

**Elżbieta A. PIECZYSKA<sup>1</sup>, M. STASZCZAK<sup>1</sup>, M. MAJ<sup>1</sup>, H. TOBUSHI<sup>2</sup>, S. HAYASHI<sup>3</sup>**

<sup>1</sup>INSTITUTE OF FUNDAMENTAL TECHNOLOGICAL RESEARCH; POLISH ACADEMY OF SCIENCES, Pawińskiego 5 B, 02-106 Warszawa

<sup>2</sup>AICHI INSTITUTE OF TECHNOLOGY, TOYOTA-CITY, JAPAN

<sup>3</sup>SMP TECHNOLOGIES INC., TOKYO, JAPAN

## Investigation of thermal effects accompanying tensile deformation of Shape Memory Polymer PU-SMP

### Abstract

Experimental results of effects of thermomechanical couplings occurring in shape memory polymer subjected to tension are presented. Stress-strain curves were recorded by testing machine, while their related temperature changes were measured with infrared camera. The mechanical and thermal characteristics were used to investigate the polymer properties. Three various stages were distinguished during the deformation process. The first, elastic, is accompanied by a drop in the specimen temperature; the second, plastic, is associated with change of the material structure and the temperature increase; the third stage, related to the specimen rupture and damage mechanisms, is accompanied by the significant increase in temperature.

**Keywords:** shape memory polymer, tension, thermomechanical coupling, temperature change, infrared camera.

### 1. Introduction

Shape memory polymers (SMPs) are new attractive materials, since like some metal alloys exhibit the shape memory properties. The mechanism of exhibiting these effects in polymers is definitely different than observed in shape memory alloys, because the crystallographic phase transition does not occur in polymers [1], [2]. 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 [3], [1]. 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 [1]. This paper presents experimental results of effects of thermomechanical couplings occurring in polyurethane shape memory polymer (PU-SMP) subjected to 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. Thus, the thermal effects accompanying the process of deformation should be studied and taken into account in new SMP applications.

### 2. Thermomechanical couplings in SMP; elasto-plastic transition

Strong thermomechanical couplings are observed in shape memory polymers subjected to loading [4], [5], [6], [7]. 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 Lord Kelvin [8], [9], [10] 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 drop in temperature, from the following, plastic one. During the tension, in the initial elastic stage, the temperature decreases due to thermoelastic couplings, while during the subsequent, plastic deformation the temperature always increases. The change of the temperature  $\Delta T$  of the specimen, subjected to adiabatic uniaxial elastic deformation can be described by the equation as follows [8]:

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

where  $\alpha$  – 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,  $\rho$  – 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 [5], [10]. Some examples obtained for the PU-SMP in tension conducted on MTS testing machine are presented in the figures below (Figs. 1-5). A fast and sensitive ThermaCamTM Phoenix infrared camera was used in order to measure in contactless manner the temperature changes accompanying the specimen deformation and analyze effects of thermomechanical couplings. The camera parameters are as follows: a wavelength range 3 μm – 5 μm, maximal frequency used in this experiment 538 Hz, window size 160 × 256 pixels; thermal sensitivity equal to 0.02 K.

The stress and temperature changes vs. strain obtained for strain rate  $10^{-2}$  s<sup>-1</sup> within range of true strain 0.065 are shown in Fig. 1.

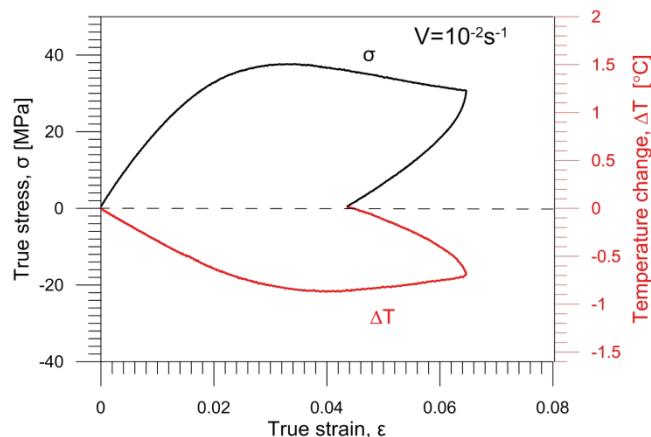


Fig. 1. Stress  $\sigma$  and related temperature change  $\Delta T$  vs. strain  $\epsilon$  obtained for SMP subjected to tension with strain rate  $10^{-2}$  s<sup>-1</sup> within strain range 0.065

It may be noticed that an amazing symmetry is observed between the mechanical and thermal results during the SMP loading: the maximal value of the stresses are related to the minimal change of the specimen temperature. Yield point estimated for the SMP as related to the maximal drop in the

specimen temperature at the strain rate  $10^{-2} \text{ s}^{-1}$  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 PU-SMP tension carried out with high strain rate ( $10^0 \text{ s}^{-1}$ ) up to the specimen rupture are presented in Fig. 2. The run of the obtained mechanical curves and temperature changes enables to distinguish 3 different deformation stages, related also to the SMP structure, developing 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, especially at the higher strain rates, which is presented in photograph (b). Due to the strain localization, the true stress (related to the current specimen cross section) decreases during this stage of the loading. Whereas, the temperature still increases, since the process has dissipative character (Some examples of the strain localization effects observed in infrared for so high strain rate are presented in the thermograms shown in Fig. 3). Stage III is related to the mechanisms of damage, which is 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 local rupture area of the specimen. 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  $T_g + 20^\circ\text{C}$  (30 min) the specimen recovers its former shape, however the decohesion still exists and is noticed even by naked eye (d).

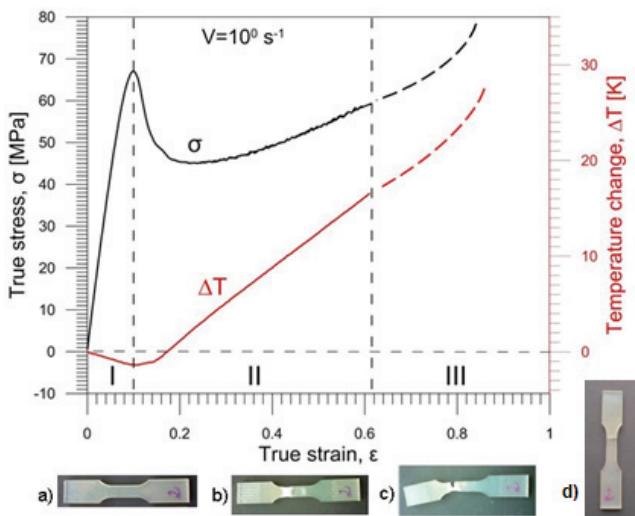


Fig. 2. Stress  $\sigma$  and temperature change  $\Delta T$  vs. strain  $\epsilon$  showing 3 stages of SMP tension: I, II, III. (Below) SMP specimens at the loading stages: a) elastic, b) plastic, c) after loading, d) after subsequent heating at  $T_g + 20^\circ\text{C}$

The experimental investigation of thermomechanical couplings in the SMP by using sensitive infrared camera allows observation and noticing many details. For example, concerning the nucleation and developing of the strain localisation (Fig. 3 b), necking (Fig. 3 c) and damage. Moreover, significant increase in the specimen temperature, depending on the strain rate, accompanies the PU-SMP loading at various stages of its deformation (Fig. 4).

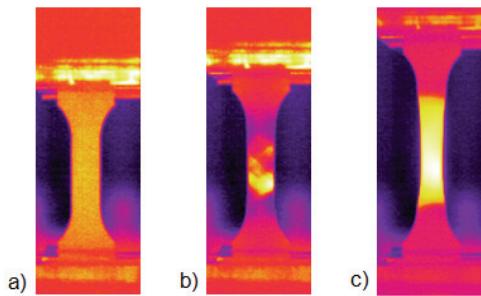


Fig. 3. Examples of strain localization effects observed in infrared for PU-SMP during tension at  $10^0 \text{ s}^{-1}$ : a) before loading; b) during loading; c) at strain 0.6

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, 5 and Table 1.

The stress and temperature changes vs. strain obtained for the PU-SMP subjected to tension at strain rate  $10^0 \text{ s}^{-1}$  within strain range 0.60 are presented in Fig. 4. After the stress increase to its maximal value of 67 MPa related to the drop in temperature approximately  $1.6^\circ\text{C}$ , the stress decreases to 46 MPa due to the strain localization phenomena. After reaching its minimal value, the stress gradually increases again which is accompanied by significant increase in the specimen temperature, up to  $16^\circ\text{C}$ . 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 (Figs 3, 4). During the specimen unloading from 58 MPa to 31 MPa, the strain localization is still observed and an increase in the specimen temperature has been recorded ( $\approx 0.8^\circ\text{C}$ ). The observed 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.

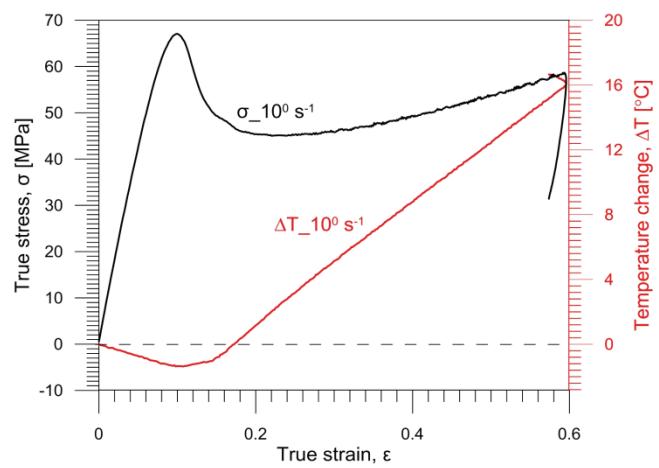


Fig. 4. Stress  $\sigma$  and temperature change  $\Delta T$  vs. strain  $\epsilon$  obtained for PU-SMP tension at strain rate  $10^0 \text{ s}^{-1}$

Stress and the related temperature change vs. strain obtained for the SMP subjected to tension performed with the lower strain rate  $10^{-2} \text{ s}^{-1}$  within the range of true strain 0.37 are presented in Fig. 5. After the stress increases to maximal value 56.5 MPa which is accompanied by the temperature drops up to  $-1.25^\circ\text{C}$  the stress decreases due to the strain localization phenomena. Beyond the strain 0.14 the stress increases again up to 38 MPa which is accompanied by increase in the specimen temperature  $\approx 0.8^\circ\text{C}$ .

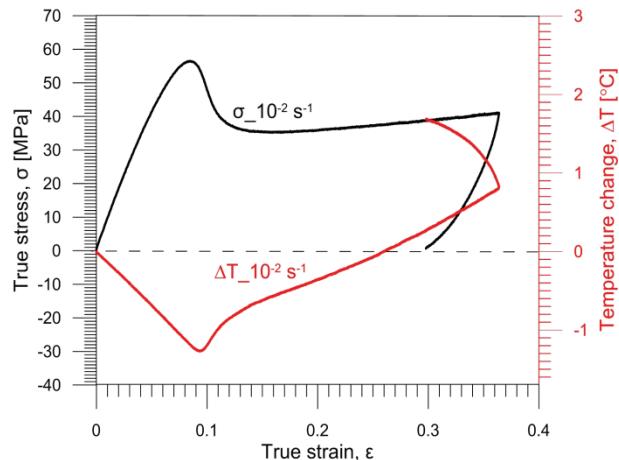


Fig. 5. Stress  $\sigma$  and temperature change  $\Delta T$  vs. strain  $\varepsilon$  obtained for PU-SMP tension at strain rate  $10^{-2} \text{ s}^{-1}$

During the further unloading from 38 MPa to null (1 MPa) an increase in the specimen temperature is observed ( $0.9^\circ\text{C}$ ), which, similarly as observed during the test shown in Fig. 4, is probably a superposition of the effects of thermoelastic unloading and the SMP exothermic relaxation processes.

Summary of the mechanical and thermomechanical data, estimated for PU-SMP during tension at two various strain rates  $10^{-0} \text{ s}^{-1}$  and  $10^{-2} \text{ s}^{-1}$ , are presented in Table 1. At the higher strain rate, more dynamic run of the deformation mechanisms and the larger temperature changes are observed.

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

Strain rate	$10^{-2} \text{ s}^{-1}$	$10^0 \text{ s}^{-1}$
$\Delta T_{\max \text{ drop}}, ^\circ\text{C}$	-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, and to observe nucleation and development of the strain localization as well as the specimen necking and damage phenomena.

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

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.

The research has been carried out with support of the Polish National Center of Science under Grant 2011/01/M/ST8/07754 and 2014/13/B/ST8/04280. Authors are also grateful to L. Urbański for obtaining mechanical data and many experimental remarks and for M. Cristea for elaborating PU-SMP parameters by Dynamic Mechanical Analysis (DMA).

#### 5. References

- [1] Tobushi H, Matsui R, Takeda K, Pieczyska EA.: Mechanical Properties of Shape Memory Materials. Nova Science Publishers, New York, 2013.
- [2] Pieczyska E.A.: Termomechaniczne aspekty przemiany fazowej w stanie TiNi z pamięcią kształtu indukowanej naprężeniem. Pomiary Automatyka Kontrola, vol.55, pp. 958-961, 2009.
- [3] Hayashi S.: Properties and Applications of Polyurethane-series Shape Memory Polymer. Int. Progress in Urethanes, vol. 6, pp. 90 – 115, 1993.
- [4] Huang WM, Young B, Fu YQ.: Polyurethane Shape Memory Polymers. Taylor & Francis Group, 2012.
- [5] Pieczyska EA, Nowacki WK, Tobushi H, Hayashi S.: Thermomechanical properties of shape memory polymer subjected to tension in various conditions. QIRT J., vol. 6, pp. 189 – 205, 2010.
- [6] Pieczyska EA, Maj M, Kowalczyk-Gajewska K, Staszczak M, Urbański L, Tobushi H, Hayashi S, Cristea M.: Mechanical and Infrared Thermography Analysis of Shape Memory Polyurethane. Journal of Materials Engineering and Performance, vol. 23, pp. 2553-60, 2014.
- [7] Pieczyska EA., Maj M, Kowalczyk-Gajewska K, Staszczak M, Grady A, Majewski M, Cristea M, Tobushi H, Hayashi S.: Thermomechanical properties of polyurethane shape memory polymer- experiment and modelling. Smart Materials and Structures, vol. 24, pp. 045043-1-16, 2015.
- [8] Thomson W. (Lord Kelvin): On the thermoelastic and thermomagnetic properties of matter. Transactions of the Royal Society of Edinburgh, 20 (161), pp. 57-77, 1853.
- [9] Chryschoos A.: Infrared thermography applied to the analysis of material behaviour: a brief overview. QIRT J., vol. 9/2, pp. 193-208, 2012.
- [10] Oliferuk W, Maj M, Litwinko R, Urbański L.: Thermomechanical coupling in the elastic regime and elasto-plastic transition during tension of austenitic steel, titanium and aluminium alloy at strain rates from  $10^{-4}$  to  $10^{-1} \text{ s}^{-1}$ . European J. of Mechanics A-Solids, vol. 35, pp. 111-118, 2012.

Received: 17.03.2015

Paper reviewed

Accepted: 05.05.2015

#### D.Sc. Elżbieta A. PIECZYSKA

She graduated from the Warsaw University of Technology, working for the Institute of Fundamental Technological Research, Polish Academy of Sciences. She completed her PhD in 1998, followed by the JSPS Post-Doc in Japan (2004-2005) and Habilitation Thesis in 2010. Her research concerns thermomechanical couplings investigated during loading and deformation of new, multifunctional materials, e.g. shape memory alloys, polymers and composites. She is an author and coauthor of 2 books, 2 book chapters, about 80 papers.



e-mail: epiecz@ippt.pan.pl