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Determination of Mechanical Spectra from Experimental Responses

Določanje mehanskega spektra na osnovi izmerjenih relaksacijskih krivulj

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A recursive computer algorithm was developed which generates line spectra from experimental response functions. The method allows storing information on the mechanical properties of polymeric materials in a convenient way. The algorithm also interconverts between relaxation and retardation spectra. From the spectra, any desired response function can then be recovered. The algorithm essentially utilizes the fact that the kernel functions resemble step functions.
Slightly different codes are used for each kernel function. The appearance of negative relaxation or retardation lines is obviated. Mathematically such lines would be acceptable, and they do not seriously affect reconstruction of responses within relaxation or retardation behavior. However, they would seriously interfere with interconversion between the two types of behavior, and they would also pose problems in the interpretation of the spectra.

Key words: viscoelasticity, relaxation, retardation, spectra, kernel function, polymers

Razvit je rekurziven računalniški algoritem, ki izračuna spekter iz eksperimentalno dobljenih odzivnih funkcij. Metoda omogoča shranjevanje informacij o mehanskih lastnostih polimernih materialov v prikladni obliki. Algoritem omogoča tudi interkonverzijo med relaksacijskim in retardacijskim spektrom. Iz spektra lahko izračunamo katerokoli materialno funkcijo. Bistvo algoritma je uporaba dejstva, da so jedra podobna koračni funkciji. Malenkostno drugačne metode so uporabljene za vsako od jeder. Pri določevanju relaksacijskega in retardacijskega linijskega spektra, se s tem algoritmom izognemo negativnim spektralnim linijam. Matematično so take linije sprejemljive in nimajo velikega vpliva na rekonstrukcijo materialnih funkcij. Problem zaradi negativnih spektralnih linij se pojavi pri interkonverziji med dvema tipoma obnašanja, poleg tega pa povzročijo nepremostljive ovire pri fizikalni interpretaciji spektra.

Ključne besede: viskoelastičnost, relaksacija, retardacija, spekter, jedro, polimeri

1. Introduction

In the response of a linearly viscoelastic material to a strain excitation, complete information on the time-dependent part of the response is contained in the relaxation spectrum. In the response to a stress excitation the same role is played by the retardation spectrum. The response then consists of the appropriate viscoelastic constants (such as the equilibrium modulus, or the glass compliance and the steady-flow fluidity), in addition to the integral over the spectrum multiplied by a kernel function characteristic of the type of excitation chosen to elicit the response. If this is a strain or a stress as a step function of time, the result is the relaxation modulus in the first, and the creep compliance in the second case. Thus, once the spectrum is known in addition to the viscoelastic constants, it is possible to generate from it the response to any desired type of excitation.

The spectrum itself is not accessible by direct experiment. From a theoretical response curve it can often be calculated[1a]. From experimental data the spectrum is necessarily obtained as an approximation to the true spectrum. A variety of methods have been proposed[1a,2] to extract approximations to the spectra from experimental data by mathematical manipulation. The well known methods based on numerical or graphical differentiation typify this approach. In another approach an attempt is made to determine a distribution of discrete spectral lines from which the original response curve can be more or less faithfully reproduced[1c]. Among the better known older methods are Procedure

X of Tobolsky and Murakami[3], the collocation method of Schapery[4], and an extension of it by Cost and Becker[5] which they call the multidata method. The two last named require matrix inversion. Both are likely to generate a negative spectrum lines, which makes virtually impossible to use this spectra for interconversion between the relaxation and retardation behavior. In the past few years several new papers have been devoted to this subject[6-14]. An extensive comparison of these methods along with the method introduced here is presented elsewhere[15].

We present here the method based on an iterative computer algorithm for calculating a distribution of spectral lines which, for a given set of data, is unique within the desired degree of accuracy. It must be emphasized, that the discrete distribution of moduli or compliances on respondance (relaxation or retardation) times obtained in this way is still an approximation. However, as will be shown below, the calculated distributions appear to yield better results than any of the other methods.

In this paper we shall sketch only the application of the algorithm to the relaxation modulus. The power of the algorithm will be than demonstrated on the experimental data obtained by Catsiff and Tobolsky[16]. These data were originally reported in terms of the tensile modulus, E(t). For the comparison reasons, presented in[17] the data were first converted to the shear modulus, as reported in[1f]. For the same reason the units of the modulus were converted from dynes/cm^2 and hours to N/m^2 and seconds.

A complete presentation of the algorithm has been published elsewhere-in the series of four papers[17-20]. The first paper in this series[17] describes the algorithm for obtaining a discrete distribution of relation times from simulated relaxation modulus data, or of retardation times from simulated creep compliance data. The second paper[18] deals with the determination of the spectra from theoretical storage and loss functions. The third paper[19] takes up the problem of converting between relaxation modulus and creep compliance. In these first three papers the algorithm have been thus applied to data sets obtained by sampling continuous theoretical curves. This has simplified presentation of the details and the power of the algorithm. The fourth paper[20] deals finally with the application of our method to experimental data, i.e., data that are not free of experimental error.

2. Theoretical

Essentially the method consists in predetermining a set of respondance times which are equally spaced on the logarithmic time-axis, and then calculating the strength of the spectral line associated with each respondance time. Our method shares this feature with the collocation method and the multidata method. However, in contrast to these methods, ours does not require matrix inversion and thus avoids mathematical difficulties associated with such an inversion (such as, e.g., occasionally generating troublesome negative respondance times). We calculate the intensity (i.e. the strength) of the kth spectral line corresponding to the kth respondance time, τ_k, from all source data lying within a fixed time interval (*Window 1*) around τk, **Fig. 1**. The contributions to the strength of this line arising from the presence of neighboring spectral lines is taken into account by making appropriate assumptions concerning the spread of the neighboring lines which will make non-negligible contributions (*Window 2*), **Fig. 2**. The spectrum is calculated by proceeding from the low end towards the high end of the response, again making appropriate assumptions. Finally, the crude distribution of spectral lines obtained in the first pass is improved by iteration.

As mentioned previously, we shall demonstrate our method on hand of the shear relaxation modulus. The method can be easily adapted to dealing with the tensile relaxation modulus or the tensile creep compliance or, for that matter, with any other response to the imposition of a strain or a stress as a step function of time[1d].

3. The Algorithm

The theory of linear viscoelastic behavior describes the shear relaxation modulus by the relation

$$G(t)=\{G_e\}+(G_g-\{G_e\})\int_0^\infty h(\tau)\ \exp-t/\tau\ d\ ln\ \tau \quad (1)$$

where $h(\tau)$ is the (normalized) continuous relaxation spectrum, and G_g and G_e are the instantaneous and the equilibrium modulus, respectively. The braces signify that $\{G_e\} = G_e$ when the modulus describes an arrheodictic material, and that $\{G_e\} = 0$ when the material is rheodictic (The term *rheodictic* refers to a material showing steady-state flow). Dividing by G_g - $\{G_e\}$ yields

$$g(t)=\{g_e\}+\int_0^\infty h(\tau)\ \exp-t/\tau\ d\ ln\ \tau, \quad (2)$$

where g(t) and g_e are the normalized relaxation modulus, and equilibrium modulus, respectively.

The source data are assumed to be available as a set of M discrete data points

$$G_j \in \{t_j,\ G(t_j);\ j=1,\ 2,\ ....,\ M\}. \quad (3)$$

Each of these data points can be normalized by the difference between the largest, G_1, and the smallest point, G_M, to yield the set

$$g_j \in \{t_j,\ g(t_j);\ j=1,\ 2,\ ....,\ M\}. \quad (4)$$

Now, the modulus can be expressed alternatively by a discrete set of (normalized) spectral lines, h_i. In terms of these we have

$$G(t)=\{G_e\}+(G_g-\{G_e\})\sum_{i=1}^{i=n} h_i\ \exp-t/\tau_i \quad (5)$$

or, in normalized form,

$$g(t)=\{g_e\}+\sum_{i=1}^{i=n} h_i\ \exp-t/\tau_i. \quad (6)$$

We intend to determine, from the set of source data, $\{g_j; j=1, 2, 3, ..., M\}$, a set of spectral lines, $\{h_i; i=1, 2, 3, ..., n\}$, which will faithfully reproduce the modulus, G(t). In proceeding to explain how this is done, we initially use the continuous representation (2), instead of its discrete equivalent (6), because this simplifies the presentation.

We begin by splitting the integral in equation (2) to obtain

$$g(t)=\{G_e\}+\int_{\tau_0}^{\tau_k} h(\tau)\ \exp-t/\tau\ d\ ln\ \tau+$$
$$+\int_{\tau_k}^{\tau_k} h(t)\ \exp-t/\tau\ d\ ln\ \tau+h(\tau_k)\ \exp-t/\tau_k+$$
$$+\int_{\tau_k}^{\infty} h(\tau)\ \exp-t/\tau\ d\ ln\ \tau. \quad (7)$$

Let the kernel in the integrals in equation (7) be represented by the function $K(t)=\exp-t/\tau$. **Figure 1** shows a plot of $K_k = \exp-t/\tau_k$ as a function of $\ln t/\tau_k$. The broken line represents the tangent to $K_k(t)$ at $\ln t/\tau_k = 0$. From the behavior of the kernel we can draw two immediate conclusions.

First,

$$K_k(100\,\tau_k)=3.72\times10^{-44}=0. \quad (8)$$

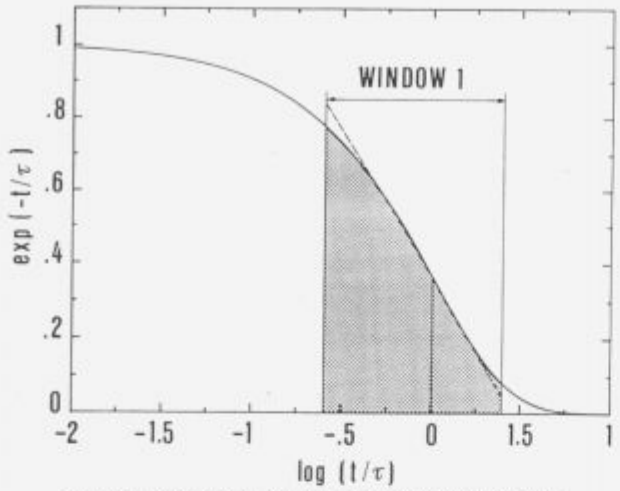

Figure 1. Definition of *Window 1* (the Boundary Window)

Slika 1. Definicija *Okna 1* (Mejno okno)

Second, the logarithmic time interval $-0.6<t/\tau_k>0.4$ defines the region over which $K_k(t)$ shows its largest time dependence. We call this interval *Window 1*. The interval from which data points will be drawn from the set of source data to calculate the k^{th} spectrum line depends on the number of lines per logarithmic decade of time. We call this interval *Window 2*. **Figure 2** shows $D_{TRAN}(t) = K'(t)$, the derivative of K(t), as a function of $\ln t/\tau_k$ for $\tau = \tau_{k-1}$, τ_k, and τ_{k+1}. The intersections of the central derivative with its neighbors to the left and to the right, designated by t_l and t_u (for *lower* and *upper*) are given by

$$t_l = \frac{\tau_k \ \tau_{k-1}}{\tau_k - \tau_{k-1}} \ ln \ \frac{\tau_k}{\tau_{k-1}} \tag{9}$$

and

$$t_u = \frac{\tau_{k+1} \ \tau_k}{\tau_{k+1} - \tau_k} \ ln \ \frac{\tau_{k+1}}{\tau_k}. \tag{10}$$

If P is the number of spectral lines per decade of *log* t, then we have *log* τ_{k+1} - *log* τ_k and, therefore,

$$t_l = \frac{2.303}{P\left(10^{1/P} - 1\right)} \ \tau_k \tag{11}$$

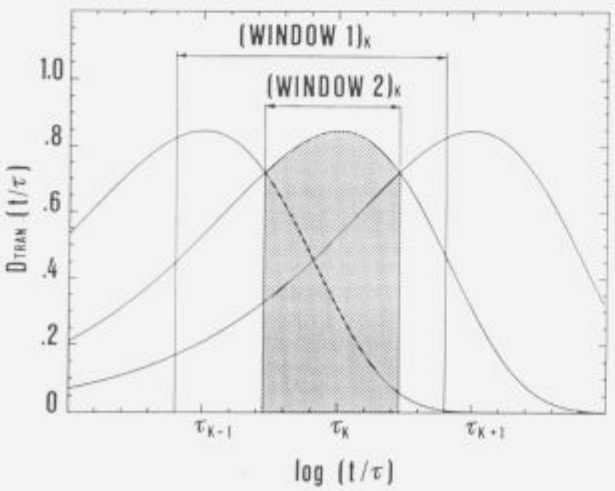

Figure 2. Definition of *Window 2* (the Modeling Window)

Slika 2. Definicija *Okna 2* (Okno modeliranja)

and

$$t_u = \frac{2.303 \times 10^{1/P}}{P\left(10^{1/P} - 1\right)} \ \tau_k. \tag{12}$$

Therefore, the spread of *Window 2* is given by $[t_l, t_u]$. The width of the window decreases as the number of spectral lines increases. Accordingly,

$$\lim_{P \to \infty} Window\ 2 = 0 \tag{13}$$

marks the transition from the discrete to the continuous form of the representation of G(t).

The third conclusion we can draw from **Fig. 1** states that *Window 2* must not be larger than *Window 1*. Outside of *Window 1* the k^{th} spectral line cannot handle data points because its contribution on the right is virtually zero, and on the left it approaches a constant value. On the other hand, we must have at least one discrete data point lying within *Window 2*. This realization allows us to determine the optimum number of spectrum lines per logarithmic decade to be chosen. This number must be such that the width of *Window 2* approaches (but does not exceed) the width *Window 1*. The number can be found by solving the transcendental equations (11) and (12). In equation (11) we let $\log t_l/\tau_k = -0.6$, in equation (12) we let it be $\log t_u/\tau_k = 0.4$, and solve for the nearest integer P. The smaller of the two solutions gives the desired optimum number of spectral lines per decade.

We can now return to equation (7). Each datum point within *Window 2* pertaining to the k^{th} spectrum line can be modeled as

$$g_j = \left\{g_\tau\right\} + \int_0^{\tau_a} h(\tau) \ \exp - t_j/\tau \ d \ ln \ \tau + \int_{\tau_a}^{\tau_k^-} h(t) \ \exp - t_j/\tau \ d \ ln \ \tau + h(\tau_k) \ \exp - t_j/\tau_k + \int_{\tau_k^+}^{\infty} h(\tau) \ \exp - t_j/\tau \ d \ ln \ \tau. \tag{14}$$

By our first conclusion from **Fig. 1**, if $\tau_a \le t_l/100$, then the first integral in (14) vanishes.

Proceeding now from the continuous to the discrete representation, we write

$$g_j = \left\{g_M\right\} + \sum_{i=m}^{i=k-1} h_i \ \exp - t_j/\tau_i + h_k \ \exp - t_j/\tau_k + \sum_{i=k+1}^{i=n} h_i \ \exp - t_j/\tau_i + \Delta_j. \tag{15}$$

In the equation above m is the discrete counterpart of τ_a and is given by m=k-2n-1. The term Δ_j has been added to take into account the absolute error introduced by switching from the continuous to the discrete representation. Using the abbreviation

$$\mathcal{Z}\left(t_j\right) = \left\{g_M\right\} + \sum_{i=m}^{i=k-1} h_i \ \exp - t_j/\tau_i + h_k \ \exp - t_j/\tau_k + \sum_{i=k+1}^{i=n} h_i \ \exp - t_j/\tau_i, \tag{16}$$

where $Z(t_j)$ denotes the theoretical (error-free) value of the normalized experimental datum point g_j, the term Δ_j can be expressed as

$$\Delta_j = g_j - \mathcal{Z}\left(t_j\right) \tag{17}$$

To avoid the instability problems caused by the large difference in magnitude of modulus on both sides of *Window 2* we introduce the *relative error of approximation* (for details see[17])

$$\delta_j = \frac{\Delta_j}{\mathscr{Z}(t_j)} = \frac{g_j - \mathscr{Z}(t_j)}{\mathscr{Z}(t_j)}. \tag{18}$$

The sum, Q_k, of the squares of δ_j within *Window 2* is

$$Q_k = \sum_{j=s_{k,1}}^{j=s_{k,u}} \delta_j^2 \tag{19}$$

where $s_{k,l}$ and $s_{k,u}$ are the first and the last discrete points in *Window 2* belonging to the k^{th} spectrum line. Minimizing the error according to

$$\frac{\partial Q_k}{\partial h_k} = 0, \tag{20}$$

where h_k is the k^{th} spectrum line, leads to the expression from which the strength of the k^{th} spectral line is to be obtained,

$$\sum_{j=s_{k,1}}^{j=s_{k,u}} \frac{g_j - \mathscr{Z}(t_j)}{\left[\mathscr{Z}(t_j)\right]^3} g_j \exp -t_j/\tau_k = 0. \tag{21}$$

Using the abbreviation

$$\mathscr{S}(t_j) = \{g_M\} + \sum_{i=m}^{i=k-1} h_i \exp -t_j/\tau_i + \sum_{i=k+1}^{i=n} h_i \exp -t_j/\tau_i, \tag{22}$$

and equation (16) in addition, we obtain the equation

$$\sum_{j=s_{k,1}}^{j=s_{k,u}} \frac{g_j - \left[\mathscr{S}(t_j) + h_k \exp -t_j/\tau_k\right]}{\left[\mathscr{S}(t_j) + h_k \exp -t_j/\tau_k\right]^3} g_j \exp -t_j/\tau_k \equiv 0. \tag{23}$$

This equation must be satisfied to minimize the sum of squares of the relative quadratic errors, Q_k, in the k^{th} window. It must be solved numerically by iteration for it cannot be made explicit for h_k as is possible when minimizing the absolute error[17-19]. We therefore now recast (23) in a form in which it becomes suitable for recursion. We let

$$h_k^{(i+1)} = \frac{\mathscr{A}\left[h_k^{(i)}\right]}{\mathscr{B}\left[h_k^{(i)}\right]} \tag{24}$$

where $h_k^{(i)}$ is the value of h_k obtained in the i^{th} iteration,

$$\mathscr{A}\left[h_k^{(i)}\right] = \sum_{j=s_{k,1}}^{j=s_{k,u}} \frac{\left[g_j - \mathscr{S}(t_j)\right] g_j \exp -t_j/\tau_k}{\left[\mathscr{S}(t_j) + h_k^{(i)} \exp -t_j/\tau_k\right]^3} \tag{25}$$

and

$$\mathscr{B}\left[h_k^{(i)}\right] = \sum_{j=s_{k,1}}^{j=s_{k,u}} \frac{\left[\exp -t_j/\tau_k\right]^2}{\left[\mathscr{S}(t_j) + h_k^{(i)} \exp -t_j/\tau_k\right]^3} g_j. \tag{26}$$

The starting set of spectrum lines for the iteration is $\{h_k^{(1)} = h^{(1)}(\tau_k);\ k=1,2,\ldots,n\}$. This starting set is obtained in a first sweep through the data using the method detailed in the paper[17]. For subsequent sweeps we then use the method just described. The iteration is broken off when an appropriately chosen limit of the absolute difference between the new and the preceding square relative error, Q_k, has been reached.

4. Results

We demonstrate the power of the algorithm by obtaining the distribution of spectral lines from the experimental data obtained by Catsiff and Tobolsky[16] - CT data. The data has been first converted as described in the introduction. In this form they are tabulated in[17], and are presented in **Fig. 3**. The solid line represents a spline function[21] through the data. **Figure 4** shows the relaxation spectrum $H_{CT}(\tau)$ calculated from these data, using the presented method.

The reconstruction of the shear relaxation modulus, G(t), from the calculated spectrum $H_{CT}(\tau)$, using the relation (5) is compared with the spline function through the original experimental data in **Fig. 5**. Both curves can not be distinguished within the resolving power of the plot.

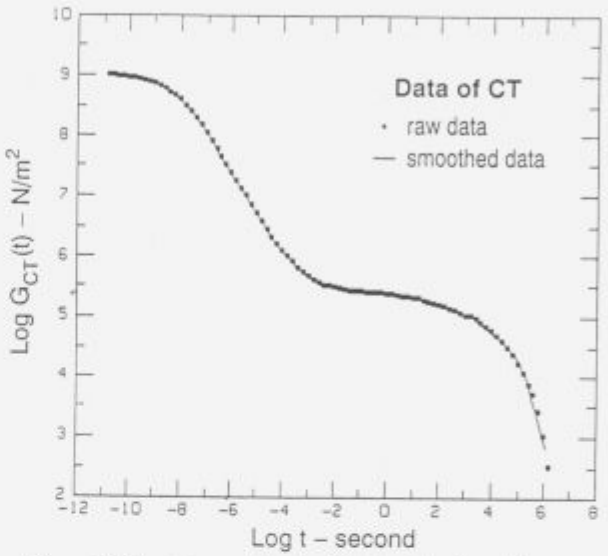

Figure 3. Relaxation modulus, *log* $G_{CT}(t)$, as function of *log* t

Slika 3. Relaksacijski modul, *log* $G_{CT}(t)$, kot funkcija *log* t

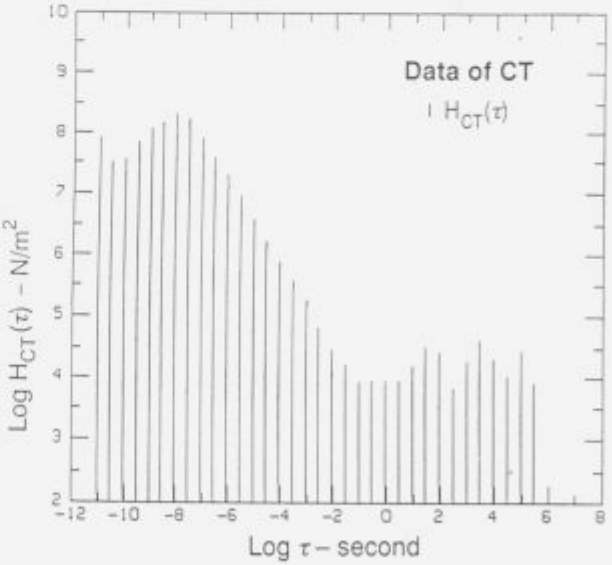

Figure 4. Relaxation spectrum, *log* $H_{CT}(\tau)$, as function of *log* τ

Slika 4. Relaksacijski spekter, *log* $H_{CT}(\tau)$, kot funkcija *log* τ

Knowing the spectrum $H(\tau)$ in addition to the viscoelastic constants one can generate from it the response to any desired type of excitation. In order to demonstrate this we first calculate $G'_{CT}(\omega)$ and $G''_{CT}(\omega)$ from $H_{CT}(\tau)$ using the relations[1r]

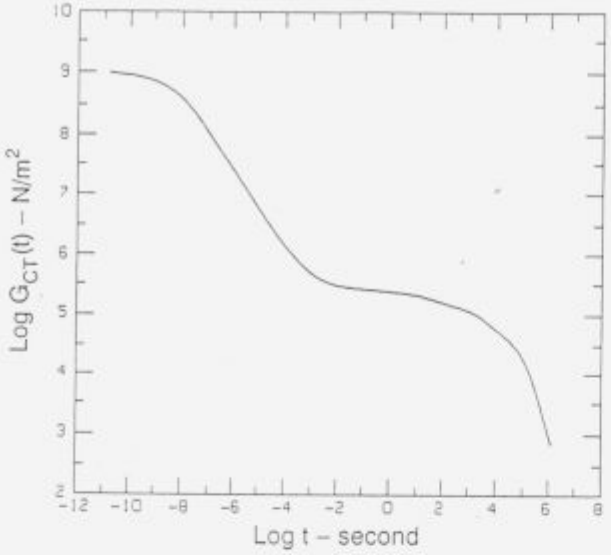

Figure 5. Reconstruction of *log* $G_{CT}(t)$ from $H_{CT}(\tau)$, compared with the spline function through the experimental data, as functions of *log* t

Slika 5. Rekonstrukcija *log* $G_{CT}(t)$ iz $H_{CT}(\tau)$ primerjana s 'spline' funkcijo skozi eksperimentalne podatke kot funcije *log* t

$$G'_{CT}(\omega) = \sum_{i=1}^{i=N} H_{CT}(\tau_i) \frac{\omega^2 \tau_i^2}{1+\omega^2 \tau_i^2} \tag{27}$$

and

$$G''_{CT}(\omega) = \sum_{i=1}^{i=N} H_{CT}(\tau_i) \frac{\omega \tau_i}{1+\omega^2 \tau_i^2}. \tag{28}$$

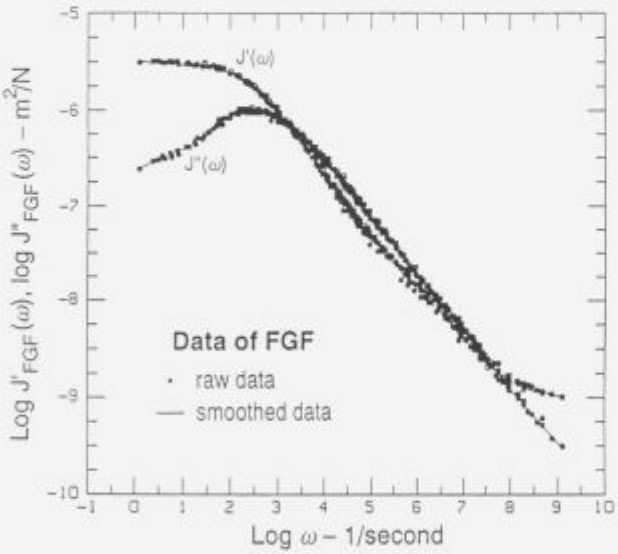

Figure 6. Storage compliance, *log* $J'_{FGF}(\omega)$, and loss compliance, *log* $J''_{FGF}(\omega)$, as functions of *log* ω

Slika 6. Shranitveni dinamični modul *log* $J'_{FGF}(\omega)$ in dinamični modul izgub *log* $J''_{FGF}(\omega)$ kot funkciji *log* ω

$G'_{CT}(\omega)$ and $G''_{CT}(\omega)$ can be than interconverted to storage compliance, $J'_{CT}(\omega)$, and loss compliance, $J''_{CT}(\omega)$, using the relations[18]

$$J'(\omega) = \frac{G'(\omega)}{\left[G'(\omega)\right]^2 + \left[G''(\omega)\right]^2} \tag{29}$$

and

$$J''(\omega) = \frac{G''(\omega)}{\left[G'(\omega)\right]^2 + \left[G''(\omega)\right]^2}. \tag{30}$$

$J'_{CT}(\omega)$ and $J''_{CT}(\omega)$ are compared with the experimental data obtained by Fitzgerald, Grandine, and Ferry[22] -FGF data. The comparison is presented in **Fig. 7**. $J'_{CT}(\omega)$ and $J''_{CT}(\omega)$, represented as broken lines, are compared with the spline functions through the experimental data, $J'_{FGF}(\omega)$ and $J''_{FGF}(\omega)$, shown as solid line. The original FGF data are shown in **Fig. 6**. The agreement between the prediction and the spline function through the experimental data is excellent.

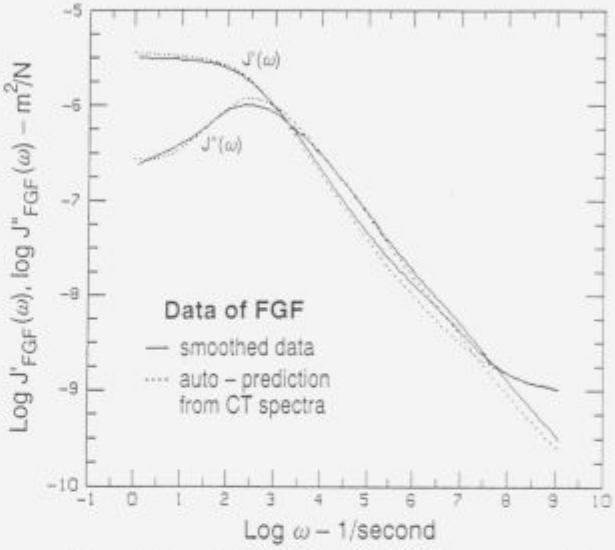

Figure 7. Smoothed $J'_{FGF}(\omega)$ and $J''_{FGF}(\omega)$ data compared with $J'_{CT}(\omega)$ and $J''_{CT}(\omega)$ derived from $H_{CT}(\tau)$

Slika 7. Zglajeni eksperimentalni krivulji *log* $J'_{FGF}(\omega)$ in *log* $J''_{FGF}(\omega)$ primerjani z *log* $J'_{CT}(\omega)$ in *log* $J''_{CT}(\omega)$ izračunanimi iz $H_{CT}(\tau)$

5. Conclusion

In this paper we have presented the algorithm for evaluation of relaxation line spectra from experimental data. The algorithm can be easily modified for the assessment of retardation spectra. The algorithm essentially utilizes the fact that the kernel functions resemble step functions. Slightly different codes are used for each kernel function, as presented elsewhere[17].

We feel that we have demonstrated that the proposed algorithm is indeed capable of generating the underlying line spectra from the experimental data without producing a negative lines that are physically unacceptable.

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6. References

[1] N. W. Tschoegl, *The Theory of Linear Viscoelastic Behavior*, Springer-Verlag, Heidelberg, 1989; a. Chapter 6; b. Chapter 4; c. Chapter 3, Section 6; d. Chapter 11; e. Chapter 6, Section 3; f. p.40; g. p. 329.

[2] J. D. Ferry, *Viscoelastic Properties of Polymeric Materials*, Wiley & Sons, NY, 1980.

[3] A.V. Tobolsky and K. Murakami, *J. Polymer Sci.* 40, 443,1955.

[4] R. A. Schapery, *Proc. Fourth U.S. Nat. Congr. Appl. Mech.*, 2, 1075, 1962.

[5] T. L. Cost and E.B. Becker, *Intern. J. Num. Methods in Eng.*, 2, 207, 1970.

[6] H. M. Laun, *J. of Rheol.*, 30, 459, 1986.

[7] M. Baumgaertel and H.H. Winter, *Rheol. Acta*, 28, 501, 1989.

[8] J. Honercamp, *Rheol. Acta*, 28, 363, 1989.

[9] J. Honercamp and J. Weese, *Macromolecules*, 22, 4372, 1989.

[10] V. M. Kamath and M.R. Mackley, *J. Non-Newt. Fluid Mech.*, 32, 1199, 1989.

[11] C. Elster and J. Honercamp, *Macromolecules*, 24, 310, 1991.

[12] C. Elster and J. Honercamp, *J. Rheol.*, 36, 911, 1992.

[13] N. Orbey and J.M. Dealy, *J. Rheol.* 35, 1035, 1991.

[14] J. Janzen and J. Scanlan, Submitted to *Rheol. Acta.*, 1992.

[15] N.W. Tschoegl and I. Emri, Submitted to *Rheol. Acta.*, 1994.

[16] E. Catsiff and A.V. Tobolsky, *Colloid Sci.*, 10, 375, 1955.

[17] I. Emri and N.W. Tschoegl, *Rheol. Acta*, 32, 311, 1993.

[18] N.W. Tschoegl and I. Emri, *Rheol. Acta*, 32, 322, 1993.

[19] N.W. Tschoegl and I. Emri, *Intern. J. Polymeric Mater.*, 18, 95, 1992.

[20] I. Emri and N.W. Tschoegl, *Rheol. Acta.* 33, 60, 1994.

[21] C. de Boer, *A Practical Guide to Splines.* Springer-Verlag, NY, 1978.

[22] R. E. Fitzgerald, L.D. Grandine Jr. and J.D. Ferry, *J. Appl. Phys.*, 24, 650, 1953.