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Experimental investigation of thermo-mechanical properties of one thermo-responsive shape memory polymer

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Abstract. The thermomechanical behaviour of Estane® ETE 75DT3 was studied experimentally. The material is the aromatic polyether-based thermoplastic polyurethane. It belongs to a group of thermo-responsive shape memory polymers (SMPs) which exhibit the thermally induced shape-memory effect. The thermal properties of the shape memory polymer (SMP) were characterized by Differential Scanning Calorimetry (DSC). The material was investigated by means of the quasi-static tensile tests at the room temperature. The Dynamic Mechanical Analysis (DMA) was carried out at various frequencies and temperatures and the values of dynamical moduli and loss tangent as the functions of the frequency and temperature were determined. The shape memory effect was also studied in the course of the thermo-mechanical loading.

Introduction

The shape memory polymers are smart materials which can change their shape upon application of an external stimulus. The shape memory effect is not an intrinsic property, meaning that polymers do not display this effect by themselves. Shape memory results from a combination of polymer morphology and specific processing and can be understood as a polymer functionalization. [1]. A change in shape caused by a change in temperature is called a thermally induced shape-memory effect. Thermo-responsive SMPs undergo a transition between two different shapes - temporary shape and permanent shape as schematically illustrated in Fig. 1.

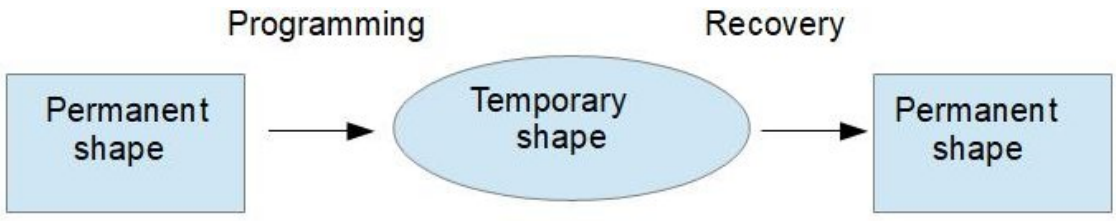


Fig.1: Thermally induced one-way shape-memory effect

First, the material is processed in injection moulding or extrusion where it got its permanent shape. Afterwards, the material undergoes the programming process in which it is heated up above the transition temperature (T_{trans}), deformed and cooled consecutively and a temporary shape is fixed. Heating the sample again above T_{trans} induces the shape memory effect so the recovery of the permanent shape. By further programming, the sample can be brought again into a temporary shape. The transition temperature depends on the type of polymer morphology and it can be either the glass transition temperature T_g or the melting temperature T_m. The shape memory effect can be formed in a number of polymers [2]. It depends on the physical properties of the polymer components, from chemistry and morphology. SMPs are mostly copolymers which consist of at least two types of constituents. One component consisting of hard segments (elastomer) with higher T_g or T_m acts as the physical cross-link and determines the permanent shape. The second soft phase (thermoplastic) enables the fixation of the temporary shape. At room temperature T_r, the hard segments prevent thermoplastic phase from showing rubber-like behaviour. However, when the temperature is increased above the glass temperature T_g, $T_r < T_g < T_m$, the material shows rubber-like behaviour governed by entropy elasticity [3].

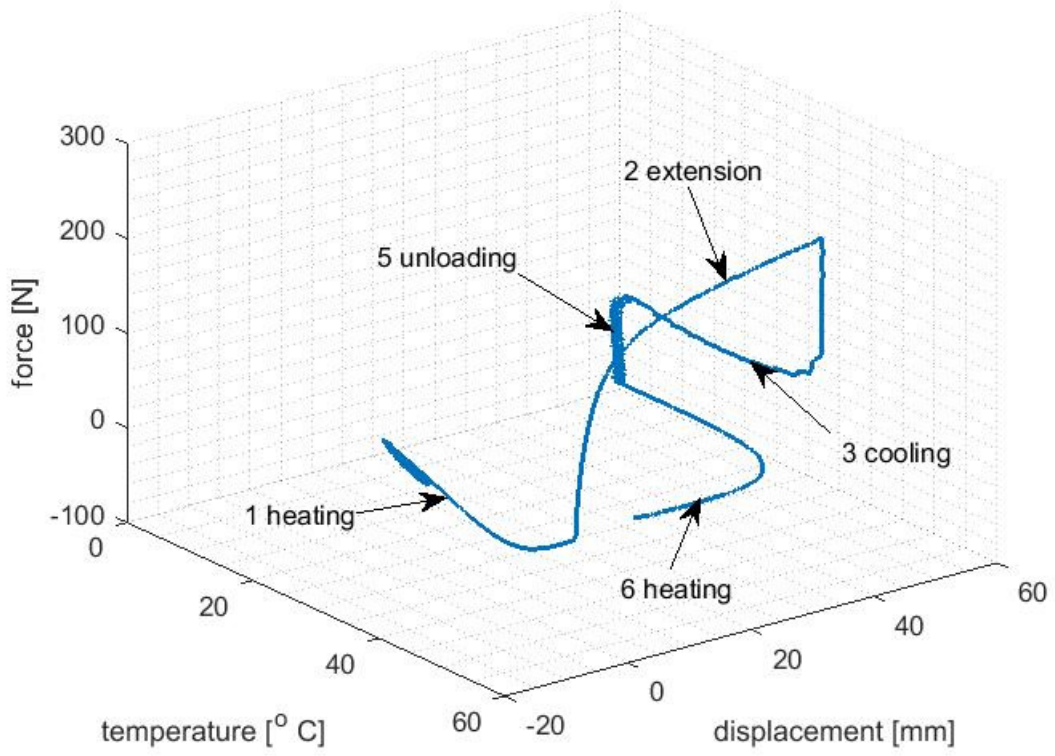


Fig. 2: Cyclic thermo-mechanical loading of thermo-responsive SMP

The thermo-responsive SMP polymer goes through cycles as indicated in Fig. 2. The material is heated in step 1 above the transition temperature ($T_g < T_{trans} < T_{melt}$) then deformed in step 2 to a predetermined shape and fixed into this shape by cooling back below the T_g in step 3 and then unloaded in step 5. The original state can be recovered by reheating the material above its T_g without the mechanical constraint in step 6.

The capability of polymers to be formed to different temporary shapes and subsequently recover their original shape can be used in many applications. Recently a number of biomedical applications have been found for polyurethane-based shape memory polymers. These materials are biocompatible, non-toxic and non-mutagenic in the human body. The

advantage of these materials is that their glass transition temperature T_g can be tailored due to self-deployment of different clinical devices and stents inserted in the human body. Textiles offer another way of SMP development. Successful application area may be deployable structures for the aircraft and space industry and in different robots.

Experiment

The thermomechanical behaviour of Estane® ETE 75DT3 was studied by several experimental methods. The material was supplied by the manufacturer Lubrizol in the form of pellets. SMP Estane is an aromatic polyether-based thermoplastic polyurethane. The producer indicates the hardness of 75 Shore D, the tensile strength 41 MPa and the elongation higher than 300% at room temperature.

Differential scanning calorimetry (DSC) was used to determine the response of the material to heating at the rate of 10 K/min according to ISO 11357. Measured values differ significantly from those indicated by the manufacturer, especially the glass transition temperature T_g. However, this temperature is close to the glass transition temperature of Estane $T_g = 54^oC$ reported in [3,4]. Results of DSC are in Fig. 3 and in Table 1.

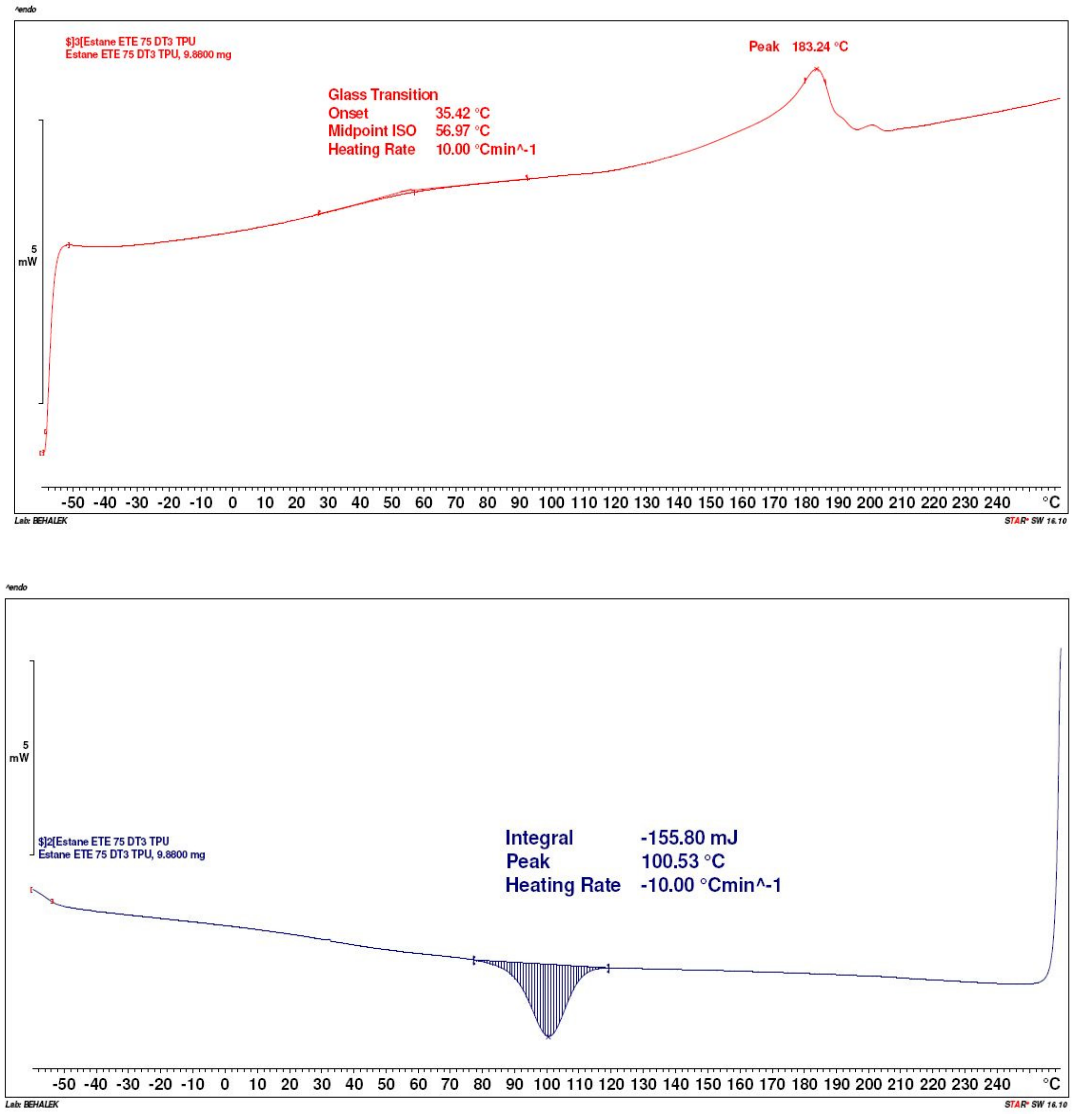


Fig. 3: Results of DSC

Table 1: Thermal properties

Temperature	Measured [°C]	Producer [°C]
T_g	57	-10
T_{melt}	183.2	218
T_{cryst}	100.5	-

The thermo-mechanical measurements were carried out on flat dog bone specimens of length 110 mm and cross section 10 x 4 mm fabricated by the injection moulding. Our measurement of hardness confirmed the value given by the manufacturer 75 Shore D. The quasi-static tensile tests showed the stress dependency on the strain rate so typical for polymers. The results of the tensile tests with rising strain rate are in Fig. 4.

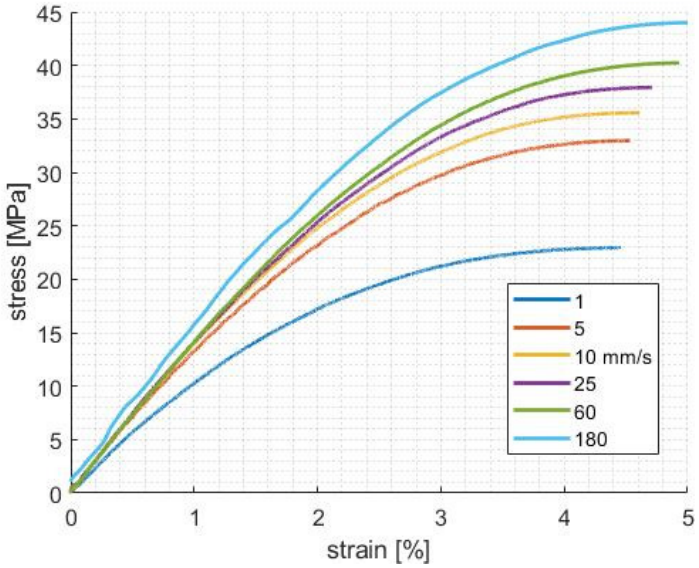


Fig. 4: Tensile tests of Estane with different strain rate

The thermo-mechanical properties were measured by the dynamic thermo-mechanical analysis (DMTA) with different frequencies and the temperature sweep around the glass transition. The dynamic moduli and the loss factor dependency on temperature, frequency and amplitude were determined. DMTA tests in tension deformation mode were performed in the temperature range from 25°C to 45°C using Instron Electropuls 3000 equipped with the temperature chamber and with standard fixtures. The small extension 1mm (around 1%) is applied to the sample in order to maintain it under tension. Then sinus cyclic strain controlled tensile loading was applied with the amplitude 0.01 mm and frequency range from 0.5 Hz to 5 Hz. In order to determine the storage E' and loss modulus E'' of the material, corresponding parameters of the force response and the phase angle δ must be extracted from the recorded raw signals. We suppose that the raw signals i.e. displacement u(t) and force response F(t), are harmonic functions approximately and we use the discrete Fourier transform (DFT) in Matlab in order to determine the phase shift δ at the main excitation frequency [5]. Amplitudes of tensile strain and tensile stress were determined from recorded signals. Dynamic moduli were calculated as

$$E' = \frac{\sigma_a}{\varepsilon_a}\cos(\delta), \quad E'' = \frac{\sigma_a}{\varepsilon_a}\sin(\delta). \tag{1}$$

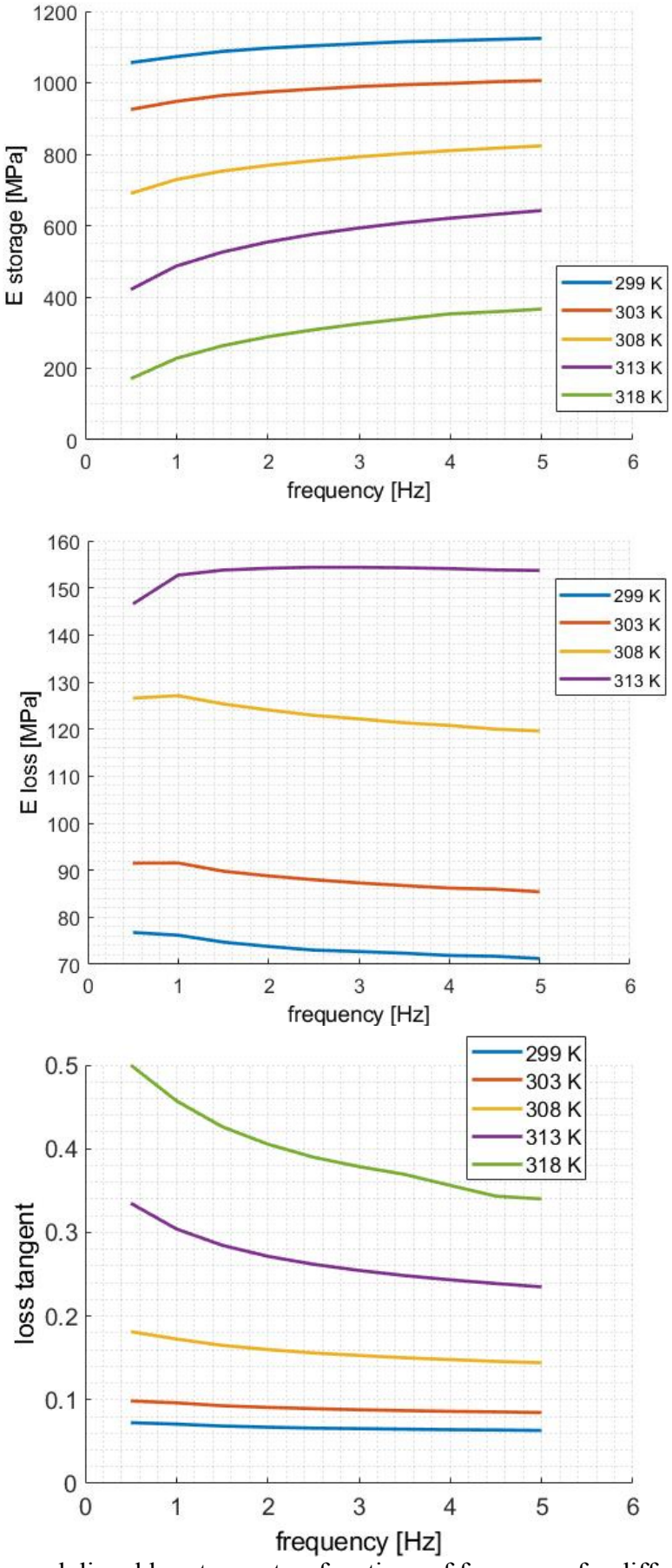
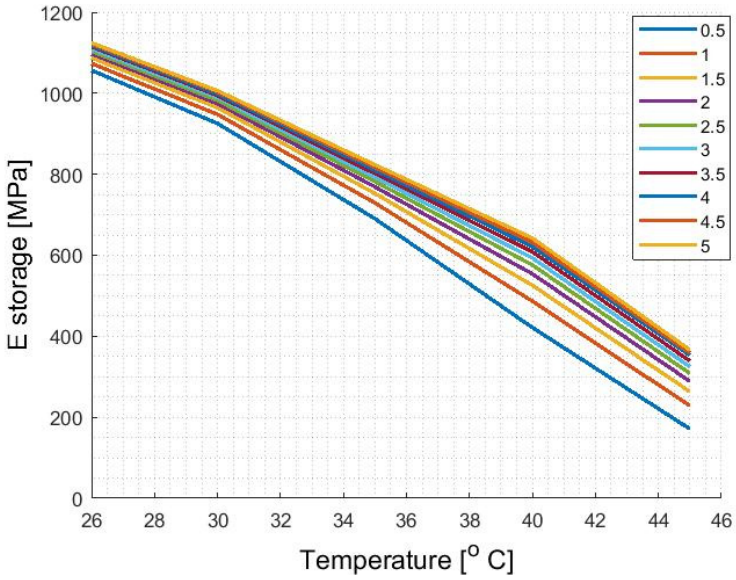
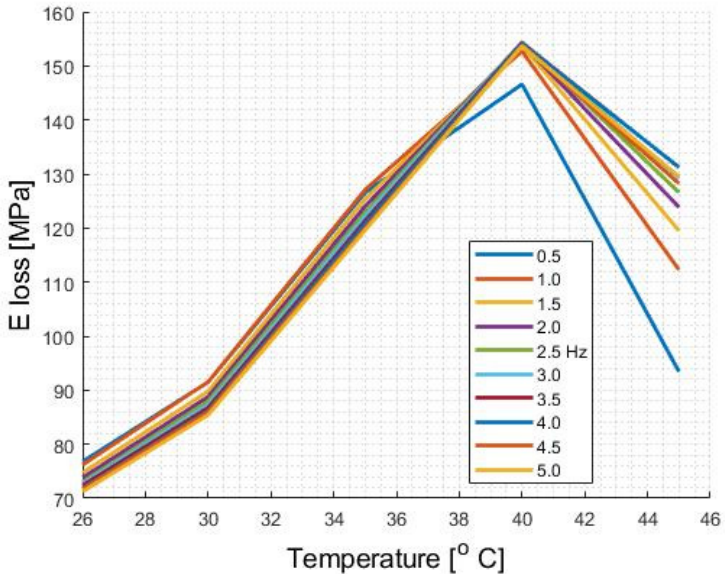


Fig. 5: Dynamic moduli and loss tangent as functions of frequency for different temperatures





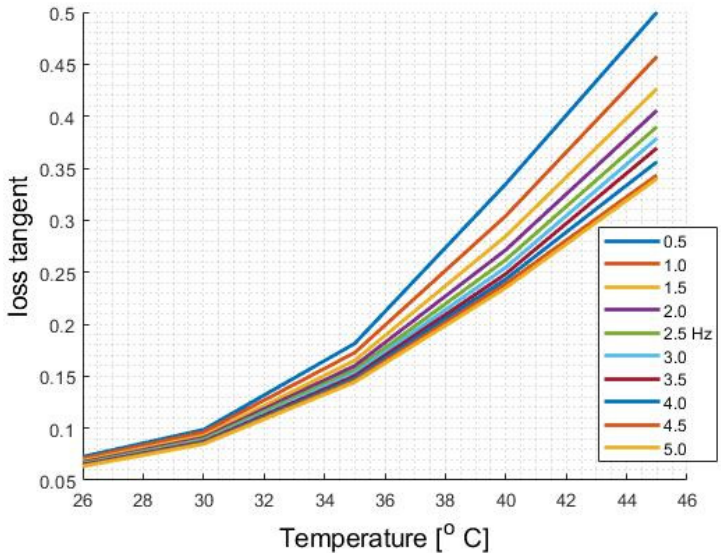


Fig. 6: Temperature dependence of dynamic moduli and loss tangent

The dynamic moduli and loss tangent as the functions of temperature and frequency are depicted in Fig. 5 and 6. It is seen that the storage modulus E' is rising with the rising frequency and decreases gradually with increasing temperature. The loss modulus E'' and loss tangent have the opposite tendency concerning frequency and they show the rising towards the glass transition temperature.

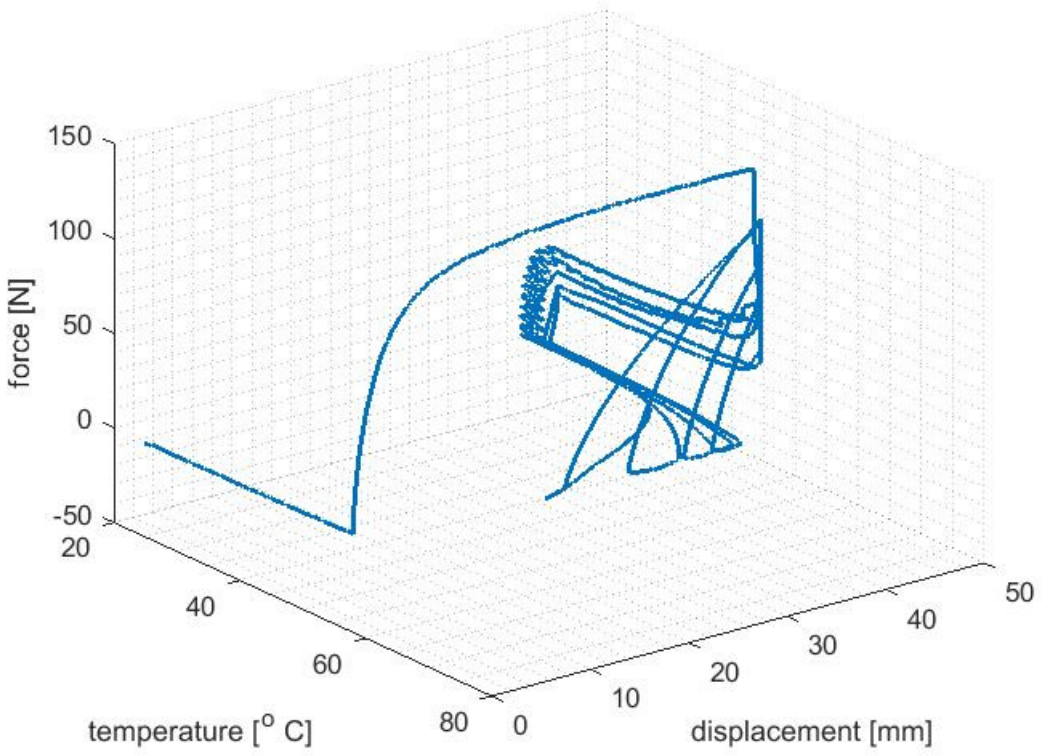


Fig. 7: Result of five cycles Programming - Shape Recovery with the programming temperature T_{max} = 57°C and cooling temperature T_{min} = 25°C

First thermo-mechanic cyclic tests Programming - Shape Recovery were carried out in this research. The result of one experiment is in Fig. 7. We can see the force relaxation at the maximum extension of the sample at the temperature T_{max}. There is also the decrease of the maximum force in subsequent cycles.

Conclusions

We present the first results of experimental research of the behaviour of the shape memory material - aromatic polyether-based thermoplastic polyurethane Estane® ETE 75DT3. The thermal properties of the shape memory polymer (SMP) were characterized by Differential Scanning Calorimetry (DSC). The material was investigated by means of the quasi-static tensile tests at the room temperature. The Dynamic Mechanical Analysis (DMA) was carried out at various frequencies and temperatures and the values of dynamical moduli and loss tangent as the functions of the frequency and temperature were determined. The shape memory effect was also studied in the course of the thermo-mechanical loading.

Acknowledgement

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