

POLYDISPERSITY INDICES OF LINEAR POLYMERS MELTS FROM RHEOLOGICAL MEASUREMENTS

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Abstract

We present here a method for determining the polydispersity indices $I_{p1}=M_w/M_n$ and $I_{p2}=M_z/M_w$ of the molecular weight distribution (MWD) for linear, entangled, polymers melts, in a direct manner, as a previous step for further characterization of polymeric systems. The method uses a simple molecular rheological model and additional experimental viscoelastic data. Specifically, the experimental rheological information required to obtain the polydispersity indices is the storage $G'(\omega)$ and loss $G''(\omega)$ moduli, ranging from the terminal zone to the plateau region.

The moments of the MWD can be derived from analytical relations between the relaxation spectrum, $H(t)$, and the MWD [Llorens et al. 2000]. The polydispersity indices can be obtained by the quotients of these moments; hence, the ill-posed inverse problem is avoided. Furthermore, it is not necessary to assume

Results show a good agreement between the a given shape of the continuous MWD in order to obtain the polydispersity indices. proposed theoretical approach and the experimental polydispersity indices of two polydimethylsiloxanes (PDMS) and binary blends.

Keywords: *Polymer rheology; Polydispersity index; Molecular weight distribution*

Resumen

Se presenta un método que permite obtener los índices de polidispersidad de un polímero lineal, definidos como la relación entre dos valores de peso molecular promedio, $I_{p1} = M_w/M_n$ and $I_{p2} = M_z/M_w$. Se calculan estos índices a partir de un modelo reológico molecular y los datos experimentales de viscoelasticidad correspondientes a los valores de los módulos de almacenamiento $G'(\omega)$ y pérdidas $G''(\omega)$ del polímero, extendidos desde la zona llamada terminal (baja frecuencia) hasta la zona Plateau, G_N^o , (donde $G'(\omega)$ varía muy lentamente con la frecuencia).

Obtenemos los momentos de la distribución de pesos moleculares, MWD, a partir de la relación analítica que existe entre el espectro de los tiempos de relajación, $H(t)$, y la MWD (Llorens et al. 2000). Los índices de polidispersidad se determinan mediante los cocientes de estos momentos.

Las ventajas de este método frente a los tradicionales es que se hacen innecesarias la presencia de disolventes y la inversión de ecuaciones integrales. Aplicamos esta metodología a polidimetilsiloxanos (PDMS) de alto peso molecular, (PDMS_H), y bajo peso molecular, (PDMS_L), y a sus mezclas binarias. Los resultados obtenidos son buenos comparados con los experimentales.

Palabras clave: reología de polímeros, distribución de pesos moleculares, índices de polidispersidad.

1. Introduction

Polymers are found nowadays in several scientific and technological fields; in most of the cases they are proposed as alternative materials for several applications, substituting classical ones. From the theoretical point of view, polymers are classified as complex systems, given the highly non-ideal they present in most of their properties: this includes their thermodynamic properties, solubility, transport properties, etc. In spite of their complex behavior, a precise knowledge of these properties is essential for the accurate design of polymer processes. One of the main characteristics of these compounds, which provide most of their unique properties, is their molecular weight: they are long molecules with a disperse molecular weight distribution (MWD); unfortunately there is not a unique way of measuring the MWD of polymeric systems, since different methods provide different molecular weights (in number, in weight, etc). A common way of circumventing this problem is by calculating some polydispersity indexes of the MWD.

The preponderant effect of polydispersity on the viscoelastic behavior of linear polymer is well recognized (Ferry JD 1980).

The viscoelastic behavior of the linear polymer can be determined by measuring the storage modulus, $G'(\omega)$, proportional to the energy storage in a cycle deformation, reflecting the elasticity of the system, and the loss modulus, $G''(\omega)$, proportional to the dissipation or loss energy as heat in a cycle deformation, reflecting the viscosity of the system.

In this work a quantitative rheological method for the calculation of the polydispersity indices is presented, based on a molecular theory, which can be applied to any kind of polymer sample, regardless the form of the distribution. The only rheological information required for this purpose is the master curves of the storage $G'(\omega)$ and the loss $G''(\omega)$ moduli, extending from the terminal zone to the plateau zone.

The viscoelastic properties in the terminal zone (at the low frequency range) are dominated by material parameters such as zero-shear viscosity, η_0 , steady-state shear compliance, J_e^0 , and if the molecular weight distribution is sharp a terminal relaxation time τ_0 .

η_0 is a measure of the polymer fluidity and a characteristic parameter for the entanglement density between chains within a material, and hence it is very susceptible to chains length (Ferry JD 1980).

The η_0 scales in the following manner with the weight-average molecular weight

$$\eta_0 = k_E \cdot M_w^\alpha \quad (1)$$

k_E is the constant of proportionality and α generally lies between 3.3 and 3.7, except for extremely broad blends, (Ferry JD, 1980; Carrot C. et al. 1996).

J_e^0 is a measure of the polymer elasticity and very sensitive to the changes of the polydispersity which can be expressed as the ratio of different moments of the molecular weight distribution. Empirical correlations of steady-state shear compliance and ratios of different moments of the

MWD have appeared in the literature (N.J.Nills, 1969; Argawal, P. K., 1979).

η_0 and J_e^0 are important parameters in extrusion and molding processes.

Commonly, polymers above a critical molecular weight, M_c , called the entanglement molecular weight, reveal a constant value of $G'(\omega)$ at the high frequency range (plateau zone), namely plateau modulus, G_N^0 . The plateau modulus is one of the material parameter constant for each type of polymer and reflects the molecular architecture of the polymers. In general G_N^0 is found to be independent of the molecular weight.

2. Theory

The molecular model used in the present study (Llorens et al. 2000) is applicable to polymeric systems when all the chains are long enough to form an entangled polymer network. Like most of the molecular models described in the literature (Daoud M et al.1979; Tsenoglou C. 1987; des Cloizeaux J. 1990). One of its main features is that it accounts for polydispersity by assuming that the relaxation time, τ_i , of a chain depends on an average molecular weight, \bar{M} , that describes the effect of the environment where the molecule reptates and its own molecular weight, M_i , according to

$$\tau_i = \left(\frac{k_E}{G_N^0} \right) \cdot \bar{M}^{\alpha-\beta} \cdot M_i^\beta \quad (2)$$

In this equation the parameters k_E and α are the same as previously described for Eq. (1), β is a parameter ($2 < \beta < \alpha$) which determines the contribution of the molecular weight of a chain in its relaxation time. Given a polymer with a given MWD, Eq. (2) can be rewritten as

$$\tau_i = K' M_i^\beta \quad (3)$$

In the model used here the normalized linear relaxation modulus, $G(t)$, for a polydisperse polymer, is formulated by the following expression

$$G(t) = G_N^0 \int_0^\infty \exp\left(\frac{-t}{\tau_i}\right) W(M) dM \quad (4)$$

This model was formulated and used in combination with rheological data in two previous works. In the first paper (Llorens et al. 2000) a unimodal MWD of commercial polymers was obtained assuming a log-normal molecular weight distribution function. The main limitation of the methodology presented there laid on the *a-priori* assumption of the shape of the MWD; hence it can be applied to polymers with this known MWD. In the second article (Llorens et al. 2003), a method was proposed for calculating the polydispersity index I_{p2} , without assuming any MDW distribution function, using the Mellin transforms; results were in good agreement with experimental data. However, the use of the Mellin transforms does not allow obtaining other polydispersity indices. The purpose of the present work is to use a mathematical procedure for calculating several polydispersity indices. For this purpose we have used Eq (4), together with classical linear viscoelastic theory, to derive two polydispersity indices, $I_{p1} = \frac{M_w}{M_n}$ and $I_{p2} = \frac{M_z}{M_w}$, from rheological data $G'(\omega)$ and $G''(\omega)$, knowing that if the relaxation modulus is used to deduce the polydispersity indices, any

inconsistency of $G(t)$ with the η_0 and J_e^0 will be directly reflected in the polydispersity calculated from $G(t)$.

Based on the previous model, the classical viscoelastic theory (Ferry JD, 1980):

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega) d \ln \omega = \lim_{t \rightarrow 0} G(t) = \sum_{i=1}^N G_i \quad (5)$$

$$\eta_0 = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{G'(\omega)}{\omega} d \ln \omega = \sum_{i=1}^N \eta_i = \sum_{i=1}^N G_i \tau_i \quad (6)$$

the Lerch theorem (Llorens et al. 2000) and after mathematical operations, we have obtained the following expression relating the molecular weight distribution of a given polymer with rheological data:

$$M_i W(M_i) = \frac{\beta \frac{G_i'}{G_N^0}}{\ln \frac{\tau_j}{\tau_i}} \quad (7)$$

This expression together with Eq (3) yields the n th-moment, $\langle M^n \rangle$, of the MWD, where

$$\langle M^n \rangle = \int_0^{\infty} M^n W(M) dM \quad (8)$$

The moments and the average molecular weights of the normalized MWD are related as follows:

$$\langle M^{-1} \rangle = \left(\overline{M_n} \right)^{-1} \quad (8a)$$

$$\langle M^1 \rangle = \overline{M_w} \quad (8b)$$

$$\langle M^2 \rangle = \overline{M_w} \cdot \overline{M_z} \quad (8c)$$

Therefore, we can use Eqs (8) to get M_w , M_n and M_z , knowing K' , G_N^0 , and β .

Usually, K' is an unknown parameter. However, if we focus on the polydispersity indices, the parameter K' is no needed:

$$I_{p1} = \frac{\overline{M_w}}{\overline{M_n}} = \left(\frac{\tau_w}{\tau_n} \right)^{\frac{1}{\beta}} \quad (9)$$

$$I_{p2} = \frac{\overline{M_z}}{M_w} = \left(\frac{\tau_z}{\tau_w} \right)^{\frac{1}{\beta}} \quad (10)$$

τ_n , τ_w and τ_z are the number-, weight-, and z- average relaxation times in the terminal zone.

$$\tau_n = K' M_n^\beta \quad (11)$$

$$\tau_w = K' M_w^\beta \quad (12)$$

$$\tau_z = K' M_z^\beta \quad (13)$$

3. Experimental

3.1. Characterising the materials

The indices M_z/M_w and M_w/M_n were obtained for different MWDs of linear polymers: polydimethylsiloxanes (PDMS). The PDMS samples were purchased from Aldrich, who also supplied the average molecular weight information.

Three bimodal PDMS mixtures were prepared by blending a sample of low molecular weight (PDMS_L) with another of high molecular weight (PDMS_H), adding either 75%, 46% or 25% (in weight) of the latter. The MWDs for the two polymers examined (PDMS_H and PDMS_L) were determined by GPC in a waters liquid chromatograph with a light scattering detector at 75 °C. The polymer solutions were prepared at a concentration of 0.05% in toluene and injected into the system at an injection volume of 50 μ L. A Styragel HR 5E column was used with toluene as the mobile phase at a flow rate of 0.35 mL/min. The average molecular weights of the blends were calculated from the known composition of the mixture.

3.2. Rheological measurements

The rheological data of the samples analyzed were obtained by dynamic oscillatory tests in a controlled stress rheometer (HAAKE RS100) with parallel plates of 20 mm diameter (gap = 0.4 mm), except for the PDMS_L sample for which a cone-and-plate sensor of 20 mm diameter and 2° angle was used. All measurements were taken in the linear viscoelastic region. The PDMS samples were analyzed at three different temperatures: 50 °C, 0 °C and -40 °C (-50 °C for the PDMS_L sample).

The isotherms were shifted in order to build up the master curves at a reference temperature of $T_0 = 0$ °C PDMS and PI, using the time-temperature superposition principle. These master curves are displayed in Fig. 2.

The figure 1 shows the Haake RS100 rheometer, from which the rheological data were obtained.

The figure 2 show the dynamic moduli $G'(\omega)$ and $G''(\omega)$ master curves for the samples PDMS_H, PDMS_L and the bimodal distributions (Llorens et al. 2000).



Figure1. Reometer

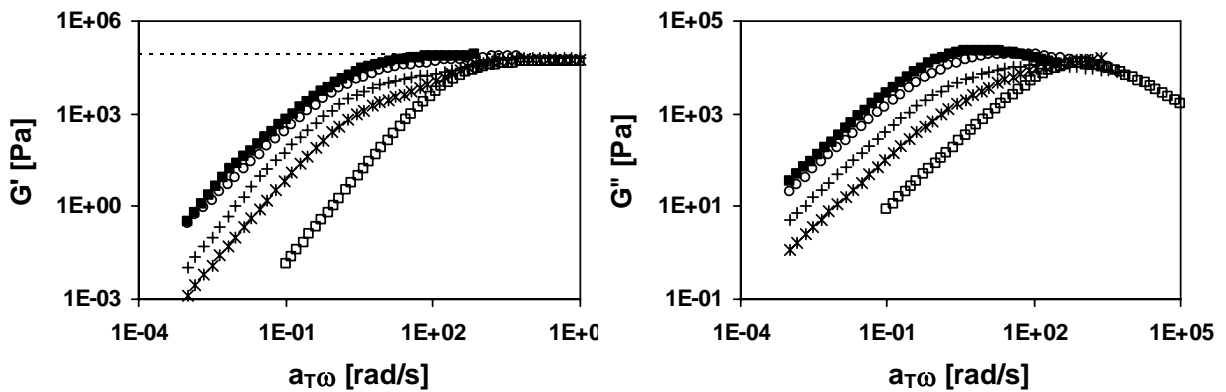


Figure 2. Dynamic moduli G' and G'' master curves at a reference temperature $T = 0\text{ }^{\circ}\text{C}$ for the PDMS mixtures series with 0% (\circ), 25% (\times), 46% ($+$), 75% (\circ) and 100% (\bullet) of the high molecular weight polymer (PDMS_H). The dotted line shows the plateau modulus for PDMS.

3.3.Determination of materials parameters

In the high frequency range, all master curves merge nearly into one curve independent of the composition. In this region the function $G'(\omega)$ reaches the plateau modulus $G_{N'}^0$, determined by the $\tan\delta$ criterion (fig. 2, horizontal line) (Wu, S. J. 1987; A. Eckstein et al. 1998).

We have determined η_0 from creep experiments [Ferry JD, 1980) in the region of linear viscoelastic behaviour for all the samples.

In order to determine the terminal relaxation time, τ_0 , one must choose the largest time for which the relaxation time spectrum posses a local maximum, (D. Maier et al. 1998).

3.4. Choice of the optimal parameter β

For calculating polydispersity indices we need to know the value of parameter β of the molecular model. This parameter must fall in the range $2 < \beta < \alpha$. The lower limit corresponds to the minimum β value from which the polydispersity indices can be calculated. The upper limit is determined by Eq. (4) with the condition $\alpha - \beta > 0$, because any relaxation time, τ_i , of a chain of molecular weight M_i , must increase when $\bar{M} > M_i$ and diminish when $\bar{M} < M_i$ with respect to the relaxation time in the monodisperse system ($\bar{M} = M_i$).

For $M \gg M_c$, two combinations of viscoelastic constants define the number and weight average terminal (longest) relaxation times τ_{on} and τ_{ow} : [Ferry JD, 1980; K. Fuchs et al., 1996)

$$\tau_{on} = \frac{\eta_{o'}}{G_{N'}^0} \quad (14)$$

$$\tau_{ow} = \eta_{o'} \cdot J_e^o \quad (15)$$

Comparing the different relaxation times Eqs (11), (12), (14) and (15) we find a value of β comprised between 2 and 3.4 for which the product $J_e^o \cdot G_{N'}^0$, is a measure of the breadth of the terminal spectrum

$$J_e^o \cdot G_{N'}^0 = \frac{\tau_{ow}}{\tau_{on}} = \frac{\tau_w}{\tau_n} \quad (16)$$

This value of β gives us the polydispersity.

4. Results and discussion

Polydispersity thus calculated has been compared with experimental polydispersity data in Table 1.

$\eta_{o'}, G_{N'}^0, J_e^o, \tau_o, \tau_n$ and τ_w values for all the polymers studied are listed in Table 2. In this Table, comparison of the different relaxation times reveals that the maximum relaxation time, τ_o , from the relaxation time spectrum is nearly identical to the weight average terminal relaxation time, τ_w , for polymers with low polydispersity. Deviations are noticeable only for polymers with a relatively high polydispersity.

Thus, for low polydisperse polymers we can calculate polydispersities just adjusting the value of β that makes $\tau_w = \tau_o$ while for highly polydisperse polymers, the ratio τ_w/τ_n can be used as a parameter to characterize the polydispersity.

Table1. Average molecular weight M_w and polydispersity indices for the polymers investigated

Sample	$M_w \cdot 10^{-3}$ (g/mol)	I_{p1} Experimental	I_{p2} Experimental	I_{p1} Calculated	I_{p2} Calculated
PDMS_H	630	1.7	1.4	1.7	1.5
PDMS_H75L25	496	3.1	2.1	3	2.1
PDMS_H46L54	341	3.6	2.7	3.5	2.7
PDMS_H25L75	228	3.1	3.5	3.1	2.7
PDMS_L	94	1.6	1.5	1.6	1.3

Table 2. Material Parameters

Sample	G_N^0 (Pa)	η_0' (Pa·s)	J_e^0 (Pa ⁻¹)	β	τ_0 (s)	τ_n (s)	τ_w (s)
PDMS H	8.56E+04	3.64E+04	1.5E-04	2.86	1.40E-01	3.20E-02	1.40E-01
PDMS H75L25	9.26E+04	1.88E+04	1.70E-04	2.5	3.71E-02	3.23E-03	5.1E-02
PDMS H46L54	5.59E+04	5.81E+03	3.37E-04	2.3	6.10E-03	1.25E-03	2.35E-02
PDMS H25L75	5.66E+04	9.61E+02	2.07E-04	2.1	2.69E-04	4.95E-04	5.33E-03
PDMS L	3.67E+04	8.96E+01	9.55E-05	2.88	1.18E-03	3.38E-04	1.18E-03

4. Conclusions

We have presented the application of a molecular model combined with rheological data to a set of PDMS polymers in order to obtain several polydispersity indices. The model provides polydispersity indices in very good agreement with available experimental data. The main advantage over previous published methods related to the same problem is that in this case several polydispersity indices can be obtained with the same procedure, while the method presented by Llorens et al 2003 allowed obtaining just one polydispersity index.

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