

Determining the Molecular Weight Distribution From Viscosity Measurements at Different Temperatures

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ABSTRACT

A constitutive model for the viscoelasticity of a polymer is formulated on the basis of molecular considerations. The inversion of 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. Some results for determining molecular weight distribution (MWD) of polyethylene (PE) starting from viscosity measurements are presented. The error of the viscosity fit is small. The accuracy of detecting MWD has been raised by using data measured at different temperatures and developed temperature conversion procedure.

INTRODUCTION

The principle of our model starts from the real structure of polymer as comparative deformations of different size molecules, and gives relations to properties. We list briefly the main features.

1. Classical dynamic system of stresses is adjusted by polymer structure function related to the flow states as shear rates or frequencies.
2. Viscoelastic properties are modelled with elastic and viscous moduli related to the molecular structures and MWD.
3. The viscous component detects the molecular collisions and the elastic component detects the reversible deformation of molecules.
4. Particular solutions of a linear differential formula generated give several properties simultaneously at different states.

The basic criteria mentioned above gives the procedure, by which the MWD and rheological properties such as wide viscosity and relaxation, elastic and viscous moduli fits are simultaneously computed from viscosity measurements.

MOLECULAR SIZE INCLUSION

The molecular weight distribution function $w(Z)$ as a function of polymer state Z is introduced. Analogically to the chemical methods, the molecular weight distribution $w(M)$ is not gained directly. The method uses the size inclusion

principle by viscoelastic properties at different shear rates according to the state function Z . At some frequency greater molecules have different entanglement structures or microstate behaviours from smaller molecules. These are also given different responses to the properties including greater or smaller molecules from all molecules and $w(Z)$ function.

In this rheological method is not needed to convert distribution fractions w , but nevertheless the state function Z at constant shear rate or frequency must be converted by Eq. (1), where H is flow transition function in the range $2 < H < 4$ and Mf is material structure factor.

$$w(Z) = w(M) \quad | \quad M = Mf Z^{-\frac{1}{H}} \quad (1)$$

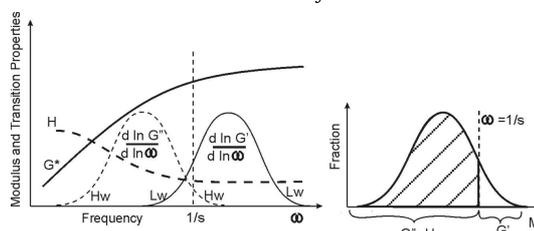


Fig. 1. Schematic illustration of the structural elements on frequency scale and ranges of definite integrals on M -scale. Component G'' and respective distribution by derivation detects the polymer flow by freely vibrating molecules. At a higher rate the reversible deformation have a relation to the elastic component G' . The scaled distributions are mirror figures, where Hw is the high weight fraction on the left and Lw respectively the small molecules on the right side. On the right is shown generation areas of MWD for definite integrals at $1/s$.

USED FORMULAS

As summarized we show used Eq. (2) for viscosity fit as follows

$$\eta^* = \eta_0^* Z^{-P'} \int_0^\infty w(Mf' Z^{-1/H}) \ln dZ - P'' \int_0^\infty w(Mf'' Z^{-1/H}) d \ln Z \quad (2)$$

Now we find one of the most important advantages of the model. We can use the same formula for different flows or states by the same polymer structure function. For example the formula for viscosity η measured with a capillary rheometer at the shear rate is the same as for an oscillating cone-plate or plate-plate rheometer, as both can be used for Z variable.

The principle is versatile covering different rheometers and also reversible. Also $w(\omega)$ is defined directly by derivation in the data range.

We are again using Eq. (1) for conversion to $w(M)$. With polymer melts the data range is mainly in the range of the elastic component and we do not need to solve the equation separately for the viscous component.

$$w(\omega) = - \frac{d}{d \ln Z} \frac{1}{P'} \left[\frac{\ln \eta^*}{\ln Z} + P'' \int_0^\infty w(Z) d \ln Z \right]$$

From Eqs. (2 and 3) we will get an appraisal solution for $w(M)$ and the transition function $H(\omega)$.

The time-dependent relaxation function $G(t)$ is found after small deformation γ_0 during a short initial time t_0 . We have to include this initial retardation by the time-dependent function $t+t_0$ to this static situation. The external deformation and stress is converted into an internal stress increase of the polymer during retardation time t_0 and stress decreases during relaxation with time t. The solution with elastic and viscous components is as follows in Eq. (4). The definite integral has the limit boundaries by t, which is also substituted in the state variable Z.

$$G(t) = G_0 e^{-\ln(1 + \frac{t}{t_0})} \left[P' \int_t^\infty w(Mf' Z^{-1/H}) d \ln Z + P'' \int_0^t w(Mf'' Z^{-1/H}) d \ln Z \right] \quad (4)$$

EXPERIMENTAL

First a data record is imported to the databases. The next step is to select the Mf and Hf constants and let the PC compute during the next few seconds. RheoAnalyzer has two modes, one is

possible to control manually and the other is an automatic procedure where processing lasts longer. The principle of computing is to combat against %RMSE error between measured data and modelled viscosity by giving priori information for MWD tails out of the respective data range and moreover suggestion of possible minor structures as LCB's. Programs offer many windows with charts and viewpoints for the computation.

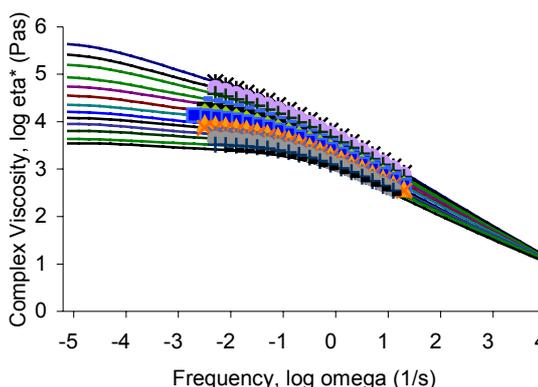


Fig. 2 shows family of 13 measured viscosity curves of Lupolen 1840H LDPE from 130°C to 250°C temperatures, where marked curves are measured data provided by BASF. Thin curves on wide scale are modelled by RheoAnalyzer.

The principal equations used for the analysis are Eqs. (2-3) for complex viscosity. A well-known fact is that polyolefins are the most difficult polymers for detecting MWD and modelling in the rheology. This is why we have selected only HDPE and LDPE samples, although the procedure has become very accurate with PS and other much easier materials.[1]

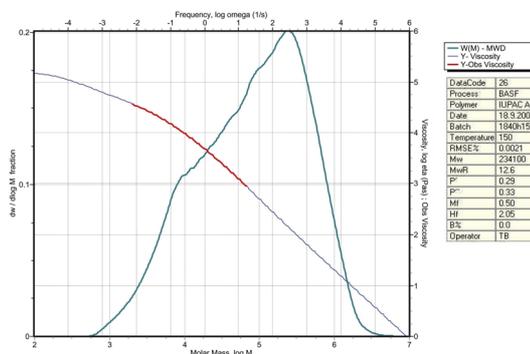


Fig. 3 shows MWD of commercial Lupolen 1840H LDPE computed from viscosity data at 150°C provided by BASF. This material is the modern version from the classical IUPAC A LDPE introduced by Meissner.[2]

All these computations were performed by means of the RheoPower software family using a standard PC. For this study we use BASF LDPE H1840, a derivative of well known IUPAC.[2] Measured viscosities at 13 different temperatures from 130°C to 250°C are shown in Fig. 2, where marked curves are measured data provided by BASF.

One example of the computation results at 150°C is shown in Fig. 3. RheoAnalyzer gives MWD and modelled viscosity flow curve, measured and used viscosity data is marked with a thicker line.

In Fig. 4 are the summarized MWD's of LDPE computed at 13 different temperatures from 130°C to 250°C. The used temperature conversion having minor effect for constants at other temperatures: $M_f = M_{f_0} + (T - T_0) * 0.0033$

We find that $M_f = 0.63$ at 190°C, or close 0.7 value for HDPE and at 250°C $M_f = 0.80$. Summarizing of these temperature tunings had minimal effect.

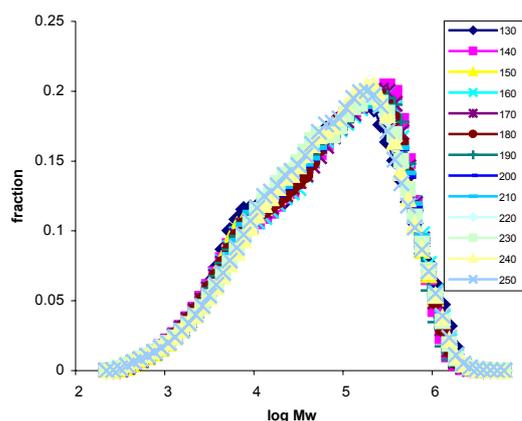


Fig. 4 shows summary of Lupolen 1840H LDPE MWDs computed from data measured at 13 different temperatures from 130°C to 250°C at 10°C steps. Prior information was measured by GPC for $M_w = 240000$ and molecular number $M_n = 17000$ giving $M_w R = 14$. Average error between measured and modelled viscosity %RMSE=0.0009 and a deviation of M_w 2.3%.

RESULT AND DISCUSSION

We found that the average error between measured viscosity data and the model is $RMSE\% = 0.0009$, which is over 50 times smaller than any other known model. Prior information was measured by GPC for $M_w = 240000$ and molecule number $M_n = 17000$ giving $M_w R = 14$. The average M_w was 234689 and $M_w R$ 14.1 of all computations deviating 2.3% from priori information.

SUMMARY

In this study the principle was used for the determination of MWD from viscosity data and vice versa. To the known ill-posed problem have been found a novel solution by partitioning to the easier solutions and MWD can be obtained directly by derivation.

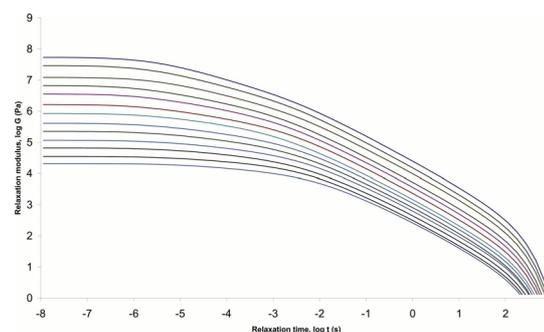


Fig.5 shows family of 13 relaxation moduli of Lupolen 1840H LDPE at temperatures from 130°C to 250°C.

The results calculated from measured data show that our model for determining MWD from for the quality control of the polymerisation process or platform for effective synchronized on line data service to CAE/CAD/CFD injection simulation software, as is shown at ICR elsewhere.[3]

An accurate viscosity data is needed to obtain the weight-average molecular weight M_w . The method presented in this paper is rapid and versatile.

The principle of the wide subject is simple, but the numerically sensitive and labile recursive exponent formulas need accurate data with fluent software to achieve high computing capacity.

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