# Planar Elongation Measurements on Soft Elastomers

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## ABSTRACT

A new fixture to the filament stretch rheometer (FSR) has been developed to measure planar elongation of soft polymeric networks. To validate this new technique, soft polymeric networks of poly(propylene oxide) were investigated during deformation.

## INTRODUCTION

Polymer networks are applied in many applications ranging from hard and brittle solid rubbers to soft and almost liquid gels. The area of soft polymer networks has obtained increasing attention due to the use of the gel-like materials as e.g. matrices for drug-delivery systems and implants[1]. Soft polymer networks are from a physical point of view very interesting materials since they possess properties of both viscous and elastic character, and the dominating behaviour depends on the applied time scale. However, soft polymer networks close to the critical gel condition are very difficult to handle and experiments have to be carefully designed in order to avoid destruction of the material. Melts can usually be measured repeatedly if allowed enough time to equilibrate while soft networks can easily be irreversibly destroyed due to the breakage of polymer chains. Soft networks can be regarded as imperfect networks where the completion of the crosslinking reaction is either hindered by stoichiometry (i.e. an excess of one of the components) or inhibition of the crosslinking reaction[2].

The aim of this work is to construct an apparatus that can measure planar elongation stresses of soft polymeric networks, without the application of rotary clamps[3]. The reason for this is the sticky nature of the samples, which seem inconvenient for this type of geometry. Planar elongational measurements on relatively soft silicone networks have been performed by Wang and Mark[4] and Urayama[5] by deforming a thin film fixed by clamps. These clamps will keep one dimension fixed during deformation. This is, however, a measurement which is very hard to perform due to the sticky nature of the samples and because it is hard to control the deformation in two directions only. A new fixture has been designed as an add-on to the Filament Stretch Rheometer (FSR)[6]. The concept for the test method is motivated by the work of Laun and Schuch[7], who introduced an apparatus for measuring planar elongation viscosities by drawing of a tube-like sample. In their measurements the perimeter of the sample is kept constant by pumping oil from a syringe into the core of the tube, while the outer pressure is controlled by a surrounding oil bath. The work done by Laun and Schuch will be simplified here such that no surrounding media is used, nor is the diameter fixed by pumping oil into the cylinder. Details about

the FSR used can be found in the work of Bach et al.[8]

The focus in this study is to evaluate the performance of this new test fixture. This is done by particle tracking as well as imaging the deviation from an ideal cylinder extension.

## EXPERIMENTAL SECTION

A draft of the test fixture is shown in Fig. 1.

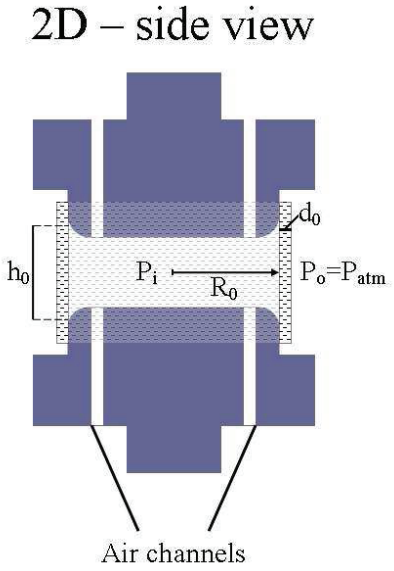


Figure 1. Draft of the new test fixture. The pressure is kept constant due to the holes in both plates. The upper plate is moved with the specified velocity profile and the initial thickness of the sample is measured at the mid-plane (indicated by $R_0$). The initial sample thickness is denoted $d_0$, and the initial plate-plate separation is denoted $h_0$.

A thin sample strip, of initial thickness, $d_0$, height $h_0$ and length $L_0$ is wrapped around the two disks to form a hollow cylinder with an inner radius of $R_0$. The length $L_0$ of the sample is slightly larger (approx. 7%) than the perimeter ($2\pi R_0$). This is to ensure an overlap where the two sample ends meet so the cylinder is properly sealed. The fixture is built to measure elongational stresses on self adhesive materials, and in most cases no extra clamps are needed to hold the sample strip in place. There are two air channels in both disks to allow airflow into the cylinder to equalize the inner and outer pressure. During an experiment the disks are pulled apart by moving the upper disk with a specified velocity profile. In the realization of steady planar elongation, the perimeter should remain constant and the cross-sectional area must decrease exponentially as $A(t) = A_0 \exp(-\dot{\varepsilon} t)$ where $A_0 = d_0 L_0$ is the initial cross-sectional area and $\dot{\varepsilon}$ the constant strain rate. An evaluation of the actual decrease in the cross-sectional area is based on digital imaging. Here particles placed on the sample surface are traced over time and from this it is possible to determine the local Hencky strain $\ln[l(t)/l_0]$, where $l_0$ is the initial distance in the axial direction between two particles and $l(t)$ is the axial distance at time $t$. In addition the mid-plane outer diameter, $D(t)$, will also be measured and compared to theoretical expectations. The aspect ratios, $\Lambda_1 = h_0 / d_0$, and $\Lambda_2 = R_0 / h_0$, are dimensionless geometrical parameters, which will be used as adjustable parameters in the evaluation of the test method. The values of the applied geometrical parameters can be seen in Table 1.

Table 1. The geometrical parameters applied in the four experiments. $\Lambda_1 = h_0 / d_0$, and $\Lambda_2 = R_0 / h_0$.

| | **TEST 1** | **TEST 2** | **TEST 3** | **TEST 4** |
|---|---|---|---|---|
| $\Lambda_1$ | 4.81 | 9.25 | 26.8 | 53.6 |
| $\Lambda_2$ | 7.34 | 3.83 | 7.34 | 3.83 |

A vinyl-terminated linear poly(propylene oxide) (PPO) is cross-linked with a silyl-terminated *f*-functional cross-linker with $f = 5$. A test sample is prepared such that it will form a gel, i.e. the degree of cross-linking, $r$, defined as the ratio of silane to vinyl groups, $r$ = [silane]/[vinyl], is larger than the lower critical degree of cross-linking[9,10] given by:

$$r > r_c = \frac{1}{f-1} \qquad (1)$$

In order to have a sample that is both very sticky but also coherent enough to handle when it is being applied on the fixture, a value of $r$ =0.6 is chosen.

The sample is prepared in a static mixer to avoid air-bubbles in the films. It is hereafter pressed in desired thicknesses in a 100°C hot-press between two sheets of silicone release liner. The sample is then cured at 100°C for one hour to make sure that it is fully reacted before further analysis Particle tracking is used to determine the local strain rate $\dot{\varepsilon}^*$ on the sample surface. If the deformation is not planar, $\dot{\varepsilon}^*$ will deviate from the imposed strain rate $\dot{\varepsilon}$. Hence the distinguishing feature of elongational flow, that neighbouring fluid elements move relative to each other at an exponential rate, is used. If $\dot{\varepsilon}^* = \dot{\varepsilon}$ then the following is valid[4]:

$$\frac{l(t)}{l_0} = \frac{h(t)}{h} = \exp\left(\dot{\varepsilon} \cdot t\right) \tag{2}$$

$h(t)$ is the plate distance at time $t$, while the distance between two neighbouring particles at time $t$ is denoted $l(t)$.

THEORY

Planar elongation is a special type of shear free deformation where the velocity field is given by following:

$$\begin{aligned} v_x &= -\frac{1}{2}\dot{\varepsilon}\left(1+b\right)x \\ v_y &= -\frac{1}{2}\dot{\varepsilon}\left(1-b\right)y \\ v_z &= \dot{\varepsilon} z \end{aligned} \tag{3}$$

where $b$=1 for planar elongation, and thus the velocity in the y direction $v_y = 0$. Hence the fluid elements will only move in the $x$ and $z$ directions. The deformation is illustrated in Fig. 2 where the height and thickness of the sample change while the length is fixed.

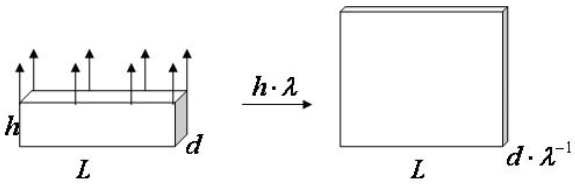


Figure 2. Illustration of planar elongation. Only the height and thickness of the sample changes while the length remains fixed.

In our case (Fig. 1), we have a tubular shaped sample, which ideally deforms in the directions of thickness ($d$) and length ($h$) only but keeps a constant sample diameter ($2R_0$).

RESULTS

The snapshots given in Fig. 3 are from test 3 at 0, 1, 1.5 and 2 Hencky strain. From this little series of pictures it is possible to see how the diameter changes with time, and it is seen that in this case it barely changes. Red particles are placed on the sample surface and the distance between them will be examined over time.

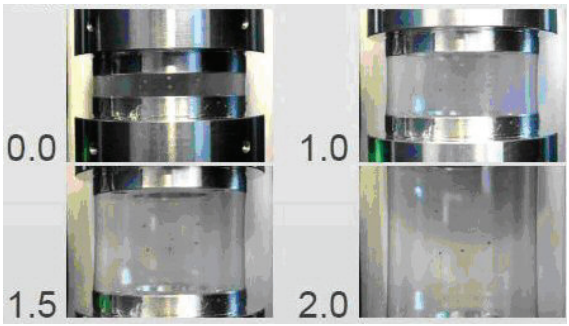


Figure 3. Snapshots of a planar elongation experiment. The snapshots are taken at 0, 1, 1.5 and 2 Hencky strain.

The results obtained from test 1 and 3 are shown in Figs. 4 and 5. It is seen that as $\Lambda_1$ increases the local strain approaches the imposed one. The results for test 2 and 4 show a similar trend with respect to $\Lambda_1$. It has now been proved how to obtain a local strain rate that is equal to the imposed one; however it is also important to check whether the cylinder diameter remains constant throughout an experiment. This is tested by changing $\Lambda_2$, which also have an

influence on the deformation. It is therefore important not to naively increase $\Lambda_1$ since it might change $\Lambda_2$ in a bad way as well.

In Fig. 6 it is shown how the cylinder diameter changes over time given as a relative measure to the initial outer diameter of the sample. It is seen that there is a significant difference from test to test. It is especially seen that by increasing $\Lambda_1$ in such a way that $\Lambda_2$ decreases the diameter will change more compared to the initial outer diameter, which is the fixture diameter plus two times the sample thickness.

Comparing the results obtained from the four samples shows that test 3 gives the best replication of planar elongation because the local strain rate is equal to the imposed strain rate and because the diameter decreases with approximately 3 % only which is negligible.

This is a very promising result since this way of measuring planar elongation is very simple compared to traditional methods and still very reliable results can be obtained without the application of rotary clamps. Both measurements, i.e. particle tracking and simple measurements of the sample diameter, agree on the ideal combination of the geometrical parameters which furthermore strengthens the measurements.

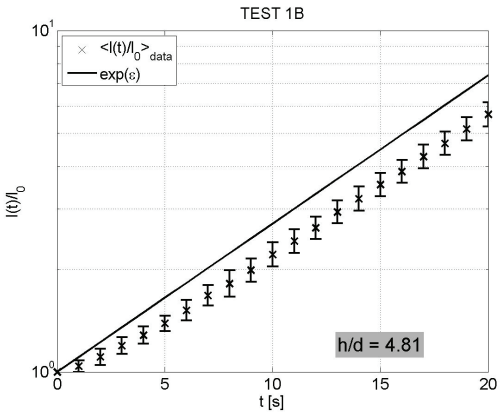


Figure 4. Particle tracking ($\Lambda_1$=4.81 and $\Lambda_1$=7.34).

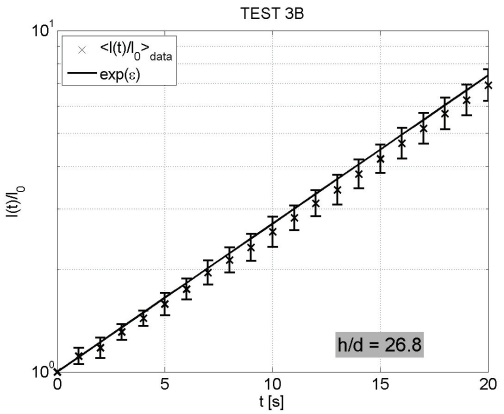


Figure 5. Particle tracking ($\Lambda_1$=26.8 and $\Lambda_2$=7.34).

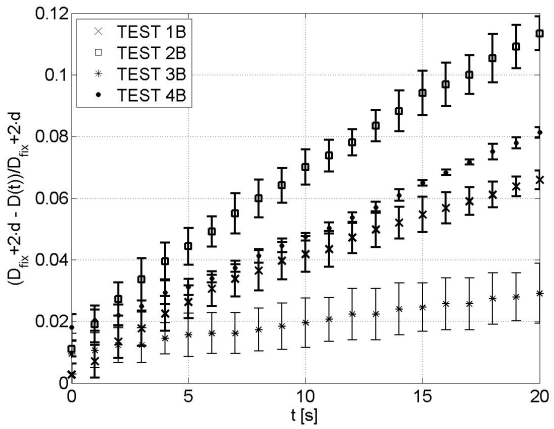


Figure 6. The decrease in cylinder diameter during the four experiments. The diameter is compared to the initial outer diameter, which is the fixture diameter plus two times the sample thickness.

## CONCLUSION

A new test fixture has been designed as an add-on to the FSR. It is made such that the sample to be deformed is a hollow cylinder. Different test conditions have been tested to find an appropriate geometric balance such that the perimeter remains constant and the local strain rate is equal to the imposed strain rate.

Two predefined aspect ratios determined from the relative sizes of the sample and the instrument, $\Lambda_1$ and $\Lambda_2$ were used for this analysis. And it was found that by increasing $\Lambda_1$ it was possible to obtain a local strain rate given by the imposed one. No significant difference was observed when changing $\Lambda_1$

from 26.8 to 53.6. Hence there is some upper limit where a further increase does not have a visible effect.

It was furthermore observed that by increasing $\Lambda_1$ in such a way that $\Lambda_2$ decreases could be a bad solution. The reason for this is that the cylinder diameter is sensitive to the size of $\Lambda_2$, and the smaller it is the more will the diameter deviate from the initial outer diameter. This means that in order to obtain planar elongation it is important to have a proper balance between $\Lambda_1$ and $\Lambda_2$. In this case the best result was obtained in test 3, where $\Lambda_1$=26.8 and $\Lambda_2$=7.34, respectively.

Further measurements on soft polymer networks will be performed in the future since in literature there seems to be large uncertainty in the published data but whereas for our experimental set-up it is believed that for the given geometrical parameters we are indeed able to produce data with high reproducibility and realibility.

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