Evaluation of the thermomechanical Shape memory polymers in equi-biaxial condition by hydraulic bulge test

M Coccia\textsuperscript{1}, E Farotti\textsuperscript{1} and A Lattanzi\textsuperscript{1}

\textsuperscript{1} Department of Industrial Engineering and Matematical Science, Via Brecce Bianche, Ancona, 60131, Italy
E-mail: m.coccia@pm.univpm.it

Abstract. Shape Memory Polymers (SMPs) are materials capable of changing their primary shape to a secondary shape thanks to the so called Shape Memory Effect (SME) phenomenon. The shape-shifting is achieved through the action of an external stimulus, such as heat, electricity, pH, etc. In this paper, experiments on a thermally actuated thin film of a Shape Memory Thermoplastic Polyurethane (SMPU) were performed to calibrate the parameters of a constitutive model which accounts the rubbery/glassy phase transition mechanism behind the shape memory behaviour. In particular, thermomechanical uniaxial tensile tests have been carried out in order to the Young modulus and Poisson’s ratio above/under glass transition temperature and the fixity/recovery ratio. Additionally, the hydraulic bulge test (HBT) in a thermally controlled loading/unloading cycle was used to study the behaviour of the SME at large strains under equi-biaxial stress state. The corresponding outcomes were, therefore, employed to validate the results of the initial calibration by means of a Finite Element (FE) simulation of the HBT.

1. Introduction
Shape memory polymers (SMPs) are mechanically functional smart materials, that are particularly interesting for biomedical applications [1, 2], aerospace applications [3, 4] and actuators [5, 6]. The SMPs own a shape memory effect (SME), i.e. under certain external stimulus such as the magnetism [7], heat [8, 9, 10], electricity [11], light [12, 13, 14] and some specific chemicals [15], it is possible to deform the material from his original shape to a temporary one and vice versa. The transition temperature which allows the shape-shifting is the glass transition temperature ($T_g$); basically, when the material is above this transition temperature, the polymer change his mechanical properties, activating the SME. The increasingly use of smart materials in different application fields requires indeed a specific characterization based on their chemical and mechanical properties.

In this paper, in order to characterize the SME behaviour, the typical thermo-mechanical cycle on uniaxial tensile tests was performed. The outcomes allows to identify the two main parameters that represent the nature of the SME: the efficiency of the material in maintaining the temporary shape, and the ability to recover an intermediate shape. A schematic of the thermomechanical cycle is depicted in Figure 1, according to[16].
Typically, the cycle is composed of five steps (i.e. heating, deformation, cooling, unloading and reheating) which are obtained by controlling the temperature and the deformation during the test [17]. In particular, in the first and the second step, the specimen is heated up to temperature above the glass transition temperature ($T > T_g$) and deformed to a prescribed value ($\varepsilon_p$), respectively. Thus, in the third step, the specimen is rapidly cooled to a temperature below the glass transition temperature ($T < T_g$) while maintaining $\varepsilon_p$ constant. In these three steps a new shape was impressed and learned to the specimen. Then, maintaining the temperature under $T_g$, the specimen is unloaded until the stress is reduced to zero; note that strain on the specimen can decrease at the end of the step to $\varepsilon_u$. This allows us to compute a measure of the SME’s capability to keep the prescribed deformation, i.e. the fixity ratio:

$$R_f = \frac{\varepsilon_u}{\varepsilon_p} \times 100$$ (1)

In the last step, the specimen is heated again, exceeding the $T_g$ with no load applied; in this phase the change of shape occurs and the specimen tends to recover its initial shape. However, at the end of the heating phase, not all of the prescribed deformation is recovered, leading to a residual deformation $\varepsilon_r$. Thereby, the so called recovery ratio can be computed as:

$$R_r = \frac{\varepsilon_p - \varepsilon_r}{\varepsilon_p} \times 100$$ (2)

In this work, a comparison between a equi-biaxial thermomechanical test and a simulation is performed. In particular, a description of biaxial test by means a HBT to determine the behaviour of the SMPs was reported. Through an optical equipment, the specimen shape was recorded during the test, and the DIC technique used to measure the deformation of the specimen, while a transducer detects the inflation pressure. Then, a numerical model on the HBT test and the material used to describe the SMPs mechanical behaviour was described. In order to simulate a SMP the determination of some parameters are necessary to describe the SME of the material. More specifically, uniaxial standard test was conducted to determine Young’s modulus and Poisson’s ratio above and below the transition temperature. Otherwise a thermomechanical uniaxial test was performed to known the principal properties for describe the SME.

2. Materials and specimens
The material used in this work is a Shape Memory Thermoplastic Polyurethane (SMPU), supplied by MAIP GROUP® in the shape of laminated foils. Both the standard uniaxial specimens (ISO 527-2) [18] and the circular bulge test specimens (with a diameter of 140 mm) were cut from the same 0.4 mm thick foil.
The external stimulus used to activate the SME of the material is the temperature. In order to determine the glass transition temperature ($T_g$) of the polymer a differential scanning calorimetry (DSC) analysis was performed. According to the procedure described in ASTM D 3418 standard [19], the sample was tested in the range from -20°C to 250°C. The analyses was carried out by means of a Seiko® EXSTAR6000 differential scan calorimeter on a 12 mg of sample cut from the foil. The scanning was conducted by using dry nitrogen having a flow rate of 50 mL min$^{-1}$ during the whole measurement session. The outcomes from the differential scanning calorimetry are reported in Figure 2.

![Figure 2. DSC of thermoplastic shape memory polyurethane. Black curve represents the heat flow depending on temperature, dashed curve represents the first derivative.](image)

It can be observed that the transition starts at the onset temperature $T_{g\text{onset}}$ equal to 53.30°C and ends at the transition $T_{g\text{end}}$ equal to 63.48°C. The glass transition temperature, $T_g$, has been determined as the inflection point, equivalent to 59.45°C [20].

3. Experimental setup and measurement technique

In order to activate the shape memory nature of the material, the mechanical tests, either uniaxial and biaxial, were conducted by controlling the temperature inside a climatic chamber. In both cases, the average temperature was monitored and recorded by using 3 K-type thermocouples suspended on the specimen. The temperature signals were acquired through National Instruments SCXI 1000DC acquisition system, equipped with Ni 1102C multi-channel signal conditioner module. The monoaxial and thermomechanical tests were performed by using an electromechanical testing machine (Zwick/Roell® Z050), equipped with a 500 N load cell with an accuracy of 0.01 N. On the other hand, the thermomechanical tests in balanced biaxial stress state were performed using a hydraulic bulge test machine. A schematic view of the set-up is reported in Figure 3. To ensure a homogeneous heating on the specimen during the HBT, also the water used for forming the specimen was maintained at temperature above $T_g$, while the fluid pressure was measured with a pressure transducer with an accuracy of 0.01 bar. The whole deformation history of specimens was recorded during all the tests employing two Pixelink® BU371F cameras (1280 × 1024 pixel$^2$ 8-bit sensor); in this way, the displacement fields – and the derived quantities – on the specimens’ surfaces were measured through 3D Digital Image Correlation (DIC) technique. Here, the image analysis has performed by commercial software MatchID® 2021, using a subset size of 29 pixel and step size of 4 pixel for the correlation. Following the ISO/DIS 16808, the equi-biaxial tensile stress has been calculated according to
the equation:

\[
\begin{align*}
\sigma_1 &= \sigma_2 = \frac{PR}{2t}, \\
\sigma_3 &= 0 \\
R &= \frac{1}{k}, \\
k &= \frac{1}{2}(k_{xx} + k_{yy}) \\
\delta_3 &= ln(\varepsilon_3 + 1) = -2\delta_1 = -2\delta_2
\end{align*}
\]

(3)

Where \( P \) was the pressure of the water, measured by a pressure transducer, \( D \) the diameter of the upper flange hole and \( t_0 \) the initial thickness of the specimen.

4. Numerical model

In order to simulate the thermomechanical cycle conducted in biaxial stress state, a numerical model of a HBT has builted, by using the finite element simulation analysis software ABAQUS/Standard®. The numerical model of the HBT is composed by two main parts: the specimen and the circular upper die, the latter modelled as analytical rigid surface. The external circumference of both parts is fixed, while pressure loads and temperature have been applied according to the sequence measured during the test illustrated in Figure 4.

The frictional contact between the upper die and the specimen surface is modelled assuming a static frictional coefficient of \( \mu_s = 0.35 \), typical of polymer-steel interfaces.

The material model used to describe the SME is proposed by Boatti et al. in [21], and implemented in the FE code by means of a material user subroutine (UMAT). This model is based on the temperature-dependent response of SMPs, identifying different regions corresponding to the glassy and rubbery region, respectively above and below the \( T_g \) (as depicted in Section 5.1). In particular, the model describes the five steps in Figure 1, and consider allows to employ the parameters describing both the imperfect shape-fixing and incomplete shape-recovery. The HBT information about the geometry and the characteristic of the used FEM model are listed in Table 1.
Figure 4. Step thermomechanical simulation

Table 1. Characteristics of the FE model

| Geometry of HBT | FEM characteristics |
|-----------------|---------------------|
| Blank size      | 140 mm              |
| Die diameter    | 90 mm               |
| Thickness       | 0.4 mm              |
| Type of element | C3D8 (8-nodes, full-integration) |
| Number of elements | 9987               |

5. Results and discussion

5.1. Uniaxial tensile test under warm condition

The calibration of the SMP constitutive model requires the elastic properties associated with the glassy and rubbery phases of the SMPU; these data were retrieved from uniaxial tensile tests under controlled temperature. In Figure 5 we report the true stress-strain curves below and above the transition temperature up to 15% of strain.

Here it is possible to observe that at 25°C the material exhibits the typical mechanical response of PU characterized by an elastic phase reaching the upper yield point, followed by a softening behaviour and a constant plateau region; here the DIC measurement highlights the formation on a necking zone, as shown in Figure 5A. Differently, above the glass transition temperature of the material, namely 70°C, the material shows an almost linear behaviour, in accordance with the rubbery nature, without the formation of necking (Figure 5B). The Young’s modulus and the Poisson’s ratio determined from the tests are reported in Table 2.

Table 2. Region properties

|                     | Glassy Region | Rubbery Region |
|---------------------|---------------|----------------|
| $E$ [MPa]           | 2460          | 13             |
| $\nu$               | 0.40          | 0.48           |

5.2. Uniaxial thermomechanical test

The efficiency of the SME of the SMPs in terms of fixity and recovery ratios, has been estimated by performing a uniaxial thermomechanical cycle. In Figure 6 is reported the cycle performed at 70°C and 20% of prescribed strain. In particular, according to (1) and (2), from the curve of the cycle is possible to determine the fixity ratio $R_f = 99.14\%$ and the recovery ratio $R_r = 83.67\%$. 


Figure 5. Experimental Stress and Strain curves at two different temperatures with DIC measured strain fields.

Figure 6. Thermomechanical monoaxial cycle

These data, together with the elastic properties of the glassy and rubbery phases of SMPU retrieved from the pure uniaxial tensile tests, have been used to calibrate the HBT simulation.
5.3. Comparison between biaxial thermomechanical test and simulation

Figure 7 shows the comparison between the experimental data and the numerical model of the HBT. The analysis shows that the ultimate strain is significantly lower in the simulated case, indicating that the SME is different from a uniaxial to a biaxial stress condition. In particular, the experimenta thermomechanical cycle in equi-biaxial condition points out a reduction of the Fixity and Recovery ratios, whose values are $R_f = 92.61\%$ and $R_r = 76.35\%$ respectively.

![Comparison of thermomechanical biaxial cycle between experimental data and numerical simulation of HBT.](image)

6. Conclusions

In this work, a HBT on a thin membrane of SMP with glass transition temperature at 60°C have been presented, exploiting the DIC technique to the deformation evolution on the specimen surface. The efficiency of the shape memory effect is evaluated by comparing the HBT experimental data with a numerical simulation of the test, whose material coefficients regulating the SMP constitutive model were calibrated from uniaxial tensile thermomechanical tests. The FE simulation provides a consistent replication of the bulge test; however, a reduction of the Fixity and Recovery ratios is observed, suggesting a small influence of the stress state on the SME of the polymer.
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