# Reversed extensional flow on polyisoprene melts

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## ABSTRACT

To gain further insight into the flow physics of polymer melts direct measurements of the stress relaxation and the bi-axial reversed flow, both following uni-axial extensional flow on a mono-disperse polyisoprene are presented in this paper. The measurements are performed on a filament stretch rheometer.

## INTRODUCTION

A linear monodisperse well-entangled polymer melt is a simple, classical system in polymer rheology and a valuable model material to gain insight into the complex physical behaviour. Only a few experimental papers has been published with data to be used for the validation of reptation based theories, like Graham et al.[1]; Ianniruberto and Marrucci[2]; Hua and Schieber[3]; Fang et al.[4].

Stresses are found to be of entropic nature and that the reversing flow experiments give particular insight into the entropic state of the melt as it mounts the work performed by the polymer.

The filament stretch rheometer (FSR) was applied by Nielsen and Rasmussen[5] to measure reversed elongational flow consisting of uniaxial elongation measurements followed by a reversed bi-axial flow on a well-defined polystyrene sample.

There are theories for entangled polymer systems which predict fundamentally different flow behaviours and some of them are based on the idea that a given polymer chain is moving by reptation in a tube made up effectively by the surrounding chains[6]. Constitutive theories which use the monodisperse polymer melt as the model molecule were initiated by Doi and Edwards[7]. Using the reptation concept of de Gennes[6], Doi and Edwards constructed a model for the dynamics of highly entangled monodisperse polymer melts.

In the present paper we write the Doi and Edwards model as a memory-weighted time integral over the Doi-Edwards strain tensor for an entangling network with instantaneous chain retraction.

$$\sigma_{ij} = \int_{-\infty}^{t} M(t-t') \frac{3.75}{\langle |E \cdot u| \rangle} \left\langle \frac{E_{in} u_n E_{jm} u_m}{|E \cdot u|} \right\rangle dt' \quad (1)$$

The terms $\sigma_{ij}$ are the integral components of the stress tensor. The angular brackets

denote an average over a unit sphere $\langle ... \rangle = 1/(4\pi)\int_{|u|=1} ...du$ where a tube segment of unit length and orientation is given by the unit vector $u$. In the stress free state $u$ is deformed into $E \cdot u$ in the current state. The components of the macroscopic displacement gradient tensor are given by $E_{ij}(x, t, t') = \partial x_i/\partial x'$, $i$ = 1, 2, 3 and $j$ = 1, 2, 3. ($x'_1$, $x'_2$, $x'_3$) are the coordinates of a given particle in the stress free reference state (time $t'$), displaced to coordinates ($x_1$, $x_2$, $x_3$) in the current state (time $t$). The memory function $M(t - t')$ is related to the relaxation modulus as $M(t - t') = dG(t - t')/dt'$.

Milner and McLeish[8] presented an analytical theory of stress relaxation in monodisperse linear polymer melts, but in the present study an empirical method developed by Baumgaertel, Schausberger and Winter (BSW)[9] is applied as it gives a more accurate prediction for the dynamic mechanical data.

The elongational flow measurement on a well defined monodisperse linear polystyrene melt was presented by Nielsen and Rasmussen by applying uniaxial extensional flow followed by a bi-axial reversed flow[5]. In that case the polystyrene melt had a number of ~10 entanglements and a value of the ratio between the relaxation time and the Rouse time of about 6. In the present paper a polyisoprene melt is used to verify the theoretical prediction of the strain recovery with the assumption of pure configurational stress, mathematically represented by Eq. 1

## MATERIALS AND METHODS

An uniaxial extensional flow followed by a bi-axial reversed flow is applied on a monodisperse polyisoprene (PI) melt with a molecular weight of $M_w$ = 483 kg/mol[10] characterized by a number of ~100 entanglements and a value of the ratio between the relaxation time and the Rouse time of about 200.

The extensional experiments are performed using a filament stretching rheometer (FSR) surrounded by a thermostatic environment, developed by Bach et al.[11]. In this FSR, a cylindrical shaped liquid sample, with height $L_i$ and radius $R_i$, is placed between two parallel solid cylinders having the same diameter as the pellet. Separation of the plates will extend the sample. The FSR measures the strain in the sample at exactly the location of the necking or the mid-filament plane of the extended sample. Subsequently, this critical region can be monitored using laser microscopy and the distance between the end-plates adjusted, thus obtaining a predefined stretch rate at the neck. To ensure a correct measurement the sample should stay symmetric across the mid-filament plane as well as axisymmetric during extension. During the extension in a FSR, a load cell measures the elongational force, F(t), and a laser micrometer measures the filament diameter, 2R(t), at the mid-filament plane. The relevant strain in the elongation is the Hencky strain (ε), which is defined as $\varepsilon(t) = 2 \ln(R_0/R(t))$ for filament stretching of cylindrically shaped samples. The transient uniaxial extension is up to a Hencky strain of $\varepsilon_0$. $R_0$ is the mid filament radius of the sample and $L_0$ the length of the sample at the start of the extension (t = 0), as the sample may have been subjected to a pre-stretch. Initially, the sample is at rest for times t < 0. The elongational rate or stretch rate is defined as $\dot{\varepsilon} = d\varepsilon/dt$.

## RESULTS AND DISCUSSIONS

The relaxation modulus is obtained using small amplitude oscillatory shear measurements and the results are fitted with a continuous BSW relaxation spectrum[9] (Fig. 1).

$$G(t-t') = \int_0^\infty \frac{H(\tau)}{\tau} e^{(-(t-t')/\tau)} dt \qquad (2)$$

$$H(\tau) = n_e G_N^0 \left[ \left( \frac{\tau}{\tau_{\max}} \right)^{n_e} + \left( \frac{\tau}{\tau_c} \right)^{-n_g} \right] h\left( \frac{1-\tau}{\tau_{\max}} \right) \quad (3)$$

where $h(x)$ is the Heaviside step function, $n_e$ is the slope of the (log(ω), logG′) curve at intermediate frequencies, $n_g$ is the slope of (log(ω), logG″) for $\omega \to \infty$ and $\tau_c$ is the crossover relaxation time.

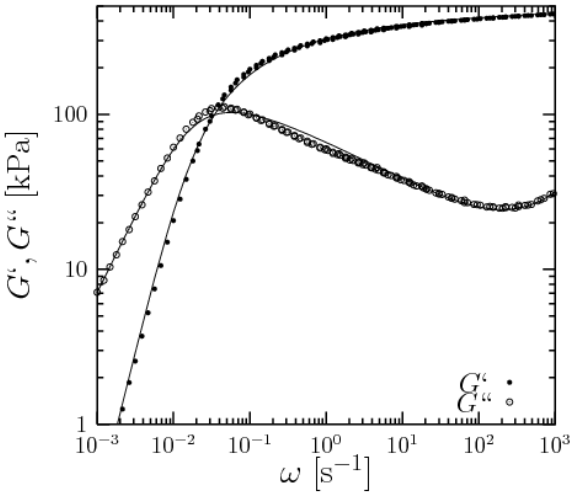


Figure 1. The linear viscoelatic data for the $M_w$ = 430 kg/mol polyisoprene[10].

The elongational stress generated within the sample filament can be calculated from the total force measured by the load cell[12] as

$$\sigma_{11} - \sigma_{33} = \frac{F(t) + \rho\pi R_i^2 L_i g/2}{\pi R(t)^2} - \frac{\sigma}{R(t)} \quad (4)$$

where $\sigma$ is the surface tension, $\rho$ is the density of the polymer melt and $g$ is the gravitational acceleration. The fluid inertia is negligibly small.

In order to calculate the Deborah number ($De = \tau_a \cdot \dot{\varepsilon}$) a characteristic relaxation time is used:

$$\tau_a = \int_0^\infty G(s)sds \Big/ \int_0^\infty G(s)ds \approx \tau_{\max}\left( \frac{1+n_e}{2+n_e} \right) = 42s \quad (5)$$

Figure 2 shows the stress as function of the Hencky strain until values of 0.5 and 1, from where the flow is reversed. The extension rate is 0.03s$^{-1}$, giving a De of 1.26. Different Hencky strain values are applied achieving higher De (De > 4). When the polyisoprene melt is subjected to higher extension rates, the sample will begin to neck and then rupture, or due to the compression force it might buckle.

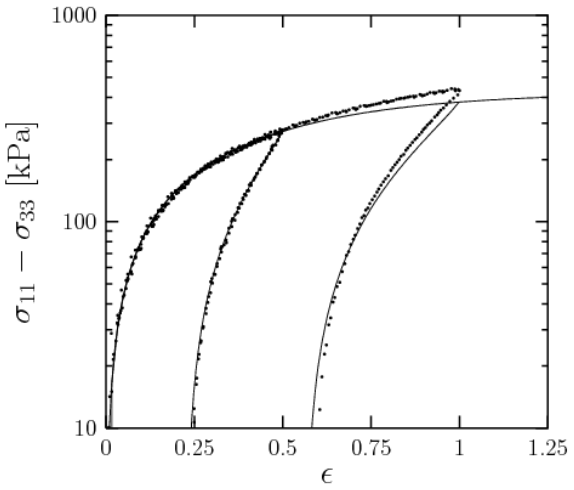


Figure 2. Extensional stress as a function of the Hencky strain. The elongational rate was 0.03s$^{-1}$ at 23ºC which result in De=1.26.

In both buckling, necking and rupture, reliable stress and strain values can not be determined.

## CONCLUSIONS

A filament stretching rheometer is used to measure uni-axial elongational flow followed by reversed bi-axial flow, both with a constant elongational rate. Pure oriental stress can be observed for the linear narrow molecular mass distribution polyisoprene as the time of the flow was considerably smaller than the Rouse time. A Doi-Edwards type of constitutive model with the assumption of pure configurational stress is capable of predicting the start-up as well the as the reversed flow.

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