

NOTES

Integral Equations Applied to Polymer Physical Property Data

The first step to an analysis of experimental data is commonly curve fitting; to obtain meaningful parameters, data are graduated by a theoretically established functional form or by an empirical expression. In either case, the parameters most often appear in a nonlinear form in the mathematical expression that describes the data. Least-squares and maximum likelihood graduating methods are difficult, if not impossible, to apply to many expressions. The least-squares criterion for graduating is refuted by nonlinear parameters. To use least-squares with nonlinear parameters, it is necessary to restrict the parameters and to use iterative computer routines.^{1,2} We propose that a graduating criterion to conserve the energy of a system by conserving the first and higher moments is more pertinent than minimizing the linear deviations from a curve. For example, the area under a stress-strain curve defined by data should equal that defined by a graduated relationship. We have developed mathematics and graduating techniques to cope with nonlinear parameters and to conserve the energy of a system. The technique is applicable to many fields of analysis, but this particular effort was directed to polymer physical properties data.

It is our experience that many polymer physical property data can be described by expressions of the forms of eqs. (1)–(5).

$$\epsilon(t) = \epsilon_0 + m(t/t_0)^n \tag{1}$$

$$\epsilon(t) = \epsilon_0 + A(1 - e^{-\lambda t}) \tag{2}$$

$$v(t) = A/(1 + \beta e^{-\lambda t}) \tag{3}$$

$$\Delta\epsilon(t) = a[\epsilon(t + 1)] + b[\epsilon(t)\epsilon(t + 1)] + \epsilon(t + 1) \sum_{s=0}^{t-1} K(s,t)\epsilon(s) \quad \Delta t = 1 \tag{4}$$

$$\Delta y = y(t) (a - t)/(b_0 + b_1 t + b_2 t^2) \quad \Delta t = 1 \tag{5}$$

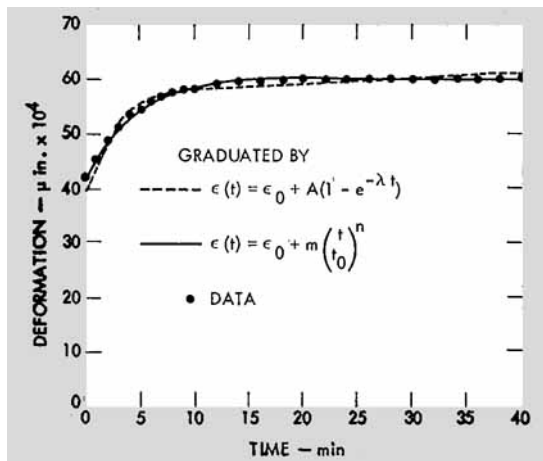


Fig. 1. Application of expressions (1) and (2) to uniaxial compressive-shear creep data for a developmental polystyrene bead foam (PSB). The curves can be shifted to the origin by subtracting the time-independent strain (ϵ_0) and graduated by expression (4) of further analysis.

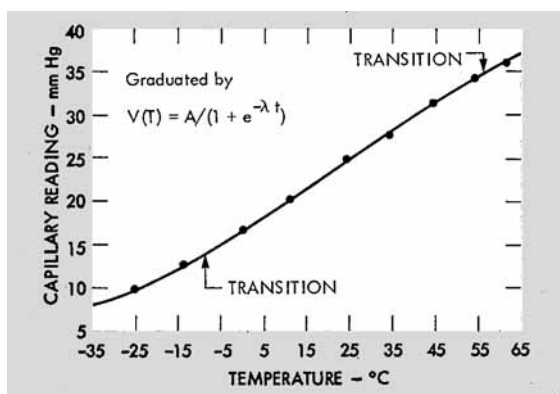


Fig. 2. Application of expression (3) to volumetric thermal expansion data for a filled ethylene-vinyl acetate. The transition temperatures were obtained analytically from the graduated curve.

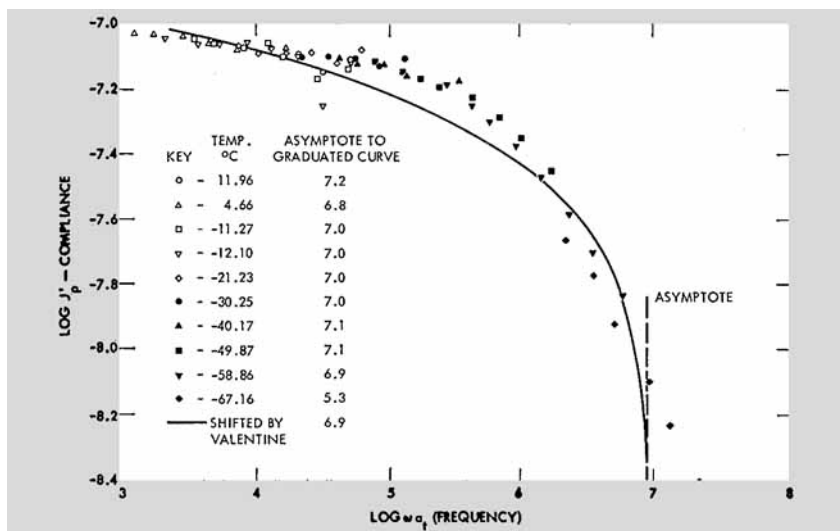


Fig. 3. Application of expression (3) to dynamic compliance data for polybutadiene. The individual test data were fitted, and the predicted asymptotes are tabulated. The predicted asymptote for the shifted data is also shown. It is obvious that expression (3) is very close to the proper functional relationship of shifting. The data at -67°C are known to be suspect because of equipment problems (Valentine and Ferry, 1967).

Expressions like (1), (2), and (4) have been useful for describing creep and stress-relaxation behavior. Expression (3) is useful for describing nonlinear rate processes such as thermal expansion and reduced-variable master creep curves. Expression (5) is used for the analysis of distributions such as creep rupture, small particle (filler) statistics, and retardation spectra.

It is necessary to rewrite expressions like eqs. (1)–(3) in a more tractable form because the parameters appear in a nonlinear form. The differential equations which have the above expressions as solutions overcome the nonlinearity in the unknown parameters.

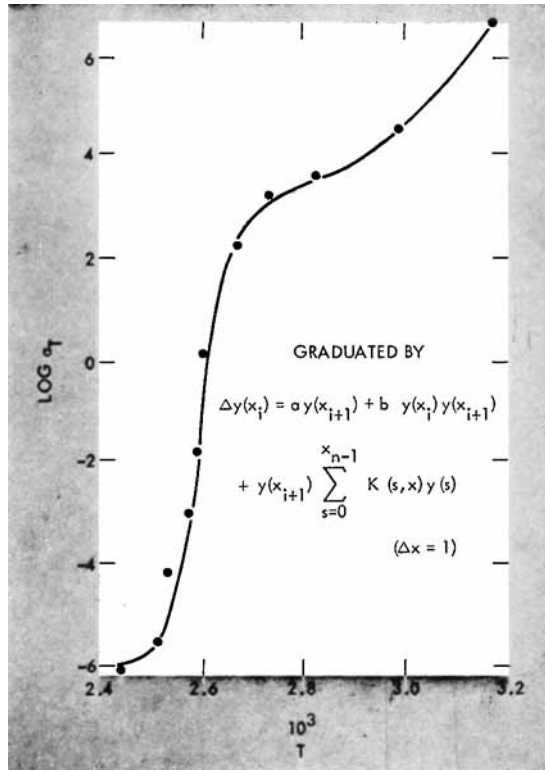


Fig. 4. Application of expression (4) to WLF shift factors for poly(methyl methacrylate) (McLouchlin and Tobolsky, 1952).

The difficulty with graduating to the differential equation occurs in determining the proper starting condition. Using the integral representation of the expression would overcome this difficulty because the boundary conditions and the parameters can be determined.³ Since we propose to conserve the energy of the system, we use a modified method of moments⁴ procedure. The method of graduating is facilitated by writing the integro-differential equations in finite difference form.

To illustrate our technique, the difference equation⁵ that has expression (3) as a solution is

$$\Delta v = v(t + 1)[av(t) + b] \quad \Delta t = 1 \quad (6)$$

and by summing, we obtain

$$v(t) = a \sum_{l=0}^{n-1} v(t + 1)v(l) + b \sum_{l=0}^{n-1} v(t + 1) + v(t = 0) \quad (7)$$

By rearranging expression (6) and setting it equal to a forcing function, we can examine a dynamic system.

To apply the method of moments to eq. (7), we multiply through by $(t - n + 1)^s$ and sum from $t = 0$ (first datum) to $t = (n - 1)$ (last datum). Using the Milne-Thompson⁶ finite summation operator P^{-r} , we write eq. (7) as

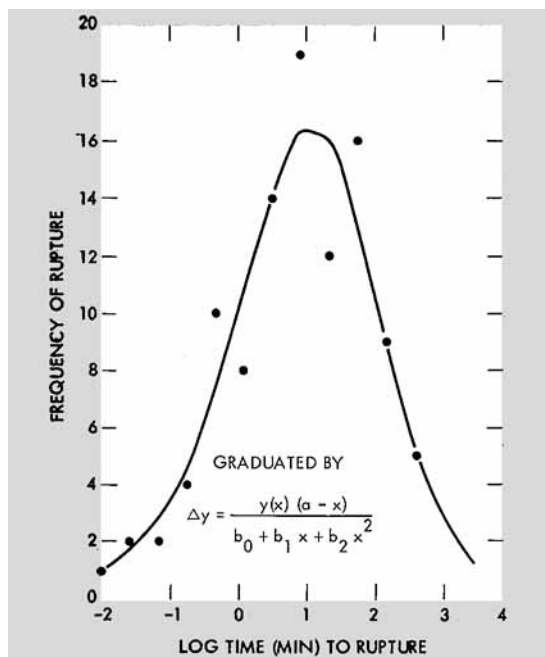


Fig. 5. Application of expression (5) to creep-rupture data of S-glass fiber. Analysis of the parameters in the generalized distribution function follows the usual procedures for extreme value statistics like a Weibull distribution, and is quite amenable to experimental confirmation.

$$\sum_{q=0}^s D_q^* P_n^{-(q+1)} v(t) = a \sum_{q=0}^s D_q^* P_n^{-(q+2)} v(t+1) v(t) + b \sum_{q=0}^s D_q^* P_n^{-(q+2)} v(t+1) + v(t=0) \sum_{q=0}^s D_q^* \frac{\Gamma(n+1)}{\Gamma(q+2)\Gamma(n-q)} \quad (8)$$

where D_q^* are the differences of zero, and Γ is the gamma function.⁷ By setting $s = 0, 1, 2, \dots$, we obtain a system of simultaneous equations from which the parameters a , b , and $v(t=0)$ are determined. The finite summation operator P^{-r} is by definition obtained from the data. The parameters of eq. (3) can be obtained from eq. (7) as follows:

$$\begin{aligned} A &= -b/a \\ B &= \frac{A - v(t=0)}{v(t=0)} \\ \lambda &= \ln(1/(1-b)) \end{aligned}$$

The graduated curve is obtained from the recursion relationship

$$v(t+1) = v(t)/[(1-a) - bv(t)]$$

where $v(t=0)$ is determined from eq. (8).

Expressions (1), (2), (4), and (5) are handled in a similar manner. Figures 1-5 illustrate some of the applications of the technique to physical-property data for polymers.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

References

1. J. B. Conway, *Numerical Methods for Creep and Rupture Analysis*, Gordon and Breach, New York, 1967.
2. J. K. Lepper and N. W. Hetherington, *J. Appl. Polym. Sci.*, **11**, 1775 (1967).
3. G. F. Hudson, *Am. J. Phys.*, **21**, 362 (1953).
4. W. P. Elderton, *Frequency Curves and Correlations*, Cambridge Univ. Press, 1938.
5. H. O. Hartley, *Biometrika*, **35**, 32 (1948).
6. L. M. Milne-Thompson, *Proc. Cambridge Phil. Soc.*, **27**, 26 (1931).
7. H. T. Davis, *Summation of Series*, Principia Press, Trinity Univ., 1962.

J. K. LEPPER
N. W. HETHERINGTON

Lawrence Radiation Laboratory
University of California
Livermore, California 94550

Received May 3, 1968