

Determination of the Discrete Relaxation Spectrum for Polybutadiene and Polystyrene by a Non-linear Regression Method

Ali Haghtalab* and Gholamhossein Sodeifian

Polymer Engineering Group, Department of Chemical Engineering, Tarbiat Modarres University, P.O. Box 14115-111, Tehran, I.R. Iran

Received 16 May 2001; accepted 31 January 2002

ABSTRACT

The relaxation spectrum is an important tool for investigating the behaviour of viscoelastic polymer melts. The most popular procedure for determining the relaxation spectrum is the use of a small-amplitude oscillatory shear experiment to determine the parameters in a multi-mode Maxwell model. However, this is an ill-posed problem and its numerical solution is along with difficulties. The determination of the discrete relaxation spectrum by a linear regression approach is widespread in practice and in the literature. In this work, a non-linear regression technique, based on Marquardt-Levenberg procedure, is applied in which the minimization is performed with respect to both the discrete relaxation times and the elastic moduli. Using this non-linear optimization, the spectrum parameters of a multi-mode Maxwell model were obtained for polybutadiene and polystyrene. It has been shown that in comparison with the other methods, the present approach is more efficient and it was found to give a very good fit with the fewest possible parameters.

Key Words: discrete relaxation spectrum, non-linear regression, rheology, polybutadiene, polystyrene

INTRODUCTION

The relaxation time spectrum describes the viscoelastic behaviour of polymeric material. The following statements can explain its central role and application in rheology. In general, using the relaxation time spectrum, one can correlate the rheological properties of a material with molecular dynamics [1, 2]. Furthermore, given this

spectrum, it is easy to convert one material function into another one [3, 4]. Additionally, in order to model polymer processing and to analyze them, rheological experiments often require the relaxation time spectrum. In fact, knowledge of the relaxation time spectrum is necessary for engineering calculations of linear viscoelastic material functions and complex flows. For example, when simulating the viscoelastic flows, one

(* To whom correspondence should be addressed. E-mail: ahaghtalab@hotmail.com

needs to have available a relaxation time spectrum where it can be used along with the constitutive equation.

Dynamic mechanical experiments can be used to measure the storage and loss modulus of polymeric liquids and solids over wide ranges of frequency. Highly sophisticated instruments are commercially available for performing these measurements.

However, the problem of converting the dynamic data from the frequency domain to the time domain is not at all a straightforward curve-fitting operation [5].

The relaxation time spectrum is not directly available from the experimental data. It has to be determined in an indirect manner. This particular calculation is one of the classical problems in rheology. In the literature various techniques have been proposed to determine the discrete relaxation spectrum from a set of experimental storage and loss modulus data.

Laun used the linear regression approach [6], however, this method may not lead to a physically meaningful spectrum. Because, as the number of Maxwell elements increases some negative elastic moduli are produced and this is physically unrealistic. Honerkamp and Weese [7] have demonstrated the use of a mathematical technique called the classical Tikhonov regularization to overcome this problem. Using this method, they were able to back-calculate their simulated relaxation spectrum using a large number of relaxation times. Therefore, the ill-posedness of the linear regression approach was well documented. According to Honerkamp and Weese, regularization method is robust and it is a general method. However, practical realization of this method leads to rather complicated and labour-consuming operations [8]. Another approach to determine the relaxation spectrum is to develop a non-linear regression to determine the relaxation times and the number of Maxwell elements as well as elastic moduli. Baumgaertel and Winter [9] used a non-linear regression method and found that the resulting elastic moduli were all positive, provided that the number of Maxwell elements was small. Unfortunately, they have not revealed the details of their method, but it is available as a commercial software product.

The objective of the present work is to show a non-linear regression method, with the fewest possible parameters and, for calculating the discrete relaxation spectrum. For this purpose, a non-linear regression approach, based on the Marquardt-Levenberg method, is used to optimize the parameters of the discrete spectrum function. Using this technique one allows to compare the results with the experimental data of polybutadiene and polystyrene (PS140) and then the accuracy of these results can be presented.

Theoretical Framework

The basic function in the theory of linear viscoelasticity is the linear relaxation modulus $G(t)$. It relates the stress tensor $\tau(t)$ to the rate of deformation tensor $\dot{\gamma}(t')$ in the following constitutive equation [10]:

$$\underline{\tau}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (1)$$

The function $G(t)$ is directly measurable by a sudden shear displacement of the material. It is necessary to represent the modulus by an explicit mathematical function. The most common function used is that of the generalized Maxwell model as:

$$G(t-t') = \sum_{i=1}^N g_i \exp\left[-(t-t')/\lambda_i\right] \quad (2)$$

Where g_i is the corresponding elastic modulus of a relaxation time λ_i ($1 \leq i \leq N$).

In small amplitude oscillatory shear flow, the shear rate in terms of frequency, ω , can be expressed in a complex form as:

$$\dot{\gamma}_{xy} = \text{Re} \{ \gamma_0 i \omega e^{i\omega t} \} \quad (3)$$

A stress tensor component $\tau_{xy}(t)$ is generated according to eqn (1), which can be written as:

$$\tau_{xy}(t) = \text{Re} \{ \gamma_0 \exp(i\omega t) (G'(\omega) + iG''(\omega)) \} \quad (4)$$

Where γ_0 , $G'(\omega)$, $G''(\omega)$ and Re are the strain amplitude, the storage modulus, the loss modulus and the real part of the complex number, respectively.

It can be shown that $G'(\omega)$ and $G''(\omega)$ are the Fourier sine and cosine transforms of the relaxation modulus, respectively [11].

$$G'(\omega) = \omega \int_{-\infty}^{\infty} G(t-t') \sin(\omega(t-t')) dt' \quad (5)$$

$$G''(\omega) = \omega \int_{-\infty}^{\infty} G(t-t') \cos(\omega(t-t')) dt' \quad (6)$$

Inserting eqn (2) into eqn (5) and (6) yields the following expressions for the dynamic moduli:

$$G'(\omega) = \sum_{i=1}^N g_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \quad (7)$$

$$G''(\omega) = \sum_{i=1}^N g_i \frac{\omega \lambda_i}{1 + \omega^2 \lambda_i^2} \quad (8)$$

In a dynamic experiment the dynamic moduli are calculated at a discrete set of frequencies. However, the discrete relaxation times are not directly available. On the other hand, the problem of determining the continuous relaxation spectrum of a viscoelastic fluid from dynamic data involves the following pair of Fredholm integral equations:

$$G'(\omega) = \int_0^{\infty} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \frac{d\lambda}{\lambda} \quad (9)$$

$$G''(\omega) = \int_0^{\infty} H(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} \frac{d\lambda}{\lambda} \quad (10)$$

Where $H(\lambda)$ denotes the continuous spectrum as a function of the relaxation time λ .

The inversion of either the eqn (9) or (10) or both as a pair is known as "ill posed" [12]. In particular, this means that small perturbations in the measurements of $G'(\omega)$ and $G''(\omega)$ can lead to arbitrarily large perturbations in the spectrum $H(\lambda)$. Therefore, great care is required to determine $H(\lambda)$ from dynamic mechanical data. In practice the discrete relaxation spectrum is determined by fitting models such as the discrete representation of the eqns (9) and (10). The non-linear nature of the eqns (7) and (8) makes them extremely difficult to solve. In the next sections optimization of the mentioned parameters are described.

Linear Regression Method

In linear regression method discrete relaxation times are given a priori and using the least square objective function, minimization is performed only with respect to the unknown elastic moduli. Having the experimental values for $G'(\omega)$ and $G''(\omega)$, one may formulate the following least square objective function:

$$\sigma = \sum_{j=1}^M \left[\left(G'(\omega_j) - \sum_{i=1}^N g_i \frac{\omega_j^2 \lambda_i^2}{1 + \omega_j^2 \lambda_i^2} \right)^2 + \left(G''(\omega_j) - \sum_{i=1}^N g_i \frac{\omega_j \lambda_i}{1 + \omega_j^2 \lambda_i^2} \right)^2 \right] \quad (11)$$

Where M and N are the number of experimental data and relaxation modes, respectively. The values $G'(\omega_j)$ and $G''(\omega_j)$ are the measured experimental data over a discrete set of frequencies $\omega_j (1 \leq j \leq M)$.

One can differentiate eqn (11) with respect to each g_i and obtain sets of equations, called the normal equations that can be solved by Gauss Jordan elimination method [13]. However, in many cases the normal equations are very close to singular and a zero pivot element may be encountered. In such cases, the minimization problem can be solved by performing a singular value decomposition (SVD) [14]. Meanwhile, the minimum of the objective function may be very flat. This means that it yields many solutions that are compatible with the given data, for example, negative values for some of the elastic moduli. Therefore, there are serious shortcomings in the use of the linear regression method to determine the discrete relaxation spectrum. In order to overcome this difficulty, Honerkamp [14] introduced an additional criterion using Tichonov's regularization method. However, as stated before, practical realization of this method leads to rather complicated and labour-consuming operations. Therefore, non-linear regression method can be considered as an alternative method.

Non-linear Regression Method

One of the shortcomings of linear regression methods,

apart from the obvious ill-posedness, is that the relaxation times are specified a priori. If some of these were placed too close together then it would lead to small singular values. In non-linear regression methods the relaxation times are as adjustable parameters. In fact, the objective function is non-linear with respect to both the relaxation times and elastic moduli. Also, the number of Maxwell elements, N , can be selected as an iteration parameter.

The number of Maxwell elements has a crucial role for the success of non-linear regression methods. When N is too few the least squares error is large. However, when a few more relaxation modes are added the mentioned error decays rapidly. Beyond some critical value of N , the least-squares errors will not improve significantly and negative values of the elastic moduli may begin to appear [15]. Winter et al. [16] chose N to be a large number, which is decreased gradually until all the elastic moduli are positive. One may use an alternative way such that the value of N is a small number. Initially, we select $N=1$, and increase it smoothly, until the problem is well posed. In order to determine the discrete relaxation times and elastic moduli, we minimize the following objective function [17]:

$$\sigma = \sum_{j=1}^M \left[\left(\sum_{i=1}^N \frac{1}{G'(\omega_j)} g_i \frac{\omega_j^2 \lambda_i^2}{1 + \omega_j^2 \lambda_i^2} - 1 \right)^2 + \left(\sum_{i=1}^N \frac{1}{G''(\omega_j)} g_i \frac{\omega_j \lambda_i}{1 + \omega_j^2 \lambda_i^2} - 1 \right)^2 \right] \quad (12)$$

Where M and N are the number of experimental data and relaxation modes, respectively. Also, the values $G'(\omega_j)$ and $G''(\omega_j)$ are the measured experimental data. In fact, the above objective function is the average square deviation between model [eqns (7) and (8)] and measured values of $G'(\omega_j)$ and $G''(\omega_j)$.

The non-linear least-squares problem at each step is solved using the Marquardt-Levenberg algorithm. Also, the discrete relaxation times and elastic moduli are determined as follows:

$$\lambda_i > \lambda_{i+1} \quad (i=1, \dots, N-1)$$

$$g_i > g_{i+1} \quad (i=1, \dots, N-1)$$

Once the discrete relaxation spectrum of a material is determined it can be used to calculate all of the material functions. This means that the discrete relaxation spectrum is an important tool for describing the viscoelastic behaviour of polymeric material.

EXPERIMENTAL

In order to evaluate the above-mentioned method, two sets of data are used. These are the dynamic mechanical data of polybutadiene melt [18] as well as polystyrene (PS140) melt with narrow molecular weight distributions. Polybutadiene has average molecular weight 57800 (g/mol), polydispersity 1.05 and the data values are obtained at 23 °C. Also polystyrene (PS140) was obtained from BASF AG with average molecular weight 145000 g/mol and polydispersity 1.03. Dynamic oscillatory shear experiment was performed on polystyrene (PS140) sample using a rheometrics mechanical spectrometer RMS-800 with parallel plate geometry of 25 mm diameter.

In general, the rheology of polymer melts depends strongly on temperature. It is well known that in the case of thermo-rheological materials, the simple and regular isotherms of $G'(\omega)$ and $G''(\omega)$ (or other material function) can be superimposed by horizontal shifts along the frequency axis (ω). Usually, two semi-empirical equations, the Arrhenius and the WLF equation, are used to evaluate the temperature dependence of the shift factors. It is possible to describe this kind of the temperature dependence of polystyrene (PS140) melt by the WLF equation with high accuracy. The dynamic moduli were measured in the temperature range 150–200 °C. Finally, the master curve was obtained by shifting the isotherms to the reference temperature 170 °C.

RESULTS AND DISCUSSION

The discrete relaxation spectrum and corresponding elastic moduli for each of these polymeric materials

Table 1. Discrete relaxation spectrum for polybutadiene.

i	λ_i	g_i
1	0.032042	23833.255732
2	0.015225	72222.542840
3	0.004007	247429.506713
4	0.000771	341514.523423

Table 2. Discrete relaxation spectrum for polystyrene (PS140).

i	λ_i	g_i
1	0.965210	10.000000
2	0.854440	39436.908400
3	0.253750	76912.360193
4	0.003789	71931.486691
5	0.004867	86562.856200
6	0.000607	83747.119628
7	0.000072	41126.348056
8	0.000001	25802973.719866

are given in Tables 1 and 2, respectively. We compare the results of the present non-linear regression to the results of other regression techniques for polybutadiene and polystyrene (PS140) in Table 3. For this purpose an appropriate criteria, average absolute deviation (AAD) [19], is used. Also the standard deviations 0.8×10^{-3} and 0.9×10^{-2} are calculated for both the samples, respectively. It can be investigated

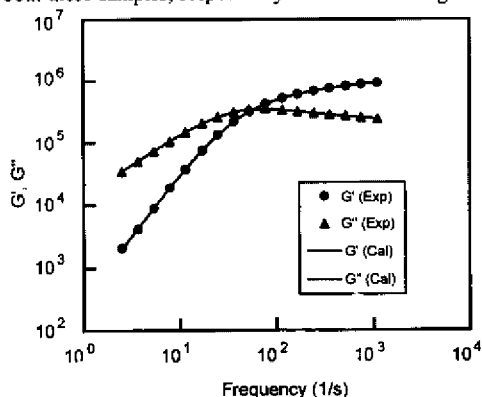


Figure 1. Comparison of the experimental data and model predictions for polybutadiene.

Table 3. Average absolute deviation AAD* for dynamic moduli of polybutadiene and polystyrene.

Material	Method	ADD (G')	ADD (G'')
Polybutadiene	Laun	16.6	13.7
	Winter	1.18	1.26
	Honerkamp	0.76	0.94
	Present study	0.95	0.85
Polystyrene	Laun	44.7	30.14
	Winter	3.23	2.71
	Honerkamp	2.16	2.24
	Present study	2.57	1.89

$$(*) \text{ AAD} = \left[\frac{1}{M} \sum_{i=1}^M \left(\frac{|G_i^{exp} - G_i^{cal}|}{G_i^{exp}} \right) \right]$$

that comparisons of the results of this work with the results from the other methods lead to conclusion that the present method has a high accuracy, especially for loss modulus. In addition, since the result of the regression is independent of starting value sets, the solution seems to be unique [20, 21]. Furthermore, there is no sign of ill-posedness.

The values of N for polybutadiene and polystyrene (PS140) were tuned to be 4 and 8, respectively. It can be seen that the results of fitting for both polybutadiene and polystyrene are excellent. In addition, the related discrete relaxation spectrum can be described by the fewest possible parameters.

Figures 1 and 2 show the changes of $G'(\omega)$ and $G''(\omega)$ against frequency for both the experimental data and the calculated values by eqns (7) and (8).

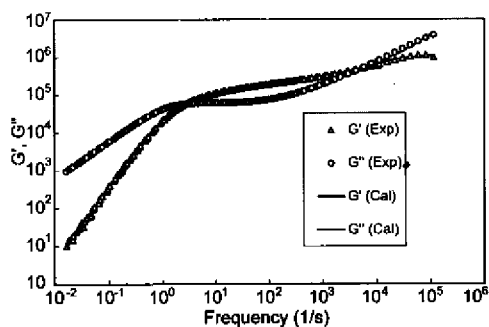


Figure 2. Comparison of the experimental data and model predictions for polystyrene (PS140).

CONCLUSION

In this work, based on Marquardt-Levenberg approach, a suitable non-linear regression technique has been presented for the determination of the discrete relaxation spectrum. The comparison with the other techniques has been performed for both polybutadiene and polystyrene materials and it has been shown that, by increasing smoothly the Maxwell elements and with the fewest possible parameters, the results of fitting are in very good agreement with experimental data.

ACKNOWLEDGEMENTS

The authors thank Professors C. Friedrich and K. Fuchs, (Freiburger Materialforschungs zentrum Germany) for their assistance in obtaining the experimental data of polystyrene (PS140) in their laboratory.

SYMBOLS AND ABBREVIATIONS

AAD	Average absolute deviation
$G(t)$	Linear relaxation modulus
$G'(\omega)$	Storage modulus
$G''(\omega)$	Loss modulus
g	Elastic modulus
$H(\lambda)$	Continuous relaxation-time spectrum
M	Number of experimental data
N	Number of relaxation modes
Re	Real part of the complex number
$\dot{\gamma}(t')$	Shear rate tensor
γ_0	Strain amplitude
λ	Relaxation time
σ	Least-square error
$\tau(t)$	Stress tensor
ω	Frequency

REFERENCES

- Elster C., Honerkamp J. and Weese J., "Regularization methods for the determination of relaxation spectra of polymeric liquids", *Rheol. Acta*, **31**, 161-174 (1992).
- Thimm W., Friedrich C., Marth M. and Honerkamp J., "On the Rouse spectrum and the determination of the molecular weight distribution from rheological data", *Rheol. Acta*, **44**, 429-438 (2000).
- Ferry J.D., *Viscoelastic Properties of Polymers*, John Wiley, New York (1980).
- Tschoegl N.W., *The Phenomenological Theory of Linear Viscoelastic Behaviour*, Springer, Berlin Heidelberg, New York (1989).
- Thimm W., Friedrich C., Marth M. and Honerkamp J., "Determination of relaxation time spectra from dynamic moduli using edge preserving regularization method", *Rheol. Acta*, **39**, 163-173 (2000).
- Laun H.M., "Prediction of elastic strains of polymer melts in shear and elongation", *J. Rheol.*, **30**, 459-465 (1989).
- Honerkamp J. and Weese J., "Tichonov's regularization method for ill-posed problems: A comparison of different methods for the determination of the regularization parameter", *Continuum Mech. Thermodyn.*, **2**, 17-30 (1990).
- Malkin A.Y. and Kuznetsov V.V., "Linearization as a method for determining parameters of relaxation spectra", *Rheol. Acta*, **39**, 379-383 (2000).
- Baumgartner M. and Winter H.H., "Determination of discrete relaxation and retardation time spectra from dynamic mechanical data", *Rheol. Acta*, **28**, 511-519 (1989).
- Dealy J.M. and Wissburn K.F., *Melt Rheology and its Role in Plastic Processing*, Van Nostrand Reinhold, New York (1990).
- Bird R.B., Armstrong R.C. and Hassager O., *Dynamics of Polymeric Liquids*, 1, 2nd ed., Wiley Interscience, New York (1987).
- Morozov V.A., *Methods for Solving Incorrectly Posed Problems*, Springer, New York (1984).
- Press W.H., Flannery B.P., Teukolsky S.A. and Vetterling T.W., *Numerical Recipes in C: the Art of Scientific Computing*, Cambridge University, Cambridge (1992).
- Honerkamp J. et al., "Ill-posed problems in rheology", *Rheol. Acta*, **28**, 363-271 (1989).
- Winter H.H. and Baumgartner M., "A parsimonious model for viscoelastic liquids and solids", in *Techniques in Rheological Measurement*, Ch. 5, Chapman and Hall, London (1993).
- Winter H.H., Baumgartner M., Soskey P. and Verkataraman S., "Computer aided rheometry", *3rd Eur. Rheology Conf. and Golden Jubilee Meeting of British Society of Rheology*, 504-506 (1990).
- Cooper L., *Applied Non-linear Programming for Engineering and Scientists*, Atoray, Englewood, NJ, 1984.

18. Honerkamp J. and Weese J., "Determination of the relaxation spectrum by a regularization method", *Macromolecules*, **22**, 4372-4377 (1989).
19. Orbey N. and Dealy J.M., "Determination of the relaxation spectrum from oscillatory shear data", *J. Rheol.*, **35**, 1035-1045 (1991).
20. Sodeifian Gh. and Haghtalab A., "Determination of the discrete relaxation spectrum from dynamic moduli using a nonlinear regression method", Australian-Korean Rheology Conference, Melbourne, **39**, September (2001).
21. Sodeifian Gh. and Haghtalab A., "Calculation of the discrete relaxation spectrum for polymeric materials using a nonlinear regression method", The Society of Rheology 73rd Annual Meeting, Bethesda, Maryland, **12**, October (2001).