(Dealy, continued from page 16)

increases. In order to take random errors into account, it is necessary to have a model for the error distribution, and this is usually assumed to be Gaussian. Elster and Honerkamp [12] have addressed this issue in some detail.

One more difficulty that arises in inferring the parameter set $\{G_i, \tau_i\}$ from the data set $\{G'_k, G''_k, \omega_k\}$ is that the magnitudes of the storage and loss moduli and of the relaxation strength vary enormously over the range of frequencies and times of interest. Honerkamp and Weese [13] addressed this problem by the use of nonlinear regression, together with regularization, in which it is the logarithm of $h(\tau)$ that is calculated rather than the spectrum function itself. The algorithm developed for this regression (NLREG) is available commercially [14]. Orbey and Dealy [15] compared discrete spectra calculated in several ways. They found that nonlinear regression with regularization, together with a sufficient density of data points, can yield a discrete spectrum whose parameter values describe very well the continuous spectrum that is characteristic of the material.

Danger Lurks Where the Data End

It is often assumed that the spectrum inferred from a set of data is valid between values of t equal to the reciprocal of the maximum and minimum frequencies of the data set. However, Davies and Anderssen [16] have shown that this gives an overly optimistic estimate. Their analysis indicates that the range of t over which the relaxation spectrum can be reliably determined is 2.36 decades less than the range of frequencies over which experimental data are available. Anderssen and Davies [17] have proposed a spacing for experimental data that optimizes the quality of the discrete spectrum inferred from them. Jensen [18] proposed a Monte Carlo method called *simulated annealing* to infer a discrete spectrum from data; in this method the range of relaxation times is constrained by the Anderssen and Davies criteria [16].

Probing the Terminal Zone

It is often necessary to use more than one measurement technique to probe the widest possible range of times or frequencies. In using rheological data to infer molecular structure, the behavior at very long times (low frequencies) is of special interest. For example, the zero-shear viscosity is very sensitive to molecular weight. However, for a material whose longest relaxation time is quite large, oscillatory shear experiments are of limited usefulness at very low frequencies because the stress is very small and the experimental time required is very long. It is in this region that creep measurements are most useful. Recent advances in the design of commercial, controlled-torque (controlled-stress) rheometers have made it possible to carry out precise measurements of creep and creep recovery on a routine basis.

However, for very polydisperse materials, particularly those with even a small amount of high-molecular-weight polymer, creep measurements become problematic as a result of the need to measure extremely slow deformations while maintaining the stress at a very low, constant value. In order to reach steady state, so that the steady-state compliance and the zero-shear viscosity can be determined, a large strain will be required, which may take the sample into the regime of nonlinear viscoelasticity. Kraft *et al*. [19] proposed a technique for determining the creep compliance up to the steady-state flow region without moving outside the regime of linear behavior and without the use of a super-sensitive creep meter. During a standard creep experiment at a stress σ_0, they reduce the stress back to zero at a time, t_1, when the deformation is still within the range of linear behavior, and monitor the resulting recoil. They show how data from the two stages of this experiment can be combined to construct the entire creep curve. Since the preferred technique for characterizing linear viscoelastic behavior at times below (or frequencies above) the terminal zone is oscillatory shear, there remains the problem of combining creep data with storage and loss modulus data to obtain a characterization valid over the broadest possible time range. He *et al*. [20] developed a method for doing this using standard commercial rheometers that appears to work quite well. They calculate continuous retardation spectra using both modulus and creep data and plot these together. The resulting graph shows clearly the zones in which each technique provides reliable data as well as the zone of overlap.

More information on this topic may be found in Ref. [1].

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(Meetings, continued from back cover)

2010

Spring 2010
6th Annual European Rheology Conference AERC 2010, location TBA

23-24 October 2010
SOR Short Course on Rheology (topic TBA), Santa Fe, NM USA

24-28 October 2010
82nd Annual Meeting of The Society of Rheology, Santa Fe, New Mexico USA, Andy Kraynik

2011

Spring 2011
7th Annual European Rheology Conference AERC 2011, location TBA

8-9 October 2011
SOR Short Course on Rheology (topic TBA), Cleveland, Ohio USA

9-13 October 2011
83rd Annual Meeting of The Society of Rheology, Cleveland, Ohio USA, Pat Mather

2012

Summer 2012
XVIth International Congress on Rheology, location TBA (every four years; in 2012 in Europe)

See also:
www.rheology.org/sor/info/Other_Meetings.htm
www.rheology-esr.org/Meetings.php
www.appliedrheology.org/ (click on conferences)

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At the Portland meeting Editor John Brady presented the JOR Publication Award to representatives of the winning team: left to right, Brady, Alex Likhtman, and Oliver Harlen. The cited paper is JOR 49(2) 501 (2005), and it is designated open access online.