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Thermomechanical Properties of Vulcanized Rubber investigated by Testing Machine and Infrared Camera

Abstract

Experimental results of effects of thermomechanical couplings occurring both in natural vulcanized rubber and rubber with self-healing polyurethane subjected to tension at different strain rates are presented. Mechanical characteristics were recorded by testing machine, while the sample temperature changes accompanying the deformation process was measured by infrared camera. The goal was to investigate influence of self-healing polyurethane on the rubber mechanical and thermomechanical properties. It was found that the introduction of the self-healing polyurethane ensures the higher elasticity and the lower tensile strength of the rubber. It was also confirmed that the material is very sensitive to the strain rate; the higher the strain rate, the higher the values of the stress and temperature increases have been obtained.

Keywords: vulcanized rubber, self-healing polyurethane, tension test, thermomechanical couplings, temperature changes, infrared camera.

1. Introduction

At present, rubber materials are of great practical interest and are often applied in different branches of industry. Because of its high elasticity and strength, a natural rubber is the basic constituent of many products used in the transportation, industrial, consumer, hygienic and medical sectors.

In order to develop new rubber materials towards the increasing applications, investigation of their mechanical as well as thermomechanical properties in various conditions are required.

The effects of thermomechanical couplings in solids often occur in nature. In general, by thermomechanical coupling we mean "strong" or "weak" interaction between mechanical and thermal effects. The problem was investigated by Lord Kelvin [1], who described the temperature change of the specimen during initial stage of loading in adiabatic conditions. Namely, the temperature insignificantly decreases during tension, increases during compression and does not change during shear or torsion. The phenomenon is called a thermoelastic effect. Whereas, at the higher strains the material temperature always increases - due to dissipative, unrecoverable mechanisms of the deformation. The effects of thermomechanical couplings have been the subject of theoretical and experimental researches, carried out by e.g. W.Nowacki [2], A.Chrysochoos [3], E.Pieczyska [4] and others.

According to the investigation of thermomechanical couplings of natural rubber, the first experiments was performed by Gough in 1805 and showed the coupled nature of its thermomechanical behavior [5]. Later Joule in his studies noticed that the loading of a vulcanized rubber caused a cooling down of the specimen for small strains, followed by a heating up for higher strains (1859) [6].

Recent researches concerning thermomechanical coupling in natural rubber were performed among others by J.R. Samaca Martinez et al. in [7]. Authors investigated the thermal effects associated with the deformation process of the natural rubber. In [8] B. Wattrisse et al. studied and quantified dissipative and cooling effects during the deformation of natural rubber. Moreover, the thermo-visco-hyperelastic model capable to predict the self-heating of the rubber-type materials under fatigue loading was proposed and discussed by Ovalle Rodas et al. in [9].

The aim of this paper is to characterize the thermomechanical response of natural vulcanized rubber (NR) and of the rubber with self-healing polyurethane (PU) in order to determine the influence of the self-healing PU on the NR thermomechanical behavior.

2. Experimental procedure

The material used in the performed experiments was a new elastomer, based on blends of two thermoset polymers: a vulcanized rubber and a self-healing polyurethane. Self-healing properties of the polyurethane mean that the material needs no outside intervention to begin its healing process, no catalyst or extra reactant. For example, such sample cut in half with a razor blade at room temperature can heal the cut during two hours [10].

The self-healing PU was incorporated in the rubber elastomer. After the incorporation, the subsequent vulcanization of the blends was performed in a hot-press under controlled conditions of the temperature and pressure. Then, the thermomechanical properties of the materials were characterized.

The samples of a gauge length approximately 25 mm (cross-section 25 mm $\times$ 2 mm) were subjected to tension test performed on MTS 858 testing machine at room temperature with different strain rates: $5 \cdot 10^{-2}$ s^{-1}, $5 \cdot 10^{-1}$ s^{-1} and $5 \cdot 10^{0}$ s^{-1}. A fast and sensitive ThermaCamTM Phoenix infrared camera was used in order to measure in contactless manner the temperature changes accompanying the rubber deformation and to analyze experimentally effects of thermomechanical couplings [11]. The black colour of the rubber provides a high emissivity, so the sample does not require any blackening. 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 is equal to 0.02 K. The infrared camera enables to find temperature distributions on the specimen surface, i.e. thermograms. Moreover, it allows determining the average temperature of the specimen during the deformation process, usually presented in the diagrams (Figs. 3-6), [11].

A schematic of the experimental setup for investigation of the mechanical characteristics and temperature changes in tension of the tested rubber is presented in Fig.1, while a photograph of the applied equipment in Fig.2, respectively.
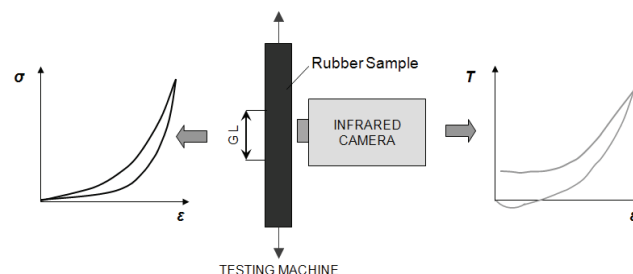

Fig. 1. Schematic of experimental setup for experimental investigation of mechanical characteristics and temperature changes in tension

3. Thermomechanical behavior of natural rubber during tension till rupture

At first, the tension test till rupture for the natural rubber sample (100% content of NR) with very high strain rate ($5 \cdot 10^{0}$ s^{-1}) was performed in room conditions. The goal was to learn something about the new rubber thermomechanical behavior and to determine a proper strain range for following tests. True stress and the related temperature changes vs. true strain obtained during the

experiment are shown in Fig. 3a. Below the diagram, thermograms 1-7 present temperature distribution on the sample surface related to the subsequent stages of the deformation process, namely: 1 – before loading, 2 - 4 – during the loading, 5 – during advanced stage of the loading, 6 – just before the sample rupture, 7 – during the sample rupture (Fig. 3b).
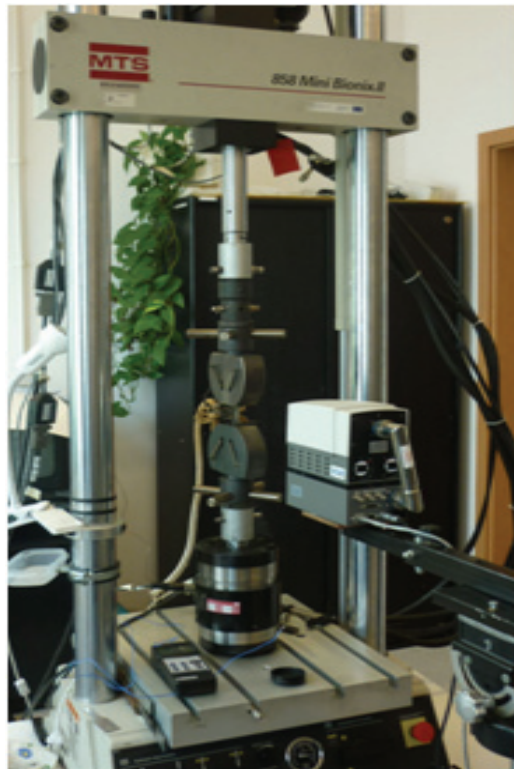

Fig. 2. Photograph of experimental setup designed for investigation of mechanical and temperature characteristics of rubber samples
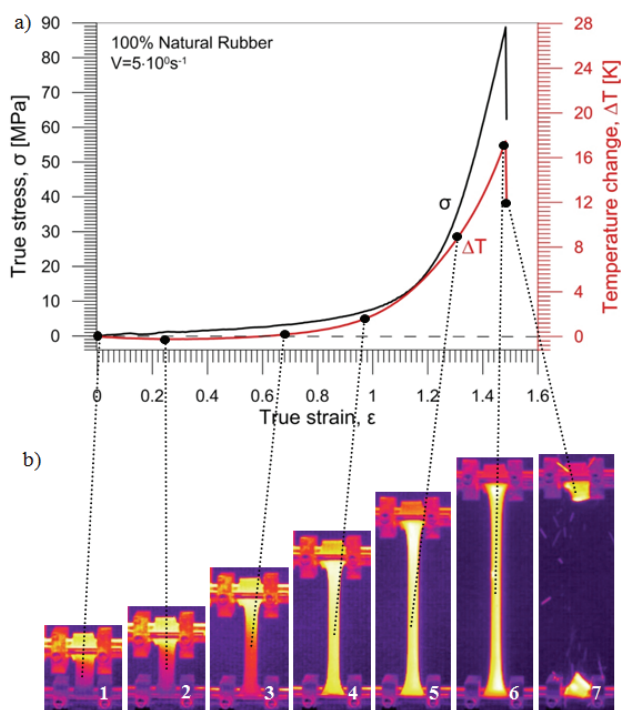

Fig. 3. a) True stress σ vs. true strain ε for NR (100%) during tension test with strain rate $5 \cdot 10^0$ s^{-1} till rupture; b) thermograms showing subsequent stages of the sample loading: 1 – before loading, 2-4 – during loading, 5 – during advanced stage of loading, 6 – just before rupture, 7 – rupture

The sample dimensions, i.e. cross-section, change continuously during the tension test. The engineering stress-strain curve is based on the original cross-section area of the sample and does not give true indication of the deformation characteristics of the material, especially in the case of large deformations. Then, measures of the stress and strain which are based on instantaneous cross-section value are needed.

Since the sample cross-section changes significantly, the stress and strain quantities in all diagrams presented in the paper are related to the instantaneous values of the sample cross-section, obtaining in this way so-called "true stress" and "true strain" values.

True stress denotes the stress determined by the instantaneous load acting on the current cross-sectional area, assuming material volume remains constant:

$$\sigma_{true} = \frac{(\Delta l + l_0) \cdot F}{l_0 \cdot S_0} = \frac{F \cdot (1+e)}{S_0}, \tag{1}$$

where: Δl denotes the sample displacement, l_0 – the initial gauge length, F – the instantaneous force, S_0 – the initial cross-section, e – the engineering strain value.

Constant values l_0 and S_0 were measured before experiments, while the changing values of F and Δl were recorded during the tension test by the testing machine.

The equation for true strain is based on instantaneous change in length. The true strain provides the correct measure of the final strain when deformation takes place in a series of increments, taking into account the influence of the strain path:

$$\varepsilon_{true} = \ln\left(\frac{\Delta l + l_0}{l_0}\right) = \ln(1+e) \cdot \tag{2}$$

The initial loading was accompanied by insignificant drop in temperature, followed by a smooth temperature increase caused by the dissipative mechanisms of the deformation. During the advanced loading, both the stress and the sample temperature increase significantly. The maximal stress value recorded at the rupture stage is 89 MPa, the obtained maximal value of its related temperature change is up to 17 K (Fig. 3).

4. Comparison of mechanical characteristics and temperature changes in NR samples and NR samples with self-healing PU

Basing on the results obtained in the test shown in Fig. 3 the strain limit of approximately 100% was given in the subsequent tension tests. The NR samples and the NR samples with self-healing PU were loaded until ≈ 100% of the true strain at room temperature with two various strain rates.

The stress and the temperature change vs. strain for the strain rate of $5 \cdot 10^{-2}$ s^{-1} are presented in Fig. 4a. Likely it was obtained for the strain rate $5 \cdot 10^0$ s^{-1}, at the beginning of the loading a small drop in temperature is observed, equal to $\Delta T \approx -0.27$ K, and then, as the strain increases for the more advanced deformation, the temperature also increases. The maximal value of the temperature increase, recorded at the maximal stress 16.54 MPa, is 2.32 K.

The next figure presents results obtained for 10 times higher strain rate, equal to $5 \cdot 10^{-1}$ s^{-1} (Fig. 4b). The value of the maximal stress is 20 MPa and its related temperature change is 4.36 K.

The higher the strain rate, the higher the stress values and the higher maximal temperature increases were obtained. The reason is that at the higher strain rate the test conditions are close to adiabatic which significantly influence both the sample structure and its thermomechanical behavior. This rule usually works also for thermoelastic effect, recorded in metals, alloys and polymers [4].
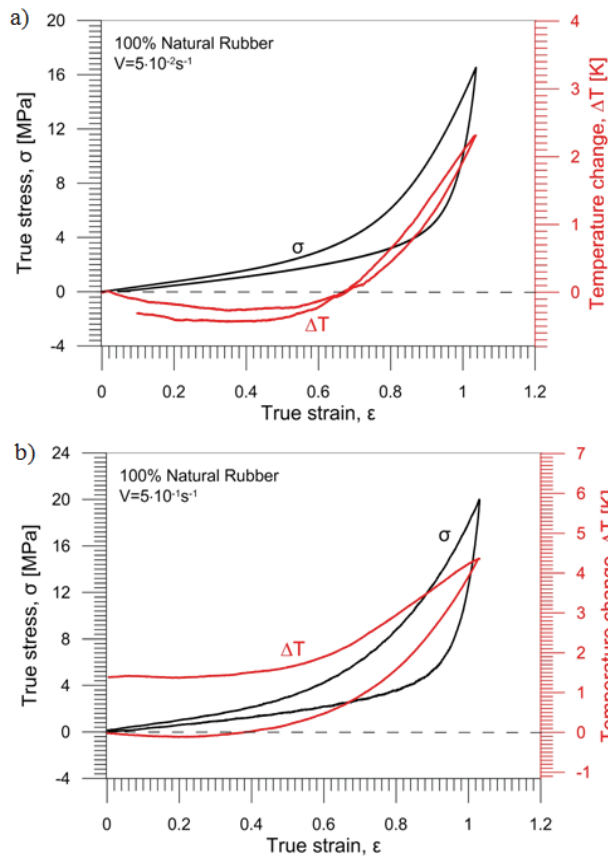
Fig. 4. True stress σ vs. true strain ε for NR (100%) during tension test with strain rates: a) $5 \cdot 10^{-2}$ s^{-1} and b) $5 \cdot 10^{-1}$ s^{-1}

Fig. 5. True stress σ vs. true strain ε for NR (70%) with 30% of PU during tension test with strain rates: a) $5 \cdot 10^{-2}$ s^{-1} and b) $5 \cdot 10^{-1}$ s^{-1}

Whereas, in the initial stage of the rubber loading the observed tendency of the decrease in temperature is opposite. Namely, the value of drop in temperature recorded at the strain $5 \cdot 10^{-1}$ s^{-1} in the initial loading stage is $-0,12$ K (Fig. 4b), smaller than obtained at the lower strain rate and shown in Fig. 4a. Such not typical thermoelastic effect tendency sometimes is observed for elastomers.

Figure 5 shows the stresses and their related temperature changes, obtained for the tension loading of the NR sample with 30% content of self-healing PU. The stress and the temperature change vs. strain for the strain rate of $5 \cdot 10^{-2}$ s^{-1} are presented in Fig. 5a, while for the strain rate of $5 \cdot 10^{-1}$ s^{-1} in Fig. 5b, respectively.

It can be noticed that at advanced stage of the deformation stress increases for both strain rates. Thus, for the strain rate $5 \cdot 10^{-2}$ s^{-1}, the stress increases up to 2,65 MPa, whereas for the strain rate $5 \cdot 10^{-1}$ s^{-1} the stress increases up to 3.32 MPa. The maximal temperature increase recorded at $\approx$ 100% of the true strain is up to -0.32 K, while for 10 times higher strain rate this value ΔT_{max} is 0.29 K.

In the initial stage of the deformation the same tendency as for the sample with 100% of natural rubber is observed. The loading causes a cooling down of the sample for small strains and at the higher strain rates lower values of thermoelastic effects were obtained: for the strain rate $5 \cdot 10^{-2}$ s^{-1} the temperature drop value is equal to -0.46 K, while for $5 \cdot 10^{-1}$ s^{-1} equal to -0.24 K. The reason of such behavior can be as follows: a rubber elastomer under tension can demonstrate negative thermal expansion coefficient in this strain range. It is connected with Gough-Joule effect, which is observed for elastomers and consists in contraction of stretched material when it is heated. It could be explained that the polymer chains absorb energy and adopt another configuration, reducing the volume of the material. These results will be a subject of our future research.
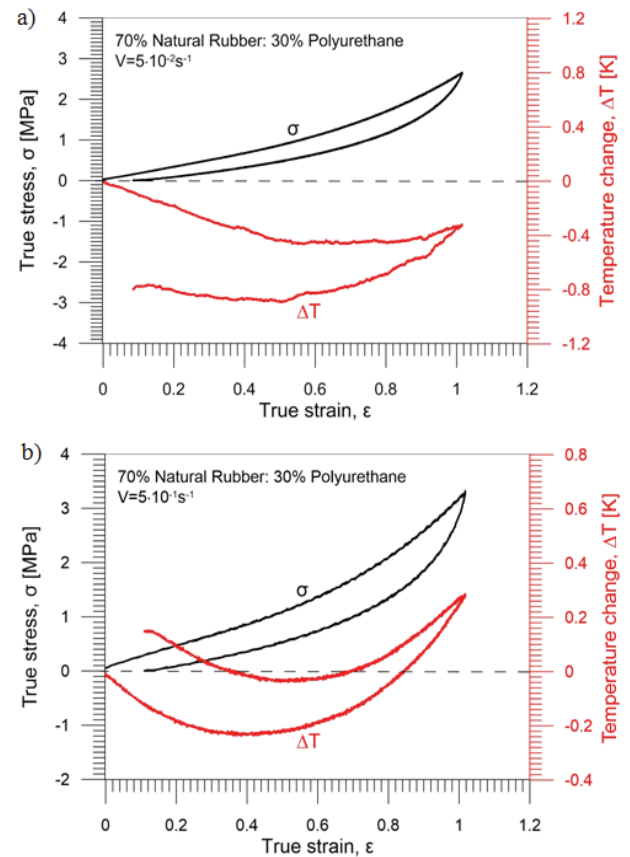
A comparison of the results, presented in Figs 4-5, namely the stress and temperature changes vs. strain for tension loading carried out with various strain rates ($5 \cdot 10^{-2}$ s^{-1} and $5 \cdot 10^{-1}$ s^{-1}) for the NR and the NR with 30% of self-healing PU, is shown in Fig. 6. The stress and the temperature changes manifest how huge is the influence of the thermomechanical couplings on the natural rubber mechanical behavior.

Looking at the results it can be noticed that addition of the self-healing polyurethane changes significantly the rubber mechanical and thermomechanical properties. Namely, the maximal stress is significantly lower and the hysteresis loop is more narrow and more regular for the NR samples with introduction of self-healing polyurethane (Fig. 6a). The values of its related temperature changes are also lower (Fig. 6b).

It was also observed that the contribution of self-healing polyurethane increases the elasticity and decreases the tensile strength of the rubber.

However, both the natural rubber (100%) and the natural rubber with 30% of self-healing polyurethane demonstrate good mechanical properties, e.g. high elasticity, high elongation, as well as high sensitivity to the strain rate.

A comparison of the results obtained for natural rubber and NR with self-healing polyurethane obtained for strain rates $5 \cdot 10^{-2}$ s^{-1} and $5 \cdot 10^{-1}$ s^{-1}, namely maximal drops in temperature during the loadings, maximal stresses and maximal temperature changes at the strain value ε equal to $\approx$ 100%, is presented in Tab.1.

One can notice that as the strain rate increases the maximal stress and their related temperature changes increase also. Whereas, the temperature drops, the decrease of the thermoelastic effect is observed.
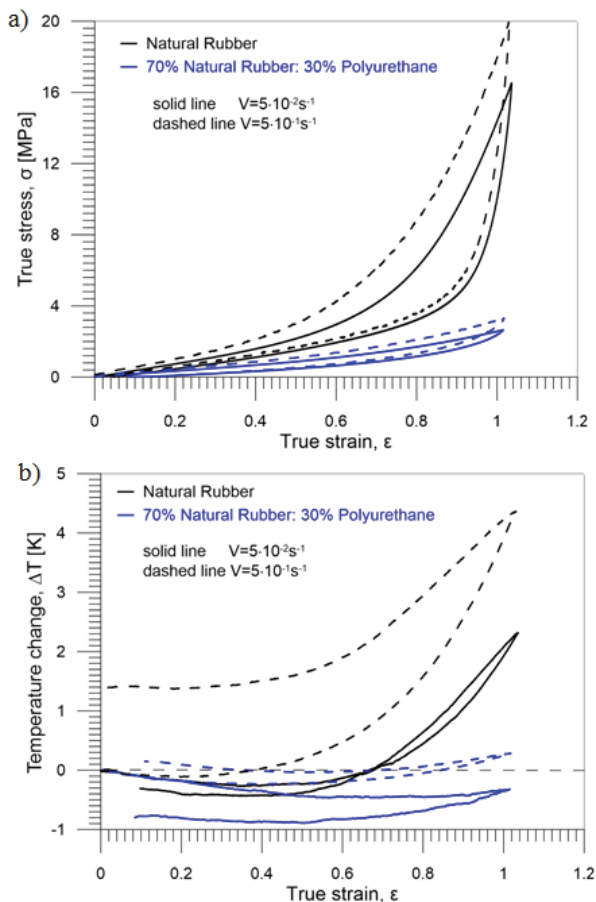
Fig. 6. Comparison of: a) true stress σ vs. true strain ε; b) temperature changes ΔT vs. true strain ε for rubber and for NR with 30% of PU during tension with strain rates: $5 \cdot 10^{-2}$ s^{-1} (solid line) and $5 \cdot 10^{-1}$ s^{-1} (dashed line)

Tab. 1. Comparison of the results obtained for natural rubber and for NR with 30% of self-healing polyurethane

Sample	Strain rate, s^{-1}	$\Delta T_{\text{max drop}}$ during loading, K	σ_{max} at maximal strain, MPa	ΔT_{max} at maximal strain, K
100% NR	$5 \cdot 10^{-2}$	−0.27	16.54	2.32
	$5 \cdot 10^{-1}$	−0.12	20.00	4.36
70% NR: 30%PU	$5 \cdot 10^{-2}$	−0.46	2.65	−0.32
	$5 \cdot 10^{-1}$	−0.24	3.32	0.29

5. Conclusions

Mechanical and thermal response associated with deformation process of the natural rubber and the natural rubber with 30% content of self-healing polyurethane has been presented.

It was shown that introduction of the self-healing polyurethane increases the elasticity and decreases the tensile strength of the rubber samples.

It was confirmed that both the natural rubber (100%) and the natural rubber with 30% of self-healing polyurethane show good elastic mechanical properties, as well as high sensitivity to the strain rate, manifested by both mechanical and thermal results.

At the higher strain rates higher values of the stresses and temperature changes related to the maximal strains were recorded.

At the higher strain rates lower values of thermoelastic effects for the natural rubber as well for the rubber with content of polyurethane were observed. These rather unusual results are

related to elastomer thermodynamic structure and will be a subject of our future research.

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