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Test Method

On necessary precautions when measuring solid polymer linear viscoelasticity with dynamic analysis in torsion

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ABSTRACT

Solid polymer linear viscoelasticity in shear is often characterized by applying torsion and using the Saint-Venant solution when rectangular prismatic specimens are considered. It is shown that experimental dynamic torsion tests can show a dependency of the storage modulus and damping factor on the dimensions of the rectangular prismatic specimen when linear temperature ramps are applied. While the discrepancy of damping factor is explained by temperature heterogeneities and can be corrected easily by applying temperature steps, the inconsistency of storage modulus is due to an invalid application of the Saint-Venant solution. Finite element simulations allowed definition of the sample dimensions for which the Saint-Venant solution provides a good approximation, and a coefficient is given to correct the results obtained with commercial instruments when other sample dimensions are used.

1. Introduction

The linear viscoelastic behavior of solid polymers is often estimated from uniaxial tension or torsion dynamic mechanical tests. While uniaxial tension is appropriate to obtain the storage and loss Young's moduli, torsion allows measuring the storage and loss shear moduli. When dealing with dynamic mechanical thermal analysers such as the Anton Paar MCR series torsion rheometers tests are often run on rectangular specimens and the storage modulus and damping factor are obtained from the Saint-Venant solution [1]. The rectangular shape is often preferred to the cylinder shape despite the fact that clamping renders the Saint-Venant solution inappropriate. Dessi et al. [2] reported a storage modulus dependency on the specimen length/width aspect ratio measured on a styrene butadiene rubber in its rubbery state. They proposed a correction coefficient to the Saint-Venant solution when dealing with rubbers (Poisson's ratio equal to 0.5), a fixed width/thickness ratio equal to 4 and a length/width ratio ranging from 0.25 to 1.85. Unfortunately, these aspect ratios do not cover the entire range of specimen dimensions recommended by instrument makers. The Anton Paar documentation recommends a length (L) x width (W) x thickness (T) product of $40 \times 10 \times 1$ mm^3. The TA instruments Ares-G2 documentation mentions that sample length and width should be 40 and 12 mm respectively, while the specimen thickness should range between 0.3 and 6 mm. Finally, the international standard ISO 4664-2 [3], designed to determine the dynamic properties of rubbers with torsion pendulum methods at low frequencies, recommends using specimens of 1 mm thickness, with a preferred width value of 10 mm and a length between 40 and 120 mm chosen to fit the clamping device. In the latter respect, note for instance that the thermal chamber CTD 600 from Anton Paar limits the specimen length to 50 mm.

In the present contribution, we expose the significant impact of the sample dimensions when characterizing the linear viscoelastic response of a solid amorphous polymer with torsion dynamic tests applied to a rectangular prismatic sample. For this purpose, two specimens with different aspect ratios were submitted to a sinusoidal torsion with constant amplitude and frequency, at various temperatures applied either with a linear ramp or stepwise in a rheometer. In order to better understand the experimental results, finite element simulations reproducing the experimental torsion tests were run. These simulations allow definition of the suitable geometries to apply the Saint-Venant solution, which is used by commercial instruments. They also allow proposal of a correction coefficient when other geometries are used.

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2. Impact of sample rectangular dimensions: experimental evidence

2.1. Material and experiment

In order to run torsion tests on rectangular geometries, plates of an amorphous polymer network were prepared in the laboratory. The material was a basic acrylate network obtained by copolymerization of benzyl methacrylate (BMA) with poly (ethylene glycol) dimethacrylate (PEGDMA) of molar weight 550 g/mol used as crosslinking agent. Products were used as received from Sigma Aldrich in proportion 90% molar mass of BMA 10% molar mass of PEGDMA. The mix was cured in a UVP ultraviolet chamber CL-1000 for 50 min between glass plates in order to obtain acrylate plates of 1 mm thickness. Rectangular specimens of either 12 or 5 mm width were punched from the plates. Finally, once set in the grips, two geometries of $46 \times 5 \times 1$ and $20 \times 12 \times 1$ mm^3 were tested.

The material viscoelasticity was measured with a MCR502 rheometer from Anton Paar. During the dynamic mechanical analysis (DMA) tests, a sinusoidal deflection angle $\theta = \theta_0 \sin(2\pi ft)$ is applied with a small angle amplitude θ_0 at a given frequency f. Due to the material linear viscoelastic behavior at low strain, the resulting torque is of the form $M = M_0 \sin(2\pi ft + \delta)$, with $\tan\delta$ characterizing the material damping factor in shear obtained directly from the phase difference between the applied deflection and the measured torque. If the Saint-Venant solution for the free-end torsion of prisms is applied, the material storage shear modulus is calculated from the measured torque as:

$$G\prime = \frac{3L}{\theta_0 W T^3} \frac{M_0 \cos\delta}{1 - 0.630\, T/W} \quad (1)$$

for width/thickness (W/T) ratios of at least 3 [4].

It is usual to submit amorphous polymers to a temperature sweep at given frequency and strain amplitude, in order to determine the glass transition temperature or the range of temperature that enhances the material viscoelasticity. Therefore, a temperature sweep was applied to the samples.

2.2. Linear temperature heating ramp

The rectangular samples were submitted to torsion oscillations at 1 Hz and 0.1% strain amplitude during linear heating ramps at 1 °C/min. Note that it was verified that the material response was linear at 0.1% strain. Fig. 1 presents the storage shear modulus $G\prime$ and the damping factor $\tan\delta$ calculated from the recorded torque M using the Saint-Venant solution (Eq. (1)), with respect to temperature. These values are very similar to those read in the report data sheet from the Anton Paar rheometer except for some discrepancies noticed at high temperatures because the Anton Paar software does not account for the variations of sample length (gap between the two grips) as it should. Indeed, due to the constant axial force applied to avoid sample buckling, the gap between grips increases with temperature. Note that it is recommended to keep the axial force as low as possible to avoid large gap changes that may occur suddenly, as we observed when the normal force was set to -1N (the minus sign stands for tension for Anton Paar reference).

Fig. 1 shows a storage modulus and a damping factor which depend on the sample geometry, and this raises the question of which (if any) data represent the actual behavior of the material. Since the long sample stands from the bottom to the top of the thermal chamber and the short sample is relatively wide, it is not guaranteed that any sample is heated homogeneously during the heating ramp. Therefore, the same oscillatory loading was applied while the temperature was set stepwise, allowing temperature to homogenize throughout the samples during long steps.

2.3. Stepwise temperature change

For these tests, once a target temperature was reached, the samples were kept for five minutes at constant temperature before applying the torsion at 1 Hz and 0.1% strain. Fig. 2 displays the storage shear modulus and the damping factor obtained for both geometries with respect to temperature. Unlike in Fig. 1, the damping factors now coincide. Note that the $\tan\delta$ curve shown in Fig. 2 does not superpose with any of the curves displayed in Fig. 1, which have broader bell shapes. The latter result shows that a linear temperature ramp, even as low as 1 °C/min and with relatively thin samples (1 mm), may induce a non homogeneous temperature that leads to inaccurate damping factors. As a consequence, temperature should be applied stepwise to reach an equilibrium before attempting any measure. The storage modulus values remain specimen shape dependent in Fig. 2, with the shorter and wider sample evidencing a significantly larger storage modulus. In order to understand this result, finite element simulations reproducing the torsion test were run. The material viscoelastic behavior, defined by a generalized Maxwell model combined the WLF equation [5] for time-temperature superposition, was fitted

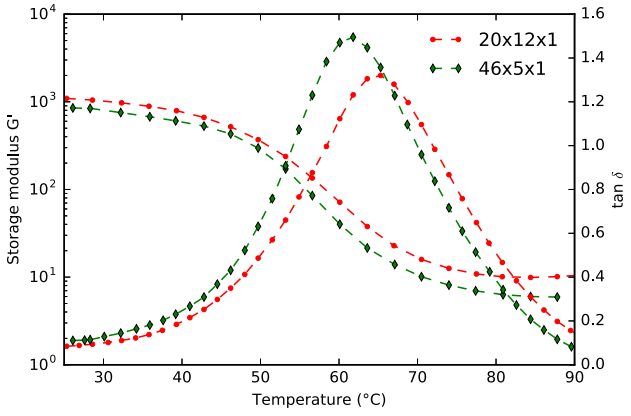

Fig. 1. Storage modulus and damping factor measured from torsion oscillations at 1 Hz and 0.1% strain during a linear temperature ramp at 1 °C/min for samples of *LxWxT* geometries.

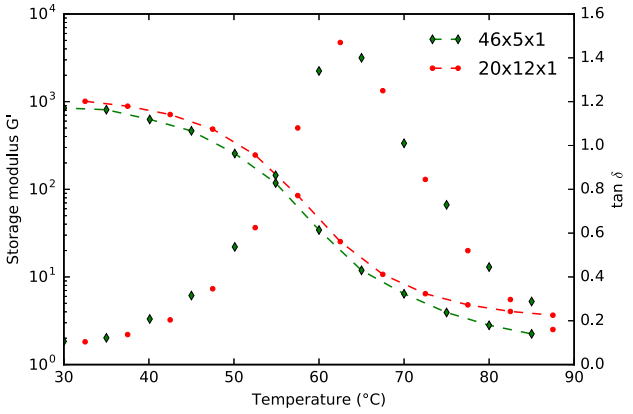

Fig. 2. Storage modulus and damping factor measured at various equilibrated temperature steps at 1 Hz and 0.1% strain for samples of *LxWxT* geometries.