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PRESSURE SENSITIVITY OF THERMOPLASTIC POLYURETHANE

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Abstract. *Mechanical material properties of polymers may change significantly when they are exposed to high pressures and/or temperatures. The effect of hydrostatic pressure on shear relaxation modulus of three thermoplastic polyurethanes has been presented in this paper. The results show that chemically identical materials may have significantly different hydrostatic pressure sensitivity. At pressure of 300 MPa, mechanical properties of two materials change "only" for a factor of 10, while for the third material, mechanical properties change* 10^9 *times!*

Key words: *thermoplastic polyurethane, shear relaxation modulus, hydrostatic pressure, pressure sensitivity*

1. INTRODUCTION

Polymeric materials are becoming increasingly important in engineering applications where extreme loading conditions are present (high pressure and temperature). An example where polymers are exposed to such extreme conditions are pipelines for offshore deep-water oil excavation, where polymeric materials are used as insulating materials for pipes [1]. Another example, where polymeric materials are exposed to severe pressures is new generation damping elements [2] for noise and vibration reduction. Here we utilize hydrostatic pressure to match the frequency range where material exhibits its maximal energy absorption properties with the frequency range of noise and/or vibrations [2] we want to eliminate. In these applications, we need materials with properties very sensitive to pressure, and at the same time with large energy absorption capability.

While the effect of temperature on mechanical properties of polymeric materials is fairly well understood, much less is known about the effect of pressure. It is important to emphasize that pressure can have enormous effect on the viscoelastic response of polymeric materials

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[3]. At this point, it also needs to be noted that material time-dependent characterization under elevated hydrostatic pressure is very time consuming, and expensive [4].

The goal of this investigation was, therefore, to measure pressure sensitivity of three different thermoplastic polyurethanes in the pressure ranges from 0.1 to 300 MPa.

2. EFFECT OF PRESSURE ON MECHANICAL MATERIAL PROPERTIES

When we expose polymeric materials to high pressures, the mobility of polymeric chains is hindered. On the macro scale, this is exhibited through the extension of the material creep and relaxation time scales [4]. Hence, under hydrostatic pressure the viscosities and viscoelastic relaxation and retardation times of polymers increase.

Stress relaxation is the process, in which a polymer relaxes after application of a sudden deformation, i.e., torsional shear deformation. Whereas, for the case of shear creep a polymer has to be exposed to a sudden shear stress, which then initiates the creep process. Deformation or stress load should be applied at particular boundary conditions, i.e., temperature and pressure, so that the material response is measured at these equilibrium conditions. Relaxation and creep of polymers are slow processes and they may last over many decades in time, thus, experimentally it is almost impossible to measure a complete (‘long-term’) relaxation or creep curve. Therefore it is a common practice to determine the relaxation modulus or creep compliance within a certain range of time called the Experimental Window (EW). Once individual segments are measured at different temperatures and/or pressures, a master curve can be generated using time-temperature (t-T) or, equivalently, time-pressure (t-P) superposition principle (SP) [5]. Different segments determined at different temperatures and at constant pressure are shifted by factor Log a_T, and segments measured at different pressures and at constant temperature are shifted by factor Log a_P, so the corresponding master curves can be generated [3, 6]. In Fig. 1 this is demonstrated for the case of creep measurements at constant temperature and different constant pressures.

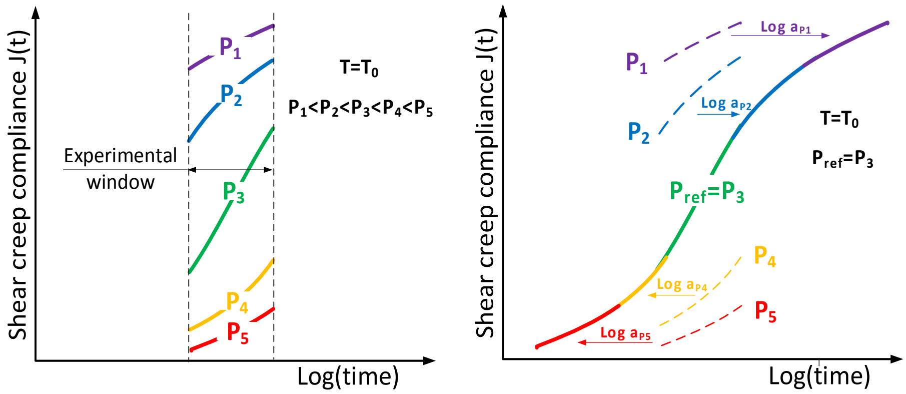

Fig. 1 Generation of creep mastercurve using t-P SP at constant temperature

Considering this, one may observe results at different reference temperatures or pressures, where master curve is appropriately shifted along the time axis. In the case of pressures, higher pressure shifts master curve to the longer times (maser curve is shifted to the right).

2. MATHERIALS AND METHODS

2.1 Sample preparation

For the research purpose, high-performance polyether-based thermoplastic polyurethane (TPU), used in new generation damping elements [2] and in underwater oil excavation [1], was chosen. All investigated materials were supplied by BASF. TPU is a thermoplastic elastomer and falls between rubbers and thermoplastics. It consists of block copolymerized alternating random-length hard and soft segments. TPU softens when heated and solidifies when cooled, which is exploited in polymer processing techniques such as extrusion and molding processes.

For the purpose of our investigation, three different TPU's were selected: 006 (75 Shore A) which is the softest material between selected TPU's, 051 (74 Shore D) which is the hardest material and 035 (95 Shore A) which is a material with intermediate hardness (figure 2).

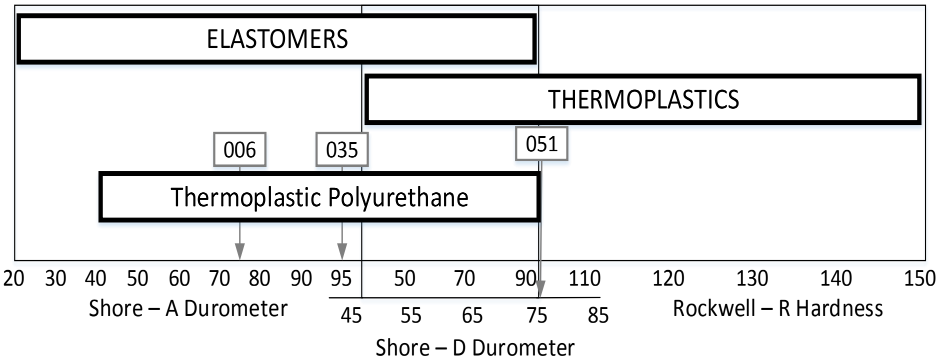

Fig. 2 Hardness for selected TPU's according to ASTM D-2240. Adopted by [7]

All three types of TPU were prepared by extrusion into a glass tube of a fixed diameter (6 or 11 mm), or via free fall in a water bath where the diameter could be altered between approximately 2.5 and 4 *mm*. After the materials were extruded, different samples were cut using a razor blade, finished with sand paper and the final dimensions were measured using a four-digit caliper. The samples were glued at both sides to metallic holders using two component epoxy glue.

2.2. Measuring principle

A unique apparatus, called CMS apparatus [4, 5, 8] was developed by the group of Center for Experimental Mechanics, Faculty of Mechanical Engineering, University of Ljubljana, to study the combined effects of temperature and hydrostatic pressure on mechanical behavior of polymers. The measuring system can measure volumetric and shear relaxation properties of solid polymer specimens simultaneously subjected to temperatures from -40°*C* to +120°*C* and pressures from atmospheric to 500 *MPa*.

CMS apparatus consists of four main parts: hydraulic system, thermal system, data acquisition system and measuring inserts. Hydraulic system includes hand pump for pressurizing silicone fluid to pressure vessel. In thermal system, a circulator and thermal bath is used to regulate temperature of specimen. In order to process and record the signals from measuring inserts, i.e., relaxometer and dilatometer, data acquisition system which constitutes of a carrier amplifier and computer is used. The CMS apparatus assembly is shown in figure 3.

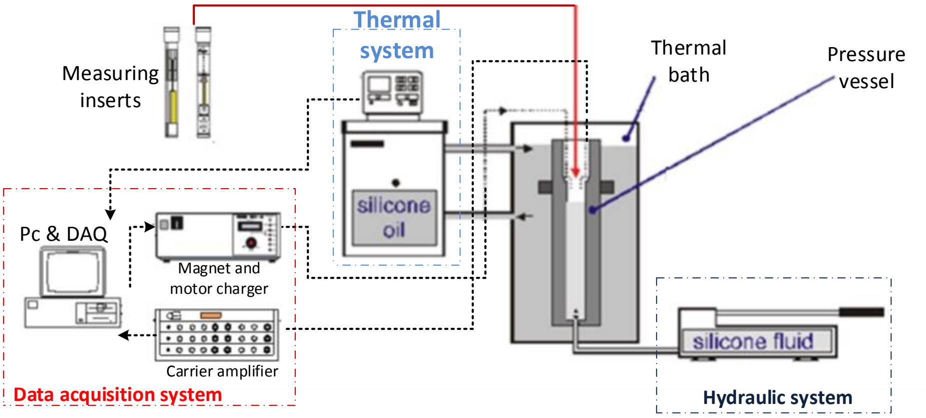

Fig. 3 Schematic representation of CMS apparatus [4, 8]

The CMS measures four physical quantities: temperature, $T(t)$, pressure, $P(t)$, specimen length, $L(t,T,P)$, and the decaying torque, $M(t,T,P)$, resulting from the initially applied torsional deformation, θ_0, on the sample. Using these quantities measured at constant or varying temperature and pressure, several other material functions can be calculated [4, 8]. In this particular case shear relaxation modulus $G(t)$ is of interest and is determined by measuring the decaying moment of a specimen exposed to selected constant temperature and pressure boundary conditions.

The shear relaxation modulus $G(t)$ is the ratio of the time-dependent shear stress $\tau(t)$ over a fixed shear strain γ_0:

$$G(t) = \frac{\tau(t)}{\gamma_0} \tag{1}$$

The shear stress of a material is determined by its geometry and its time-dependent internal resistance to an applied deformation. The internal resistance of a cylindrical specimen can be expressed in terms of a time-dependent moment $M(t)$ and the polar moment of area I_p:

$$\tau(t) = \frac{M(t)D_0}{2I_p} \tag{2}$$

Where D_0 is the specimen diameter and I_p is defined as:

$$I_p = \frac{\pi}{32} D_0^4 \tag{3}$$

For a cylindrical specimen of length L_0, the shear strain can be written in terms of the applied angular deformation θ_0 in radians:

$$\gamma_0 = \frac{D_0 \theta_0}{2L_0} \tag{4}$$

Rewriting these equations, results in the final expression for the shear relaxation modulus:

$$G(t,T,P) = \frac{32 L_0 M(t)}{\pi D_0^4 \theta_0} \tag{5}$$

2.3 Experiments

As mentioned before a set of shear relaxation tests was performed on three different types of TPU's at pressures 0.1, 50, 100, 150, 200, 250, 300 M*Pa* and at constant temperature 20°*C*. Measurements at each boundary condition and each material were repeated three times. Segments of shear relaxation were measured in experimental window of 1000 s. In order to erase material's thermo-mechanical history, annealing procedure was used, where the samples were heated to temperature of 90°*C* and left there for three hours. Following this rejuvenation stage, the samples were slowly cooled to 20°*C* with an average cooling rate of -15°C/min. After this, the experiments were conducted.

3. RESULTS AND DISCUSSION

As an example, segments of shear relaxation modulus of TPU 051 as a function of logarithmic time, measured at different pressures, are presented in Figure 4. Using Close Form Shifting (CFS) algorithm [5], master curve of selected material was constructed at reference conditions of T_{ref}=20°*C*.

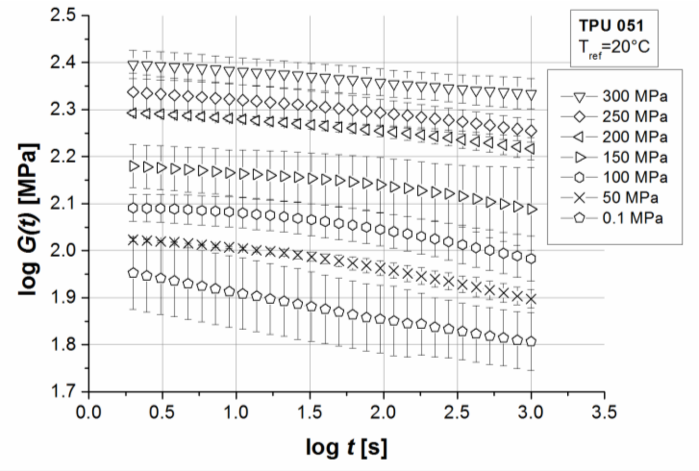

Fig. 4 Shear relaxation modulus for material TPU 051

In figure 5 and figure 6, master curves of shear relaxation modulus as a function of logarithmic time for all three materials, 051, 006 and 035 are shown. Figure 5 shows the shear relaxation of materials at "room conditions", i.e, at $T_{ref}=20°C$ and $P_{ref}=0.1MPa$, while figure 6 shows shear relaxation at $T_{ref}=20°C$ and $P_{ref}=300MPa$.

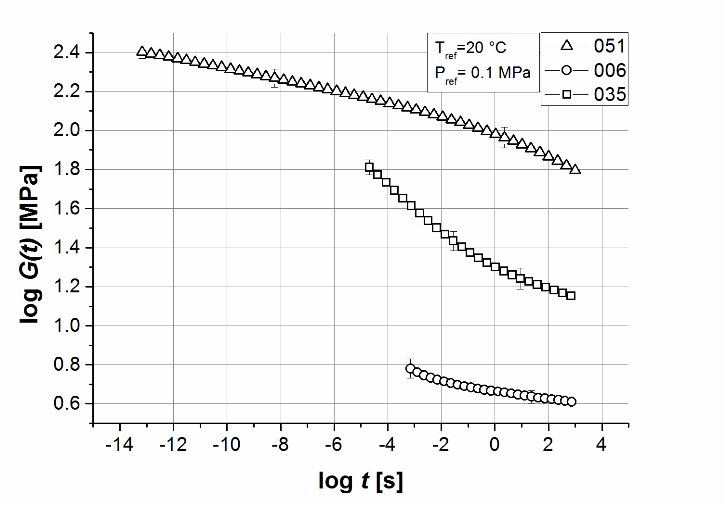

Fig. 5 Master curves for materials 051, 006 and 035 at T_{ref}=20°C and P_{ref}=0.1 MPa;

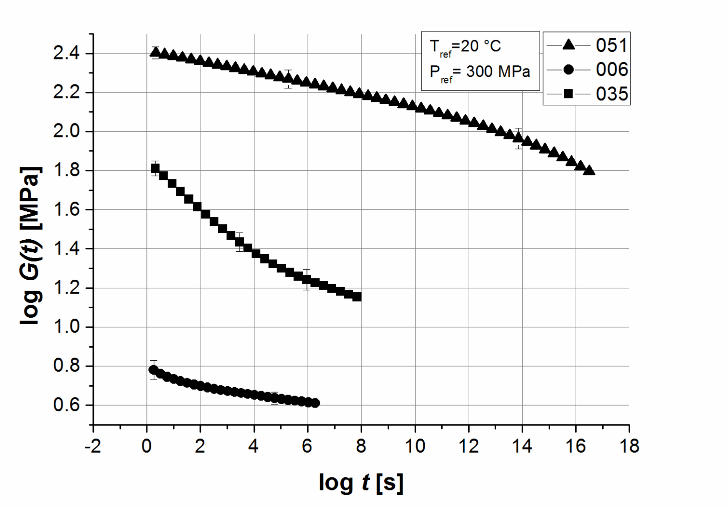

Fig. 6 Master curves for materials 051, 006 and 035 at T_{ref}=20°C and P_{ref}=300 MPa.

We clearly see that hydrostatic pressure has significantly different effect on the three investigated materials. The difference is seen even clearer when we plot horizontal shift factors belonging to each of the three materials as a function of pressure, shown in Fig. 7.

The diagram shows the way the relaxation process slows down as the hydrostatic pressure to which material is exposed is being increased. We clearly see that pressure sensitivity of the material 051 is several orders larger than that of the other two materials.

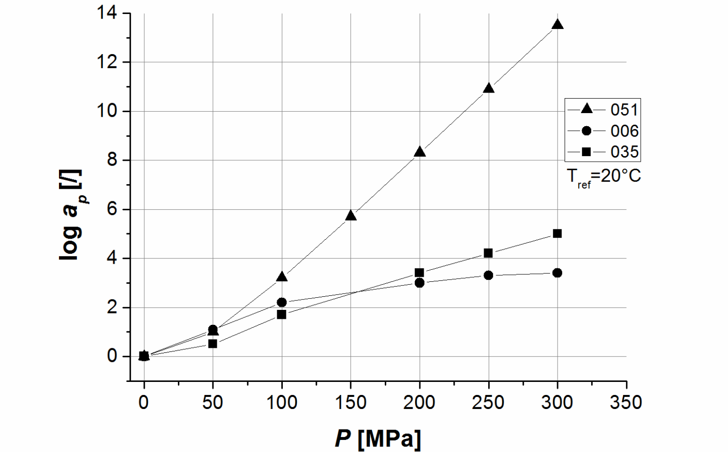

Fig. 7 Shift factors a_P for TPU 006, 035 and 051

4. CONCLUSION

Pressure can have extremely large effect on the viscoelastic response of polymeric materials. In this study we have shown that polymeric materials belonging to the same group (i.e., have the same chemical structure) can have several orders of magnitude and different sensitivity to pressure.

Pressure sensitivity of all three investigated materials is at lower end of measured pressures (100 *MPa*) similar for all materials, whereas above 100 *MPa* the difference starts to increase. At the highest measured pressure (300 *MPa*), pressure sensitivity of 035 and 006 materials proves to be very similar, the difference is “only 10 times”. However, at the same time, time-dependency in terms of shear relaxation modulus of 051 material at 300 *MPa* changes 10^9 times (!) more then time-dependency of other two materials.

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OSETLJIVOST TERMOPLASTIČNOG POLIURETANA NA PRITISAK

Mehaničke osobine polimernih materijala se mogu značajno promeniti kada su izloženi visokim pritiscima i/ili temperaturama. U okviru ovog rada je predstavljen uticaj hidrostatičkog pritiska na modul smicaja pri relaksaciji za tri termoplastična poliuretana. Rezultati pokazuju da hemijski identični materijali imaju znatno različitu osetljivost na hidrostatički pritisak. Na pritisku od 300 MPa , mehaničke osobine dva materijala se menjaju "samo" za faktor 10, dok se za treći material mehaničke osobine menjaju 10^9 *puta.*

Ključne reči: *termoplastični poliuretan, modul smicanja pri relaksaciji, hidrostatički pritisak, osetljivost na Pritisa*