EXPERIMENTAL INVESTIGATION ON THERMOPLASTIC POLYURETHANE HAVING PARTIAL SHAPE MEMORY EFFECT

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Summary: In the present work, a multi-cycles shape memory tests are performed on thermoplastic polyurethane (TPU) at 70°C which can regain only 67% of its initial shape. This partial shape memory effect (SME) has been improved by successive cycles of shape memory tests. After fourth cycles the polymer is able to regain 100% of its shape. The results of fifth and sixth cycles confirm this modification. These original results indicate that a polymer with partial shape memory effect may be transformed into a shape memory polymer without any chemical modification. This increase of shape memory effect could be related to the creation of residual stresses during the tensile tests. The residual stresses are the origin of the driving force responsible for shape memory effect.

1 INTRODUCTION

Shape memory polymers (SMPs) are polymeric smart materials that have the ability to return from a deformed state to their original shape when an external stimulus is applied. The behavior, known as the shape memory effect (SME), is normally looked at on a macroscopic scale, i.e. visual shape changes. In the case of heating stimuli, the process can be summarized in successive steps: heating, deformation, relaxation, fixation and recovery [1, 2].

It is generally accepted that shape memory effect (SME) is related to the presence of two different (hard and soft) segments in the structure of polymers [3-6]. The hard segment morphology stabilizes the permanent shape of the structure while the soft segment morphology allows the passage from permanent to temporary state or vice versa. Even though this explanation is correct, it cannot be the answer to all of the questions related to the SME mechanism; it cannot illustrate the chemical and physical origin of SME. So our objective is to explain the mechanism of SME and to show the role of driving force during recovery.
One of the questions is related to the relationship between shape memory effect (SME) and properties memory effect (PME). In our previous work [7], we have shown that after recovery a SMP does not necessarily exhibits the same properties; that means even after regaining 100% of initial shape, the polymer may not always show the same properties.

It is worth mentioning that between the SMP and those without SME, there are polymers which have an intermediate behavior. Partial shape memory effect is the properties of the polymers that can recover only a part of deformation imposed on them during mechanical loading [8]. This property is found practically in all the polymers. In fact the polymers may be divided in two categories: shape memory polymers and partial shape memory polymers (PSMP).

In the present study we have used thermoplastic polyurethane (TPU) having partial shape memory effect. We will demonstrate how the shape memory capacity of this polymer will be increased by multi-cycle tests.

The polyurethanes are well known to have different interesting properties, besides shape memory effect [9-12] such as high resistance to organic solvent, stability against sunlight and oxidation, high elastic property, and possible biocompatibility. The preparation of these polymers is not very difficult [13].

2 MATERIALS AND METHODS

The polymer used in this study is a TPU (thermoplastic polyurethane). The formulations of this polymer are based on 1,6-hexamethylene diisocyanate (Sigma Aldrich, France), polyethylene glycol (PEG 1000; VWR International, France) as macrodiol, and 1,3-propanediol (PDO; Sigma Aldrich) as petrochemical CE or Susterra® 1,3-propanediol (bio-PDO™; DuPont Tate & Lyle Bio Products, USA) as bio-based CE, which is a 100% renewably sourced material derived from corn sugar, in the presence of dibutyl tin dilaurate (Fluka, France) as catalyst. Recently, this polymer has been developed as a new polymer for reactive rotational molding [14].

Segmented TPUs generally display several thermal transitions, corresponding to the soft and hard segments. Thus, the soft segment could present a (low) glass transition temperature, and, if semicrystalline, a melting transition, whereas the hard segment may display a glass transition and/or multiple melting transitions. In the current study, the glass transitions ($T_g$) and melting peaks ($T_m$) of SS and HS were determined using differential scanning calorimetry (DSC). The result shows two distinct $T_g$ (-54°C and 89°C) and two distinct $T_m$ (16°C and 128°C) corresponding to soft and hard segment respectively.

A shape memory cycle test consists of the following successive steps: tensile test, stress-relaxation test, fixing and recovery test. For reproducibility of the results, the shape memory tests have been carried out on at least three samples, each time. In multi-cycle experiments successive shape memory tests on the same sample was conducted. After the first cycle (at the end of the recovery test) the sample has been used for a second cycle in order to do the same tests successively; that means tensile, fixing (without relaxation test) and recovery test. The cycle has been repeated several times.

3 RESULTS AND DISCUSSION

Tensile tests have been carried out with the Instron 5881, loading cell of 1 kN. This machine is equipped with a temperature-controlled thermochamber for heating the samples and performing the tests at different temperatures. The dimensions of the samples are as follows: length 75 mm, length of rectangular part 25 mm, width 4 mm, and thickness 1 mm.
The strain rate is 5 mm/min.

The results of the tensile tests at 23 and 70°C are presented in figure 1. Unfortunately, the test at 70°C has been stopped before rupture of sample because of the limit of the height of the thermochamber. However, the result shows that the strain at break (at 70°C) is higher than 550%.

![Figure 1: Tensile tests of TPU at 23 and 70°C.](image1)

The stress relaxation isothermal test (at 70°C) has been performed at the end of the tensile after 100% of deformation. The strain has been taken constantly, and the decrease of stress has been measured versus time up to 300min (Figure 2). This test has been performed to eliminate the residual stress induced during the tensile test in the samples.

![Figure 2: Stress relaxation tests of TPU at 70°C.](image2)
All stress relaxation curves show two different regimes. At the beginning, the decrease of stress is relatively fast and then it becomes slow. For example, at 70°C, the value of stress has been decreased from 2.9 to 2.1 MPa after 15 min. Then, it decreased to 1.8 MPa after 300 min before reaching to a relatively stable level. It can be seen that the relaxation does not lead the sample to zero stress.

Fixing can be performed after tensile tests or after stress relaxation tests. During this step, the sample obtains a temporary shape. By cooling the sample with ventilator to room temperature, the maximum deformation (100% and/or 150%) obtained at the end of tensile tests has been conserved in the sample.

The recovery tests are carried out in a thermal chamber at 90°C after fixing at 100% (or 150%) of deformation. The percentage of recovery has been determined using the following equation:

\[
R(\%) = \frac{L_n - L_{fn}}{L_n - L_{0n}} \times 100
\]  

Where:
- \(L_{0n}\) is the initial length at the begining of cycle number n (mm)
- \(L_n\) represents the length of sample after fixing test of cycle number n (mm)
- \(L_{fn}\) is the length of sample after recovery test of cycle number n (mm)

Figure 3 show that the percentage of recovery is about 67% after 64 h, which means that this polymer is not 100% SMP, and thus, it has partial SME. The recovery curve presents two different stages. In the first stage, the recovery rate is relatively high. During 10 min, the sample regains 55% of its initial shape. In the second stage, to regain 10% of its initial shape, the sample needs more 80 min.

Figure 3: Recovery test at 90°C.
4 PARTIAL SHAPE MEMORY EFFECT

The multi-cycle tests have been performed on the same sample according to the procedure, as explained before. At each cycle, the sample has been stretched up to 100% before recovery tests. The results of the tensile tests (at 70°C) of the different cycles have been presented in figure 4 where real stress is plotted versus strain. These tests have been repeated with at least two other samples; the same results have been obtained.

![Figure 4: Real stress versus strain at the beginning of each cycle of shape memory tests.](image)

The different cycles may be analyzed as follows:

i) Cycle 1 can be divided into two zones with:
   - Elastic stage up to 10% of deformation and with a Young modulus of 10.83 MPa
   - Wide transition zone from 10% to 50%
   - Plastic linear stage up to 100% of engineering strain. After recovery test, the sample regains 67.3% of its initial shape.

ii) Cycle 2 begins at the end of the first cycle and after the recovery test. This cycle is also divided into 2 linear stages.
   - Elastic zone with practically the same yield stress and yield strain as the first cycle.
   - Transition zone
   - Plastic zone up to 100% of deformation. After recovery test, the sample regains 80.5% of deformation.

iii) Cycle 3 begins at the end of the second cycle and after the recovery test. This cycle is also divided in 2 linear stages; linear elastic and plastic zones with a transition zone between them. At the end of this cycle, and after recovery test, the sample regains 93.7% of its shape of the beginning of this cycle.

iv) Cycle 4 begins at the end of the third cycle and after the recovery test. As in previous cycles, it is separated in to 2 different stages, elastic and plastic zone. After recovery test at the end of this cycle, the sample becomes practically a polymer with 100% shape memory effect.
As we can see, TPU initially has a partial shape memory effect. At the end of each cycle this property improves and shape memory capacity of the polymer increases. After fourth cycle, it becomes a shape memory polymer (table 1).

<table>
<thead>
<tr>
<th>N° of cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (MPa)</td>
<td>E₁</td>
<td>10.83</td>
<td>11.49</td>
<td>12.09</td>
<td>12.85</td>
<td>11.15</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>2.8</td>
<td>5.13</td>
<td>5.95</td>
<td>6.78</td>
<td>7.17</td>
</tr>
<tr>
<td>% Recovery</td>
<td></td>
<td>67.4</td>
<td>80.5</td>
<td>93.7</td>
<td>99.0</td>
<td>99.2</td>
</tr>
</tbody>
</table>

Table 1: Modulus and percentage of recovery at the end of each cycle.

Table 1 shows also the evolution of modulus at end of each cycle. The modulus related to the elastic (E₁) and plastic (E₂) deformation zones have been reported in this table.

At the beginning, the polymer has a partial shape memory effect with a recovery rate of 67%. Figure 5 shows schematically the results of 6 successive cycles of shape memory tests. As it can be seen, at the end of each cycle and at the beginning of next one, the sample is the same. This figure shows also that the recovery rate, obtained from equation 1, increases after each cycle; from 67% to 80.5% after the second cycle, 93.7% after the third cycle and reaches 99%, 99.2% and 99.5% after respectively fourth, fifth and sixth cycle.

The evolution of shape memory capacity of a polymer which is not originally an SMP can reinforce the following idea: A polymer with partial shape memory effect can be transformed into a 100% SMP by multi-cycle loading.

Figure 5: Evolution of SME capacity of TPU by successive shape memory tests.
5 CONCLUSION

This study has focused on partial shape memory effect (PSME) of TPU. The multi-cycle shape memory tests showed that the TPU regains only 67% of its initial shape at the end of the first cycle. These tests also showed that the shape capacity of polymer to regain its initial shape increases by the number of cycles. The same polymer after the second, third, fourth, fifth, and sixth cycles regains 80.5, 93.4, 99, 99.2, and 99.5% of its initial shape, respectively. This new concept of SME has very important value. We can in a legitimate way suppose that a polymer without SME can be transformed into an SMP. This study also demonstrates that the driving force for the SME is in fact the residual stress introduced in the sample during the tensile test. At the end of each cycle, this residual stress increases and the driving force becomes more and more prominent.

REFERENCES


