By using small-angle X-ray, this study aims to identify the role of the morphological structures of linear segmented thermoplastic polyurethane during shape memory cycle. A deformed specimen was placed on a heating stage mounted at the beamline; the shape recovery was measured during 20min. Furthermore, to study the influence of the temperature during recover, the specimens were subjected to different thermo-cycle. In each condition, the phase morphology and composition were investigated. Recovery process was separated into three stages. Bulk incompatibility and entropic recovery were the two controlling features for determining the final polyurethane morphology.

Keywords: Segmented polyurethanes, SAXS, microphase separation, and nano-morphology

Introduction

Linear segmented thermoplastic polyurethane (PU) elastomers are multiblock copolymers which consist of the so-called hard and soft segments which can microphase separate to form hard and soft domains. The properties of these materials are dependent of phase morphology and phase separation of these domains\(^[1, 2, 3]\). Recent approaches have tailored PUs properties to yield thermo-responsive materials that can be used to create smart devices with the ability to memorize a permanent shape that can substantially differ from their initial temporary shape\(^[4]\). Described as shape memory polymers (SMP), they have many advantages over shape memory metal alloys. (i) low density (1.0–1.3 g/cm\(^3\)), (ii) wide range of actuation temperature, (iii) high shape recovery (maximum shape recovery ratio larger than 400%), (iv) low manufacturing cost, and (v) easy processing\(^[5]\).

Generally, a SMP can be thought of as a material with morphology consisting of two phases: a shape fixing matrix phase and a shape memorizing dispersed phase. Above the actuation transition of the shape fixing phase, the polymer can be deformed from its primary shape to a secondary shape by the application of stress, and then locked into the secondary shape by cooling to below the actuation transition\(^[6]\). Although some research have been done in the past, the details of the morphological changes during shape memory cycle are still poor understood, mainly because segmented PUs exhibit a complex phase structure depending on the type and size of segments used
as well as on the processing conditions. By using small-angle X-ray, this study aims to identify the role of the morphological structures of PU’s during shape memory cycle.

**Materials and Methods**

**Prepolymer synthesis**

Poly(caprolactone diol) (PCL – Mn = 2000 g mol\(^{-1}\)), isophorone diisocyanate (IPDI), 2,2-bis(hydroxymethyl), propionic acid (DMPA) and dibutyl tin dilaurate (DBDLT) were obtained from Aldrich (St. Louis, MO). Triethylamine (TEA, 98%) and hydrazine (HZ, 25%) were purchased from Vetec (RJ, Brazil). All these chemicals were employed throughout this work without any previous treatment.

PU was synthesized by the conventional prepolymer method, using a 250mL three neck glass flask equipped with a heating mantel, a mechanical stirrer, a thermometer under nitrogen atmosphere. In the first step, prepolymer was obtained by reacting PCL (23.9 wt%), DMPA (1.2 wt%) and IPDI (9.3 wt%) at 2 NCO/OH ratio for about 3.5h. During this time, DBDLT was added twice. The reaction was carried out at 70–75°C. After cooling down to 40°C, the carboxylic acid groups were neutralized by the addition of TEA (0.9 wt%). The mixture was then gentle stirred for 40min. The dispersion in water and PU chain extension were achieved by adding HZ (0.7 wt%) and deionized water (64 wt%) to the neutralized prepolymer under high-speed stirring. To ensure that the reaction was completed, the mixture was stirred for 60min. This chemical procedure was successful in producing PUs water dispersions with solid content about 35%. The weight fraction (%) of hard segment, \(W(HS)\), is 38% (IPDI + HZ). PU synthesis procedure is detailed described in a previous work\(^{[7]}\).

**Infrared spectroscopy**

Infrared spectra were collected in a Fourier transform infrared spectrophotometer (FTIR; Perkin–Elmer, model Spectrum 1000). Measurements were carried out using the attenuated total reflectance (ATR) technique. Each spectrum was a result of 64 scans with a resolution of 4 cm\(^{-1}\).

**Synchrotron small angle X-ray scattering (SAXS)**

SAXS measurements of synchrotron small angle X-ray scattering were performed using the beam line of the National Synchrotron Light Laboratory (LNLS, Campinas, Brazil). After passing through a thin beryllium window, the beam is monochromatized (\(\lambda = 1.488\text{Å}\)) and horizontally focused by a
cylindrically bent and asymmetrically cut silicon single crystal. The X-ray scattering intensity, \( I(q) \), was experimentally determined as a function of the scattering vector, \( q \), whose modulus is given by Eq. 1:

\[
q = \frac{4\pi}{\lambda} \sin \theta
\]  

(1)

where \( \lambda \) is the X-ray wavelength and \( \theta \) being half the scattering angle.

Each SAXS pattern corresponds to a data collection time of 900 s. From the experimental scattering intensity produced by all the studied samples, the parasitic scattering intensity produced by the collimating slits was subtracted. All SAXS patterns were corrected for the non-constant sensitivity of the PSD, for the time varying intensity of the direct synchrotron beam and for differences in sample thickness. Because of the normalization procedure, the SAXS intensity was determined for all samples in the same arbitrary units so that they can be directly compared. The sample-detector distance of 551.6 mm was used during the measurements.

**Mechanical Properties and Shape memory properties (SM)**

Shape memory experiments were done at room temperature using a universal testing machine (DL3000, EMIC). The sample length between the clamps was 20mm. A shape recovery cycle consisted of the following steps: (1) Samples DIN60 were deformed to a defined strain, \( L_m = 120 \) mm, at 10 mm/min crosshead speed. (2) While maintaining the strain at \( L_m \), samples were cooled with liquid N\(_2\). (3) Mechanical constraints on the polymers were removed. (4) The samples were subsequently submitted to a thermo-cycle to recover its original shape. Figure 1 illustrates a shape-memory thermomechanical cycle test.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Temperature</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle-A</td>
<td>37°C</td>
<td>17hs</td>
</tr>
<tr>
<td>Cycle-B</td>
<td>37°C, 50°C</td>
<td>17hs, 10min</td>
</tr>
<tr>
<td>Cycle-C</td>
<td>50°C</td>
<td>30min</td>
</tr>
<tr>
<td>Cycle-E</td>
<td>80°C</td>
<td>20min</td>
</tr>
</tbody>
</table>

Figure 1 – Shape memory cycle

Table 1 – Thermo-cycle
During Cycle-A, the deformed sample was heated to 37°C in an oven, and stayed at this temperature for 17hs. The recovery during thermo-cycle “B” was carried out within two heating stages. First, the specimen was heated to 37°C for 17hs then heated for 10 min at 50°C. During thermo-cycle “C”, the sample was heated to 50°C for 30min. Finally, in Cycle-E the sample stayed at 80°C for 20min. The thermo-cycle parameters are described in Table 1.

The SM properties of the materials were described by the strain recovery ratio, $R_R$, and the strain fixity ratio, $R_f$. Both can be determined according to Eq. 2 and Eq. 3: The mechanical properties were described by the yield strength ($\sigma_y$), and the initial modulus ($E$).

$$R_R(\%) = \frac{L_m - L_{res}}{L_m - L_o} \times 100$$  \hspace{1cm} (2)

$$R_f(\%) = \frac{L_{ret} - L_o}{L_m - L_o} \times 100$$  \hspace{1cm} (3)

where: $L_o$ is the original length, $L_m$ is the deformed length, $L_{ret}$ is retained length and $L_{res}$ is the length after the recover.

**In situ recovery**

One deformed specimen was placed on a heating stage mounted at the beamline. The specimen was heated to 50°C–60°C and the shape recovery was measured during 20min. The SAXS patterns were recorded at 7.2min, 8.3min, 9.3min, 11.0min, 12.1min, 13.1min, 14.2min, 15.2min, 16.3min, 17.3min, 18.4min and 19.4min.

**Results and discussion**

A typical infrared spectrum of obtained PU is shown in Figure 2(a). The characteristic bands of poly(ester-urethane) are marked in the figure. The primary amine stretching modes appear at 3600–3150cm$^{-1}$. The carbonyl group stretching vibrations, C=O, appear at 1760–1600cm$^{-1}$. The secondary amide absorption, >N–H, appears at 1640–1540cm$^{-1}$. The band at 1150cm$^{-1}$ is assigned to the stretching of the –C–O–C– group.$^{[7]}$ Figure 2(b) shows typical stress–strain curves of shape memory specimens.
PU’s are characterized by good mechanical properties: $\sigma_e = 8.2 \pm 0.5$ MPa and $E = 2.2 \pm 0.5$ MPa. $R_R$ of Cycle-A, Cycle-B, Cycle-C and Cycle-E are, respectively, 71%, 82%, 88% and 98%. Low values of strain fixity ratio were observed, $R_f = 31 \pm 2.2\%$. Upon removing the strains at Step3 a significant recover of strain occurs and thus low values of $R_f$ were observed. Different factors, derived from the SM cycle configuration, may have contributed to the present results. To maintain a deformed shape in a stable manner, new chain positions must be fixed by new bonds. The development of the new physical entanglements (temporary bonds) between the polymeric chains is a result of a temperature decrease and/or forced chain alignment\cite{8}. In the present work, after Step1, samples were gripped to an apparatus, removed from the testing machine and immersed in liquid nitrogen. In consequence, the metastable structure, developed during the strain, were partially released, contributing to low values of $R_f$. A second factor, temperature, may also contribute to low values of $R_f$. According to Ping et al\cite{9}, when the $T_d$ is too low ($30^\circ$C below the melting temperature of the soft segment), the shape recovery starts at a lower temperature and takes place over a wide temperature range. As room temperature is superior to $25^\circ$C, the lowest recovery temperature of obtained PUs might be lower than the room temperature and shape recovery may start after Step3.

Figure 3 illustrates SAXS patterns of the obtained PU during different stages of shape-memory thermomechanical cycle and during in situ recovery. SAXS measures the scattering intensity as a function of the incident X-ray beam. The technique is informative for fine morphologies at the nanometer level because it is sensitive to the differences in electron density within a material. The patterns and intensity distribution of SAXS are dependent on the shape, the size and size distribution of scattering objects\cite{10}. In Figure 3(b), it is observed two maxima occurring along the
stretching direction on both sides of the beam. The maxima are due to the scattering from the oriented structure formed during deformation process. The patterns indicate a high degree of orientation obtained from deformation process[11]. When the deformation is applied to the specimen polymer chains will align to the extension direction and promote crystallization. During in situ recovery tests, the anisotropic orientation of the lamellae in the samples disappears. The different thermo-cycle promotes unlike reorientation of the deformed structure. The new patterns are function of the energy injected in the system. Higher temperature treatment brought more energy to the system which returned do the original configuration. However, as observed, the initial high scattering intensity phase was restored.

Figure 3 – SAXS pattern of: (a) undeformed specimen, (b) deformed specimen, in situ recovery, (c) Cycle-A, (d) Cycle-B, (e) Cycle-C, (f) Cycle-E.

Figure 4(a) illustrates SAXS data of the obtained PU during different stages of shape-memory thermomechanical cycle. The scattering peak observed arises due to local heterogeneities in the electron density of the materials and it is usually interpreted as a consequence of the presence of distinct microphases with different electronic densities. However, to discuss the phase separation, it
is convenient to employ the Lorentz correction, \( Q_{\text{inv}} \), which describes the electron density fluctuation of polymer and is a good approximation to estimate the overall degree of phase separation in segmented polymers, Figure 4(b)\(^ {10, 12, 13} \). The Lorentz correction, the invariant quantity, \( Q_{\text{inv}} \), can be obtained by integrating \( I_{(q)}q^2 \) over the range of scattering angles, Eq. 4\(^ {10, 12, 13} \).

\[
Q_{\text{inv}} = \int_0^\infty I_{(q)}q^2 dq
\]

where \( I_{(q)} \) is X-ray scattering intensity and \( q \) the scattering vector.

Figure 4 – (a) SAXS curves of obtained and (b) Deconvoluted Lorentz SAXS pattern

The contribution of each phase to the Lorentz corrected SAXS patterns was separated by a deconvolution procedure. Figure 5 illustrated the obtained deconvoluted curves.

Figure 5 – Deconvoluted Lorentz SAXS pattern: (a) deformed specimen, (b) in situ recovery, (c) Cycle-A, (d) Cycle-B, (e) Cycle-C, (f) Cycle-E.
$Q_{inv}$ of each phase was obtained as fraction of the total area. As observed in Figure 6(a), shape recovery during SAXS experiment occurred within three stages. The stages are distinguished at the hard domain curve. During the first seven minutes of recovery, the hard domain content decrease (first phase) followed by a fast increase in the hard segment fraction (second phase) and, finally, the hard domain fraction become stable (third phase). During the *in situ* tests, the crystalline fraction decreases because the soft segment crystals melt, enriching the matrix phase with soft segments. As consequence, in the matrix, the repulsive interaction between the dissimilar hard and soft segments increases, increasing their immiscibility and leading to hard domain formation. However, the hard domain segregation is limited by the hard segment nature. The hard segment low mobility stops the segregation process and the hard domain formation stabilizes$^{[13]}$. Figure 6(b) illustrates PU morphology after the different thermo-cycles. *In situ* results may be extrapolated to the results observed after the thermo-cycle. According to SM tests, the thermo-cycle “A” promotes shape recovery, however, the energy injected in the system is enough to ensure only the first stage of shape recovery. As observed at Figure 6(b), during Cycle-A the hard domain fraction decrease, but the temperature treatment is not enough to melt the crystals, change the matrix composition increasing the incompatibility and promoting domain formation. Cycle-B ensures the three stages of shape recovery. However, higher values of $R_R$ were not achieved due to the first step of the thermo-cycle. The cycle-B first step acts as stress release treatment, decreasing the energy stored during deformation. Therefore, the polymeric chains are not able to recover their strongly coiled conformation consequently lower values of $R_R$ are obtained. Thermo-cycle “C” and “E” complete the 3 stages of shape recovery. Thermo-cycle “E” ensures higher $R_R$ values mainly because the higher temperature treatment guarantees melting of larger crystals fraction.

![Figure 6](image)

**Figure 6** – (a) PU multi-phase evolution during *in situ* tests; (b) PU multi-phase during SM cycle.
Conclusions
The evolution of the phases during shape memory cycles applied to polyurethanes was successfully monitored by using in situ SAXS experiments. It was shown that during the recovery stage of the PU shape, soft segment crystallites are progressively melted while phase separation becomes increasingly important until a new thermodynamic equilibrium point is reached that defines the final PU nanostructure.

Acknowledgments
The authors acknowledge the financial support from the following institutions: National Council for Scientific and Technological Development (CNPq), a foundation linked to the Ministry of Science and Technology (MCT) of the Brazilian Government; the State of Minas Gerais Research Foundation (FAPEMIG); and the National Synchrotron Light Laboratory (LNLS-Brazil) for the use of the SAXS beamline facilities.

References