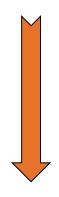


DEFINITION OF THE RELAXATION SPECTRUM

since $G(t) = \sum E_j \exp(-t/\lambda_j)$,



$$G(t) = \int_{-\infty}^{\infty} F(\lambda) \exp(-t/\lambda_j) d\lambda,$$

but , since the viscoelastic response spans several decades of time and of relaxation times, it is typical to describe the information in a logarithmic fashion, and this is accomplished by multiplying and dividing the integrand by λ :

relaxation spectrum and represents a distribution of moduli for the

viscosities which is known as viscosity density function (VDF).

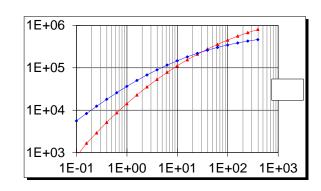
generalized Maxwell model. Conversely, $\lambda H(\lambda)$ is a distribution of

$$G(t) = \int_{-\infty}^{\infty} \lambda \, F(\lambda) exp(-t/\lambda_j) \, (d\lambda/\lambda), \qquad \qquad G(t) = \frac{\text{Stress/deformation}}{\text{G(t)}} \quad \text{units: Pa} \\ F(\lambda) \quad \text{units in Pa/s} \\ H(\lambda) \quad \text{units in Pa} \\ \\ K(\lambda) = H(\lambda), \qquad \qquad G(t) = \int_{-\infty}^{\infty} H(\lambda) \, exp(-t/\lambda_j) \, d\ln\lambda. \qquad \qquad G(t) = \frac{\text{Stress/deformation}}{\text{G(t)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{G(t)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{G(t)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{G(t)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/deformation}}{\text{F(\lambda)}} \quad \text{units in Pa} \\ \\ G(t) = \frac{\text{Stress/$$

GETTING A DISCRETE RELAXATION SPECTRA

Remember that:

 η_i is the viscous modulus of the ith Maxwell analog g_i is the elastic modulus of the ith Maxwell analog



and that you need the Dynamic Mechanical Data to get the loss and the elastic modulus:

$$\eta_i = g_i \lambda_i \tag{1}$$

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

$$G''(\omega) = \sum_{i=1}^{N} g_i \frac{\omega \lambda_i}{1 + \lambda_i^2 \omega^2}$$
 (3)

The continuous function can be obtained (see paper)

A dynamic nonlinear regression method for the determination of the discrete relaxation spectrum

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Abstract. The relaxation spectrum is an important tool for studying the behaviour of viscoelastic materials. The most popular procedure is to use data from a small-amplitude oscillatory shear experiment to determine the parameters in a multi-mode Maxwell model. However, the discrete relaxation times appear nonlinearly in the mathematical model for the relaxation modulus. The indirect calculation of the relaxation times is an ill-posed problem and its numerical solution is fraught with difficulties. The ill-posedness of the linear regression approach, in which the relaxation times are specified *a priori* and the minimization is performed with respect to the elastic moduli, is well documented. A nonlinear regression technique is described in this paper in which the minimization is performed with respect to both the discrete relaxation times and the elastic moduli. In this technique the number of discrete modes is increased dynamically and the procedure is terminated when the calculated values of the model parameters are dominated by a measure of their expected values. The sequence of nonlinear least-squares problems, solved using the Marquardt–Levenberg procedure, is shown to be robust and efficient. Numerical calculations on model and experimental data are presented and discussed.

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SOME MATERIAL PARAMETERS AS A FUNCTION OF $H(\Lambda)$

• zero shear viscosity

$$\eta_0 = \int_{-\infty}^{\infty} H(\lambda) \lambda \cdot d \ln \lambda$$

• instantaneous modulus

$$Gg = \int_{-\infty}^{\infty} H(\lambda) d \ln \lambda$$

steady state recoverable compliance

$$Je^{0} = \frac{\int_{-\infty}^{\infty} H(\lambda) \cdot \lambda^{2} \cdot d \ln \lambda}{\left(\int_{-\infty}^{\infty} H(\lambda) \lambda \cdot d \ln \lambda\right)^{2}}$$

YOUR JOURNEY

 $G'(\omega)$, $G''(\omega)$, $\eta(\gamma)$, G(t), J(t) Measurements

Introduction to

- ✓ Polymer processing
- ✓ Polymer chemistry

Estimate

J(t), N1(t), n(g,t), Jr(t) to avoid unnecessary laboratory measurements and relate it to:

- MWD data and/or to
- polymer processing problems and/or to
- taylor a new polymer





Master curves

 $G'(\omega)$, $G''(\omega)$, $\eta(\omega)$, G(t),J(t), etc.

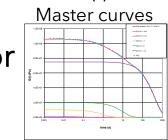
Get $H(\lambda)$

From

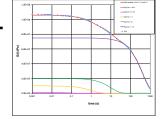
 $G'(\omega)$, $G''(\omega)$ Master curves

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

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



G(t)

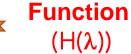


Get materials constants

$$\eta_0 = \int_{-\infty}^{\infty} H(\lambda) \lambda \cdot d \ln \lambda$$

$$Je^0 = \int_{-\infty}^{\infty} H(\lambda) \lambda \cdot d \ln \lambda$$

$$Gg = \int_{-\infty}^{\infty} H(\lambda) d \ln \lambda$$



Discretized

 g_i, λ_i

Apply Navier Stokes Equation to Polymer Processing: Fiber Spnng, Blow Molding, Blown Film



Simulate Process using a given material and evaluate the

- ✓ resin performance or
- ✓ redesign the process



Constitutive Model

- ✓ Wagner model
- ✓ Pan-Thien-Tanner (PTT) model
- Rubber Like Liquid model



Memory Function