COMPREHENSIVE INVESTIGATION OF THERMOMECHANICAL PROPERTIES OF SMP FOR DEVELOPMENT OF SMART DEVICES

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SYNOPSIS

Shape memory polymers (SMPs) are multifunctional materials that can change their shape under external stimuli, usually temperature. In the case of polyurethane shape memory polymers (PU-SMP) or shape memory epoxy (SMEp), a relatively high strength and beneficial shape memory properties are found which enables various applications in the medical, industrial fields and daily life. Particularly interesting is a new generation of multiple SMPs that demonstrate the ability to memorize more than two shapes. The property significantly broadens the functionality of SMPs making them attractive for applications from robotics to biomedicine. The multiple shape memory effect (SME) can be achieved through additive manufacturing (AM), particularly 4D printing. The approach facilitates the design and development of devices with complex structures unattainable by traditional techniques.

INTRODUCTION

A comprehensive investigation of the structure and shape memory performance of a thermoset PU-SMP with a glass transition temperature T_g of 45 °C, denoted by MP4510 was conducted. The chemically crosslinked network of the SMP ensures exceptional shape memory behavior, making it highly desirable for various applications. In addition, its activation temperature range close to room and human body temperature opens up possibilities for use in biomedical and industrial applications, e.g. fast-response actuators. In order to better understand the SMP behavior in various conditions and to select the appropriate parameters for the thermomechanical loading, the extensive program of the PU-SMP structural characterization was performed by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), atomic force microscopy (AFM). The obtained results confirmed the high strength and high shape memory properties of the PU-SMP.

Shape memory properties, i.e. shape fixity and shape recovery parameters, were determined in the thermomechanical loading program. A modified experimental approach that considered the polymer's sensitivity to external conditions, such as temperature and humidity variations, was applied. The obtained results indicate that the PU-SMP exhibits a shape fixity ratio of approximately 98%, which remains relatively consistent throughout subsequent cycles of thermomechanical loading due to the stability of chemical crosslinks in the thermoset material's structure. In terms of shape recovery, the polymer demonstrated a value of about 90% in the first cycle, which progressively improved to surpass 99% in the third cycle.

TESTING AND RESULTS - PROGRAM OF THERMOMECHANICAL LOADING

The PU-SMP specimen (T_g 45°C; gauge length 15mm) was subjected to a thermomechanical loading program using the modified experimental setup presented in Fig. 1a. The experimental results obtained during one cycle of the subsequent stages of the thermomechanical loading (I – IV), i.e. the stress, strain and temperature vs. time curves are depicted in Figs. 1 a, b and c, respectively. Selected colors used in the diagrams indicate each stage of the loading I (black)- loading up to ε_m at T_h ($T_g + 20$ °C), II (red)- cooling down to T_l ($T_g - 20$ °C), III (blue)- unloading at T_l, IV (green)- heating up to T_h.

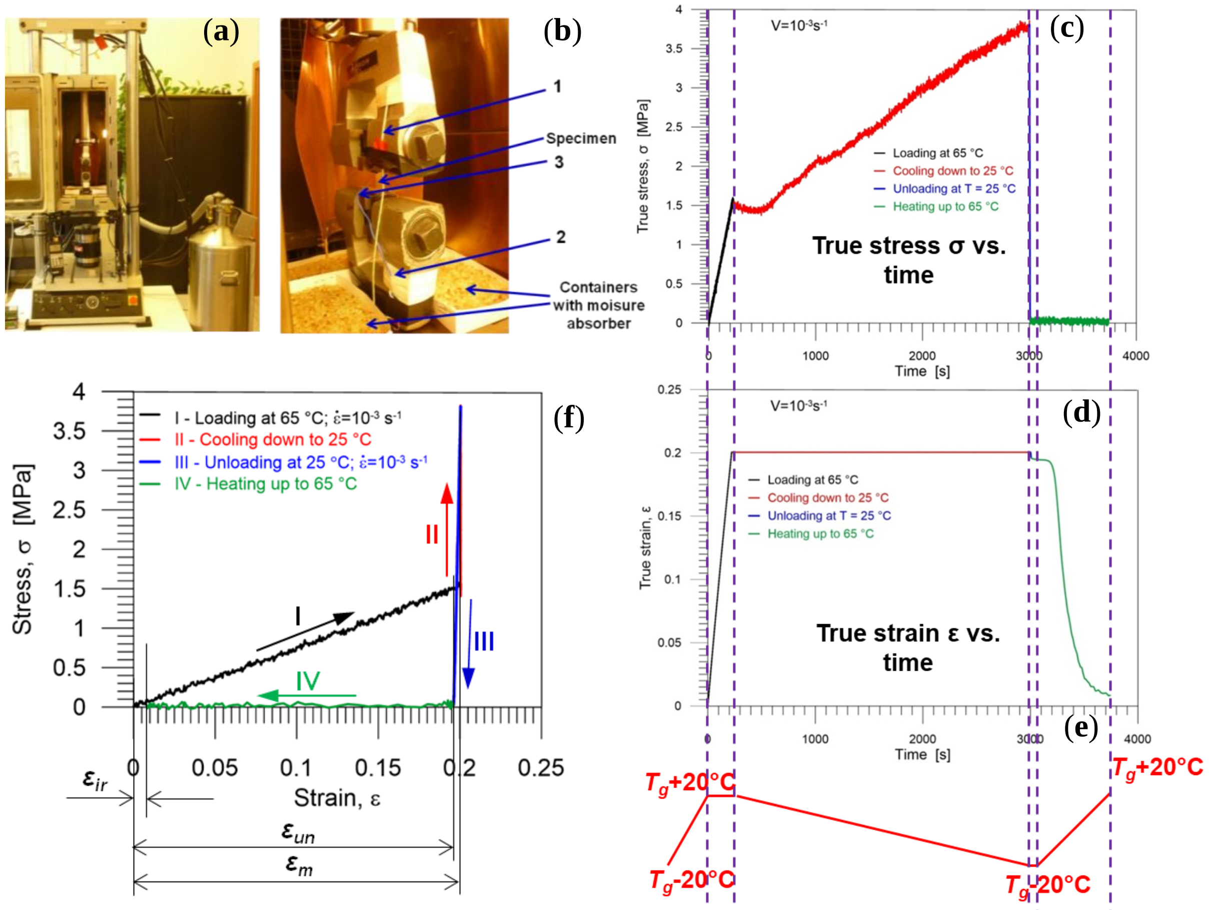

Fig. 1 Photographs of experimental setup: a testing machine with a thermal chamber (a); PU-SMP specimen in grips of testing machine with additional thermocouples (1, 2, 3) and moisture absorbers in the boxes (b). Stress (c), strain (d), temperature (e) vs. time and stress vs. strain (f) obtained during the subsequent stages of one cycle of thermomechanical loading-unloading program.

The functional parameters of shape memory polymers, crucial for their applications, namely shape fixity R_f and shape recovery R_r were determined using the obtained experimental data (Fig. 1f) and equations (1) and (2), proposed by Hisaaki Tobushi and Shunichi Hayashi [30]:

$$R_f = \frac{\varepsilon_{un}}{\varepsilon_m} \cdot 100\% \,, \qquad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_{ir}}{\varepsilon_m} \cdot 100\% \,, \qquad (2)$$

where: ε_m - the maximum strain, ε_{un} - the strain obtained after unloading at T_l,
ε_{ir} - the irrecoverable strain obtained after heating up to T_h under no-load conditions.

For SMP with excellent shape memory properties, the values of both shape fixity and shape recovery ratios are approximately 100%. However, in reality, the temporarily fixed shape resulting from cooling the deformed specimen differs from the deformed shape obtained right after the loading. The recovered shape after heating at the temperature above T_g is also slightly different from the original one. Therefore, performing the thermomechanical loading cycle in a thermal chamber on the PU-SMP with T_g = 45 °C allowed us to determine the realistic values of these functional parameters. For checking of repeatability of the results, the program of the thermomechanical loading cycle was performed for 5 PU-SMP specimens. The obtained shape fixity and shape recovery ratios are compared in Table below. A low discrepancy was found.

Specimen	**Shape fixity R_f, %**	**Shape recovery R_r, %**
1	98.1	87.5
2	97.9	96.0
3	97.9	94.9
4	97.8	93.8
5	97.8	92.1
Average value	97.9 ± 0.12	92.5 ± 3.32

The average value of the shape fixity is 98% which confirms the high shape fixity properties of the PU-SMP produced by *SMP Technologies Inc*. The mean value of the shape recovery is approximately 93%, which denotes that during the one cycle the property is lower. as high as the shape fixity property.

CONCLUSIONS

The shape memory properties of the PU-SMP – shape fixity and shape recovery – were determined with an increased accuracy of the measurements thanks to a modified setup considering the polymer sensitivity to temperature and humidity changes.
The PU-SMP shape fixity parameter was found to be around 98%, independent of the number of thermomechanical loading cycles. The reason was attributed to the huge dependency of the soft segments mobility on temperature, resulting in the fixation of the oriented soft segments at a temperature below T_g. This behavior remains unchanged in the subsequent cycles.
The shape recovery was determined to be approximately 90% in the first cycle and it reached 99% in the third cycle. The behavior was explained by the fact that during the first cycle a great amount of effective physical entanglements are stretched and loosened and fewer entanglements remain to be recovered during the heating in the second and third cycles. This confirmed that the values of shape recovery enhance with the number of cycles and the training can improve the shape memory properties of the PU-SMP.

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