THERMOMECHANICAL ANALYSIS OF POLYURETHANE SHAPE MEMORY POLYMER IN CYCLIC LOADING – SHAPE RECOVERY AND SHAPE FIXITY

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1. Introduction

Recently shape memory polymers (SMP) have been attracting broad interest because they can change their shape in a predefined way when exposed to an appropriate stimulus. Among the shape memory polymers the largest group represent those, whose shape memory properties are triggered by temperature. The temperature at which the polymer returns to the original shape is usually its glass transition temperature (T_g). If the polymer is heated to the temperature above T_g, it can be deform easily. After cooling down below its T_g, followed by unloading to remove the stress, the modified shape is largely maintained (shape fixity). Heating again to temperature above the T_g enables the polymer to return to the original shape (shape recovery) [1]. Thermally responsive polymers found applications in various fields, e.g. in smart textiles, in medical devices, in actuators and sensors, heat-shrinkable tubes for electronics, etc. In order to guarantee sufficient reliability and predict the shape memory behavior of these materials it is important to obtain knowledge about the shape fixity and shape recovery properties.

2. Experimental procedure

In the presented research a polyurethane shape memory polymer (PU-SMP) was used. The material has been characterized by dynamic mechanical analysis (DMA); its glass transition temperature T_g is approximately equal to 45°C and degree of crystallinity is in the range of 5%. The results of DMA confirmed that the SMP fulfills some initial requirements to work as shape memory polymer; namely high value of glass elastic modulus E_g' = 1250 MPa, proper value of the rubber modulus E_r' = 12.1 MPa and a high ratio of E_g'/E_r' = 103 were obtained.

In order to determine the SMP shape recovery and shape fixity parameters, the specimens have been subjected to thermomechanical loading program performed on testing machine (TM) equipped with a thermal chamber. The temperature has been controlled by three thermocouples placed in the specimen area, as well as on upper and lower grips of the TM, respectively.

General description of the thermomechanical loading program can be described as follows. At first, the specimen was heated up to high temperature T_h = 65°C (T_g+20°C). Then, it was loaded by tension at T_h till maximum strain of 20% with strain rate of $10^{-3}s^{-1}$. While maintaining the maximal strain 20%, the specimen was cooled down to T_l=25°C (T_g-20°C). After that, the specimen was unloaded at T_l with the same strain rate. During the subsequent heating from T_l to T_h under no-load conditions the SMP specimen almost recovered its original shape; however a residual strain ε_{ir} was recorded. The thermomechanical loading cycle was repeated three times and the shape recovery and shape fixity parameters were calculated for the subsequent cycles.

3. Results and discussion

An example of the experimental results of the SMP thermomechanical cyclic loading (3 cycles) performed at strain rate of $10^{-3}s^{-1}$ is presented in Fig.1. Using the obtained data, important polymer parameters, namely the shape recovery R_r and shape fixity R_f have been determined. In the material with the best shape memory properties these values should be equal to 100%.

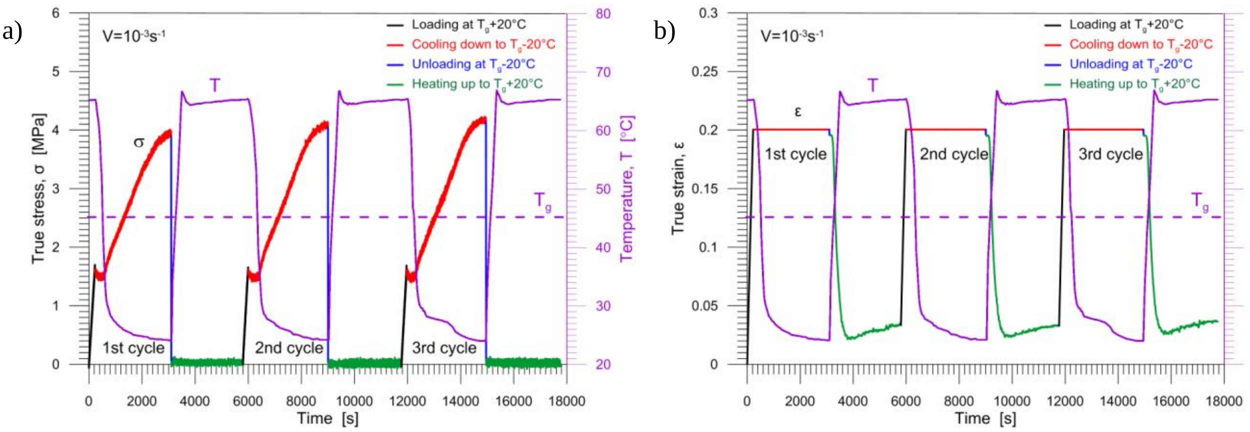

Fig. 1. Results obtained during the SMP three thermomechanical loading: a) true stress σ and temperature T vs. time; b) true strain ε and temperature T vs. time

The values of these parameters in the Nth cycle can be calculated using following equations:

$$R_f = \frac{\varepsilon_{un}(N) - \varepsilon_{ir}(N-1)}{\varepsilon_{\max} - \varepsilon_{ir}(N-1)} \cdot 100\% \; ; \quad R_r = \frac{\varepsilon_{un}(N) - \varepsilon_{ir}(N)}{\varepsilon_{un}(N) - \varepsilon_{ir}(N-1)} \cdot 100\% \; ,$$

where ε_{max} denotes maximum strain, ε_{un} – the strain obtained after unloading at T_l and ε_{ir} – irrecoverable strain, i.e. the strain obtained after heating up to T_h under no-load conditions [2].

It has been found that average value of the shape fixity parameter is approximately 98% and the shape recovery parameter about 95% which confirms good shape fixity and shape recovery properties of this material. Moreover, it can be noticed that for all tests and all performed cycles the values of shape fixity have not changed significantly in subsequent cycles of the thermomechanical loading, whereas the values of shape recovery parameters increase with number of cycle.

4. Conclusions

The cyclic thermomechanical analysis was conducted in order to quantify the shape memory effects of the rigid polyurethane shape memory polymer (T_g=45°C).

Important parameters, crucial for the SMP applications, were evaluated in three thermomechanical loading cycles. It was found that the shape fixity parameter oscillates around 98% and did not change significantly in subsequent loading cycles. Whereas the average value of shape recovery is equal to ≈95% and increases with number of cycle. Estimation of the application parameters allowed to confirm good shape memory properties of the PU-SMP.

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5. References

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