APPARATUS FOR TIME-DEPENDENT MEASUREMENTS OF MECHANICAL PROPERTIES UNDER HYDROSTATIC PRESSURE

NAPRAVA ZA ČASOVNO-ODVISNE MERITVE MEHANSKIH LASTNOSTI POD HIDROSTATIČNIM TLAKOM

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Although high hydrostatic pressures commonly appear in demanding structural applications and during several manufacturing processes, there is little information available about their effect on material properties. This is because, world-wide, very few instruments exist that can measure the effects of hydrostatic pressure on mechanical properties. Fillers, Moonan, and Tschoegl built such on instrument several years ago. We have improved and upgraded this apparatus with the intention of researching the influence of pressure and temperature on the mechanical properties of time dependent polymeric materials. In this study, special emphasis is put on the Filles-Moonan-Tschoegl (FMT) [1] model, which can describe the combined effect of temperature and pressure. The model is based on the time, temperature, and pressure superposition principle, for which parameters are obtained using the presented apparatus. As an example we present measurements on PVAc for bulk creep compliance and shear relaxation.

Key words: polymers, pressure, relaxation, creep, superposition

Čeprav se visok hidrostatični tlak pojavlja v zahtevnih konstrukcijskih uporabah in pri več predelovalnih procesih, je še vedno zelo malo znanega o vplivu tlaka na lastnosti materialov. To je zaradi pomanjkanja naprav za meritve vpliva hidrostatičnega tlaka v svetovnem merilu. Fillers, Moonan in Tschoegl so pred leti zgradili takšno napravo. To napravo smo sedaj prenovili in jo izboljšali z namenom, da bi z njo merili vpliv tlaka na časovno-odvisne mehanske lastnosti polimernih materialov. V tej študiji je poseben poudarek na Filles-Moonan-Tschoegl (FMT) [1] modelu, ki lahko popisuje kombiniran učinek temperature in tlaka. Model sloni na časovno-temperaturno-tlačni superpoziciji za katerega parametre dobimo z meritvami na predstavljeni napravi. Kot primer navajamo rezultate meritev volumskega lezenja in strižne relaksacije.

Ključne besede: polimeri, tlak, relaksacija, lezenje, superpozicija

1 THE APPARATUS

The apparatus presented in this paper (**Figure 1**) consists of a beryllium-copper pressure vessel located in a thermally controlled silicon bath with two measurement inserts, designed to fit in the pressure vessel. The first insert is the dilatometer, which provides us with information on polymer's bulk behavior. The second is the insert for shear relaxation measurements, which provides data on the polymer's time dependent shear behavior. Either of the two inserts can be connected to the data acquisition system (**Figure 1**) when in use.
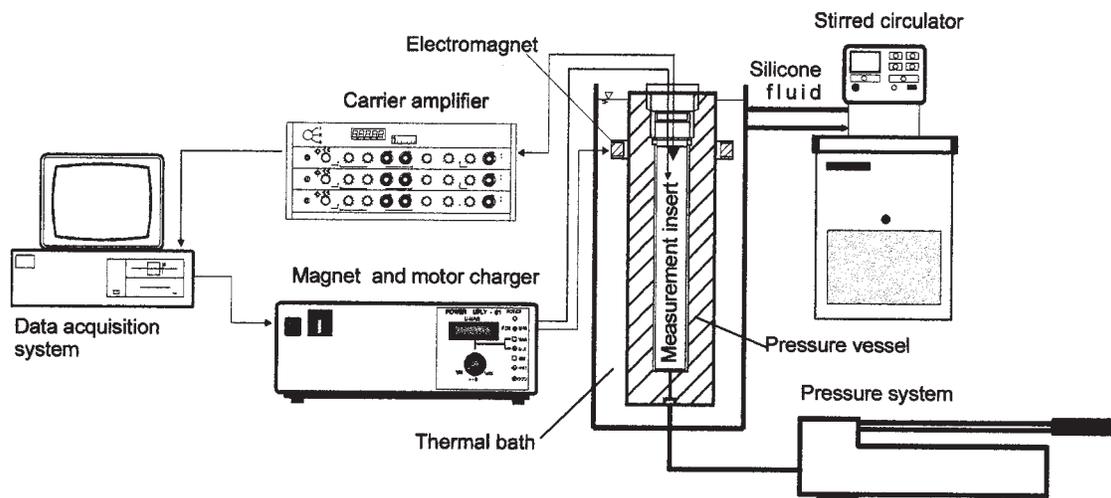

Figure 1: Schematic apparatus layout
Slika 1: Shematični prikaz aparata

1.1 Pressurizing system and thermal bath

The pressurizing system is built around a system of cylinders and handpumps that provide pressures up to 620 MPa. The silicone fluid used on the high-pressure side is General-Electric SF 96 5 with a molecular weight of approximately 500. Such a fluid has sufficient molecular weight to prevent significant penetration into the polymeric specimens while at the same time sufficiently low viscosity, to allow motion of the measurement insert's mechanical components at increased pressures and/or lowered temperatures. Pressure on the high-pressure side is determined by an Autoclave-Engineers cell, connected to the data acquisition system. As a backup, a classical Burdon-tube manometer provides information about the pressure on the lower-pressure side.

The temperature of the experiment, conducted in the pressure vessel, is controlled by a stirred thermal bath in which the pressure vessel is fully immersed. The bath liquid (Haake SIL 180) is forced into convection by an external circulator. The circulator is equipped with a cooler and heater, which allow testing conditions ranging from -30 to +120°C. The circulator provides temperature regulation to ±0.01°C in the bath.

1.2 Insert for volume measurements

The Dilatometer (**Figure 2, left**) measures various bulk properties, such as the P-v-T relations, bulk creep compliance, *B(t)*, equilibrium bulk modulus, K, and the coefficient of thermal expansivity, β, by monitoring the specimen's volume change, after pressure and temperature conditions have been applied. The change in volume is estimated by measuring the specimen's change in length. This estimate can be considered accurate if the change is small (up to a few percent) and the material isotropic. The built-in LVTD monitors changes in length

of the specimen and sends data to the data acquisition system. The LVDT has been modified with holes in its steel body which allows equalization of the hydrostatic pressure.

The dilatometer has been calibrated over a range of pressures and temperatures against a steel bar with known compressibility and thermal expansivity.

The measurement pod is suitable for specimens with diameters up to 16 mm and heights up to 50 mm. Testing conditions range from -55°C to +150°C and up to 600 MPa of hydrostatic pressure. Measurements are accurate to within 0.1 percent of specimen's specific volume and allow a measurement resolution of better than 0.0001 cm^3/g.

1.3 Insert for shear relaxation measurements

The Relaxometer (**Figure 2, right**) measures the shear relaxation modulus, G(t), by applying a constant torsional strain to a cylindrical specimen, in which the induced moment is monitored over time.

The two main parts of the insert are the Loading Device and the Load Cell. The Loading Device applies a torsional strain by twisting the specimen for a few degrees in less than 0.01 seconds. This time interval is short enough for the load to be considered a step function, which according to linear viscoelastic theory, is a theoretical requirement[2].

The induced moment is then measured by the Load Cell, which is attached to a slider to compensate for the specimen's length changes resulting from various temperature and pressure conditions. After the shear relaxation measurement is complete, the loading device brings the specimen to its original, undeformed state, while ensuring the pressure vessel remains fully pressurized.

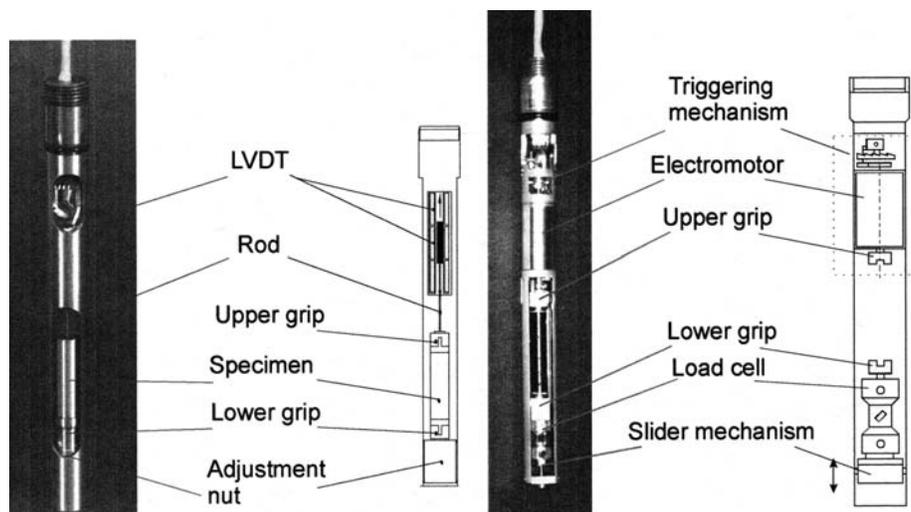The Relaxometer is limited to specimens with diameters from 2.5 mm to 12 mm. Its allowed testing

Figure 2: Insert for volume and shear relaxation measurements
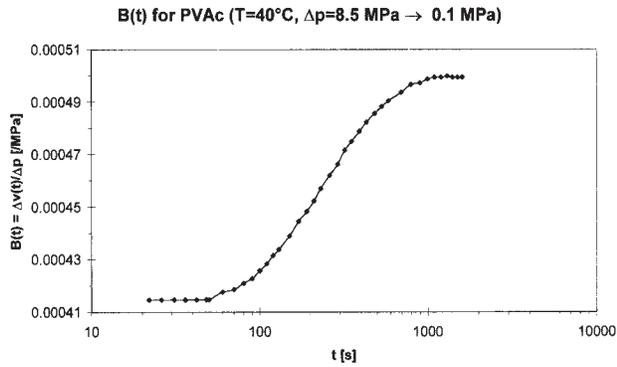**Slika 2:** Vložka za meritve volumna in strižne relaksacije

Figure 3: Bulk Creep Compliance B(T) for PVAc at 40C subjected to a pressure drop from 8.5 MPa to 0.1 MPa
Slika 3: Volumsko lezenje B(T) za PVAc pri 40C izpostavljen tlačnemu padcu od 8.5 MPa do 0.1 MPa

Figure 4: Shear modulus for PVAc at various pressures
Slika 4: Strižni modul za PVAc pri različnih tlakih

conditions range from -75°C to +105°C and pressures up to 600 MPa. The relaxometer can successfully measure a shear modulus ranging from 0.01 MPa to 10000 MPa, accurate to within ±5% of the measured value.

2 EXAMPLE MEASUREMENTS WITH PVAc

2.1 Volume Measurements

Using the dilatometer, which measures the specimen's volumetric response to a given pressure or temperature stimulus, one can measure several bulk behavior properties. These are bulk creep compliance, equilibrium bulk modulus, specific volume and thermal expansion dependence on pressure (**Figure 3**).

Bulk creep compliance B(t) determines the specific volume response $\Delta v(t)$ to a unit step function h(t) in hydrostatic pressure P according to the following equation[3]:

$$B(t) = -\frac{\Delta v(t)}{v}\frac{1}{h(t)P} \qquad (1).$$

The dilatometer measures B(t) by monitoring the specimen's volume change over time after a pressure drop is applied, while the temperature is maintained at a constant value. The plot in shows $B(t)$ for a PVAc (T_g=30C) specimen, which after achieving steady state at approximately 10 MPa, is suddenly brought to atmospheric pressure (0.1 MPa). The data indicates how the volume change lags behind the pressure drop. Only after about 45 minutes, does the specimen's volume reach steady state.

2.2 Shear Relaxation Measurements

The relaxometer gives the shear relaxation modulus $G(t)$ for $t>0$, by measuring the decaying moment $M(t)$, after a sudden shear strain per unit length $\vartheta_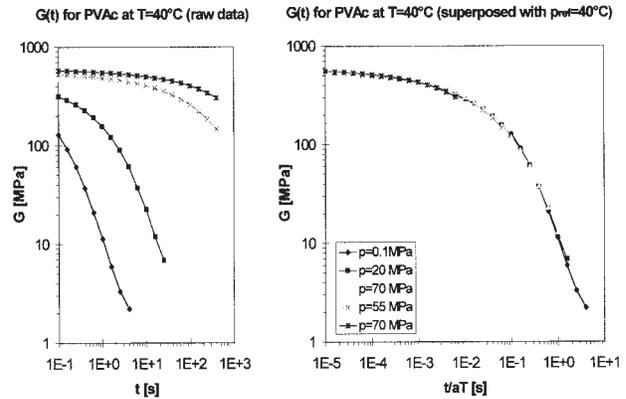0$ has been applied to a cylindrical specimen at time t=0. If $G(t)$ measurements take place at different temperatures with a constant pressure, the WLF [2] equation can be applied to perform time-temperature superposition. On the other hand, if $G(t)$ is taken at different pressures while maintaining a constant temperature, the FMT model is used.

The relaxometer also measures $G(t)$ for various pressures while maintaining the specimen at a constant temperature. The measurements shown in started at atmospheric pressure and continued with ascending pressure order. The specimen was held at each pressure for 2.5 hours before $G(t)$ was measured (**Figure 4**).

3 CONCLUSION

This paper presents apparatus used to research the effects of pressure on the mechanical properties of polymers. Pressure is an important factor in practically all processes of polymer treatment. Some more demanding applications, such as the construction of submersible vessels, also requires good knowledge of polymers under high hydrostatic pressures.

The presented apparatus enables research on the influence of pressure within the domain of the linear theory of viscoelasticity, yet it enables investigation of phenomena in the nonlinear thermo-viscoelastic domain. Physical ageing or so-called structural relaxation is one such phenomena.

4 REFERENCES

[1] Fillers, R.W. and Tschoegl, N.W., 'The Effect of Pressure on the Mechanical Properties of Polymers', *Transaction of the Society of Rheology*, 21 **(1977)** 51-100

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[3] Tschoegl, N.W., The Phenomenological Theory of Linear Viscoelastic Behavior, Springer-Verlag, Berlin, **1989**