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Linear viscoelastic models
Part II. Recovery of the molecular weight distribution using viscosity data

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ABSTRACT

The constitutive models for the viscoelasticity of polymers are presented for determining molecular weight distributions (MWDs) from viscosity measurements. The inversion of this model derived from control theory and melt calibration procedure connects the relaxation modulus, viscosity, and other flow properties of a polymer. The linear principle enables simultaneous and accurate modelling of the relaxation modulus and of viscosity flow curves over a wide range. Starting from viscosity measurements, the new model is used to determine the MWD, linear viscoelastic relaxation moduli, and the relaxation spectra of polyethylene of different grades. In addition, two benchmark analyses of bimodal polystyrene are reported, and the capability of the model is proven by the two-box test of Malkin. The error of the modelled viscosity is smaller than that for previously reported models. One of the main features of this work is that no relaxation time or spectrum procedures were used to generate and model linear viscoelasticity.

1. Introduction

Bersted et al. made one of the most successful early attempts to find a relationship between the viscosity flow curve and molecular weight distribution (MWD), using the partition model [1–7]. The inverse problem of how to determine the MWD from viscosity was described by Malkin [8], and is known to be an ill-posed problem [9–16].

In our model, once the relation between the structure and measured data is set up, other properties are computed simultaneously on a frequency or time scale.

Our companion paper [17] presents the main concepts of the procedure, viscoelasticity, relationships to chain structures and dynamics, and the mathematical treatment by linear viscoelastic relaxation modulus. This paper presents the computations and results for the complex viscosity.

For a constant frequency it is misleading to use entangle and Rousean relaxations and relaxation times, since chain dynamics differ (as explained in Sections 2.1 and 2.2). We simply consider (mainly) elastic rheologically effective distribution (RED′) $w'(\log\,\omega)$ and viscous RED″ $w''(\log\,\omega)$.

2. Theory

2.1. Modelling viscosity at different steady-state flow rates

We have developed a principle for using complex viscosity data obtained from a dynamic rheometer measured in the frequency-sweep mode. As described in the companion paper for the relaxation modulus, modern control theory as applied to dynamic systems can be used to derive the formulas for frequency rate ω and relations to distributions by the melt calibration. In this paper we use MWD as a function of frequency $w'_i(\omega) = w_i(M)$ from function of molecular weight M in which w_i is the weight fraction of component i in the mixture. Now the development procedure can be started from the principle $\eta*(\omega) = \sum w_i(M)\eta_i^*(\omega)$ as the sum of independent contributions according to Graessley [18] to get complex viscosity functional [19] for $\eta*(\omega) = \sum w_i(\omega)\eta_i^*(\omega)$.

The basic idea is to model steady impulses and the summed stress resulting from chain dynamics between molecules of different molecular sizes at a steady frequency rate ω. With the normalized rheologically effective distribution (RED), $w(\omega)$, and the impulse response, $h(\omega)$, we obtain system response $y(\omega)$ according to control theory as follows:

$$y(\omega) = \int_{-\infty}^{\omega} w(\psi)h(\omega - \psi)\,\mathrm{d}\psi. \tag{1}$$

As the MWD function is normally a function of logarithmic variables, or here RED $w(\log\,\omega)$, we have to rewrite all variables and

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Nomenclature

Hf	conversion factor between M and ω scales
$M(\omega)$	calibration curve for melts
Mf	structural value
Mf_0	structural value at the reference temperature
P'	elasticity value
P''	viscosity value
R	ratio of effective distribution ranges
$w'(\omega)$, $w'(\log\,\omega)$	rheologically effective distributions, (elastic) RED
$w''(\omega)$, $w''(\log\,\omega)$	rheologically effective distributions, (viscous) RED″
$w'_c(\omega)$, $w'_c(\log\,\omega)$	characteristic effective distributions, (elastic) RED
ω_c	characteristic frequency
η^*_c	characteristic complex viscosity
%RMSE	percentage root-mean-square error function between observed and fitted viscosity curves

functions in Eq. (1) on a logarithmic scale: $\log\omega - \log\psi = \log(\omega/\psi)$, and $d\psi$ is written as $d(\log\psi)$. System response $y(\log\,\omega) = \log(\eta*(\omega)/\eta^*_0)$ is a normalized complex viscosity η^* with zero viscosity η^*_0. We can rewrite the presented complex viscosity functional for the normalized complex viscosity in the steady frequency rate as follows:

$$\log\frac{\eta*(\omega)}{\eta^*_0} = -P'\int_{-\infty}^{\log\omega} w(\log\,\psi)\left(\log\frac{\omega}{\psi}\right)\,\mathrm{d}\,\log\,\psi. \qquad (2)$$

We use entanglement relaxation modulus and Rouse relaxation and the respective REDs to illustrate the procedure. Complex viscosity $\eta^*(\omega)$ has a different physical origin and chain dynamics at a steady frequency. At higher steady frequencies, an oriented and disentangled chain tries to relax and re-entangle, conforming mainly to constant stress with an elastic response according to RED′ $w'(\log\,\omega)$. At very low steady frequencies, molecular friction generates mainly constant stress with a viscous response according to RED″ $w''(\log\,\omega)$. During the constant state it is misleading to use entangling and Rousean relaxations; instead we simply consider (mainly) elastic RED′ $w'(\log\,\omega)$ and viscous RED″ $w''(\log\,\omega)$ over the normal data measurement range. The complete formula for $\eta^*(\omega)$ at different frequencies can be expressed by common logarithmic distributions as

$$\log\frac{\eta*(\omega)}{\eta^*_0} = -\int_{\log\,\omega/T}^{\log\,\omega}\left(P'w'(\log\,\psi) + P''w''\left(\log\frac{\psi}{R}\right)\right)\log\frac{\omega}{\psi}\,\mathrm{d}\,\log\,\psi. \qquad (3)$$

where scalar values P' and P'' are elastic and viscous constants, respectively. This is achieved simply by copying function $w'(\log\,\omega)$ after dividing ω by the ratio, R, of the frequency-rate ranges to obtain the distribution, $w''(\log(\omega/R))$, if better information is not available. Viscous RED″ $w''(\log(\omega/R))$ is outside the range of standard viscosity measurements, but at very low frequencies ω also has elastic effects. During steady-state frequency, the longest chains are no more effective for the viscosity and we have to use the lower bound of integration $\log\omega - \log T = \log(\omega/T)$ instead of the minus infinity limit. The sampling band is still wide in the range $T = 100{,}000/\mathrm{s}$ for polydisperse polymers.

The model described by Eq. (3) includes complex viscosity $\eta^*(\omega)$ without difficulty, but solving distribution $w'(\omega)$ is known to be a severely ill-posed problem.

2.2. Conversion from the distribution $w(\omega)$ to $w(M)$ (MWD) by melt calibration

When an effective distribution function (RED′) $w'(\log\,\omega)$ is found from the best fit to the viscosity, we must convert $w'(\log\,\omega)$ to a function of molecular weight, MWD $w(\log\,M)$, using a conversion factor between scale Hf and the polymer structural value Mf. The background of the melt calibration is presented earlier [17]; in the present paper we present the modelling of the steady shear conforming to a statistical orientated or stressed sphere linked to its midpoint.

The relation between the molecular weight scale M and the frequency scale ω is obtained using a homogeneous linear differential formula. The additional decrease in $\mathrm{d}M$ – converted by Hf on the M scale according to – $\mathrm{d}M/\mathrm{d}\omega$ – must equal the molecular weight scale divided by frequency M/ω:

$$Hf\frac{\mathrm{d}M}{\mathrm{d}\omega} + \frac{M}{\omega} = 0 \qquad (4)$$

Solving Eq. (4) yields a simple relation for the melt calibration, $M(\omega)$, as a function of frequency, where the value of Mf is M at $\omega_1 = 1/\mathrm{s}$:

$$M = Mf\left(\frac{\omega_1}{\omega}\right)^{1/Hf} \qquad (5)$$

Conversions can be performed using a standard variable transformation as multivariate change-of-variable formula, Eq. (5), and the exponent (i.e. conversion factor between scales Hf and the polymer structural value Mf). MWD $w(M) = \mathrm{d}W(M)/\mathrm{d}M$, and $W(M)$ is the cumulative distribution of weight fractions of chains that, in the most-used semilogarithmic scale, is $w(\log\,M) = \mathrm{d}W(M)/\mathrm{d}(\log\,M)$. All distributions are normalized using an integral as for the following example for $w'(\log\,\omega)$:

$$\int_{-\infty}^{+\infty} w'(\log\,\omega)\,\mathrm{d}\,\log\,\omega = 1 \qquad (6)$$

The correct value of Mf for each polymer type is found by fitting data from gel-permeation chromatography (GPC) and size-exclusion chromatography (SEC), and dynamic measurements and models.

The inversion $\omega \propto 1/M$ generated from Eq. (5) is used in evaluations. High and low frequency rates correspond to small and large molecules, respectively. The calibration curves for melt (i.e. $M(\omega)$) may also be numerical function in practice.

2.3. Effective distribution $w(\omega)$ from viscosity measurements

We have to extract effective distribution $w'(\omega)$ from analytical Eq. (3), but solving this directly is known to be a severely ill-posed problem. Using a procedure similar to that described for the relaxation modulus, we obtain characteristic η^*_c for constant characteristic frequency ω_c as

$$\log\frac{\eta_c*(\omega)}{\eta^*_0} = -\log\frac{\omega}{\omega_c}\int_{-\infty}^{\log\omega}\left(P'w'(\log\,\psi) + P''w''\left(\log\frac{\psi}{R}\right)\right)\,\mathrm{d}\,\log\,\psi \qquad (7)$$