A Numerical Approach for Obtaining Nonlinear Viscoelasticity Parameters of Polymeric Materials and Composites

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Synopsis

A least-squares fitting procedure is developed for application to determine the parameters of the power law for nonlinear creep and recovery behavior of polymeric materials. The nonlinear power law, developed by Schapery from thermodynamic principles, is linearized, and an iterative approach is used to determine the desired parameters. The iteration is stopped after the standard deviation of the calculated points with respect to the fitted points reaches a minimum value. The purpose of this method is to avoid the inherent ambiguities present in the more familiar graphical fitting procedure. In order to study the sensitivity and limitations of an experimental approach for determining the viscoelastic parameters, sets of artificial experimental data points were generated for use as a control. These points were obtained by varying the theoretical functional values with normally-distributed random numbers within a preset error band.

INTRODUCTION

Except for very small stresses or strains, most polymers show a considerable degree of nonlinear viscoelastic behavior. It is, therefore, desirable to extend the characterization of these materials into the nonlinear viscoelastic range. A frequently used formulation of nonlinear viscoelastic behavior and analysis of polymeric and composite materials has been thoroughly discussed among others by Schapery.[1-3] Other descriptions of the nonlinear viscoelastic behavior have been suggested. A recent overview on this subject was given by Christensen.[4]

In this paper we consider a numerical approach for the determination of the parameters for the nonlinear Schapery formulations[5] from experimental data and to obtain an estimate of the errors one may expect. As originally suggested by Schapery, the parameters are determined by a graphical method which requires simultaneous horizontal and vertical shifts of an experimental curve to give a best fit with one of a series of master curves. Since we found this procedure rather time consuming and quite difficult to reproduce, we developed a numerical method which is rapid, considerably more accurate and less ambiguous than the graphical method, and easily adaptable to modern data gathering systems via microprocessors. The method involves a least-squares fit of experimental data to the nonlinear power-law equations of the Schapery formulation for creep and recovery strain by varying the parameters of the model.

A major objective of this investigation is to illustrate how precisely our numerical procedure can determine the parameters of the fit as a function of the error spread of the experimental data. In order to do this, we have

Journal of Applied Polymer Science, Vol. 30, 4203-4233 (1985)

CCC 0021-8995/85/114203-31$04.00
Published by John Wiley & Sons, Inc.

artificially generated experimental points by varying the true functional values obtained for the creep and recovery equation with a Gaussian distribution to represent experimental errors with a chosen error. We do this, despite the fact that we are presently using the method successfully in an experimental program to study the nonlinear viscoelastic behavior of expoxy resins, in order not to deal with the rather inflexible and, possibly, unknown pecularities of real material and equipment behavior. We thus have the freedom to change the material parameters and experimental errors at will.

The method proposed here of using a least-squares fit to determine the parameters of a function to describe a set of data is not new, but it does not seem to be well known in the present application. Hence, we felt it worthwhile to discuss it in some detail in the context of the Schapery formulation, with particular emphasis on results that pertain to establishing the most appropriate form for various ranges of the parameters. Fundamentally, we assume that we are given a set of data, f_i, at the points x_i, which we want to fit by a function $f(x_i, \alpha)$. The quantities α_j, which for convenience we denote by the vector α, are the parameters to be determined from the data. The method consists of minimizing the sum S:

$$S = \sum_i [f_i - f(\mathbf{x}_i, \alpha)]^2$$

where the sum is over the data points. There are several techniques available to minimize S. What we do here is to linearize the function $f(x,\alpha)$ in the parameters α_j by expanding f in a Taylor series and by keeping the first two terms. The problem is thus reduced to the familiar linear regression, which, in the present context, provides first-order correction terms to initial estimates for the parameters which must be given. This procedure is continued until the standard deviation of the functional values from the experimental values is minimized.

A characteristic feature of nonlinear analysis is a sensitivity in the determination of the parameters of the fit to their initial values, which must be specified, in the sense that values which are sufficiently far from the true values will lead to absurd results. This situation can be determined quickly from an inspection of the results. If this happens, new initial values need to be tried. We mention this merely to warn the reader of this possibility.

Among various other formulations for describing the nonlinear viscoelastic behavior of polymeric materials,[4,6,7] the approach taken by Schapery[5] appeared particularly attractive to us for the following reasons: The experiments to be carried out are simple (uniaxial) creep or relaxation measurements; the theory was developed from thermodynamical principles.[1,2] The parameters g_0, g_1, g_2, and a_σ in the Schapery formulation are not simple curve-fitting parameters; but they reflect third and higher order dependence of the Gibb's free energy on the applied stress, and a_σ arrives from similar high-order effects in entropy production and free energy. (Similarly, the parameters h_0, h_1, and h_2 are higher-order strain effects in the Helmholtz

free energy, and a_ϵ arises from strong strain influences in both entropy production and free energy.) It should be noted that the Schapery expressions reduce to those of the well-known linear viscoelastic equations when the Schapery parameters g_0, g_1, g_2, and a_σ (or h_e, h_1, h_2, and a_ϵ) approach 1, or to another widely used nonlinear theory, the modified superposition principle (MSP) (when the parameters $g_0 = a_\sigma = 1$).[8]

In the following, a short review of the Schapery formulation is given, and the numerical approach is described with enough detail to allow the experimentalist to set up a computer program to meet his specific needs. Finally, a number of sample runs were made to give the reader some feeling of the magnitude of the uncertainty he may expect in the determination of the parameters for certain material parameter ratios or ranges. We included several parameter curve-fitting examples, because the uncertainties can be generally reduced if one parameter is already known and one has to solve only for two or one instead of three. The paper is not intended to discuss procedures on how to do creep and recovery measurements but rather to guide the experimentalist in the data analysis. Numerical data manipulation does not replace the experimental skill and physical intuition.

DISCUSSION

The Schapery Formulation

The time-dependent nonlinear strain and stress behavior of polymeric materials as derived by Schapery is given in eqs. (1) and (2):

$$\epsilon(t) = g_0 D(0)\sigma + g_1 \int_0^t \Delta D(\Psi - \Psi') \frac{dg_2\sigma}{d\tau} d\tau \tag{1}$$

where $D(0)$ and $\Delta D(\Psi)$ are initial and transient components of the creep compliance, Ψ is the reduced time defined by

$$\Psi \equiv \int_0^t \frac{dt'}{a_\sigma [\sigma(t')]}$$

and

$$\Psi' \equiv \Psi(\tau) \equiv \int_0^\tau \frac{dt'}{a_\sigma[\sigma(t')]}$$

and the material properties g_0, g_1, g_2, and a_σ are functions of stress;

$$\sigma(t) = h_e E_e \epsilon + h_1 \int_0^t \Delta E(\rho - \rho') \frac{dh_2\epsilon}{d\tau} d\tau \tag{2}$$

where ϵ is the strain ($\Delta l/1$), E_e, and $\Delta E(\rho)$ are the equilibrium and transient relaxation moduli and the reduced time, ρ, defined as

$$\rho \equiv \int_0^t \frac{dt'}{a_\epsilon[\epsilon(t')]}$$

and

$$\rho \equiv \rho(\tau) \equiv \int_0^\tau \frac{dt'}{a_\epsilon[\epsilon\,(t')]}$$

and the material properties h_e, h_1, h_2, and a_ϵ are functions of strain.

For constant stress (creep) or constant strain (relaxation) eqs. (1) and (2) become expressions (3) and (4) for the nonlinear creep and relaxation behavior:

$$\epsilon(t) = g_0 D(0)\sigma + g_1 g_2 \Delta D\,(t/a_\sigma)\,\sigma \tag{3}$$

$$\sigma(t) = h_e E_e \epsilon + h_1 h_2 \Delta E\,(t/a_\epsilon)\,\epsilon \tag{4}$$

The creep function $\Delta D(t)$ could for instance be expressed by an exponential series:

$$\Delta D(t) = \sum_{r=1}^{N} D_r\left(1 - e^{-t/\tau_r}\right) + D_s t \tag{5}$$

where D_r, D_s, and τ_r are positive constants; τ_r is usually called retardation time. The term $D_s t$ is the so-called steady flow component (which can be neglected except for uncrosslinked amorphous polymers above their glass-transition temperature). Equation (5) is not only an expression for the familiar Kelvin model, consisting of springs and dashpots, but it is also obtained from molecular models and from the STT.

A particular simple expression for $\Delta D(t)$, however, is

$$\Delta D(t) = C_1 t^n \tag{6}$$

It was pointed out by Schapery[5] and Williams[9] that eq. (6) can be derived from eq. (5) if a continuous retardation time spectrum is used instead of a finite series of retardation times.

Thus, one obtains a rather simple expression for the nonlinear creep strain,

$$\epsilon(t) = g_0 D(0)\sigma + g_1 g_2 C_1 (t/a_\sigma)^n \sigma \tag{7}$$

and for the stress–relaxation,

$$\sigma(t) = h_e E_e \epsilon + h_1 h_2 E_1\,(t/a_\sigma)^{-m}\,\epsilon \tag{8}$$

where n and m are generally less than 0.5.

Since g_1 and g_2 appear as a product in the second term of eq. (7) [h_1 and h_2 in eq. (8)], it is not possible to obtain both parameters from single creep

or relaxation experiments. Shapery suggested to perform creep and subsequent recovery measurements to determine all nonlinear parameters (g_0, g_1, g_2, and a_σ) and multistep relaxation experiments to determine h_e, h_1, h_2, and a_ϵ.[10]

The equation for the recovery strain is given by

$$\epsilon_r(t) = \frac{\Delta\epsilon_a}{g_1}[(1 + a_\sigma\lambda)^n - (a_\sigma\lambda)^n] \tag{9}$$

where $\epsilon_r(t)$ is the recovery strain, $\Delta\epsilon_a$ the net strain just before the time t_a of unloading, and λ the reduced time $(t-t_a)/t_a$.

On performing an experiment at small stresses (in the linear range) where $g_0 = g_1 = g_2 = a_\sigma = 1$, one obtains the constants $D(0)$ and C_1. Now g_0, g_1, g_2, and a_σ can be obtained.[10]

Schapery described a graphical method for determining the exponent n from the recovery curves where the experimental log λ curves are simultaneously shifted vertically and horizontally to match best with one of a series of master curves (with different n's).

We found this procedure very time-consuming and very difficult to get reproducible results, even from the same set of creep strain data. This and the recent availability of automatic data gathering via digital microprocessors prompted us to develop a numerical approach for a rapid creep data analysis. Since the stress–relaxation has a similar form and can be readily adapted, we will discuss here only the equations for the creep compliance and the equations for the recovery curve.

Numerical Approach

Substituting $D_0 = g_0D(0)$, $\epsilon_0 = D_0\sigma$, $D_1 = Cg_1g_2/a_\sigma^n$, $\Delta\epsilon_1 = D_1\sigma$ and $A = \Delta\epsilon_a/g_1$ into eqs. (7) and (9) and dividing by the applied stress, we can rewrite eqs. (7) and (9) in terms of

$$\epsilon(t) = \epsilon_0 + \Delta\epsilon_1 t^n \tag{10}$$

$$\epsilon_r(t) = A\left[(1 + a_\sigma\lambda)^n - (a_\sigma\lambda)^n\right] \tag{11}$$

Thus, eq. (10) is a three-parameter equation with time t as the independent and the creep strain, $\epsilon(t)$, as the dependent variables to be measured, and the parameters, ϵ_0, $\Delta\epsilon_1$, and the exponent n are to be obtained from the experimental points. (This three-parameter creep curve fit will be called 3PC.) Similarly, in eq. (11) λ is the independent and $\epsilon_r(t)$ the dependent variable with A, a_σ, and n to be determined. (This curve fit will be called 3PR.) One can see that n can be obtained from either expression.

In order to obtain a best fit for all the experimental points to the given equations, the parameters are adjusted such that the standard deviation of all points becomes a minimum.

Equations (10) and (11) were linearized by expansion into a Taylor series and truncation after the first derivative to give

$$\epsilon(t) = \epsilon_0 + \Delta\epsilon_1 t^{n_0} + \Delta\epsilon_1^* \delta n t^{n_0} \ln t \tag{12}$$

where n_0 and $\Delta\epsilon_1^*$ are initial input values for the following iteration, and $\delta n = n - n_0$, and

$$\begin{aligned}\epsilon_r(t) = {} & A\,[(1 + a_0\lambda)^{n_0} - (\lambda a_0)^{n_0}] \\ & + B\,[(1 + a_0\lambda)^{n_0} \ln(1 + a_0\lambda) - (\lambda a_0)^{n_0} \ln(\lambda a_0)] \\ & + C\left[(1 + a_0\lambda)^{n_0} \frac{n_0\lambda}{1 + a_0\lambda} - (\lambda a_0)^{n_0} \frac{n_0}{a_0}\right]\end{aligned} \tag{13}$$

where $A = \Delta\epsilon_a / g_1$, $B = A\delta n$, $C = A\delta a$, $\delta a = (a_\sigma - a_0)$.

After substitution for $\epsilon_0 = \alpha$, $\Delta\epsilon_1 = \alpha_2$, and $\Delta\epsilon_1^*\delta n = \alpha_3$ in eq. (12) and variation with respect to the α's,

$$\delta \sum_{i=1}^{N} [\alpha_1 + \alpha_2 t_i^{n_0} + \alpha_3 t_i^{n_0} \ln t_i - \epsilon(t_i)]^2 = 0$$

we obtain a set of linear simultaneous equations:

$$\begin{aligned} a_{11}\alpha_1 + a_{12}\alpha_2 + a_{13}\alpha_3 &= b_1 \\ a_{21}\alpha_1 + a_{22}\alpha_2 + a_{23}\alpha_3 &= b_2 \\ a_{31}\alpha_1 + a_{32}\alpha_2 + a_{32}\alpha_3 &= b_3 \end{aligned}$$

where

$$a_{11} = N,\ a_{12} = \sum_{i=1}^{N} t_i^{n_0},\ a_{13} = \sum_{i=1}^{N} t_i^{n_0} \ln t_i$$

$$a_{22} = \sum_{i=1}^{N} t^{2n_0},\ a_{23} = \sum_{i=1}^{N} t_i^{2n_0} \ln t_i$$

$$a_{33} = \sum_{i=1}^{N} t_i^{2n_0} (\ln t_i)^2,\ a_{21} = a_{12},\ a_{32} = a_{23}$$

$$b_1 = \sum_{i=1}^{N} \epsilon(t_i),\quad b_2 = \sum_{i=1}^{N} \epsilon(t_i) t_i^{n_0},\ b_3 = \sum_{i=1}^{N} \epsilon(t_i) t_i^{n_0} \ln t_i$$

N is the number of measured creep points $\epsilon(t_i)$ and t_i are the respective times. n_0 is chosen as the initial value for the exponent and $\Delta\epsilon^*{}_1$ is the

netstrain after 1 h (which was chosen as the time unit). Obviously, any time unit at which $\Delta\epsilon_1$ can be measured reliably will suffice.

The introduction of $\Delta\epsilon_1^*$ as an initial value was chosen in order to separate the product of unknowns $\Delta\epsilon_1\delta n$. Solving these equations for α_1, α_2, α_3 results in new values of n_0 and $\Delta\epsilon_1^*$ which are now entered in the loop. This iteration is continued until the standard deviation including all points reaches a minimum.

A similar variation with respect to the unknown parameters is carried out with eq. (13):

$$\delta \sum_{i=1}^{N} \left[\epsilon_r(t_i) - Af_1(i) - Bf_2(i) - Cf_3(i) \right]^2 = 0$$

where f_1 is the first bracket term of eq. (13), f_2 the second bracket term, and f_3 the third bracket term. Let $f_1, f_2, f_3 \rightarrow f_k$ and $A,B,C, \rightarrow A_k$, where $k = 1,2,3$; then we obtain again a set of simultaneous linear equations.

$$\sum_{k=1}^{3} A_k \sum_{i=1}^{N} f_k(i) * f_l(i) = \sum_{i=1}^{N} \epsilon_r(t_i) f_l(i)$$

where $l = 1,2,3$. Defining

$$M_{lk} = M_{kl} = \sum_{i=1}^{N} f_l(i)\, f_k(i)$$

$$B_l = \sum_{k=1}^{3} M_{lk} A_k$$

then we obtain

$$M_{11}A_1 + M_{12}A_2 + M_{13}A_3 = B_1$$

$$M_{21}A_1 + M_{22}A_2 + M_{23}A_3 = B_2$$

$$M_{31}A_1 + M_{32}A_2 + M_{33}A_3 = B_3$$

which is solved for the A_k, giving new values for A, n_0, and a_0. The iteration is continued until the standard deviation with all points included obtains a minimum value.

Thus, the exponent n can be obtained from either the 3PC or the 3PR method. In the case where one method has a lower error probability for determining n, it might further reduce the error probability for determining the rest of the parameters by reducing the second curve fit to be performed as a two-parameter curve fit. Also, from the shape of the creep curves, it may appear that $\Delta\epsilon_1$, the net strain (transient strain) after 1 h, can be

obtained with high accuracy; thus again, one obtains a two-parameter curve fit with $\Delta\epsilon_1$ as constant input. This curve fit will be called 2PC1. The corresponding two-parameter creep curve fit, where the initial strain ϵ_0 is entered as constant will be called 2PCO. The two-parameter recovery curve fit, where n (obtained from the creep experiment) is set constant, will be called 2PRn. Or vice versa, the two-parameter curve fit where n was determined from 3PR curve fit is called 2PCn. For the derivations of the two-parameter curve fits the same Taylor expansion eqs. (12) and (13) are used where the variations are carried out for the unknown parameters.

Test Functions and Simulated Experiments

The thermodynamic theory gives only a qualitative meaning to the parameters g_0, g_1, g_2, a_σ, and n. For obvious reasons they cannot be predicted by theory but must be determined from experiment. The graphical method of vertical and horizontal curve shifting makes an error analysis for the various parameters very difficult if not impossible, while the numerical method allows one to obtain reasonable error estimates.

If we can exclude all instrument sources of errors (such as misalignments, large variabilities or nonlinearities and temperature fluctuations) which are not related to the curve fitting method itself, the errors in the parameters to be determined will then depend on the data spread in the collected strain readings, on the number of points collected, on the form of the creep or recovery curve (i.e., on the magnitude of the parameters themselves and their relation to each other), and on the specific curve fitting method. The finite loading time, during which time creep and relaxation will occur, makes it sometimes difficult to obtain a reasonable estimate of the initial compliance or relaxation modulus. Schapery analyzed this problem[10] and concluded that if the collected data are taken after a time which is larger than five times the time necessary to complete sample loading, the error in the creep compliance or relaxation modulus will be less than 5%.

Instead of using actual experimental creep and recovery curves which do not show a direct error measurement, we used theoretical test functions of the form of equations (10) and (11) with reasonable, assumed parameters ϵ_0, $\Delta\epsilon_1$, and n or A, a_σ, and n, respectively. As experimental curves, we took samples of N points which were artificially randomized to give a normal distribution around the theoretical values using the algorithm of[11]

$$X = (-2 \ln R_1)^{1/2} \cos(2\pi R_2) \tag{14}$$

where R_1 and R_2 are random numbers from 0 to 1 and X are numbers which are normally distributed from -1 to $+1$. (For the desired data spread in $\pm\%$ this number is multiplied by $p/100$.)

Thus, artificial experimental points were produced through which curves were fit using the above curve-fitting techniques. This allows one to change the parameters and their ratio to one another at will, as well as to change the number of points and the width of their normal distribution and the time after which data collection starts. The iteration is continued until the standard deviation of the "experimental" points to the fitted curve becomes a minimum. The parameters of this curve are then taken as best fit.

It should be noted that each set of randomized, normally distributed experimental points gives parameters that differ from each other and from the theoretical value. In order to obtain a measure for these errors, 10 individual runs were made for each set of parameters such that for every run a new set of random numbers was used. The mean error of these 10 runs and its standard deviation is reported.

Relations of Polymers and Composites

In evaluating viscoelastic parameters in composites, great care should be taken, particularly if the experimental loading process is not extremely short (which in many cases it is not). For many composite constructions, the ratio of $\epsilon_0/\Delta\epsilon_1$ of initial strain to net strain after 1 unit of time (say 1 h) is much larger than that for the neat resin. This could mean that the creep curve of a composite can mimic a considerably lower n value than one might find for the pure resin. An example is shown in Figure 1, curve 1, and Figure 2. By graphically superposing these two curves, they seem to be indistinguishable (except for extremely short times).

These are two theoretical curves: 1 of Figure 1 has $\epsilon_0 = 8000$, $\Delta\epsilon_1 = 8000$, and $n = 0.01$, i.e., $\epsilon_0/\Delta\epsilon_1 = 1$; the curve of Figure 2 has $\epsilon_0 = 15{,}000$, $\Delta\epsilon_1 = 1000$, and $n = 0.1$ Thus, a very large error may be expected if such a curve was analyzed without further knowledge. (This example should only caution the experimentalist that mindless automation and uncritical data analysis may easily lead to erroneous conclusions.)

In Figure 1 we also have included curves 2, 3, and 4, which all have the same $\epsilon_0/\Delta\epsilon_1$ ratio but different exponents n, which are 0.1, 0.4, and 1, respectively. We have done this for two reasons: first it provides a better feeling for the functional form of eq. (10); second, and more importantly, it

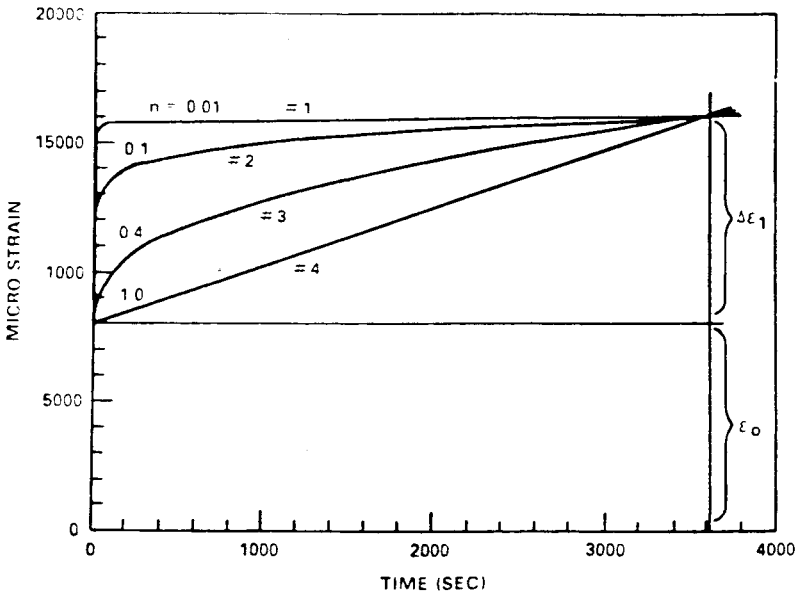

Fig. 1. Creep strain curves for different values of the exponent n. $\epsilon_0 = 8000$, $\Delta\epsilon_1 = 8000$; the unit time = 1 h.

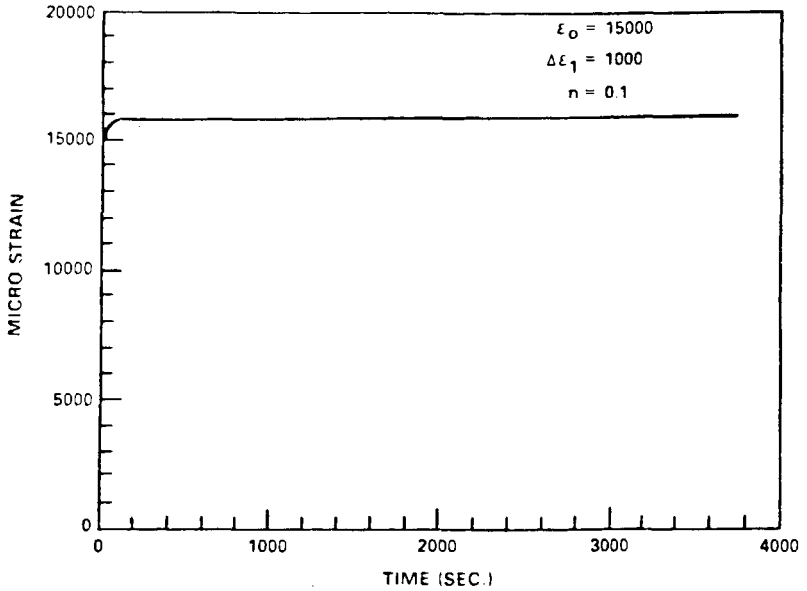

Fig. 2. Creep strain curve for $n = 0.1$, $\epsilon_0 = 15000$, $\delta\epsilon_1 = 1000$. Note this curve is, except for very short times, for all practical purposes indistinguishable from the curve in Figure 1 with $n = 0.01$.

shows immediately that if we have no further knowledge of the material, we may, even with good measurements, get large errors for small n's. On the other hand, if we know that this polymer is in the glassy state, we would obviously not expect a creep curve of a shape of curve 1, which would mean that the viscous deformation is almost finished by the time the loading is complete (i.e., the glassy viscosity is low which is contrary to any observation and a resulting $\epsilon_0 = 8000$, $\Delta\epsilon_1 = 8000$, and $n = 0.01$ would not make sense).

At this point it may be useful to remember the meaning of n. Williams[9] has shown that n is the log–log slope of the retardation (or relaxation) curve through the transition region between glassy and rubbery behavior. This statement has two consequences: First, n should be independent of temperature since a change in reference temperature of the log–log master curve for the creep compliance (or relaxation modulus) leads only to a horizontal shift but not a change in slope; second, n (being a material constant) should carry over unchanged to composites (at least for angle ply composites with fibers that do not creep, as is the case with carbon fibers). This is obviously not true for Kevlar composites since Kelvar also shows a creep behavior. The reason that n should be the same for angle ply composites with creep-free fibers as for the neat resin arises from micromechanical considerations. The theoretical details for that cannot be discussed here. However, on a qualitative basis one might argue as follows. The only constituent in such a composite that can creep is the matrix. (The fact that in a loaded composite the resin between the fibers is in a nonuniform multiaxial stress–strain field is not important.) The local stresses can be represented by octahedral shear stress–strain components[5] and the ana-

lytical approach is normally a finite element analysis as used, for instance, by Schaffer and Adams[12] or Crossmann et al.[13] The effective resin stress will remain constant during a creep experiment and, therefore, the ratio of the net strain, $\Delta\epsilon(t)$, at some time, t, and the net strain after one unit of time, $\Delta\epsilon_1$, should remain the same for both the matrix and the composite, since $\Delta\epsilon(t) = \Delta\epsilon_1 \cdot t^n$. For this reason, it may be more useful to determine the exponent n from the neat resin and the other parameters ϵ_0, $\Delta\epsilon_1$, A, and a_σ from the two-parameter curve fits 2PCn and 2PRn.

Unidirectional composites in the zero direction, crossply composites, and multiangle ply composites may not have the same exponent. This can also be understood if one considered a unidirectional composite loaded in the fiber direction. Usually the fibers carry the main load. After the initial load application, the fiber is strained to its equilibrium. The resin is stressed not only longitudinally but through the Poisson effect also transversely. The resin does not creep longitudinally since it is restrained by the fibers, but it will relax and transfer the relaxed stresses (a small portion of the total stress in the composite) to the fibers which will be slightly more loaded and strained. In this case, it is the stress–relaxation of the resin that governs the creep of the composite. (For nonlinear viscoelasticity there is no direct conversion from relaxation modulus to creep compliance.) A similar argument holds for crossply composites and for multiangle composites.

However, if the loads applied to the composite are not very high (for instance under storage), the stresses in the resin (as calculated via micromechanics and lamination theory) may be well within the linear elastic range, and creep compliance and stress relaxation modulus are related by the well-known convolution integral,

$$t = \int_0^t D(\tau)E(t-\tau)\,d\tau$$

where $D(\tau)$ is the linear creep compliance and E is the linear relaxation modulus. Thus, the log–log slope (n) of D is the same as that of E (with a negative sign). Again, the 2PCn or 2PRn curve fit can be used if n was determined from resin creep or relaxation experiments. Measuring the composite and the resin creep exponent independently may even yield additional information on various composite nonlinearities which are of a different nature than the nonlinearities resulting from the matrix itself (for instance, microcrack formation or fiber breakage, all of which are irreversible phenomena and can mimic a "nonlinear" viscoelastic behavior of the composite, based, however, on a different mechanism).

The above remarks should be a reminder that at present we do not want to give the impression that an automation of the experiments (without a certain understanding of the experimenter on the subject and on the nature of the material) will lead to unambiguous and reliable results.

In the following section, we shall investigate what errors we may expect as a result of the number of points entered into the analysis, the effect of spread (width) of the measured data, and how the magnitude of the various parameters effect each other.

TABLE I
Results of Test Runs Using the 3PC Curve Fitting Method

Test no.	Theoretical value			Spread	Initial input			Average error (%) standard deviation					
	ϵ_0	$\Delta\epsilon_1$	n	(±%)	$\Delta\epsilon_1^*$	n_0	ϵ_0	SD	$\Delta\epsilon_1$	SD	n	SD	$\epsilon_0/\Delta\epsilon_1$
1	8000	1000	0.4	0.5	900	0.5	0.85	1.13	6.67	8.19	11.89	10.42	8
2	8000	1000	0.4	0.5	900	0.5	0.50	0.35	3.96	2.66	7.59	4.74	8
3	8000	1000	0.4	0.5	900	0.5	0.36	0.38	2.89	2.82	4.46	4.46	8
4	500	8000	0.4	0.5	10,000	0.5	5.09	4.64	0.29	0.25	0.63	0.64	1/16
5	1000	8000	0.4	0.5	10,000	0.5	3.31	2.85	0.36	0.27	0.75	0.73	1/8
6	2000	8000	0.4	0.5	10,000	0.5	1.54	0.89	0.25	0.18	0.92	0.70	1/4
7	4000	8000	0.4	0.5	10,000	0.5	1.90	1.71	0.77	0.71	1.96	1.65	1/2
8	8000	8000	0.4	0.5	8000	0.5	1.05	0.80	1.04	0.80	1.84	1.12	1
9	8000	4000	0.4	0.5	6000	0.5	0.70	0.77	1.45	1.54	2.67	2.33	2
10	8000	2000	0.4	0.5	3000	0.5	0.66	0.72	2.71	2.95	4.69	4.19	4
11	8000	500	0.4	0.5	1000	0.5	0.79	1.28	12.60	18.66	17.21	16.55	16
12	8000	250	0.4	0.5	1000	0.5	1.01	0.74	26.81	22.34	40.22	16.46	32
13	8000	1000	0.4	0.25	900	0.5	0.22	0.15	1.75	0.76	3.23	2.70	8
14	8000	1000	0.4	0.75	900	0.5	1.29	1.27	9.74	10.88	17.66	11.62	8
15	8000	1000	0.4	1.0	900	0.5	1.49	1.15	11.40	8.26	21.33	13.07	8
16	8000	1000	0.4	1.25	900	0.5	1.57	0.92	11.17	6.25	26.07	16.97	8
17	8000	1000	0.4	1.5	900	0.5	2.46	3.00	18.01	22.90	36.70	33.11	8
18	8000	8000	0.4	1.0	8000	0.5	2.72	1.86	2.37	1.92	4.80	2.84	1
19	8000	8000	0.15	0.5	10,000	0.5	30.58	11.98	30.96	12.14	106.32	49.35	1
20	8000	8000	0.20	0.5	10,000	0.5	10.35	10.84	10.48	11.34	27.61	31.01	1
21	8000	8000	0.25	0.5	10,000	0.5	2.75	1.42	2.58	1.24	4.31	2.78	1
22	8000	8000	0.30	0.5	10,000	0.5	1.02	0.89	0.88	0.72	2.02	1.70	1
23	8000	8000	0.40	0.5	6000	0.5	1.09	1.01	1.02	0.80	2.18	1.66	1
24	8000	8000	0.40	0.5	8000	0.2	0.90	1.01	0.85	0.89	1.87	1.87	1
25	8000	8000	0.40	0.5	10,000	0.5	0.60	0.49	0.55	0.32	1.27	1.08	1

Expected Errors in the Experimental Determination of the Nonlinear Viscoelastic Parameters

From eqs. (10) and (11) and the definitions of the following parameters: $\epsilon_0 \equiv g_0 D(0)\,\sigma$, $\Delta\epsilon_1 \equiv Cg_1g_2/a_\sigma^n$, $A \equiv \Delta\epsilon_a/g_1$, and from the fact that, for experiments at low stresses (linear region), $g_0 = g_1 = g_2 = a_\sigma = 1$, one can obtain the stress dependent parameters $g_0 \neq g_1 \neq g_2 \neq a_\sigma \neq 1$ from a series of single uniaxial creep and recovery experiments at different loading levels. For the sake of clarity, we shall use here only the parameters ϵ_0, $\Delta\epsilon_1$, a_σ, A, and n.

We shall consider examples with the three- and two-parameter curve fitting methods 3PC, 3PR, 2PRn, 2PCO, 2PC1, and 2PCn.

Each entry in Tables I–VI is the average of 10 individual test runs, each with a new set of random numbers. In addition to the average errors

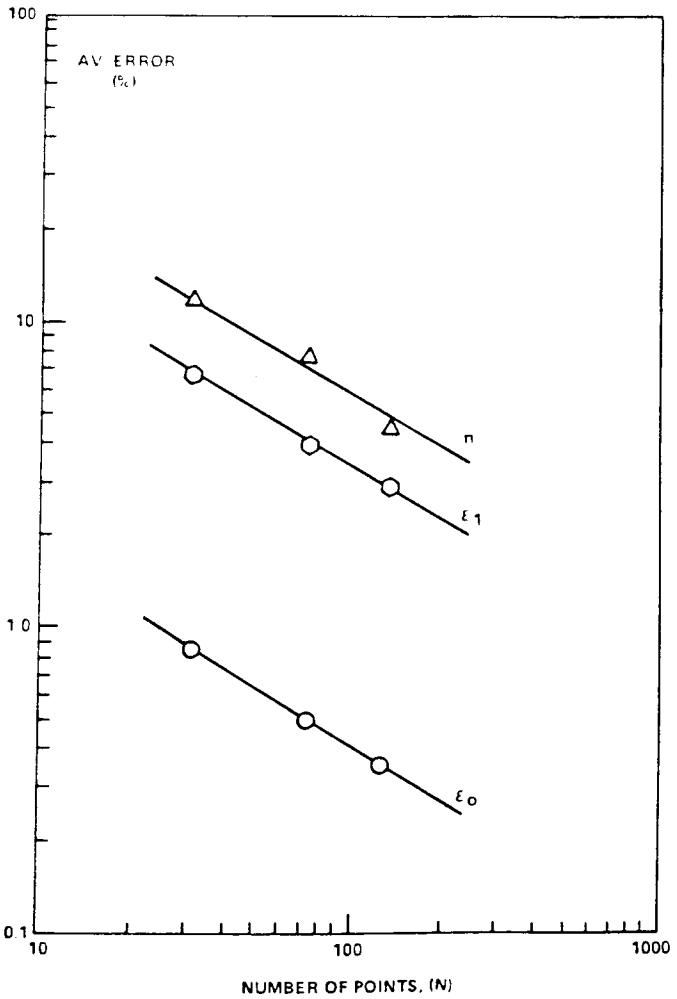

Fig. 3. Average errors for ϵ_0, $\Delta\epsilon_1$, and n as a function of the number of data points (N) for the 3PC curve fit. Theoretical values: $\epsilon_0 = 8000$, $\Delta\epsilon_1 = 1000$, $n = 0.4$; data spread: $\pm 0.5\%$.

($\Sigma|\text{Err}|/n$), their standard deviation is also given. Under the columns "Theoretical values" are listed the parameters that were chosen to represent a theoretical reference function from which a number of points were taken and normally distributed to give a set of "experimental" points with a preset data spread, indicated in the column, spread ($\pm$%). Since in some cases the final result was significantly dependent on the choice of initial trial values of the parameters for the iteration, they are listed in the columns Initial Inputs. The data points were assumed to start after 60 s and spaced to fall within 1 h to simulate a typical creep experiment.

For reference purposes, all entries are numbered consecutively. For all runs except runs 2 and 3, a total of 31 data points were used (run 2 had 73 and 3 had 126 points). For the two-parameter curve fits, a preset error was given to the third parameter which was assumed to be known within that range. For obvious reasons, we neither can, nor do we intend, to give a complete description of the total error space governed by all three parameters and their relations to one another. The sample runs were chosen to show trends and to provide a better feel for the errors that may be expected from actual creep and recovery experiments. Once the program is set up, it is easy to investigate these specific cases of interest which are not covered here.

Effect of the Number of Experimental Points on the 3PC Curve Fit

If no artificial error was introduced in the functional values of the selected points of the test function, the parameters were obtained exactly (within the roundoff error of the computer).

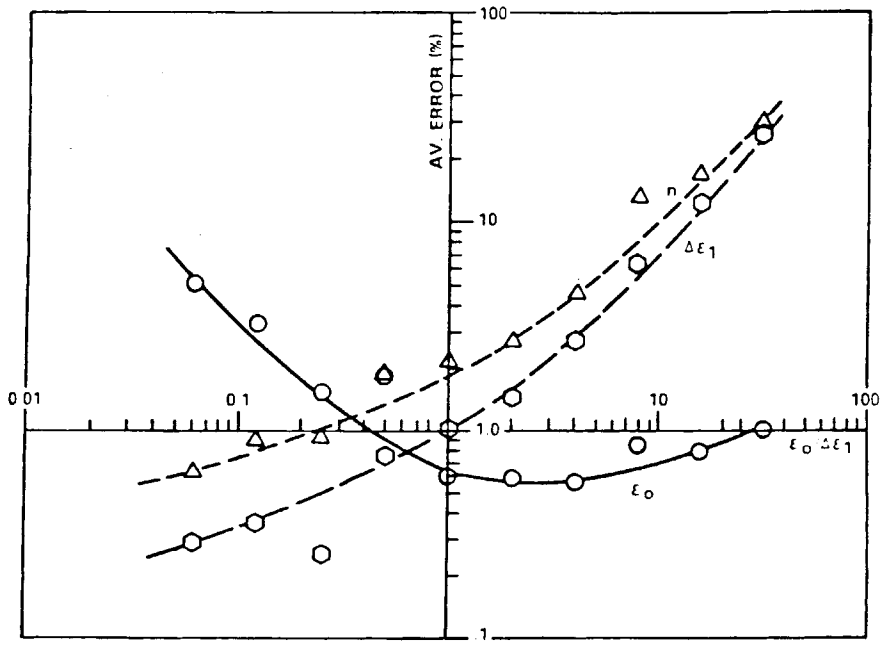

Fig. 4. Average errors in ϵ_0, $\Delta\epsilon_1$, and n as a function of the ratio $\epsilon_0/\Delta\epsilon_1$ for the 3PC curve fit with $n = 0.4$. Data spread: $\pm 0.5\%$; $N = 31$.

By introducing normally distributed errors of $\pm 0.5\%$ bandwidth for the data points around the true functional value for the 3PC curve fit, the average errors for each parameter were different; however, they decreased approximately to 1/2 when the number of experimental points was increased threefold (see Table I, runs 1–3, and Fig. 3).

Effect of the Ratio $\epsilon_0/\Delta\epsilon_1$ on the 3PC Curve Fit

As we have indicated in the section Relations of Polymers and Composites, with a high ratio of $\epsilon_0/\Delta\epsilon_1$ and in the absence of reliable measurements at very short times, one may expect large errors for n, as can be indeed seen from the results of Table I (runs 1, and 4–12) and Figure 4.

Effect of the Data Bandwidth on the 3PC Curve Fit

For this set of runs, a ratio $\epsilon_0/\Delta\epsilon_1$ of 8 was chosen which may be useful for many polymers. From the results of Table I (runs 1, and 13–17) and

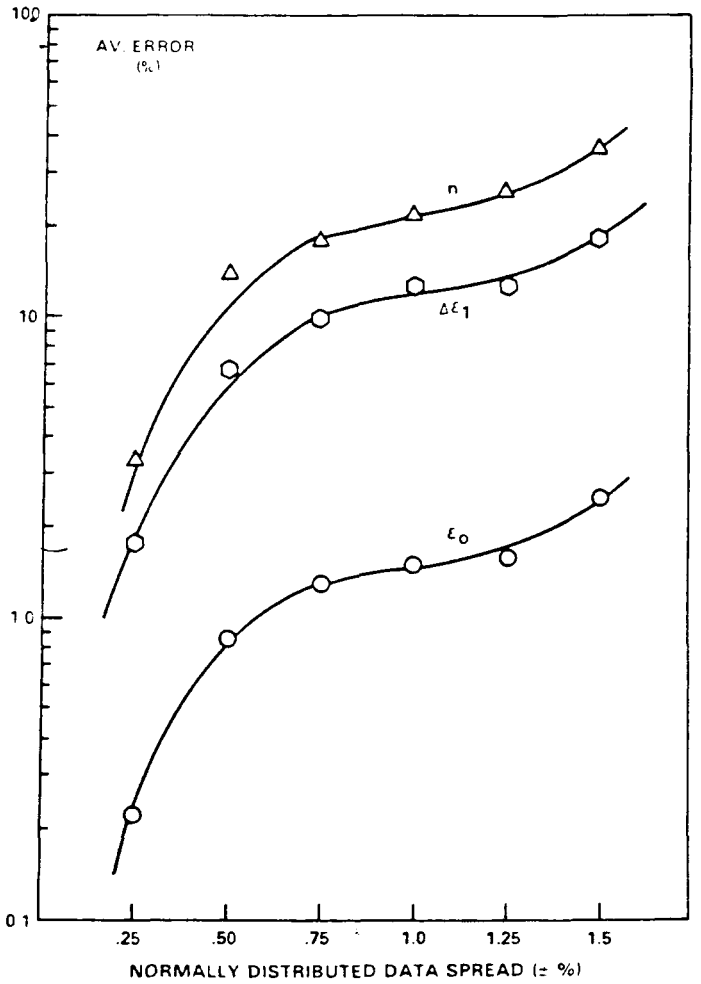

Fig. 5. Average errors in ϵ_0, $\Delta\epsilon_1$, and n as a function of the width of the normally distributed data for the 3PC curve fit. Theoretical values: $\epsilon_0 = 8000$, $\Delta\epsilon_1 = 1000$, $n = 0.4$, $N = 31$.

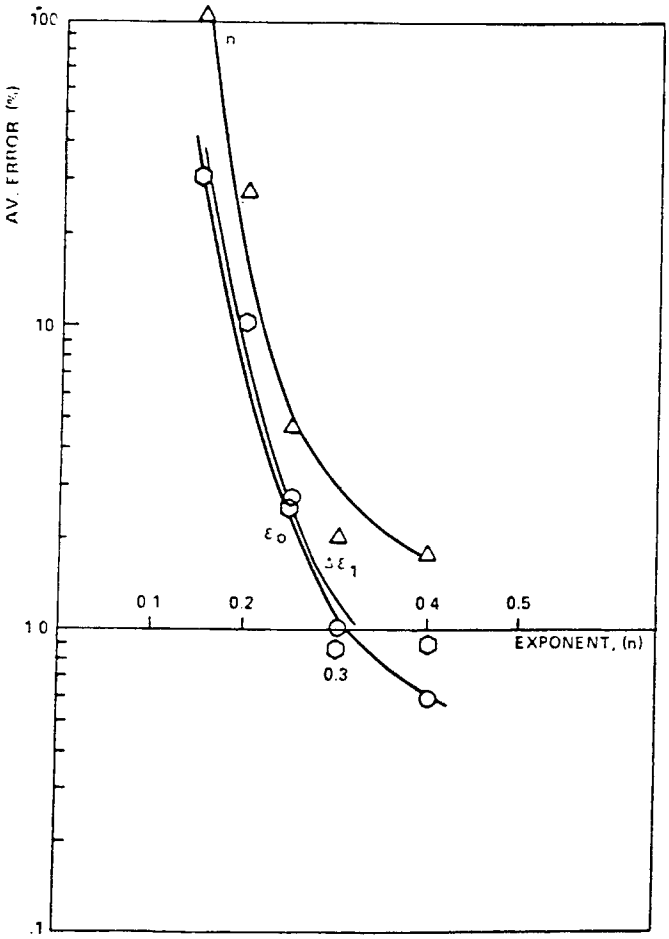

Fig. 6. Average errors in ϵ_0, $\Delta\epsilon_1$, and n as a function of n for the 3PC curve fit. Theoretical values: $\epsilon_0 = 8000$, $\Delta\epsilon_1 = 8000$, $N = 31$; data spread: $\pm 0.5\%$.

Figure 5, it is obvious that a data bandwidth of $\pm 1\%$ or higher gives unacceptable errors in n and $\Delta\epsilon_1$. (Either the number of points or the accuracy of the data must be significantly increased to assure that the parameters obtained are useful.) Of course, if the ratio of $\epsilon_0/\Delta\epsilon_1$ is smaller, the error for n and $\Delta\epsilon_1$ is also considerably smaller (see run 18).

Effect of the Exponent of the 3PC Curve Fit

Figure 6 and Table I (runs 19–23) show that the error in determining n with the 3PC method increases drastically as n becomes smaller than 0.2, even for an $\epsilon_0/\Delta\epsilon_1$ ratio as small as 1. It should be noted here that curve fits to the experimental points (using these high error n values) still look excellent on the computer graphics printouts. Obtaining a good curve fit with experimental points in this case does not mean that the parameters obtained are equally good. The 3PC curve fitting method is insensitive to the initial input values for $\Delta\epsilon_1^*$ or n_0 as can be seen in runs 23–25. (This is not the case for the 3PR curve fit.)

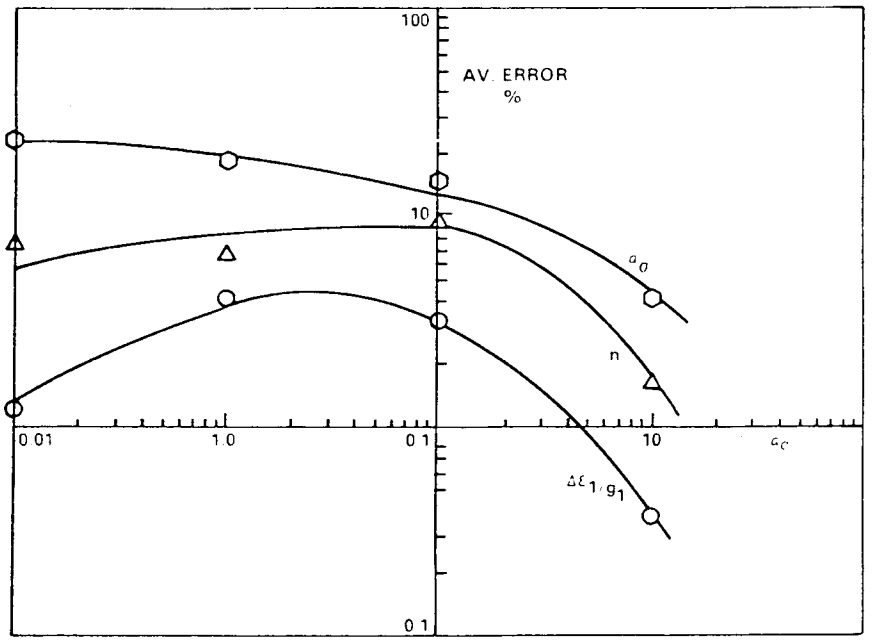

Fig. 7. Average errors in $\Delta\epsilon_1/g_1$, a_σ, and n as a function of a_σ for the 3PR curve fit. Theoretical values: $\Delta\epsilon_1/g_1 = 8000$, $n = 0.3$, $N = 31$; data spread: $\pm 0.5\%$.

Effect of Change in a_σ on the 3PR Curve Fit

From Figure 7 and Table II (runs 26–29), one can conclude that as the horizontal shift factor a_σ becomes very small, the error in a_σ increases slowly, while the errors in n and in the "vertical shift factor" $A = \Delta\epsilon_a/g_1$ remain within acceptable bonds.

Effect of the Exponent n on the 3PR Curve Fit

From Figure 8 and Table II (runs 30–34), one can see that for small exponents $n < 0.2$ the 3PR method is better for determining n but for large exponents $n > 0.2$ the 3PC method is superior. Also, it does not seem to matter much whether $\Delta\epsilon_a/g_1$ is large or small (compare run 30 with 35 and run 33 with 36). However, as will be seen in the next paragraph, fine tuning of the trial input values for n_0 may be required for best results.

Effect of the Trial Input Value of n On the 3PR Curve Fit

In contrast to the 3PC method, the 3PR curve fitting method is very sensitive to the initial trial input values for the exponent n_0 (see Fig. 9 and Table II, runs 37–42 and run 32). As a matter of fact, there is usually an overflow error if the difference between the true value of n and the initial input value n_0 is larger than 0.1. An error recovery and fine tuning algorithm is advisable here. This is fairly independent of whether $\Delta\epsilon_a/g_1$ is large or small (compare with runs 41 and 42).

TABLE II
Results of Test Runs Using the 3PR Curve Fitting Method

Test no.	Theoretical value			Spread (±%)	Initial input			Average error (%) standard deviation					
	A	a_σ	n		A_0	a_0	n_0	A	SD	a_σ	SD	n	SD
26	8000	0.01	0.3	0.5	8000	0.02	0.3	1.21	0.64	23.56	9.27	7.41	3.38
27	8000	0.1	0.3	0.5	8000	0.2	0.3	4.17	4.03	18.92	10.90	6.74	6.52
28	8000	1.0	0.3	0.5	9000	1.0	0.3	3.26	3.26	14.81	15.80	9.64	10.49
29	8000	10.0	0.3	0.5	8000	15	0.3	0.39	0.27	4.18	3.29	1.60	1.14
30	250	1.0	0.1	0.5	240	1	0.1	9.00	9.30	6.78	9.43	14.71	19.41
31	250	1.0	0.2	0.5	240	1	0.2	9.29	6.69	18.92	15.55	20.10	16.91
32	250	1.0	0.3	0.5	240	1	0.3	2.69	2.44	15.50	12.56	10.21	7.04
33	250	1.0	0.4	0.5	240	1	0.4	1.63	1.35	14.92	8.06	7.14	4.51
34	8000	1.0	0.5	0.5	8000	1	0.5	0.84	0.68	19.43	12.04	6.90	4.76
35	8000	1.0	0.5	0.5	9000	1	0.1	12.46	9.67	8.80	9.50	18.73	19.64
36	8000	1.0	0.4	0.5	8000	1	0.4	3.11	2.96	23.11	15.82	11.65	8.54
37	250	1.0	0.3	0.5	240	1	0.15	11.63	7.22	48.01	30.02	39.83	28.11
38	250	1.0	0.3	0.5	240	1	0.20	4.48	5.04	7.98	4.61	6.94	4.34
39	250	1.0	0.3	0.5	240	1	0.40	3.68	2.02	19.91	18.97	11.60	8.63
40	250	1.0	0.3	0.5	240	1	0.50	11.85	1.06	100.87	32.44	48.95	9.52
41	8000	1.0	0.3	0.5	9000	1	0.50	11.63	0.81	94.36	26.56	46.91	7.93
42	8000	1.0	0.4	0.5	8000	1	0.50	1.99	1.27	16.91	7.49	8.14	3.78
43	8000	1.0	0.4	0.25	8000	1	0.4	0.76	0.67	7.89	4.74	3.63	2.47
44	8000	1.0	0.4	0.50	8000	1	0.4	1.77	1.37	16.35	8.54	7.79	4.59
45	8000	1.0	0.4	0.75	8000	1	0.4	2.96	1.12	27.38	12.31	12.99	5.49
46	8000	1.0	0.4	1.00	8000	1	0.4	3.36	2.55	27.68	15.68	13.58	8.56
47	8000	1.0	0.4	1.25	8000	1	0.4	3.45	3.10	28.47	11.93	13.79	7.74
48	8000	1.0	0.4	1.50	8000	1	0.4	5.44	5.38	35.20	19.74	18.47	11.90

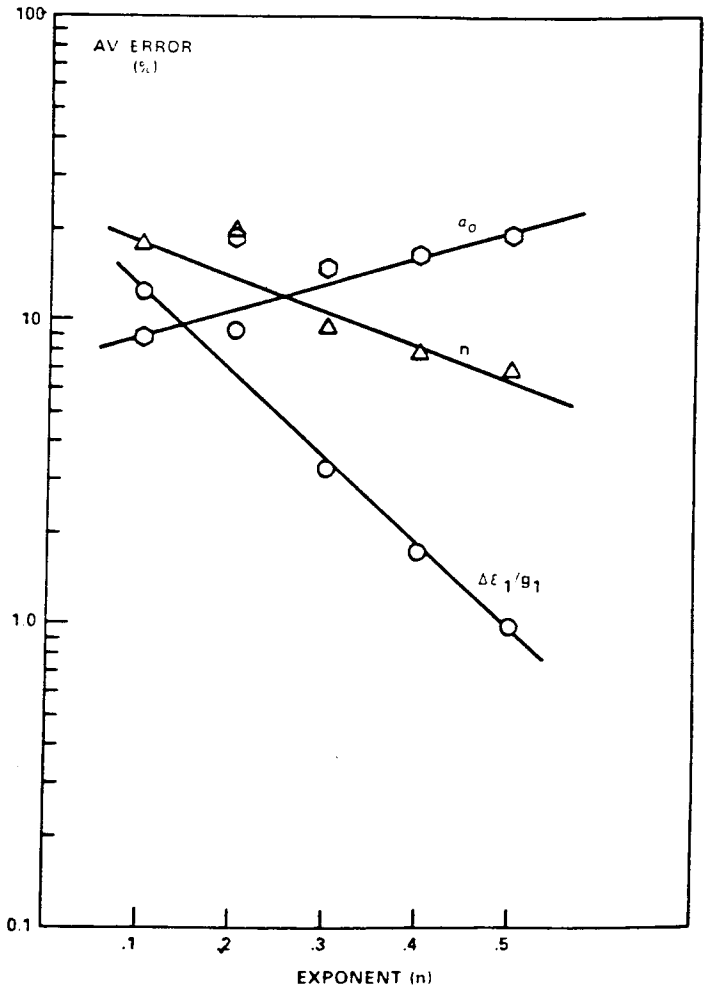

Fig. 8. Average errors in $\Delta\epsilon_1/g_1$, a_σ, and n as a function of n for the 3 PR curve fit. Theoretical values: $\Delta\epsilon_1/g_1 = 250$, $a_\sigma = 1$, $N = 31$; data spread: $\pm 0.5\%$.

Effect of Data Bandwidth on the 3PR Curve Fit

Comparing Figure 10 (Table II, runs 43–48) with Figure 5, it seems that the error in n is less sensitive to the data bandwidth for the 3PR method than for the 3PC method. However, one still has to keep the remarks of the previous paragraph in mind.

Effect of the Exponent n on the 2PRn Curve Fit

From Table III (runs 49–53) and Figure 11 one can see that if n were known exactly for the 2PRn curve fit, one would obtain very small errors in a_σ and $\Delta\epsilon_a/g_1$, fairly independent on n itself. If the error of the assumed exponent n increases above 8%, so does the error of a_σ and $\Delta\epsilon_a/g_1$, and the 2PRn may no longer be superior to the 3PR method (see Fig. 12 and Table III, runs 54–57). On the other hand, if $n > 0.22$, the error in n decreases

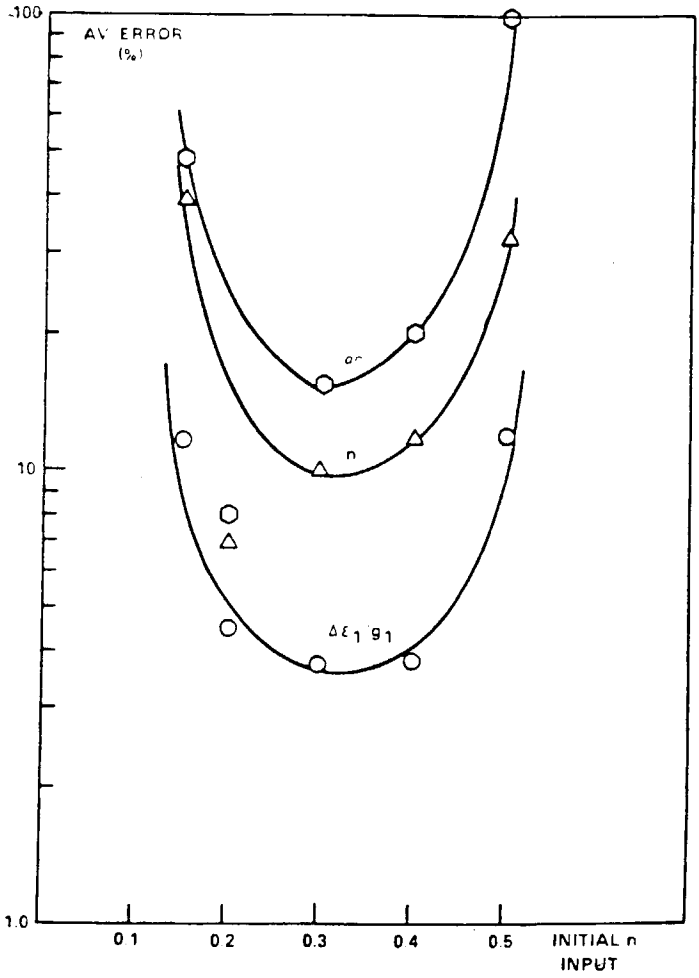

Fig. 9. Average errors in $\Delta\epsilon_1/g_1$, a_σ, and n as a function of the initial input value of n when the theoretical value of $n = 0.3$. Theoretical values: $\Delta\epsilon_1/g_1 = 250$, $a_\sigma = 1$, $N = 31$; data spread: $\pm 0.5\%$.

rapidly if the 3PC method is used. This means that if $n > 0.22$, a combination of 3PC and 2PRn may give better results than the combination of 3PC and 3PR where one still has to make a compromise with the two different n values that are most likely obtained.

Results with the 2PCO Curve Fitting Method

In using the 3PC method, we have mentioned that as the ratio $\epsilon_0/\Delta\epsilon_1$ becomes larger than 15, the errors in n and $\Delta\epsilon_1$ become unacceptably large. On the other hand, for large $e_0/\Delta\epsilon_1$ it seems quite easy to make a good guess for ϵ_0 from the creep curve, even by visual inspection. One might ask whether an improvement could be made with a two-parameter curve fit, where ϵ_0 is given with a small error. The answer can be seen immediately from

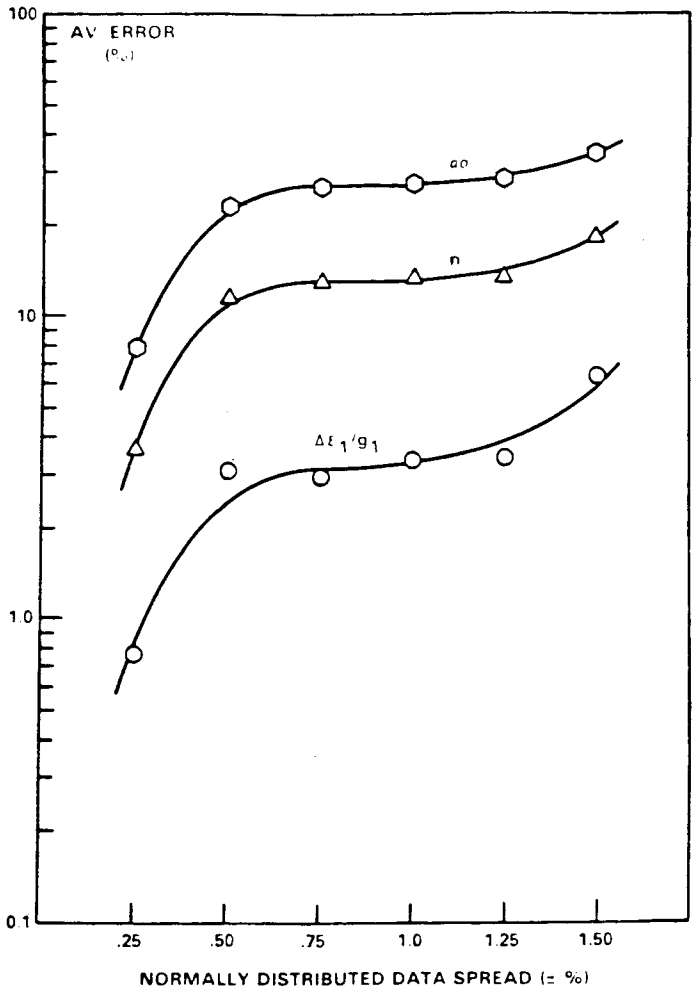

Fig. 10. Average errors in $\Delta\epsilon_1/g_1$, a_σ and n as a function of the width of the normally distributed data for the 3PR curve fit. Theoretical values: $\Delta\epsilon_1/g_1 = 8000$, $a_\sigma = 1$, $n = 0.4$, $N = 31$.

Table IV. Even very small errors in ϵ_0 lead to very large errors in $\Delta\epsilon_1$, and even larger errors in n. The 2PCO method is not recommended under any circumstances.

Results with the 2PC1 Curve Fitting Method

In cases where we have both a large ratio of $\epsilon_0/\Delta\epsilon_1$ and a small exponent $n < 0.2$, we will expect a large error in $\Delta\epsilon_1$ and n if we use the 3PC method. However, for large $\epsilon_0/\Delta\epsilon_1$ it becomes rather easy to estimate $\Delta\epsilon_1$ (the transient creep strain after 1 h). Figure 13 (Table V, Runs 66–70) shows a particularly unpleasant case where $\epsilon_0/\Delta\epsilon_1 = 32$ and $n = 0.15$. Under such circumstances one may find the 2PC1 method superior to the 3PC method. Comparing runs 66 and 71, one finds no great change in error with changing

TABLE III
Results of Test Runs Using the 2PRn Curve Fitting Method

Test no.	Theoretical value			Spread (±%)	Initial input			Average error (%) standard deviation				Set error for n
	A	a_0	n		A_0	a_0	n_0	A	SD	a_σ	SD	
49	8000	1.0	0.1	0.5	9000	1.0	0.1	0.40	0.27	0.92	0.63	0
50	8000	1.0	0.2	0.5	9000	1.0	0.2	0.31	0.23	0.94	0.62	0
51	8000	1.0	0.3	0.5	9000	1.0	0.3	0.18	0.15	0.48	0.33	0
52	8000	1.0	0.4	0.5	9000	1.0	0.4	0.13	0.12	0.59	0.43	0
53	8000	1.0	0.5	0.5	9000	1.0	0.5	0.25	0.16	0.90	0.80	0
54	8000	1.0	0.4	0.5	9000	1.0	0.408	0.61	0.30	3.57	1.04	2.0
55	8000	1.0	0.4	0.5	9000	1.0	0.438	1.65	0.26	18.44	1.02	8.0
56	8000	1.0	0.4	0.5	9000	1.0	0.464	2.80	0.23	42.04	0.98	16.0
57	8000	1.0	0.4	0.5	9000	1.0	0.496	3.66	0.34	70.97	2.14	24.0

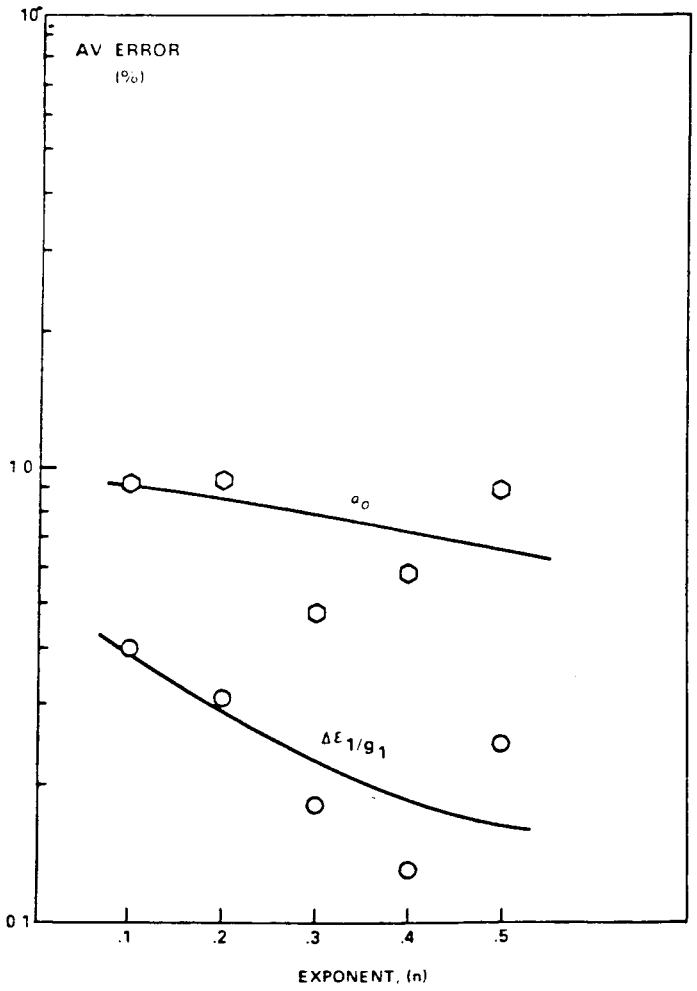

Fig. 11. Average errors in $\Delta\epsilon_1/g_1$ and a_σ as a function of n for the 2 PRn curve fit. Theoretical values: $\Delta\epsilon_1/g_1 = 8000$, $a_\sigma = 1$, $N = 31$; data spread: $\pm 0.5\%$.

n. For a preset error in $\Delta\epsilon_1$ of 10% (which may be quite reasonable), and for a ratio of $\epsilon_0/\Delta\epsilon_1 = 32$, Figure 14 and Table V (runs 69, and 72 through 74) show the change in error as a function of n. Again, for small n the 2PC1 method is preferrable.

From Figure 15 and Table V (runs 75–84), one can see that the error of n obtained from the 2PC1 method is quite insensitive to the ratio of $\epsilon_1/\Delta\epsilon_1$, and the error of ϵ_0 becomes very small as this ratio increases.

Results with the 2PCn Curve Fitting Method

This method is applicable for determining ϵ_0 and $\Delta\epsilon_1$ if n is known already from previous experiments with sufficient accuracy. It might be especially useful for angle ply composites where the ratio $\epsilon_0/\Delta\epsilon_1$ is usually large and where the resin exponent has been determined on the neat resin. (As was

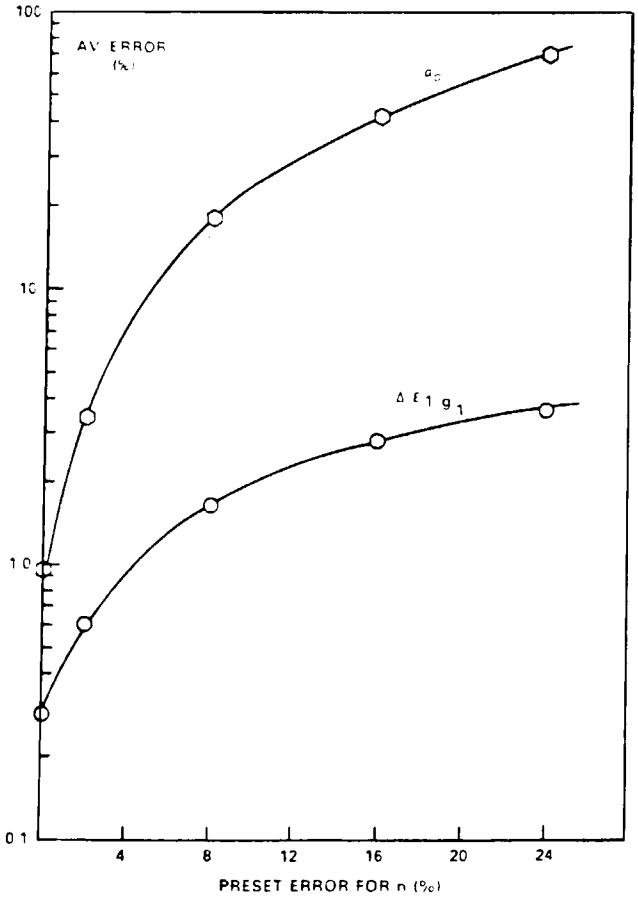

Fig. 12. Average errors in $\Delta\epsilon_1/g_1$ and a_σ as a function of the preset error in n for the 2PRn curve fit. Theoretical values: $\Delta\epsilon_1/g_1 = 8000$, $a_\sigma = 1$, $n = 0.4$, $N = 31$; data spread: $\pm 0.5\%$.

mentioned before, micromechanical arguments predict the same exponent for angle ply composites as for the neat resin.)

From Table VI one can see that the errors in ϵ_0 and $\Delta\epsilon_1$ remain low, even for a small exponent and for high $\epsilon_0/\Delta\epsilon_1$ ratios. Even if the n used has an error of 10%, the increase in the error of ϵ_0 and $\Delta\epsilon_1$ is not dramatic (compare run 93 with 97 and run 95 with 96). Comparing run 12 of Table I with run 96, one can see that the 2PCn method becomes rapidly more attractive where the ratio of $\epsilon_0/\Delta\epsilon_1$ becomes large and where n becomes small.

General Appearance of Computer Graphics for the Curve Fitting Procedures

It was observed that even when there were considerable errors in the parameters extracted from these curve-fitting procedures, the resulting curves seemed to fit very nicely through the "experimental points," and, also, they were generally difficult to resolve from the theoretical test curves. This could mean that, under certain circumstances, the physical meaning of a change in parameter becomes less significant and is washed out, or,

TABLE IV
Results of Test Runs Using the 2PCO Curve Fitting Method

Test no.	Theoretical value			Spread (±%)	Initial input			Average error (%) standard deviation				Set error for ϵ_0
	ϵ_0	$\Delta\epsilon_1$	n		ϵ_0	$\Delta\epsilon_1$	n_0	$\Delta\epsilon_1$	SD	n	SD	
58	8000	250	0.4	0.5	8010	240	0.5	9.16	5.69	11.47	6.78	0.125
59	8000	250	0.15	0.5	8010	240	0.5	6.28	4.75	19.78	16.74	0.125
60	8000	250	0.15	0.5	8010	500	0.5	6.07	3.82	15.97	9.13	0.125
61	8000	250	0.2	0.5	8010	240	0.5	3.68	3.82	23.87	13.94	0.125
62	8000	250	0.3	0.5	8010	240	0.5	3.99	4.95	21.06	12.23	0.125
63	8000	250	0.15	0.5	8100	500	0.5	39.70	4.73	99.38	59.59	1.25
64	8000	250	0.3	0.5	8080	240	0.5	29.85	4.88	84.46	35.25	2.0
65	8000	250	0.3	0.5	8160	240	0.5	57.68	4.47	561.91	190.40	4.0

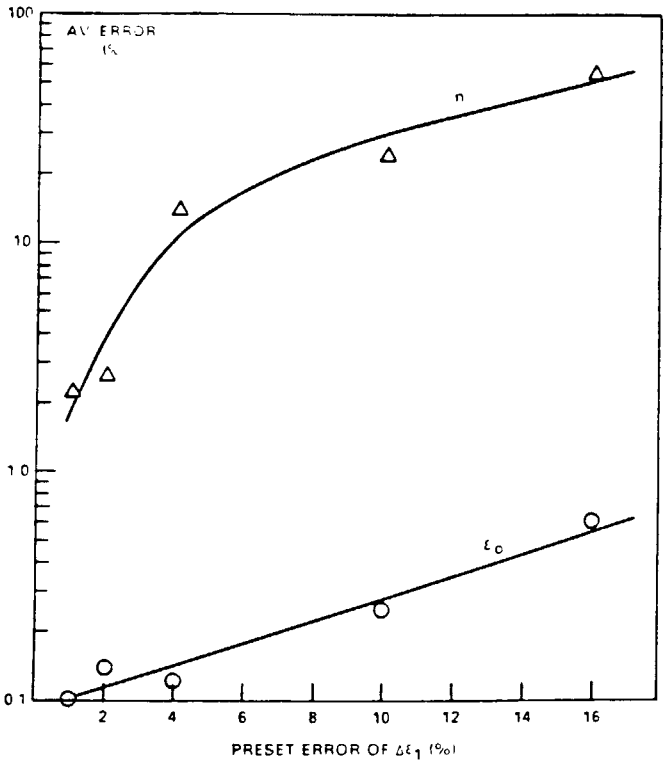

Fig. 13. Average errors in ϵ_0 and n as a function of the preset error in $\Delta\epsilon_1$ for the 2PC1 curve fit. Theoretical values: $\epsilon_0/\Delta\epsilon_1 = 32$, $n = 0.15$, $N = 31$; data spread: $\pm 0.5\%$.

that the method itself, which uses only a limited number of points, cannot resolve the underlying physics. Sometimes improved experiments may help to resolve the physics better, such as very rapid loading conditions to obtain reliable data at less than 1 s, or more accurate strain measurements with less noise. Sometimes additional knowledge about the material may resolve the question of whether the material parameters should be better represented by a curve such as 1 in Figure 1, or by parameters as indicated in Figure 2. In spite of the fact that these curves look almost identical for times larger than a few seconds after load application, the physics is actually quite different.

CONCLUSIONS

1. The 3PC curve fitting method is recommended for analyzing creep strains for polymeric materials or composites where $0.05 < \epsilon_0/\Delta\epsilon_1 < 15$ and where the creep exponent $n > 0.22$. The average errors in the determined parameters may be reduced to one-half if the number of experimental points is increased threefold. (With a strain data bandwidth of 1%, the errors in ϵ_0, $\Delta\epsilon_1$, and n are then within 6, 10, and 15%, respectively.)

2. The 3PR curve fitting method is superior for determining the exponent

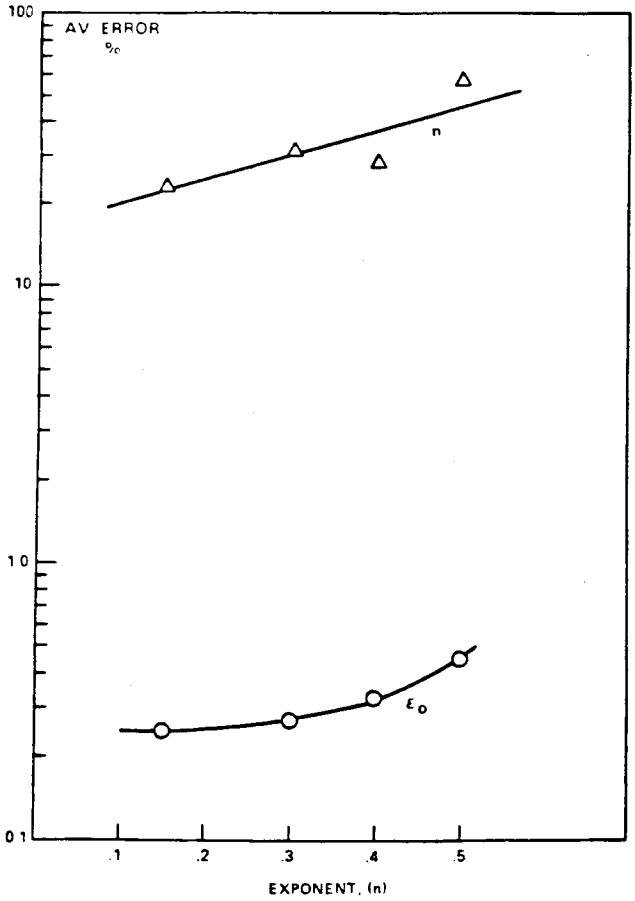

Fig. 14. Average errors in ϵ_0 and n as a function of n for the 2PC1 curve fit. Theoretical values: $\epsilon_0/\Delta\epsilon_1 = 32$, preset error for $\Delta\epsilon_1 = 10\%$, $N = 31$; data spread: $\pm 0.5\%$.

n only if $n < 0.22$. The results of the 3PR iteration procedure are quite sensitive to the initial trial input value for n. The iteration may even diverge if $n_0 = n \pm 0.1$ (an error recovery and a fine tuning algorithm must be incorporated). The iteration of the 3PR method may also diverge when the trial input value of a_σ deviates more than a factor of 10 from the true value. The magnitude of a_σ also affects the mean errors of all parameters. As a_σ goes from 10 to 0.01 (for $n = 0.3$), the mean errors of $\Delta\epsilon_1/g_1$ and n remain less than 10% while the error of a_σ increases from 4 to more than 30%; however, at such low values of a_σ this error is of minor significance. That the mean errors for all parameters increase with any of the curve fitting methods when the data bandwidth increases is obvious.

3. The 2PRn curve-fitting method is superior to the 3PR curve-fitting method when $n > 0.22$ and $\epsilon_0/\Delta\epsilon_1 < 10$ because n can then be obtained more accurately from the 3PC procedure and put into the 2PRn method as a known constant.

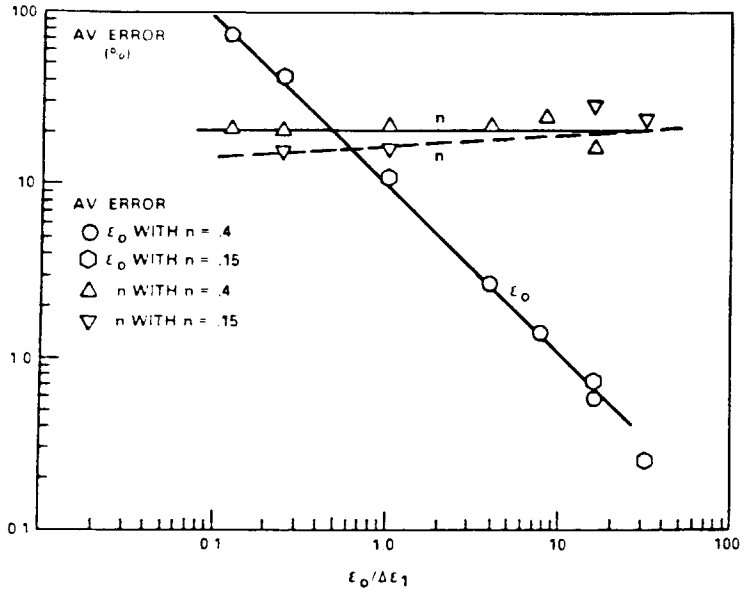

Fig. 15. Average Errors of ϵ_0 and n as a function of the ratio $\epsilon_0/\Delta\epsilon_1$ for the 2PC1 curve fit. Theoretical values: for both $n = 0.4$ and 0.15, $N = 31$, preset error for $\Delta\epsilon_1 = 10\%$; data spread: $\pm 0.5\%$.

4. The 2PCO method is inferior under any circumstances and should not be used.

5. The 2PC1 method is superior to the 3PC method when $n < 0.2$ and when $\Delta\epsilon_1$ can be obtained with an error less than 10% (then n can be obtained more accurately from the 3PR method).

6. The 2PCn method is superior if n is sufficiently well known from previous experiments since the resulting errors in ϵ_0 and $\Delta\epsilon_1$ remain low. The method is especially suitable for low n and high ratios of $\epsilon_0/\Delta\epsilon_1$, and for composites where the resin exponent has been determined independently.

7. Neither of these curve-fitting methods should be used without careful consideration of their shortcomings. Large errors will result if $\epsilon_0/\Delta\epsilon_1$ is large or if n is small. The question of what constitutes an acceptable error must obviously be left to the engineering or scientific requirements. Improvements in the analysis may be possible, for instance, by changing the experimental conditions such as carrying out the experiment at different temperatures, getting data at shorter times (which requires high loading rates), reducing the noise level of the measurements to obtain a smaller data bandwidth, including a larger number of points, etc., and, under certain conditions, using a combination of curve fitting procedures may be advantageous. Even if the automation of the data analyses should not be carried out mindlessly, we believe that this numerical approach to the nonlinear viscoelastic parameter analysis will increase the reliability of the data analyses and materials characterization in this field.

TABLE V
Results of Test Runs Using the 2PCl Curve Fitting Method

Test	Theoretical value			Spread	Initial input			Average error (%) standard deviation				Set error	
	ϵ_0	$\Delta\epsilon_1$	n	(±%)	ϵ_0	$\Delta\epsilon_1$	n_0	ϵ_0	SD	n	SD	for $\Delta\epsilon_1$	$\epsilon_0/\Delta\epsilon_1$
66	8000	250	0.15	0.5	9000	247.5	0.5	0.10	0.03	22.50	11.31	1.0	32
67	8000	250	0.15	0.5	9000	245	0.5	0.14	0.10	26.17	20.11	2.0	32
68	8000	250	0.15	0.5	9000	240	0.5	0.12	0.08	14.06	12.02	4.0	32
69	8000	250	0.15	0.5	9000	225	0.5	0.25	0.12	23.47	13.64	10.0	32
70	8000	250	0.15	0.5	9000	210	0.5	0.60	0.16	56.00	28.85	16.0	32
71	8000	250	0.4	0.5	9000	247.5	0.5	0.19	0.14	25.06	19.75	1.0	32
72	8000	250	0.3	0.5	9000	225	0.5	0.27	0.16	31.50	22.39	10	32
73	8000	250	0.4	0.5	9000	225	0.5	0.33	0.20	28.44	15.80	10	32
74	8000	250	0.5	0.5	9000	225	0.5	0.45	0.22	57.56	40.10	10	32
75	1000	8000	0.4	0.5	1200	7200	0.5	82.97	1.64	20.49	0.85	10	1/8
76	2000	8000	0.4	0.5	2500	7200	0.5	41.34	0.69	20.45	0.53	10	1/4
77	2000	8000	0.15	0.5	2500	7200	0.5	40.73	0.59	15.18	4.40	10	1/4
78	8000	8000	0.4	0.5	9000	7200	0.5	10.54	0.32	21.47	1.20	10	1
79	8000	8000	0.15	0.5	9000	7200	0.5	10.32	0.33	15.85	2.37	10	1
80	8000	8000	0.15	0.5	8000	7200	0.5	10.16	0.21	14.80	1.86	10	1
81	8000	2000	0.4	0.5	9000	1800	0.5	2.64	0.18	21.31	3.95	10	4
82	8000	1000	0.4	0.5	9000	900	0.5	1.40	0.20	24.26	7.73	10	8
83	8000	500	0.4	0.5	9000	450	0.5	0.58	0.16	15.90	11.35	10	16
84	8000	500	0.15	0.5	9000	450	0.5	0.74	0.17	28.75	14.40	10	16

TABLE VI
Results of Test Runs Using the 2PCn Curve Fitting Method

Test no.	Theoretical values			Spread (±%)	Input	Average error (%) standard deviation				% Set error for n	
	ϵ_0	$\Delta\epsilon_1$	n		n	ϵ_0	SD	$\Delta\epsilon_1$	SD		$\epsilon_0/\Delta\epsilon_1$
85	500	8000	0.2	0.5	0.2	5.72	3.70	0.45	0.35	0	1/16
86	1000	8000	0.2	0.5	0.2	1.52	0.99	0.28	0.19	0	1/8
87	2000	8000	0.2	0.5	0.2	1.21	0.54	0.40	0.26	0	1/4
88	8000	8000	0.2	0.5	0.2	0.53	0.51	0.78	0.67	0	1
89	8000	4000	0.2	0.5	0.2	0.32	0.20	0.89	0.71	0	2
90	8000	2000	0.2	0.5	0.2	0.62	0.51	2.88	2.51	0	4
91	8000	1000	0.2	0.5	0.2	0.37	0.18	3.62	1.86	0	8
92	8000	500	0.2	0.5	0.2	0.45	0.34	8.00	7.01	0	16
93	8000	250	0.2	0.5	0.2	0.26	0.22	10.42	9.61	0	32
94	8000	100	0.2	0.5	0.2	0.40	0.27	48.39	26.15	0	80
95	8000	250	0.5	0.5	0.5	0.12	0.11	8.24	4.39	0	32
96	8000	250	0.5	0.5	0.45	0.21	0.18	11.54	7.11	10	32
97	8000	250	0.2	0.5	0.22	0.38	0.33	14.11	15.03	10	32

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Received January 9, 1984
Accepted February 1, 1985