

## Determination of discrete relaxation and retardation time spectra from dynamic mechanical data \*

M. Baumgaertel and H.H. Winter

Department of Chemical Engineering, University of Massachusetts, Amherst (USA)

**Abstract:** A powerful but still easy to use technique is proposed for the processing and analysis of dynamic mechanical data. The experimentally determined dynamic moduli,  $G'(\omega)$  and  $G''(\omega)$ , are converted into a discrete relaxation modulus  $G(t)$  and a discrete creep compliance  $J(t)$ . The discrete spectra are valid in a time window which corresponds to the frequency window of the input data. A nonlinear regression simultaneously adjust the parameters  $g_i$ ,  $\lambda_i$ ,  $i = 1, 2, \dots, N$ , of the discrete spectrum to obtain a best fit of  $G'$ ,  $G''$ , and it was found to be essential that both  $g_i$  and  $\lambda_i$  are freely adjustable. The number of relaxation times,  $N$ , adjusts during the iterative calculations depending on the needs for avoiding ill-posedness and for improved fit. The solution is insensitive to the choice of initial values  $g_{i,0}$ ,  $\lambda_{i,0}$ ,  $N_0$ . The numerical program was calibrated with the gel equation which gives analytical expressions both in the time and the frequency domain. The sensitivity of the solution was tested with model data which, by definition, are free of experimental error. From the relaxation time spectrum, a corresponding discrete set of parameters  $J_0$ ,  $\eta$ ,  $J_{d,i}$  and  $\Lambda_i$  of the creep compliance  $J(t)$  can then readily be calculated using the Laplace transform.

**Key words:** Relaxation modulus; complex modulus; relaxation spectrum; retardation spectrum; critical gel

### 1. Introduction

Modelling of polymer processing and analysis of processing experiments often require the relaxation or retardation time spectrum,  $G(t)$  or  $J(t)$ , instead of the readily available dynamic moduli,  $G'$ ,  $G''$ . Therefore it is of great practical use to convert dynamic mechanical data (dynamic moduli  $G'$ ,  $G''$  which are easy to measure) from the frequency domain into data in the time domain (linear relaxation modulus  $G(t)$  which is easy to interpret). This data conversion should preferably be performed by a self-contained computer program which does not require any material specific input beyond the  $G'$ ,  $G''$  data set.

The determination of the relaxation time spectrum has been recognized as an ill posed problem with degree of ill-

posedness increasing as the number of relaxation times increases [1, 2]. We will show that the problem can be avoided by simply keeping the number of relaxation modes small. The restriction to a small number of relaxation modes is therefore not just a matter of convenience (convenient for data storage or for numerical calculations of viscoelastic liquid flow) but it is a necessity for a meaningful description of viscoelastic data. Due to this relatively small number of relaxation modes, the values of the relaxation times can not be pre-set but they have to be optimized to avoid waviness. In fact, in our approach waviness is not a noticeable problem even with a reduced number of relaxation modes.

Dynamic mechanical experiments are most effective for measuring the relaxation modes of polymeric liquids and solids over wide ranges of frequency. Highly sophisticated equipment is commercially available for that purpose. The sample is deformed sinusoidally at small amplitudes and the stress response is measured to obtain the dynamic moduli, i.e. the storage modulus,  $G'$ , and the loss modulus,  $G''$  [3]. It is a classical problem of rheology to convert the dynamic data from the frequency domain to the time domain [4, 5, 2]. The problem could be avoided by directly measuring the relaxation modulus,  $G(t)$ , in the time domain (step strain experiment). However, the gained simplicity in the analysis comes at the expense of the accuracy which is not nearly as good as for the dynamic mechanical experiment. It there-

\*) This paper is dedicated to Professor Hanswalter Giesekus on the occasion of his retirement as Editor of Rheologica Acta.

fore is preferable to determine  $G(t)$  from dynamic mechanical data.

The objective of this study is to express dynamic mechanical data with discrete spectra which allow prediction of linear viscoelastic behavior in the time domain. The number of relaxation modes shall be kept small. Initial results have been presented at ANTEC 1989 [6].

## 2. Background

### 2.1 Linear viscoelastic material behavior

In the range of small deformations, the relation between the deformation and stress can be described by a constitutive equation which is based on Boltzmann's superposition principle [3]

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

where  $\tau$  is the stress tensor,  $\dot{\gamma}$  is the strain rate tensor and  $G(t)$  is the linear relaxation modulus. An alternative linear viscoelastic constitutive equation expresses the strain in terms of the history of the time derivative of the stress  $\dot{\tau}$

$$\gamma(t) = \int_{-\infty}^t J(t-t') \dot{\tau}(t') dt' \quad (2)$$

where  $J(t)$  is the creep compliance. The linear relaxation modulus  $G(t)$  and the creep compliance  $J(t)$  are related [3]

$$\int_0^t G(t') J(t-t') dt' = t \quad (3)$$

Physical models of chain motion give a discrete relaxation spectrum. For linear polymers of uniform length, the relaxation modes are well defined. However, in real polymers the spectrum is "smeared out" due to the non-uniformity of the chains and the relaxation modes lose their distinct physical meaning. In the following, we will consider a discrete relaxation (and retardation) spectrum even if it cannot be interpreted physically. The relaxation modulus,  $G(t)$ , will conveniently be expressed as a discrete set of exponential decays

$$G(t) = G_e + \sum_{i=1}^N g_i \exp(-t/\lambda_i) \quad (4)$$

realizing that other decays would be also acceptable [7]. The  $N$  relaxation modes are defined by their relaxation strength  $g_i$  and their relaxation times  $\lambda_i$ . The equilibrium modulus  $G_e$  is finite for solids ( $G_e > 0$ ) and zero for liquids ( $G_e = 0$ ). Using this discrete spectrum in Eq. (1), the dynamic moduli,  $G'$  and  $G''$ , become

$$G'(\omega) = G_e + \sum_{i=1}^N g_i \frac{(\omega \lambda_i)^2}{1 + (\omega \lambda_i)^2}, \quad (5)$$

$$G''(\omega) = \sum_{i=1}^N g_i \frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2}. \quad (6)$$

From these equations, it can be seen that the discrete relaxation spectrum (DRS) may be determined from measured values of the dynamic moduli or vice versa.

### 2.2 Critical gel

For the development of our method, it is convenient that there exist viscoelastic materials for which the linear relaxation modulus, the creep compliance, and dynamic moduli are known in analytic form. These are materials at the gel point, the critical gels [8] with a relaxation modulus (gel equation [18])

$$G(t) = S t^{-n}. \quad (7)$$

It should be noted here, that Heindl and Giesekus [9] have discussed materials with power law relation and realized that they are neither liquid nor solid. However, they did not expect that such behavior does exist in nature. Some polymers (others than gels) exhibit power law relaxation at intermediate frequency [10].

The continuous spectrum may be written in discrete form

$$G(t) = \sum_{i=0}^{\infty} g_0 \left( \frac{\lambda_0}{\lambda_i} \right)^n e^{-t/\lambda_i}, \quad t/\lambda_0 \gg 1. \quad (8)$$

For simplicity, the spacing  $\alpha$  of the relaxation times may be chosen equidistant in a log scale,  $\lambda_i = \lambda_0 10^{i\alpha}$ .  $\lambda_0$  is the shortest mode in the power law spectrum.

The creep compliance of gels also has power law format

$$J(t) = \frac{(1-n)t^n}{S\Gamma(2-n)\Gamma(1+n)} = \sum_{i=0}^{\infty} J_{d,0} \left( \frac{\Lambda_i}{\Lambda_0} \right)^n (1 - e^{-t/\Lambda_i}), \quad t/\Lambda_0 \gg 1. \quad (9)$$

and it also can be expressed in discrete form, where the spacing of the retardation times may be chosen equidistant in the log scale,  $\Lambda_i = \Lambda_0 10^{i\alpha}$ .

The complex modulus  $G^*$  of a critical gel is given by

$$G^* = G' + iG'' = S\Gamma(1-n)\omega^n \times [\cos(n\pi/2) + i \sin(n\pi/2)]. \quad (10)$$

We will use the explicit relations as an independent check of our solution. It is especially useful that the

continuous spectra are expressible in discrete form because our method relies on the choice of a discrete spectrum.

### 3. Conversion from the frequency to the time domain

Three methods of conversion are found in the literature. The first method uses a Fourier transformation

$$G(t) = G_e + \frac{2}{\pi} \int_0^{\infty} \frac{(G'(\omega) - G_e)}{\omega} \sin(\omega t) d\omega \quad (11)$$

or

$$G(t) = G_e + \frac{2}{\pi} \int_0^{\infty} \frac{G''(\omega)}{\omega} \cos(\omega t) d\omega \quad (12)$$

which is commonly split into 3 parts:

$$G(t) = \frac{2}{\pi} \left( \int_0^{\omega_{\min}} \dots d\omega + \int_{\omega_{\min}}^{\omega_{\max}} \dots d\omega + \int_{\omega_{\max}}^{\infty} \dots d\omega \right). \quad (13)$$

The first and the third term require data extrapolation in the frequency range from  $\omega = 0$  to  $\omega_{\min}$  and from  $\omega_{\max}$  to  $\infty$ , while experimental data are only available in the intermediate window (second term). It is obvious that this extrapolation process is highly arbitrary. A detailed description of the Fourier Transform method has been given recently [19].

A second method utilizes empirical correlations which are successful for wide classes of materials [3, 5]. However, for complex materials one would like to have a more general conversion method.

In the third method, the parameters of a discrete relaxation spectrum are found by simply fitting Eqs. (5) and (6) to  $G'$ ,  $G''$  data. The coefficients,  $g_i$ , and relaxation times,  $\lambda_i$ , are determined such that the average square deviation between predicted  $G'$ ,  $G''$  values and measured  $G'$ ,  $G''$  data is minimum (least squares fit):

$$\sum_{j=1}^m \left( \left[ \frac{G'(\omega_j)}{\hat{G}'_j} - 1 \right]^2 + \left[ \frac{G''(\omega_j)}{\hat{G}''_j} - 1 \right]^2 \right) = \min. \quad (14)$$

$\hat{G}'_j$ ,  $\hat{G}''_j$  are the measured data at  $m$  frequencies  $\omega_j$  and  $G'$ ,  $G''$  are calculated values from Eqs. (5) and (6). From here one might progress by prescribing a set of  $\lambda_i$  and calculating the coefficients  $g_i$  [11, 12]. Differentiating this function with respect to  $g_i$  leads to a set of linear equations which can be solved numerically. The convergence of the solution can be improved

by using the classical Tikhonov regularization method [2, 13]. Negative coefficients,  $g_i < 0$ , may appear if the spacing of the relaxation times is too small [2].

In this study, we also use the third method, however, with a major difference. In our experience, it is necessary to keep not only all  $g_i$  but also all  $\lambda_i$  freely adjustable. Additionally, the number of relaxation modes,  $N$ , has to be a freely adjustable parameter. The resulting coefficients are necessarily all positive.

The choice of  $N$  is crucial for the success of our method. With too few relaxation modes, the average deviation (residual in Eq. (14)) is large. However, it decays rapidly when increasing the number of relaxation modes,  $N$ . Above a certain value of  $N$ , the residual starts levelling off and a further increase of the number of relaxation modes is not justified since one would not want to reduce the average deviation below the error bar of the measured  $G'$ ,  $G''$ . At that high number of relaxation modes, negative  $g_i$ -values start to occur and the problem becomes ill-posed. Also, in most practical cases the finite number of data points is not sufficient to determine the excessive number of parameters  $g_i$  and  $\lambda_i$  at high value of  $N$ . In our numerical program, the initial number of relaxation modes is chosen empirically between 1 and 2 per decade. It was found to be advantageous to start with a large number of relaxation modes and let the program merge or eliminate unnecessary ones. One criterium for reducing the number of relaxation times was the occurrence of negative  $g_i$ -values.

The program also applies to viscoelastic solids, even in cases where the equilibrium modulus can not be determined since it would require extrapolation beyond the accessible frequency window of the dynamic experiment. In most cases we found that more modes are necessary to describe the relaxation of viscoelastic solids than of a liquid in a comparable time range.

### 4. Relation between discrete retardation and relaxation spectra

The calculated relaxation spectrum also defines the retardation spectrum. Methods of calculating the retardation spectrum from a relaxation spectrum are well known [3, 4, 14]. The calculation is especially simple for discrete spectra. The relations are easiest to understand when derived from the beginning. Since the relaxation spectrum is given in analytical form, one can solve the convolution integral, Eq. (3), using the Laplace transform

$$\hat{G}(s)\hat{J}(s) = 1/s^2. \quad (15)$$

The Laplace transform of the linear relaxation modulus of a viscoelastic liquid, ( $G_e = 0$ ),

$$\hat{G}(s) = \sum_{i=1}^N \frac{g_i}{s + 1/\lambda_i} \quad (16)$$

is substituted into Eq. (15) to give the retardation spectrum in the Laplace domain<sup>1)</sup>

$$\hat{J}(s) = \frac{1}{s^2} \frac{\prod_{k=1}^N (s + 1/\lambda_k)}{\sum_{i=1}^N \left( g_i \prod_{k=1, i}^N (s + 1/\lambda_k) \right)} \quad (17)$$

This may be rearranged by using partial fractions:

$$\hat{J}(s) = \frac{K_0}{s} + \frac{K_1}{s^2} - \sum_{i=1}^{N-1} \frac{c_i}{(s + 1/\lambda_i)} \quad (18)$$

with the constants

$$K_0 = -K_1 + \frac{1}{G_0} \frac{\prod_{k=1}^N (1 + 1/\lambda_k)}{\prod_{k=1}^{N-1} (1 + 1/\lambda_k)} + \sum_{k=1}^{N-1} \frac{c_k}{(1 + 1/\lambda_k)} \quad (19)$$

$$K_1 = \frac{1}{G_0 \lambda_N} \prod_{k=1}^{N-1} \frac{\lambda_k}{\lambda_k} \quad (20)$$

$$c_i = -\frac{1}{G_0} \frac{\prod_{k=1}^N \left( 1 - \frac{\lambda_i}{\lambda_k} \right)}{\prod_{k=1, i}^{N-1} \left( 1 - \frac{\lambda_i}{\lambda_k} \right)}; \quad i = 1, \dots, N-1 \quad (21)$$

$$G_0 = \sum_{i=1}^N g_i \quad (22)$$

The  $N-1$  discrete retardation times are the inverse of the real roots of

$$\sum_{i=1}^N g_i \left( \prod_{k=1, i}^N (s + 1/\lambda_k) \right) = G_0 \prod_{i=1}^{N-1} (s + 1/\lambda_i) \quad (23)$$

The ordering of the relaxation and retardation times is found to be [15]:

$$\lambda_1 < \lambda_1 < \lambda_2 < \dots < \lambda_{N-1} < \lambda_{N-1} < \lambda_N \quad (24)$$

The retardation spectrum  $\hat{J}(s)$  can then be transformed back into the time domain

$$J(t) = J_g + t/\eta + \sum_{i=1}^{N-1} J_{d,i} \Psi_i(t), \quad J_{d,i} \equiv c_i \quad (25)$$

with the instantaneous compliance  $J_g$

$$J_g = K_0 - \sum_{i=1}^{N-1} c_i, \quad (26)$$

the steady shear viscosity

$$\eta = 1/K_1 = \sum_{i=1}^N g_i \lambda_i, \quad (27)$$

and the retarded compliance

$$J_{d,i} \Psi_i(t) = c_i (1 - e^{-t/\lambda_i}) \quad (28)$$

The derivation for viscoelastic solids ( $G_e > 0$ ) is accordingly as shown in Appendix A.

## 5. Calculated discrete relaxation and retardation spectra

Three spectra will be discussed in the following. Starting from measured data  $G'$ ,  $G''$  the discrete relaxation spectrum will be calculated first and from that, the discrete retardation spectrum is obtained.

Our method can be demonstrated on a blend of two monodisperse polystyrenes of different molecular weight using the published dynamic mechanical data of Schausberger et al. [16, 17] as shown in Fig. 1. The

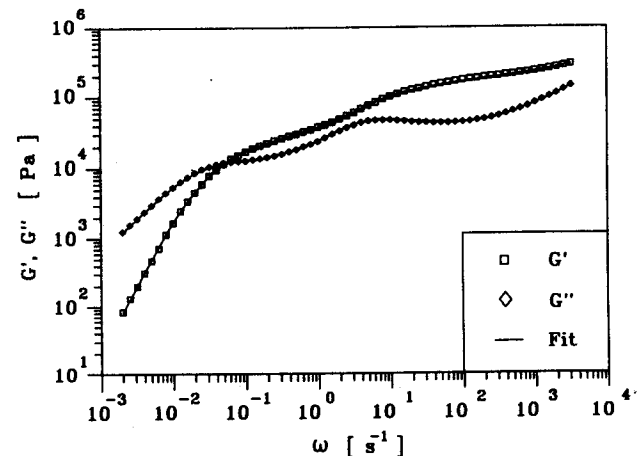


Fig. 1. Dynamic moduli vs. frequency for a blend of two monodisperse polystyrenes of different molecular weight (50% of  $M_w = 125000$  and 50% of  $M_w = 750000$ ) [16, 17]

<sup>1)</sup> Notation

$\prod_{k=1, i}^N a_k$ . Multiply all  $a_k$  except  $a_i$

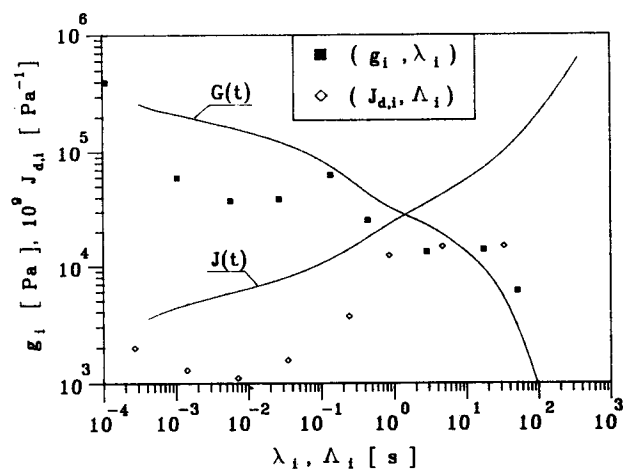


Fig. 2. Discrete relaxation and retardation spectrum calculated numerically from data of Fig. 1. The corresponding relaxation modulus and creep compliance are calculated with discrete spectra

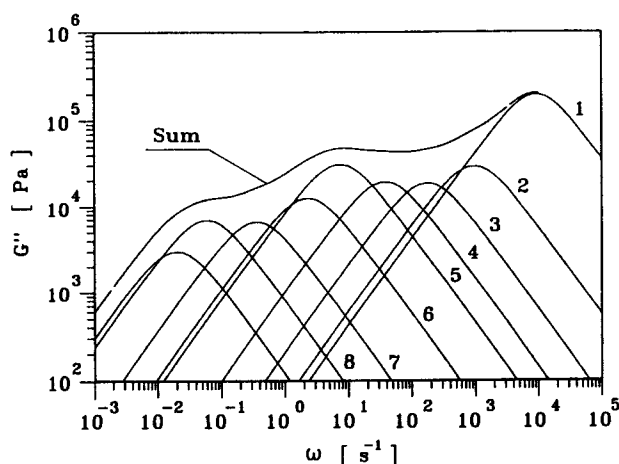


Fig. 4. Contribution of each mode to the loss modulus,  $G''$ , of Fig. 1

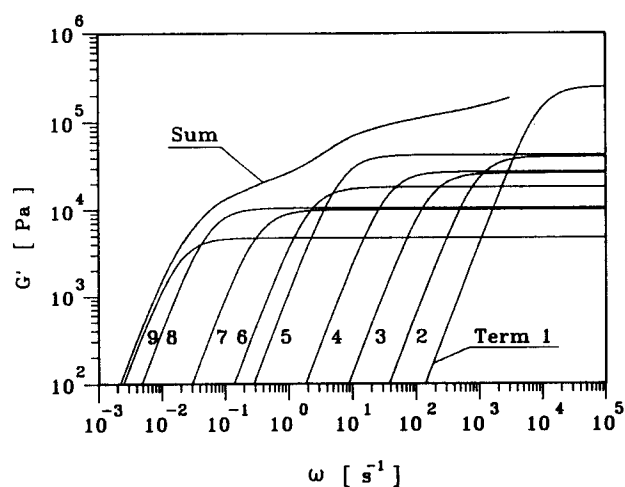


Fig. 3. Contribution of each mode to the storage modulus,  $G'$ , of Fig. 1

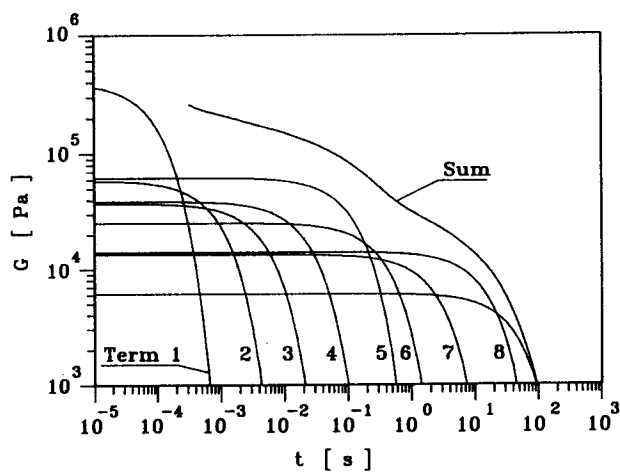


Fig. 5. Calculated relaxation modulus and contribution of each mode for data of Fig. 1

Table 1. Parameters of the discrete relaxation and retardation spectra for the sample of Fig. 1

$i$	$g_i$ [Pa]	$\lambda_i$ [s]	$c_i$ [Pa $^{-1}$ ]	$A_i$ [s]
1	399000	$1.106 \cdot 10^{-4}$	$1.987 \cdot 10^{-6}$	$2.688 \cdot 10^{-4}$
2	59200	$1.066 \cdot 10^{-3}$	$1.109 \cdot 10^{-6}$	$7.185 \cdot 10^{-3}$
3	37300	$5.837 \cdot 10^{-3}$	$1.293 \cdot 10^{-6}$	$1.419 \cdot 10^{-3}$
4	38800	$2.716 \cdot 10^{-2}$	$1.562 \cdot 10^{-6}$	$3.502 \cdot 10^{-2}$
5	62500	$1.397 \cdot 10^{-1}$	$3.662 \cdot 10^{-6}$	$2.432 \cdot 10^{-1}$
6	25300	$4.468 \cdot 10^{-1}$	$1.247 \cdot 10^{-5}$	$8.697 \cdot 10^{-1}$
7	13400	$2.861 \cdot 10^0$	$1.485 \cdot 10^{-5}$	$4.677 \cdot 10^0$
8	14100	$1.743 \cdot 10^1$	$1.505 \cdot 10^{-5}$	$3.332 \cdot 10^1$
9	6120	$5.142 \cdot 10^1$		

line through the data points is calculated with the fitted relaxation time spectrum. The calculated values of the parameters of the discrete relaxation and retardation spectrum are given in Table 1 (see also Fig. 2). The instantaneous compliance and the zero shear viscosity are  $J_g = 1.526 \cdot 10^{-6} \text{ Pa}^{-1}$  and  $\eta = 6.202 \cdot 10^5 \text{ Pa s}$  respectively.

The contribution of the discrete relaxation modes are shown for the dynamic moduli, Figs. 3 and 4, and the linear relaxation modulus, Fig. 5. Domination can be seen by the relaxation modes No. 1, 5 and 8. These relaxation modes can be considered to be characteristic of this polymer blend, while No. 9 has the longest

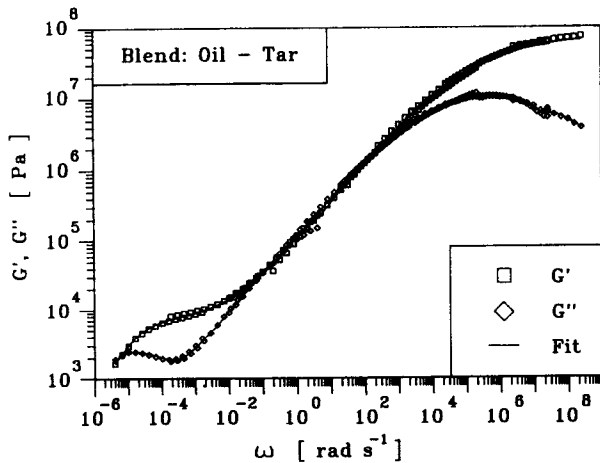


Fig. 6. Dynamic moduli vs frequency for polymer modified bitumen

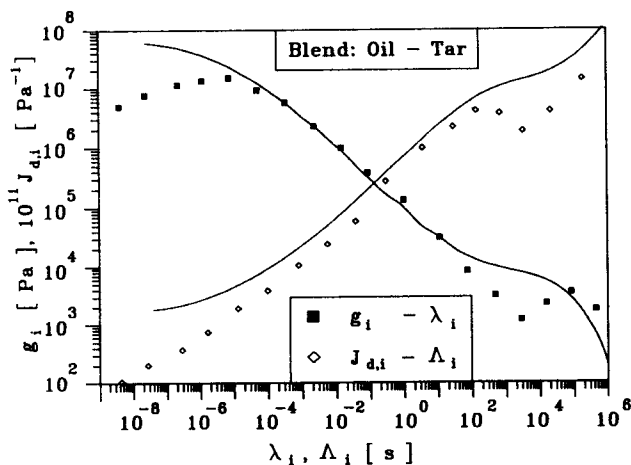


Fig. 7. Discrete relaxation and retardation spectrum calculated numerically from data of Fig. 6. The corresponding relaxation modulus and creep compliance are calculated with discrete spectra

relaxation time. Notice that the spacing between the relaxation times is not equidistant. Since the result of the regression is independent of starting value sets, the solution seems to be unique in the case of a small number of relaxation modes. There is no sign of ill-posedness. Obviously, the solution changes when altering the value of  $N$  or the weight factor in Eq. (14).

The "plateaus" in the measured dynamic moduli and the calculated  $G(t)$  have a physical meaning as

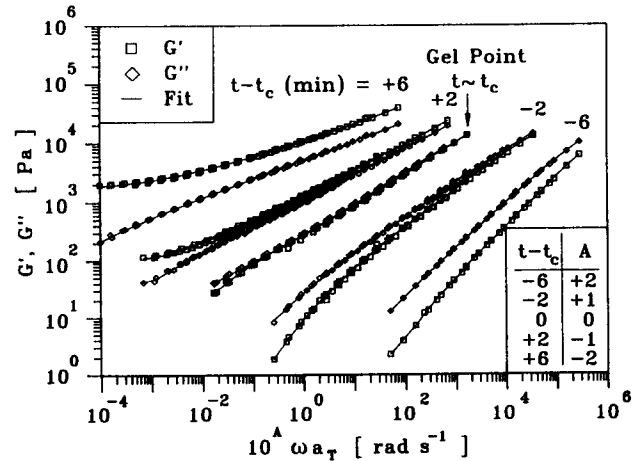


Fig. 8. Evaluation of the dynamic moduli of a crosslinking polymer at increasing degree of crosslinking (increase crosslinking time) [18]. The lines are calculated with discrete spectra. Data in the liquid and in the solid range are approximated equally well. No attempt is made to extrapolate to the equilibrium modulus

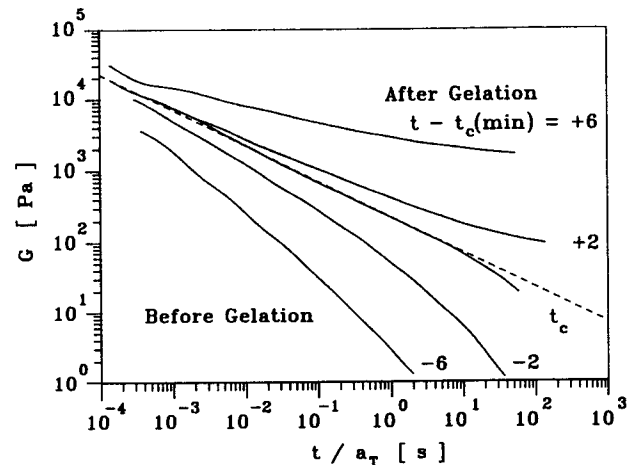


Fig. 9. Evolution of relaxation modulus during liquid/solid transition as calculated from Fig. 8

discussed by Schausberger. Unfortunately, experimental data of the relaxation modulus of this polymer blend are not available to compare with the calculation.

The second example, a commercial blend of tar and oil, demonstrates the ease with which the approximation of complex data over a frequency range of 14 decades is achieved, see Figs. 6 and 7. The data scatter does not cause a major problem except that it slightly increases the computation time.

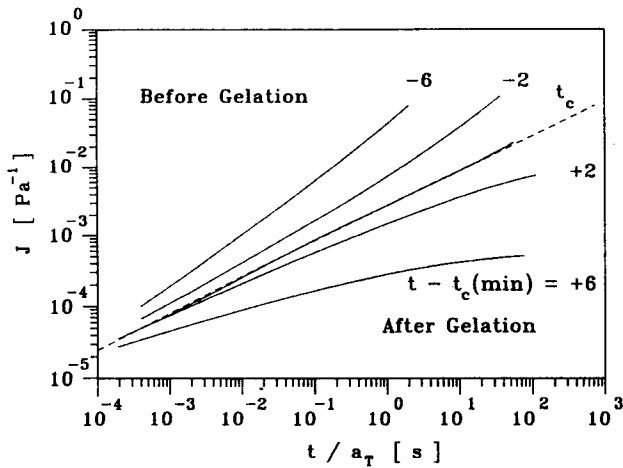


Fig. 10. Evolution of creep compliance calculated from Fig. 8

A third demonstration uses published dynamic data of a crosslinking polymer which undergoes gelation. The dynamic data of Chambon and Winter [18] consist of five spectra (Fig. 8), each of which corresponds to a specific extent of crosslinking. The evolution of the relaxation modulus (Fig. 9) and the creep compliance (Fig. 10) can now be seen clearly: Before the gel point, the polymer can relax completely, at the gel point the polymer relaxes in a power law, and beyond the gel point the polymer can only relax to an equilibrium value (equilibrium modulus).

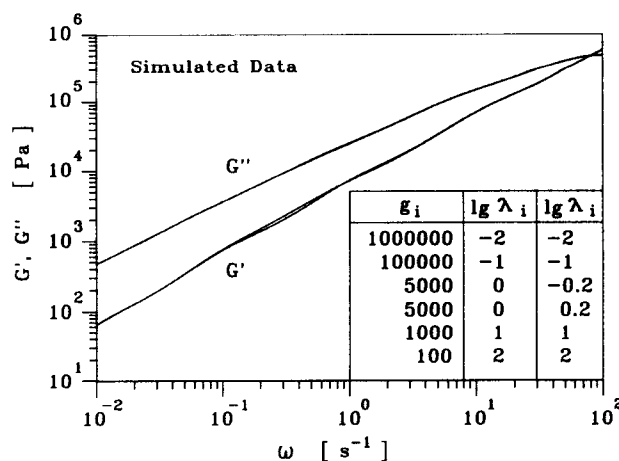


Fig. 11. Test of sensitivity. Dynamic moduli are calculated for two discrete model spectra. Note the small deviations in  $G'$  due to variations in  $\lambda_3$  and  $\lambda_4$ . The  $g_i$ -values are the same for both spectra. The waviness is produced by the artificial choice of relaxation spectrum

### 6. Test of sensitivity

Experimental data are obviously biased by noise and the calculated spectra do not only reflect the actual relaxation modes of the material but they also depend on the experimental error. In other words, the same material measured dynamically with different noise will give a different calculated spectrum. We often realized how easily our program follows the details of some scatter in the data. For the following sensitivity test, we use model data which do not contain the experimental noise. The model data are generated by choosing a set  $g_i, \lambda_i$  and calculating  $G'(\omega), G''(\omega)$  in the corresponding frequency window (rounding errors are insignificant here).

Two sensitivity tests of the iterative data fitting program were performed with the objective to answer the following questions:

- 1) Does the program recover a set of  $g_i, \lambda_i, N$  from model data  $G'(\omega), G''(\omega)$ ?
- 2) How close can two relaxation times be without being lumped into a single mode?

Concerning the first question it is found that the program recovers the known DRS independently of the start values  $N_0, g_{i,0}$ , and  $\lambda_{i,0}$ .

To answer the second question, dynamic moduli are simulated for two DRS. Both DRS consist of 6 relaxation times (Fig. 11). In the second DRS the relaxation times  $\lambda_3 = \lambda_4 = 1 \text{ s}^{-1}$  are replaced by 2 relaxation times  $\lambda_3 = 0.63 \text{ s}^{-1}$  and  $\lambda_4 = 1.58 \text{ s}^{-1}$  which are relatively close together. The coefficients,  $g_i$ , are the same for both DRS. The calculated dynamic data for these two DRS are plotted in Fig. 11. The deviations of these two curves are very small. However, the program recovers both DRS exactly.

The conclusion from this test is that the DRS can be recovered from model data sets even if 2 relaxation times are relatively close together. This result also indicates that the problem is not ill posed in the range of a small number of relaxation modes, since the only unique solution is recovered. This is an encouraging result. However, it should be noted again that for real experimental data, relaxation times which are close together are lumped into a single mode because of the experimental scatter.

In a further simulation, relaxation modulus and creep compliance of a critical gel are simulated and compared with the solution using discrete spectra (Fig. 12). Simulated dynamic data (Eq. (10)) serve as input data to calculate the discrete relaxation and retardation spectra. The resulting relaxation modulus and creep compliance agree very well with the analytic power law solution. This is an additional demonstra-

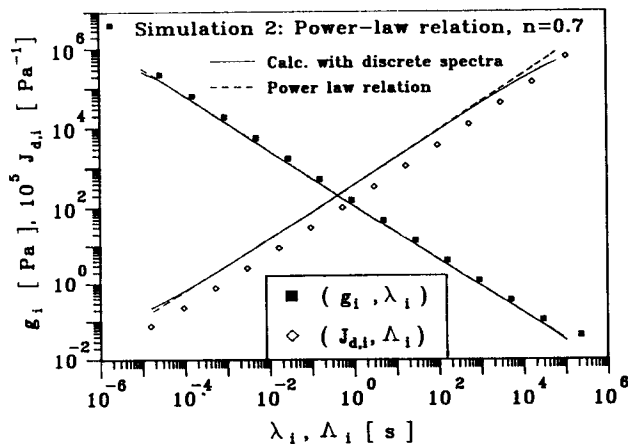


Fig. 12. Comparison of the relaxation modulus and creep compliance: The analytic power law spectra are shown with the corresponding discrete spectra

tion of the accuracy of the employed data conversion methods.

## 7. Conclusions

The parameters of a discrete relaxation spectrum  $g_i$ ,  $\lambda_i$ ,  $i = 1 \dots N$  have been determined by simply fitting dynamic mechanical data. Ill posedness of the problem was avoided by keeping the number of relaxation modes small. Recognizing this requirement, one can apply a non-linear regression in which not only the  $g_i$  and  $\lambda_i$  are adjustable parameters, but also  $N$  has to be variable. The discrete relaxation spectrum can be directly transformed into a discrete retardation spectrum. The longest relaxation and retardation time and the characteristic shorter modes are determined with an accuracy which depends on the quality of the experimental data  $G'$ ,  $G''$ .

One advantage of the robustness of the proposed method is its simple conversion into a fully automated numerical program. On a personal computer, a typical computation time is about 10 min. The solution is independent of the starting parameter set  $g_i$ ,  $\lambda_i$ ,  $i = 1, 2, \dots, N$ . Any dynamic data measured in our laboratory or made available to us by others have been successfully converted into the time domain. It is a most useful tool in our laboratory, especially for establishing a rheological data bank, for analyzing viscoelastic experiments, and for numerical simulation of polymer processing. Creep experiments for testing the retardation spectra are in progress.

## Appendix A

### Discrete retardation spectrum of a viscoelastic solid

The discrete retardation spectrum of a viscoelastic solid can be calculated in the same way as shown for the liquid, except the equilibrium modulus  $G_e$  has to be accounted for. The retardation times and relaxation times are now related as

$$G_e \left( \prod_{k=1}^N (s+1/\lambda_k) \right) + \left( \sum_{i=1}^N g_i \left( \prod_{k=1, i}^N (s+1/\lambda_k) \right) \right) = G_0 \prod_{i=1}^N (s+1/\Lambda_i) \quad (\text{A } 1)$$

where  $G_0 = G_e + \sum g_i$  and the constants  $K_0$  and  $c_i$  are given here by

$$K_0 = \frac{1}{G_0} \prod_{k=1}^N \frac{\Lambda_k}{\lambda_k} \quad (\text{A } 2)$$

$$c_i = \frac{\frac{\Lambda_i}{G_0} \prod_{k=1}^N \left( 1 - \frac{\Lambda_i}{\lambda_k} \right) - K_0 \Lambda_i \prod_{k=1}^N \left( 1 - \frac{\Lambda_i}{\Lambda_k} \right)}{\prod_{k=1, i}^N \left( 1 - \frac{\Lambda_i}{\Lambda_k} \right)} \quad (\text{A } 3)$$

The discrete retardation spectrum contains now  $N$  modes where the ordering of the retardation times is found as:

$$\lambda_1 < \Lambda_1 < \lambda_2 < \dots < \Lambda_{N-1} < \lambda_N < \Lambda_N \quad (\text{A } 4)$$

Since no permanent deformation is observed in viscoelastic solids the creep compliance is found to be

$$J(t) = J_g + \sum_{i=1}^{N-1} J_{d,i} \Psi_i(t) \quad (\text{A } 5)$$

The instantaneous compliance  $J_g$  and the retarded compliance are given by the same relation as before, Eqs. (27) and (28).

### Acknowledgement

M. Baumgaertel thanks Prof. Buggisch of the Univ. of Karlsruhe (TH) for his support and for allowing that his diploma thesis could be written during a stay at the University of Massachusetts. Discussions with Dr. P. Soskey during the testing of our program were very helpful.

## References

1. Tanner RI (1968) *J Appl Polym Sci* 12:1649
2. Friedrich G, Hoffmann B (1983) *Rheol Acta* 22:425
3. Ferry JD (1980) *Viscoelastic Properties of Polymers*. Wiley, New York
4. Gross B (1953) *Mathematical Structure of the Theories of Viscoelasticity*, Hermann & Cie., Paris
5. Staverman AJ, Schwarzl F (1956) In: *Die Physik der Hochpolymeren*, Vol 4. Springer-Verlag, Berlin



6. Baumgaertel M, Winter HH (1989) Proceedings Antec 89
7. Friedrich J, Blumen A (1985) Phys Rev B. Rapid Com 32(2):1434
8. Winter HH (1989) "Gel Point" In: Kroshwitz J, Bikales N (ed) Encycl Polym Sci Eng. Supplement (1989) p 343
9. Heindl W, Giesekus H (1972) Rheol Acta 11:152
10. Larson RG (1985) Rheol Acta 24:327
11. Laun HM (1978) Rheol Acta 17:1
12. Soskey PR, Winter HH (1984) J Rheol 28(5):625
13. Honerkamp J, Weese J (1989) Macromolecules. In press
14. Leaderman H (1958) Rheology, Theory and Applications, Vol 2. Academic Press, New York
15. Giesekus H (1970) Lecture notes
16. Schausberger A, Schindlauer G, Janeschitz-Kriegl H (1985) Rheol Acta 24:220
17. Schausberger A (1986) Rheol Acta 25(6):595
18. Chambon F, Winter HH (1985) Polymer Bulletin 13:499
19. Kamath VM, Mackley MR (1989) J Non-Newtonian Fluid Mech 32:119

(Received July 25, 1989)

Correspondence to:

Prof. H. Henning Winter  
University of Massachusetts  
Dept. of Chemical Engineering  
154 Goessmann Laboratory  
Amherst, MA 01003, USA