

# Determining The Molecular Weight Distribution From Viscosity Measurements

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## INTRODUCTION

A constitutive model for the viscoelasticity of a polymer is formulated on the basis of molecular considerations [1]. It takes the form of a linear differential equation. The inversion of this differential equation allows the viscosity, modulus and other flow properties of a polymer to be related to its molecular structure.

The model connects different shear rates and deformation states of flow and orientation of molecules to the structure and viscoelastic properties.

The error of the viscosity fit is small compared to the procedures published earlier. Main features are:

1. Viscoelastic properties are modelled by active and passive component functions influenced by the properties and related structure.
2. Passive component  $P''$  detects the deformation of flow and active component  $P'$  by the deformation of molecules.
3. Particular solutions of linear differential formula generated from molecular relations give properties at different states.
4. Relaxation spectra procedures are not used, but sum of components  $P=P'+P''$  to make formulas linear.

Principle gives simultaneously MWD, viscosity, relaxation modulus and spectrum.

## LINEAR DIFFERENTIAL EQUATION

We will start from the basis of the well-known mechanics of polymers by generating fundamental differential equation for a dynamic system in the equilibrium state. The steady state flow system consists of a deformed body and a wall. The change of the externally measured stress difference  $d\sigma$  must be equal to the shear stress in the body under study but in the opposite direction or expressed as

$$d\sigma + G_p d\gamma = 0 \quad (1)$$

The formula is true in every time interval, thus we can avoid the use of a time variable in the formula. The modulus  $G_p(\gamma)$  of the internal body is a function of strain  $\gamma$ . Unfortunately this modulus  $G_p$  is known only by measurements for complex polymers. For the solution of the problem we scale the modulus by a polymer structure function  $P$ . Measured stress  $\sigma$

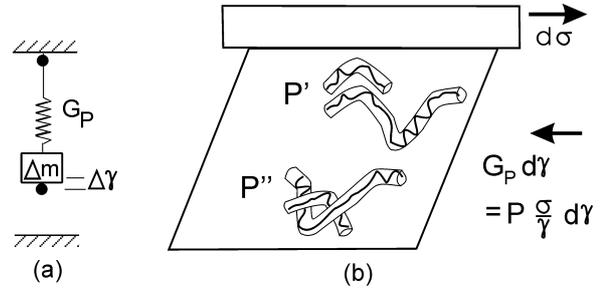


Figure 1. a) Mechanical spring model where increase of mass  $m$  give deformation  $\Delta\gamma$ . b) The complete system consists of internal body and external wall. Function  $P$  has strain information of molecules by  $P''$  and  $P'$  functions, where  $P''$  has a relation to extensions and  $P'$  disentanglements of molecules. High  $P$  values are damping elastic influences of structure and at  $P=0$  formula returns to the pure Hookean state.

and strain  $\gamma$  have a relation as follows  $G_p = P \sigma / \gamma$ , where the values of the non-dimensional  $P$  make equation (2) true and linear. The complete system is illustrated in Fig 1.

Next we can use a well-known conversion  $d\gamma = \gamma d \ln \gamma$  and the differential equation transforms

$$\frac{d\sigma}{d \ln \gamma} + P\sigma = 0 \quad (2)$$

Initially, the main formula of the principle is generated, but before that we present the normalised macroscopic material state  $Z = \gamma / \gamma_0$  giving us a simpler form of formulas. Shear rate or frequency have linear relation to the strain and we can write  $Z = \omega / \omega_0$ .

Shear modulus  $G$  and viscosity  $\eta$  have a linear relation to the stress  $\sigma$ . Thus, we can write Eq. 2 directly for viscosity. With the integrating factor

$e^{Pd \ln Z}$  we obtain the general solution  $\eta e^{Pd \ln Z} = C$  and the following particular solution for the shear viscosity by the integral constant  $C = \eta_0$ .

$$\eta = C e^{-\ln Z P} = \eta_0 Z^{-P} \quad (3)$$

## FLOW TRANSITION FUNCTION

Not only viscosity, but also flow structure changes at different states  $Z$  or shear rates. The shear

viscosity is proportional to the molecular size with the exponent value 2 according to Rouse theory and tube model by the exponent value 3. It has been shown by many measurements to be in the range of 2.0-3.7.

We have solution in Eq. (4) of a differential equation for molecular weight  $M$  and *structural factor*  $Mf$ , where the exponent called *flow transition function*  $H$  has values in the range of 2-4.

$$Z = \left( \frac{Mf}{M} \right)^H \quad (4)$$

#### ACTIVE P' AND PASSIVE P'' COMPONENTS

We present two important tools for structure; the passive component detects the deformation of flow and the active component detects the deformation of molecules. The passive component  $P''(M)$  can be set up as a product of the scalar value  $P''_0$ , the integral of  $w(M)$  and  $P''(M)$  is converted to  $P''(Z)$  by Eq. (4)

$$P''(M) = P''_0 \int_0^{\infty} w(M) d \ln M \quad (5)$$

Only some molecules of the  $w(M)$  distribution have an influence on the properties during flow according to the  $P''_0$  constant due to co-operation. This practical scalar value is the maximum of component  $P''(M)$ . Thus  $P''_0$  is the limit value at small  $M$ .

During an influenced shear rate at some point the greatest entangled molecules start to disentangle and orientate. We are interested only in the molecules, which will perform their induction; this time the interest is orientation and deformation. We set up the active component  $P'(M)$  can be set up as a product of the scalar value  $P'_0$  for these molecules as follows

$$P'(M) = P'_0 \int_0^M w(M) d \ln M \quad (6)$$

#### STEADY FLOW

The solutions of formulas for a rheometer are presented. The complex viscosity of the dynamic oscillating rheometer is marked briefly by  $\eta$ . By connecting Equations (3),(4),(5) and (6) to the complete function, we obtain form for viscosity  $\eta$  shown in Eq. (7).

$$\eta = \eta_0 Z \left[ -P'_0 \int_0^M w(M) d \ln M - P''_0 \int_0^{\infty} w(M) d \ln M \right] \quad (7)$$

The principle is versatile covering different rheometers and also reversible. Also  $w(M)$  is defined directly by derivation of Eq. (7) in the data range shown in Eq. (8) where we are again using Eq. (4) for conversions between  $M$  and  $Z$  scales.

$$w(M) = - \frac{\partial}{\partial \ln M} \frac{1}{P'_0} \left[ \frac{\ln \eta}{\ln \frac{\omega}{\omega_0}} + P''_0 \int_0^{\infty} w(M) d \ln M \right] \quad (8)$$

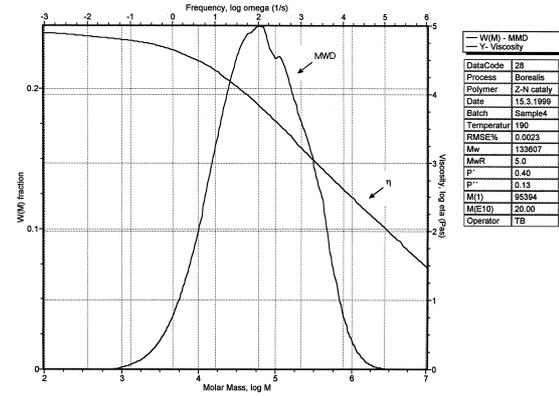


Figure 2. The MWD curve of HDPE coded by Ziegler-Natta Sample 4 arranged by Borealis Polymers. The curve has been computed by RheoAnalyzer [2] from viscosity data in the ASCII form. For this narrow MWD it was possible to measure the average molecular weight  $w=132000$  and the polydispersity index  $MwR=4.1$  rather accurately by GPC. The differences are minimal.

With polymer melts the data range is mainly in the range of the active component and we do not need to solve the equation separately for the passive component as the value of  $P''$  component is constant.

Our results are fundamental and we now have the linear relation between molecules and properties.

#### TIME-DEPENDENT RELAXATION MODULUS

In the relaxation procedure the system is not in an equilibrium state, which need some additional procedure not shown here. We rewrite the principal differential Equation (2) for convenience directly for relaxation modulus  $G$ .

$$G(t) = G_0 Z \left[ -P'_0 \int_0^M w(M) d \ln M - P''_0 \int_0^{\infty} w(M) d \ln M \right] \quad (9)$$

The time-dependent relaxation function  $G(t)$  is found after an infinitesimal deformation  $\gamma_0$  during a short time  $t_0 > 0$ . Now the flow state  $Z$  also has the time-dependent function or  $Z = (\dot{\gamma}_0 / \dot{\gamma}_0 + t) / (\dot{\gamma}_0 / \dot{\gamma}_0)$ , which turn as follows after infinitesimal strain.

$$Z = \frac{t_0 + t}{t_0} \quad (10)$$

#### REFERENCES

1. Borg T. Pääkkönen E. J., submitted to *J. Non-Newtonian Fluid Mech* (2002).
2. <http://www.TomCoat.com>