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Thermal effects accompanying tensile deformation of shape memory polymer PU-SMP

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Streszczenie

In the paper experimental results of the effects of thermomechanical couplings occurring in polyurethane shape memory polymer (PU-SMP), produced by SMP Techno Tokyo, subjected to tension with various strain rates are presented. Stress-strain curves were recorded by MTS 858 testing machine with a high accuracy, while using a fast and sensitive infrared camera (Phoenix FLIR IR System) enables to obtain the temperature distribution on the specimen surface, estimate the average temperature and investigate effects of the strain localization during the deformation process. The higher the strain rate the higher the changes in the stress and in temperature are observed, since the deformation mechanisms occur in more dynamic manner and the loading process is closer to adiabatic conditions.

1. Introduction

Shape memory polymers (SMPs) are new attractive materials, since like some metal alloys exhibit the shape memory properties. The mechanism of exhibiting this effect in polymers is definitely different than observed in shape memory alloys, because the crystallographic phase transition does not occur in polymers (Tobushi *et al.*, 2013), (Pieczyska *et al.*, 2009). Whereas, the functional characteristics of SMP, e.g. the rigidity, elastic modulus, coefficient of thermal expansion, change drastically above and below the glass transition temperature (T_g). This is caused by differences of molecular motion depending on temperature (Hayashi S., 1993), (Tobushi H. *et al.*, 2013). In family of SMPs, the polyurethane shape memory polymers can be especially distinguished. The polyurethanes are currently of great practical interest because of their good mechanical and shape memory properties and also low weight, good shape fixity and recovery, easy production techniques, the transition temperature which can be set around the room and human body temperature, as well as low cost in comparison to Ti-based shape memory alloys. These properties allow to use them in different fields, e.g. in medical, protection of food, textile, space and aviation industries (Tobushi *et al.*, 2013). This paper presents experimental results of effects of thermomechanical couplings occurring in polyurethane shape memory polymer subjected to cyclic tension loading at different strain rates. The SMP glass transition temperature (T_g) is approximately equal to 45°C, so the polymer is rigid at room temperature. The degree of crystallinity estimated by DSC is approximately 5%. Since the melting point is relatively low in polymers, the effects of thermomechanical couplings can substantially influence their behaviour under load, so should be studied and taken into account in new SMP applications.

2. Theory - Thermomechanical couplings in PU-SMP; elasto-plastic transition

Strong thermomechanical couplings are observed in shape memory polymers subjected to loading (Huang *et al.*, 2012, Pieczyska *et al.* 2010, 2014, 2015). Thermomechanical couplings, i.e. the “strong” or “weak” interactions between the mechanical and temperature fields, play a significant role in nature, technology and our daily life, causing heating or cooling objects under loading and straining. The effects of thermomechanical couplings have been the subject of theoretical and experimental research, carried out by L. Kelvin (Thomson, 1853), (Chrysochoos, 2012), (Oliferuk *et al.*, 2012) and others. The stress and temperature

change vs. strain curves obtained during the solid tension enable to distinguish reversible stage of the deformation, related to the insignificant change in temperature, from the following, plastic one. During the tension, in the initial, elastic stage the temperature changes due to thermoelastic couplings are negative, while during the subsequent, plastic deformation the temperature changes are always positive. The change of the temperature ΔT of the specimen, subjected to adiabatic uniaxial elastic deformation can be described by the equation as follows (Thomson, 1853):

$$\Delta T_{el} = -\frac{\alpha T \Delta \sigma_s}{c_p \rho}, \quad (1)$$

where α – the coefficient of linear thermal expansion, T – the sample absolute initial temperature, $\Delta \sigma_s$ – the isentropic change of stress, c_p – the specific heat at constant pressure, ρ – the material density.

So, the value of maximal drop in the material temperature can be used for evaluating of a limit of its reversible deformation with high accuracy.

Empirical identification of the boundary between the elastic and the plastic stage of the deformation is really complex. Especially it is difficult to identify it in materials without pronounced Yield point, like most of polymers. In this case, the methods utilizing a thermal emission and based on a qualitative change of the temperature behaviour of the specimen under mechanical loading are usually very efficient (Pieczyska *et al.* 2010), (Oliferuk *et al.*, 2012). Some examples are presented in the figures below. The stress and temperature changes vs. strain obtained for the SMP in tension conducted with strain rate 10^{-2}s^{-1} within range of true strain 0.065 are shown in Fig. 1.

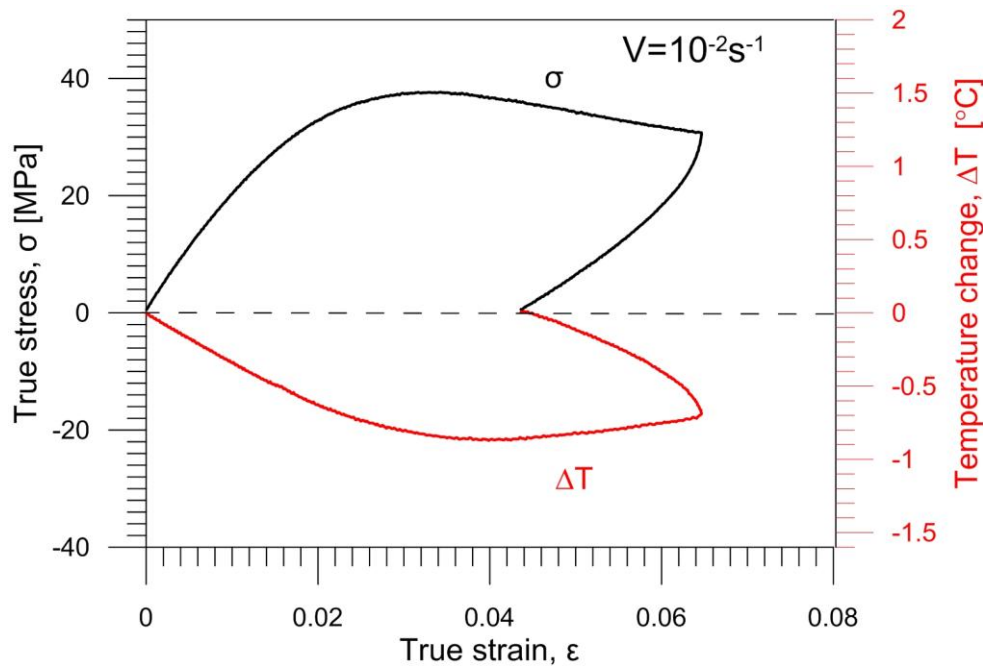


Fig. 1. Stress σ and related temperature change ΔT vs. strain ϵ obtained for SMP subjected to tension with strain rate 10^{-2}s^{-1} within true strain range 0.065.

It may be noticed that an amazing symmetry is observed between the mechanical and thermal results during the SMP loading: the maximal values of the stresses are related to the minimal changes of the temperature. Yield point estimated for the SMP as the maximal drop in the specimen temperature at the strain rate 10^{-2}s^{-1} is approximately 38 MPa.

3. Thermomechanical couplings in PU-SMP - investigation of strain localization

The stress and their related temperature changes vs. strain curves obtained during the SMP tension carried out with high strain rate up to rupture are presented in Fig. 2. The run of the curves enables to distinguish 3 different deformation stages, related also to the SMP structure, evaluating under the loading. The first (I) is the elastic stage of the reversible deformations, described by theory of elasticity (equation 1). The strain is low and the SMP specimen does not change significantly, as we can see at the photograph (a). The second (II) is the plastic stage, associated with substantial change of the material structure, namely the polymer chains straightening. Moreover, the strong strain localization effects can be observed at this stage, which are presented in photograph (b). Due to the localization, the stress decreases during some stage, however the temperature still increases. Some examples of the strain localization effects observed in infrared for so high strain rate are presented in Fig. 3. Stage III is related to the mechanisms of damage, which was shown in photograph (c). In this stage a breaking of the polymer chains occurs, leading to the specimen rupture. A huge increase in the specimen temperature is observed then, especially in the rupture area. However, in this figure, this stage, denoted by a dashed curve, is only an approximation of the stress and temperature changes. During the subsequent heating at temperature $T_g + 20$ °C (30 min) the specimen recovers its former shape, however the decohesion still exists and is noticed even by naked eye (d).

The experimental investigation of thermomechanical couplings in the SMP by using sensitive infrared camera allows noticing many details, especially concerning the nucleation and developing of the strain localisation, necking and damage. Like in metals, a significant increase in the specimen temperature, depending on the strain rate, accompanies the SMP loading process at various stages of its deformation (Fig. 3).

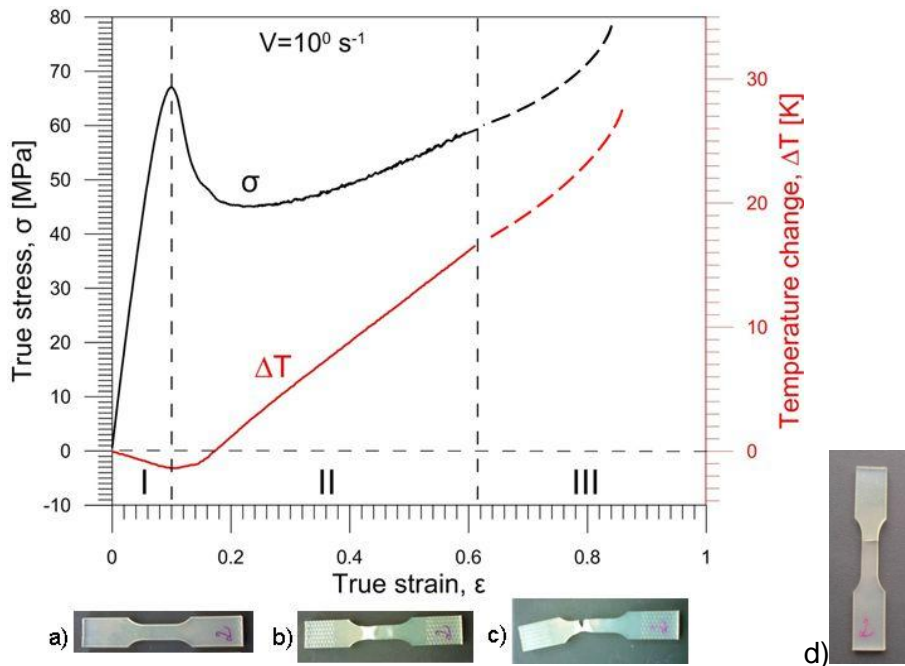


Fig. 2. Stress σ and temperature change ΔT vs. strain ϵ showing 3 stages of SMP tension: I, II, III. (Below) SMP specimens at the loading stages: a) elastic, b) plastic, c) after loading, d) after subsequent heating at $T_g + 20$ °C.

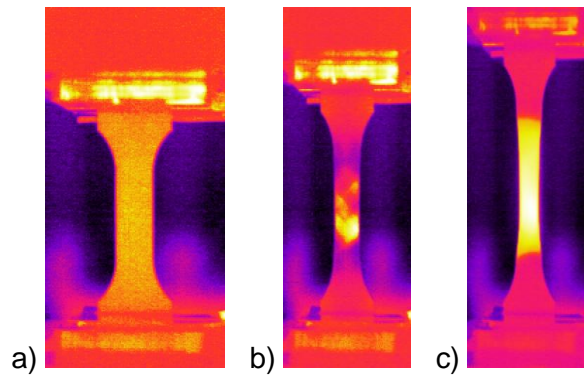


Fig. 3. Examples of strain localization effects observed in infrared for PU-SMP during tension at 10^0s^{-1} : a) before loading; b) during loading; c) at strain 0.6.

The higher the strain rates, the more dynamic run of the deformation mechanisms and the larger temperature changes have been observed. The influence of the strain rate on the mechanical and thermal behavior is shown in Figs 4 and 5.

The stress and temperature changes vs. strain obtained for the SMP subjected to tension at strain rate 10^0s^{-1} within strain range 0.60 are presented in Fig. 4. After the stress increase to 67 MPa related to the drop in temperature approximately $1.6 \text{ }^\circ\text{C}$, the stress decreases to 46 MPa due to the strain localization phenomena. After reaching a minimal value, the stress gradually increases again which is accompanied by significant increase in the specimen temperature, up to $16 \text{ }^\circ\text{C}$. The temperature increases due to dissipative mechanisms of the SMP deformation, e.g. straightening of the polymer chains, origin and development of the exothermic crystal defects, leading to nucleation and evolution of the localization phenomena, related to a heat production (Fig. 3). During the unloading from 58 MPa to 31 MPa, the localization is still observed and an increase in the specimen temperature has been recorded ($\approx 0.8 \text{ }^\circ\text{C}$). The temperature increase is probably a superposition of the positive effect of thermoelastic unloading, similar to those occurring during compression process of any solid, as well as due to the SMP exothermic relaxation processes, often observed in visco-elastic-plastic materials, as polymers.

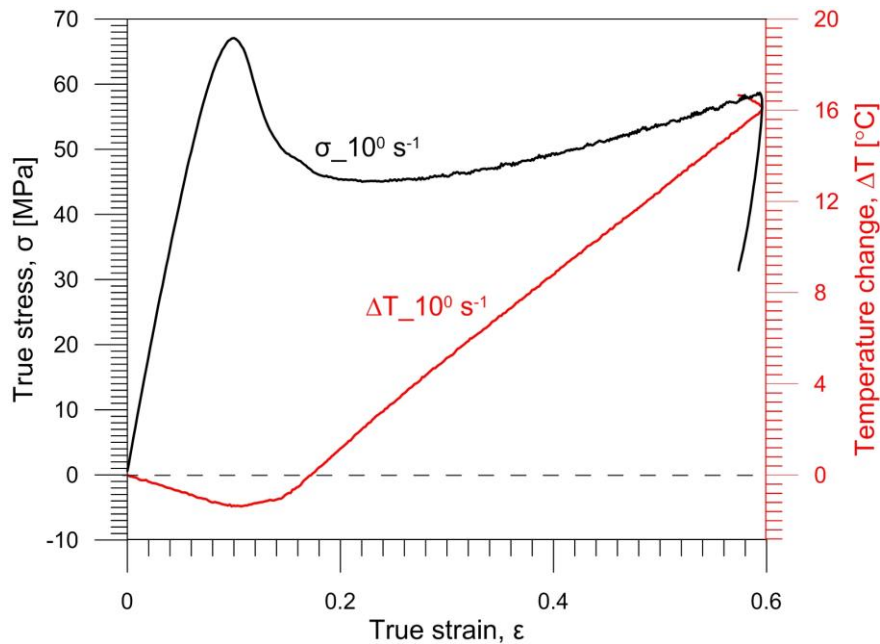


Fig. 4. Stress σ and temperature change ΔT vs. strain ϵ obtained for PU-SMP tension at strain rate 10^0s^{-1} .

Stress and the related temperature change vs. strain obtained for the SMP subjected to tension performed with the lower strain rate 10^{-2}s^{-1} within the range of true strain 0.37 are presented in Fig. 5.

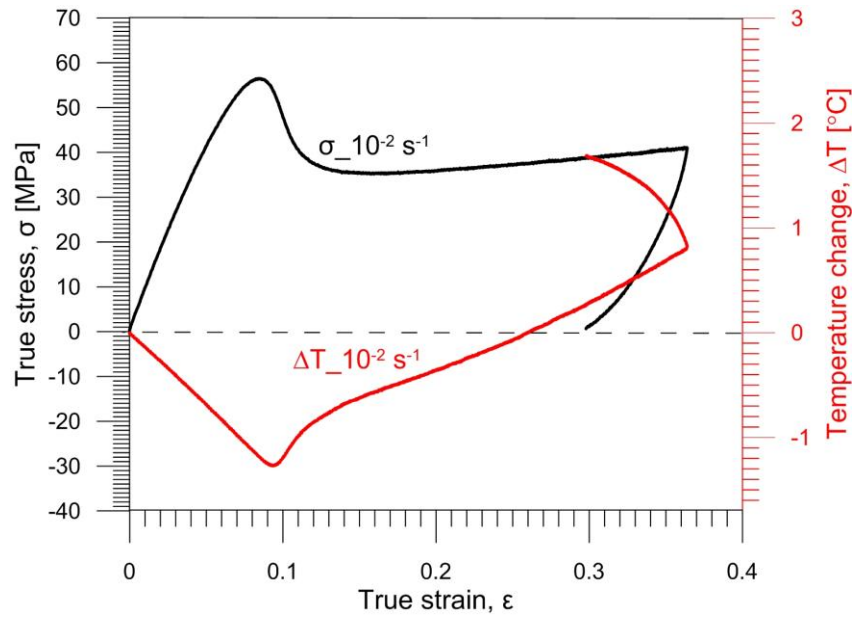


Fig. 5. Stress σ and temperature change ΔT vs. strain ϵ obtained for PU-SMP tension at strain rate 10^{-2}s^{-1} .

After the stress increases to 56.5 MPa related to the temperature drops to $-1.25\text{ }^{\circ}\text{C}$ the stress decreases due to strain localization phenomena. Beyond the strain 0.095 the stress increases again which is accompanied by increase in the specimen temperature up to $0.8\text{ }^{\circ}\text{C}$ for the strain rate 10^{-2}s^{-1} and the strain range 0.37. During the unloading from 37 MPa to 1 MPa an increase in the specimen temperature is observed ($0.9\text{ }^{\circ}\text{C}$) which, similarly as observed for the higher strain rate and shown in Fig. 4, is probably a superposition of the effect of thermoelastic unloading and the SMP exothermic relaxation processes.

Like in metals, this deformation stage beyond the Yield limit is characterized by a dissipative character. A significant increase in the SMP specimen temperature, depending on the strain rate, accompanies the deformation process.

Yield point values estimated for PU-SMP during tension at two various strain rates, namely 10^0s^{-1} and 10^{-2}s^{-1} , are presented in Table 1. The higher the strain rate, the more dynamic run of the deformation mechanisms and the larger drops in temperature and their related stress values indicating the SMP Yield points are observed.

Tab. 1. Yield point values estimated for PU-SMP during tension at two strain rates

Strain rate	10^{-2}s^{-1}	10^0s^{-1}
$\Delta T_{\text{max drop}} [^{\circ}\text{C}]$	- 1.25	- 1.6
$\sigma_{\text{reversible}} [\text{MPa}]$	56.5	67

4. Conclusions

The stress-strain characteristics and their related temperature changes elaborated for the PU-SMP tension loading, as well as results of dynamic mechanical analysis, confirmed that the polymer is characterized by good mechanical and shape memory properties, as well as high sensitivity to the strain rate, manifested by both mechanical and thermal behavior.

Effects of thermomechanical couplings, working out for polyurethane shape memory polymer during the loading, enable to determine the material yield point with high accuracy, observe

nucleation and development of the strain localization phenomena leading to the specimen necking and damage.

Using the fast and sensitive infrared camera it can be observed how the strain localization is nucleating and developing. It was found that the localization develops in particular at the higher strain rates whereas at the lower strain rate the deformation occurs more homogeneously.

ACKNOWLEDGMENTS

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