol CO3 feature well ordered soft domains even at high HS contents, due to the highly crystalline nature of CO3. As can be observed from the values presented in table 2, the E' value of STPU CO3-46 dropped from 385 MPa (at 45°C) to 105 MPa (at 75 °C) upon melting of the soft phase. By contrast, the E' values of STPU CO1-46 and STPU CO2-46 did not exhibit such a huge drop (from 115 to 75 MPa for STPU CO1-46 and from 215 to 165 MPa for STPU CO2-46), because in these cases the soft phases exhibit lower crystallinity values (figure 4(a)). Furthermore, as was observed in the literature [34, 35], with increasing HS content, hard ordered domains change from an isolated state to an interconnected state, owing to higher urethane content, which leads to higher hydrogen bonding between urethane groups, contributing to the formation of interconnected hard domains. The interconnected hard domains form a rigid framework which prevents the polymer from softening when the soft segment phase melts, which explains why the decrease in storage modulus is less pronounced with increasing HS content. At temperatures higher than T_{mSS} , a rubbery plateau in the storage modulus was observed, with higher E' values for polyurethanes with high HS content (table 2), due to the more ordered hard domains formed by longer HS units. Finally, at high temperatures, a dramatic decrease of storage modulus was observed, associated with the melting temperature of the hard phase. The increase in HS content leads to higher thermo-mechanical stability, due to the formation of more ordered domains formed by the longer HS units, as also observed by DSC.

The two characteristic values that summarize the performance of shape-memory polymers are the shape fixity (R_f) and shape recovery (R_r), as well as the temperature regimes in which the material can be used and programmed/released, which in our case are dictated by T_{mSS} and T_{mHS} . Therefore, the plateau regions between the former and latter transitions are very important in terms of shape-memory properties. As can be observed from figure 3, all the synthesized polyurethanes exhibit an extended rubbery plateau between T_{mSS} and T_{mHS} , and should therefore lend themselves to easy programming of a temporary shape [36].

Regarding the thermally activated shape-memory properties, the shape fixity and shape recovery values were established by DMA, applying thermo-mechanical cycles as illustrated in figure 2, and taking into account equations (3) and (4), as detailed in the experimental section. The programming/release temperature selected for these experiments was 60 °C, as the soft phase crystallites melt above this temperature. Figure 5 shows the data obtained for the first thermo-mechanical cycle applied to each sample as a function of composition, while figure 6 shows a schematic representation of the stipulated molecular mechanism of thermally activated shape-memory effect for low, medium and high HS content polyurethanes.

Figure 5(a) shows that R_f decreases with increasing HS content. This is consistent with the DSC and DMA data discussed above, which have shown that the soft phase crystallinity decreases with increasing HS content; consequently, the capacity to fix the temporary shape decreases, because the shape fixity is intimately related to the strain-induced crystallization of the soft phase [14, 34, 37]. Accordingly, the highest values for R_f were obtained for polyurethanes based on polyol CO3 (97–98%), due to the high crystallinity of that polyol. However, all polyurethanes exhibit very high shape fixity values between 90 and 98%, which compare favourably with literature values [38, 39].

Figure 5(b) presents the R_r values for the first thermomechanical cycles. Since the hard domains form physical crosslinks that are responsible for permanent shape or shape recovery, one would initially expect that with increasing



Figure 5. (a) Shape fixity and (b) shape recovery values for the three STPU series as a function of hard segment content, measured in the first shape-memory cycle.

HS content, R_r would also increase. However, as can be observed in figure 5(b), the R_r values of all the series exhibit a maximum when the HS content is 25 wt%. Polyurethanes with 17 wt% of HS content exhibit lower R_r values, since they do not contain a sufficiently large number of physical crosslinks formed by the hard segments, so that the driving force for shape recovery is low (figure 6(a)). At HS contents of more than 25 wt%, the number of urethane groups increases, and consequently the number of hydrogen bonds increases, presenting more interactions among hard segments. During the stretching process of the thermo-mechanical tests, as samples are stretched over the yield point, plastic and non-reversible deformation occurs, and therefore those interactions among hard segments decrease (figure 6(c)) [15, 34]. Furthermore, an increasing SS molecular weight leads to polyurethane formulations with higher chain extender amounts, increasing the amount of urethane groups and also the hydrogen bonds between urethane groups. This explains why the STPU CO3 series exhibits the lowest R_r values, as the increase of interactions among hard segments leads to lower yield strain values, resulting in higher plastic and non-reversible deformation.



Figure 6. Schematic representation of the molecular mechanism of the thermally activated shape-memory effect for (a) low HS content STPU, (b) medium HS content STPU and (c) high HS content STPU.

Figure 7 summarizes the data obtained for the second shape-memory cycles, resulting in quite similar values for the shape fixity as the first cycles (figure 5(a)). This result is in accordance with similar results observed in the literature, as the soft segment capacity to act as a switching segment in several cycles is not impacted as long as its ability to form comparable crystalline domains is not impacted [38–40]. The highly crystalline nature of the castor-oil-derived polyols used in this study as SSs leads to microphase separated polyurethanes, where the soft segments crystallize easily during the thermo-mechanical tests, even for the polyurethanes based on the less crystalline polyol (the STPU CO1 series). However, the R_r values were considerably improved for the second cycles (figure 7(b)), and all investigated polyurethanes exhibited values in the range of 80-100%. As was explained before, samples were deformed well above their yield point in the first thermo-mechanical cycle, resulting in high plastic and non-reversible deformation values. Nevertheless, for the second thermo-mechanical cycle, due to the pre-orientation of the polyurethane chains that occurred in the first thermo-mechanical cycle, the yield point experiments an improvement (higher yield strain values), and therefore less plastic and non-reversible deformation occurs, a phenomenon known as hysteresis, thus improving shape recovery values. Polyurethanes with 17 wt% of HS content are the exception, as they present similar R_r values for the first and second cycles, owing to the low HS content and lack of physical crosslinks. Taking into account the $R_{\rm f}$ and $R_{\rm r}$ values obtained for the first two thermo-mechanical cycles, polyurethanes with 25 wt% of HS content present the best shape-memory properties, as the amount of HS content is enough to form physical crosslinks for shape recovery and, also, the SS acts as a switching segment giving high $R_{\rm f}$ values. At lower HS contents, the materials present higher $R_{\rm f}$ values, but the R_r values are quite low. On the other hand, at higher HS contents, the increase of interactions among hard segments leads to lower yield strain values, resulting in lower R_r values. Therefore, as STPU CO2-25 and STPU CO3-25 present



Figure 7. (a) Shape fixity and (b) shape recovery values for the three STPU series as a function of hard segment content, measured in the second shape-memory cycle.

longer hard segments and consequently more interactions among hard segments, STPU CO1-25 presents the best shape-memory properties among polyurethanes synthesized in this study.



Figure 8. Stress–strain–temperature diagram for several consecutive shape-memory cycles, starting with the third cycle, for STPU CO2-46.

Finally, after the second cycles of stretching and recovery, all samples gave R_r values close to 100% (except polyurethanes with 17 wt% of HS content) and similar shape fixity values to the ones obtained in the first and second thermo-mechanical cycles. Figure 8 presents the curves obtained after the first two thermo-mechanical cycles for STPU CO2-46, corroborating cyclic shape-memory properties, as values close to 100% were obtained for R_f and R_r even for the sixth cycle (blue line in figure 8).

4. Conclusions

Segmented thermoplastic polyurethanes showing a thermally activated shape-memory effect were synthesized with HS contents varying from 17 to 46 wt%. Polyols from castor oil and corn-sugar-based chain extender were used as renewable resources, in order to minimize the content of starting materials derived from petrochemical raw materials. Thereby, STPUs with shape-memory properties and high contents of carbon from renewable resources were synthesized.

The thermal properties of the STPUs were characterized by DSC, which revealed that the soft phase crystallinity decreased with increasing HS content, while the hard phase crystallinity increased. DMA measurements corroborated the results obtained by DSC, and also revealed a plateau in storage modulus between the two main transitions (T_{mSS} and T_{mHS}), which is characteristic of shape-memory polymers. High HS contents led to low yield strain values, resulting in high plastic and non-reversible deformation values during the first thermo-mechanical cycles, and, therefore, low shape recovery values. However, after the first cycles, all the polyurethanes presented $R_{\rm f}$ values close to 100% and $R_{\rm r}$ values in the range of 80-100%. The materials synthesized in this work are presented as candidates to be used as smart materials in applications where a thermally activated shape-memory effect is required.

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