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Nonlinear Viscoelastic Behavior of Plasticized Poly(vinyl Chloride)

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Synopsis

This paper shows how an empirical nonlinear creep relation suggested by Leaderman might be justified on the basis of an approximate nonlinear viscoelastic constitutive equation. In addition, experimental evidence is presented which tends to support the proposed theory.

INTRODUCTION

In 1962 Leaderman[1] presented an approximate constitutive equation which he suggested could be used to linearize the creep and recovery behavior of plasticized poly(vinyl chloride) under moderately large uniaxial strain conditions. He stated in that paper that the equation was considered to be quasiempirical, but its form was suggested by the equilibrium behavior of rubber-like solids in simple tension. Leaderman, McCracklin, and Nakada[2] later interpreted Leaderman's experimental results in terms of the multiintegral expansion of Green and Rivlin[3] and showed that under proper conditions, Leaderman's empirical relation could be found from continuum concepts.

The purpose of the present study was to show an alternate derivation of one form of Leaderman's equation based on Lianis'[4] approximation to the theory of finite linear viscoelasticity originally proposed by Coleman and Noll.[5] It is shown that inversion of the Leaderman equation leads to an equation similar to the Lianis equation for uniaxial relaxation assuming that certain material response is present.

THEORY

The empirical creep relation proposed by Leaderman is given by

$$\mathrm{p(t)} = \int_{-\infty}^{t} \psi(\mathrm{t} - \tau)\, \frac{\mathrm{d}\sigma}{\mathrm{d}\tau}\, \mathrm{d}\tau \tag{1}$$

where $p(t)$ is a deformation measure given in either of the equivalent forms

$$p(t) = \frac{(\lambda - 1/\lambda^2)\,(1 + k_1/\lambda)}{3(1 + k_1)} \tag{2a}$$

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or

$$p(t) = \frac{(\lambda^2 - 1/\lambda)(1 + k_2/\lambda)}{3(1 + k_2)} \tag{2b}$$

depending whether $\sigma(t)$ is taken as the nominal or true stress.

If k_1 is taken equal to zero, eq. (2a) was found by Leaderman to be an adequate measure of the creep and recovery of plasticized PVC for strains up to approximately 27%. If the true stress is used, then Leaderman found that eq. (2b) is applicable to plasticized PVC if k_2 is taken equal to 0.6. Since the constants k_1 and k_2 are selected to give the best possible fit to experimental creep data, one presumably could find other materials for which the Leaderman equation would be applicable.

We now seek to establish the validity of the Leaderman equation on the basis of the Lianis theory. It has been shown by Lianis that the nonlinear uniaxial viscoelastic behavior of many materials can be represented in the form

$$\begin{aligned}\sigma(t) = {} & [a + b(\lambda^2 + 2/\lambda - 3) + c/\lambda](\lambda^2 - 1/\lambda) + 2\int_{-\infty}^{t} \phi_0(t-\tau) \\ & \frac{d}{d\tau}[\lambda^2(\tau)/\lambda^2 - \lambda/\lambda(\tau)]^{\bullet} d\tau + 2\int_{-\infty}^{t} \phi_1(t-\tau)\frac{d}{d\tau}[\lambda^2(\tau) - 1/\lambda(\tau)]\,d\tau \\ & + 2\int_{-\infty}^{t} \phi_2(t-\tau)\frac{d}{d\tau}[\lambda^2\lambda^2(\tau) - 1/\lambda\lambda(\tau)]\,d\tau + (\lambda^2 - 1/\lambda) \\ & \int_{-\infty}^{t} \phi_3(t-\tau)\frac{d}{d\tau}[\lambda^2(\tau) + 2/\lambda(\tau)]d\tau \end{aligned} \tag{3}$$

where a, b, and c are constants defining the long-time (equilibrium) behavior and the $\phi_i(t)$ are time-dependent relaxation functions such that $\lim_{t\to\infty} \phi_i(t) \to 0$; $\lambda = \lambda(t)$ is the uniaxial extension ratio at the present time t.

If we consider a uniaxial relaxation test such that

$$\lambda(\tau) = 1 \qquad \tau < 0, \qquad \lambda(\tau) = \lambda \text{ (constant)} \qquad \tau > 0 \tag{4}$$

then it can be shown that eq. (3) reduces to

$$\begin{aligned}\frac{\sigma(t)}{\lambda^2 - 1/\lambda} = {} & [a + b + 2\phi_1(t) - 2\phi_3(t)] + [2b + c + 2\phi_0(t) + 2\phi_2(t) \\ & + 2\phi_3(t)]\frac{1}{\lambda} + [b + 2\phi_2(t) + \phi_3(t)][\lambda^2 - 1).\end{aligned} \tag{5}$$

Lianis has shown that eq. (5) is useful for viscoelastic materials which exhibit isochrones (curves at constant time) which are similar to the Mooney-Rivlin curves shown in Figure 1. Moreover, if we consider only the linear range, then eq. (5) reduces further to

$$\frac{\sigma(t)}{\lambda^2 - 1/\lambda} = [a + 2\phi_1(t) - 2\phi_2(t)] + [c + 2\phi_0(t) + \phi_3(t)]\frac{1}{\lambda} \tag{6a}$$

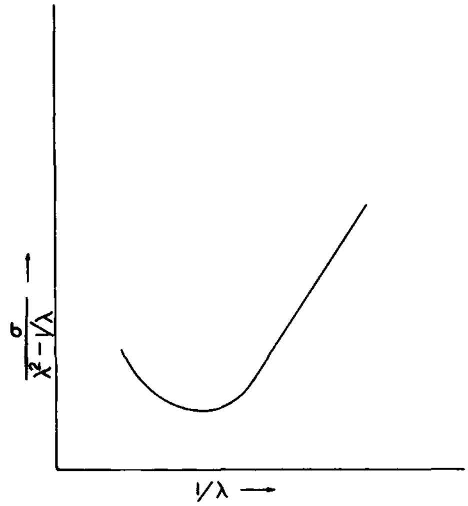

Fig. 1. Typical relaxation isochrone required for the Lianis approximation.

where it is required that

$$b = 2\phi_2(t) + \phi_3(t) = 0. \tag{6b}$$

Ordinarily, the constants a and b are determined from a long-time (equilibrium) uniaxial test. However, in the present study we assume that plasticized PVC demonstrates no long-time equilibrium so that $a = c = 0$. Further, we are not interested in evaluating the individual relaxation functions but simply group them in the form

$$\frac{\sigma(t)}{\lambda^2 - 1/\lambda} = \Phi_1(t) + \Phi_2(t)\,\frac{1}{\lambda} \tag{7}$$

where obviously we have taken

$$\Phi_1(t) = 2\phi_1(t) - 2\phi_2(t) \tag{8a}$$

$$\Phi_2(t) = 2\phi_0(t) + \phi_3(t). \tag{8b}$$

At this point we leave eq. (7) for the moment and reconsider the Leaderman equation in the form given by eq. (1). We can invert this equation by applying the well-known convolution theorem from LaPlace transforms. Performing the indicated inversion leads to

$$\sigma(t) = \int_0^t \phi^L(t - \tau)\,\frac{dp(\tau)}{d\tau}\,d\tau \tag{9}$$

where

$$\mathcal{L}\{\phi^L(t)\} = \phi^L(s) = \frac{1}{s^2\Psi(s)}. \tag{10}$$

If we use the Leaderman deformation measure given by eq. (2b) and apply a uniaxial relaxation deformation such that

$$\lambda(\tau) = 1 \qquad t < 0, \qquad \lambda(\tau) = \lambda(t) = \lambda \qquad t > 0 \tag{11}$$

eq. (9) can be integrated to obtain

$$\frac{\sigma(t)}{\lambda^2 - 1/\lambda} = \frac{\phi^L(t)}{3(1 + k_2)} + \frac{k_2\phi^L(t)}{3(1 + k_2)}\,\frac{1}{\lambda}. \tag{12}$$

A comparison of eqs. (7) and (12) leads us to conclude that the restricted Lianis theory and the inversion of the Leaderman creep equation will lead to the same uniaxial relaxation results if

$$\Phi_1(t) = \frac{\phi^L(t)}{3(1 + k_2)} \tag{13a}$$

$$\Phi_2(t) = \frac{k_2\,\phi^L(t)}{3(1 + k_2)}. \tag{13b}$$

In order for eqs. (13) to be valid, we can easily observe that $\Phi_1(t)$ and $\Phi_2(t)$ cannot be independent but must be related in the sense that

$$\Phi_2(t) = k_2\Phi_1(t) \text{ (all time)}. \tag{14}$$

Additionally, we observe that $\Phi_1(t)$ and $\Phi_2(t)$ represent the intercept and slope, respectively, of a straight-line isochrone on the Mooney-Rivlin plot of $[\sigma(t)/(\lambda^2 - 1/\lambda)]$ versus $1/\lambda$. Thus, eq. (14) requires that the ratio of slope to intercept remain constant and equal to k_2 for every isochrone.

With these rather restrictive conditions, we have thus shown that the Leaderman equation leads to results which can be obtained from a theory based on continuum concepts.

In the following sections, we discuss some creep and relaxation experiments conducted with a commercial plasticized poly(vinyl chloride) film which tend to give some credence to the development which has been presented.

EXPERIMENTAL PROCEDURE

The material used for the experimental phase of this study was commercial plasticized poly(vinyl chloride) purchased from Reed Plastics, Inc., in sheets 0.012 in. thick. The sample configuration was simply a strip 4 in. long with a rectangular cross section 0.50 in. wide and 0.12 in. thick.

The uniaxial creep and relaxation tests were conducted at 74°F in a CO_2 controlled environment. The strain input, in the case of relaxation, was provided by means of a hydraulic pump system with the strains being determined by measuring the change in a 1-in. gauge length with a traveling telescope. The loads were measured through a SR 4 load cell and recorded by a light trace-galvanometer recording system. The creep tests, which were of the constant nominal stress type, were run in the same environmental system, with the load being applied by a dead-weight system. The longer-time strains were measured with the traveling telescope, whereas the short-time strains were measured by photographic techniques.

EXPERIMENTAL RESULTS

Relaxation tests were first run to determine whether the conditions indicated by eq. (14) could be satisfied by the Reed Plastic's stock plasticized

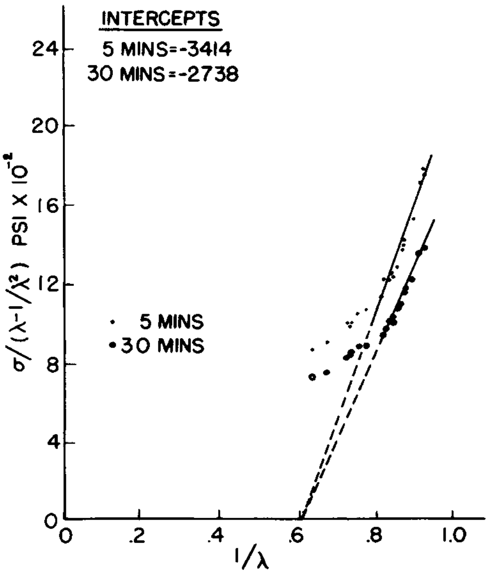

Fig. 2. Stress relaxation isochrones for commercial plasticized PVC.

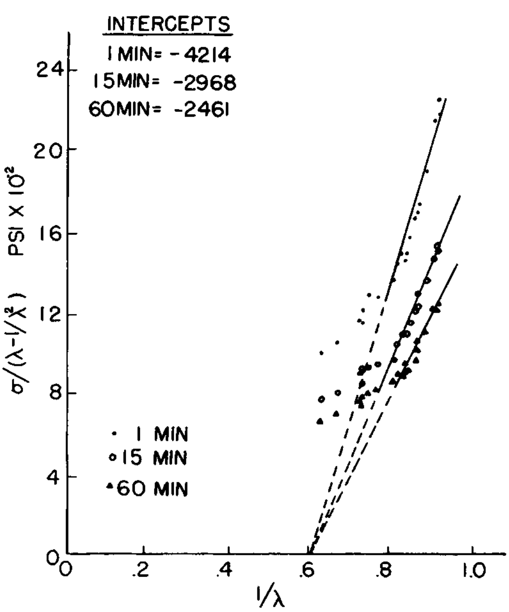

Fig. 3. Stress relaxation isochrones for commercial plasticized PVC.

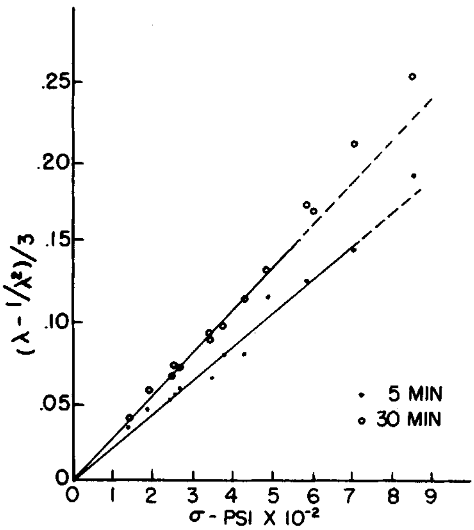

Fig. 4. Leaderman creep measure with $k_2 = 0$.

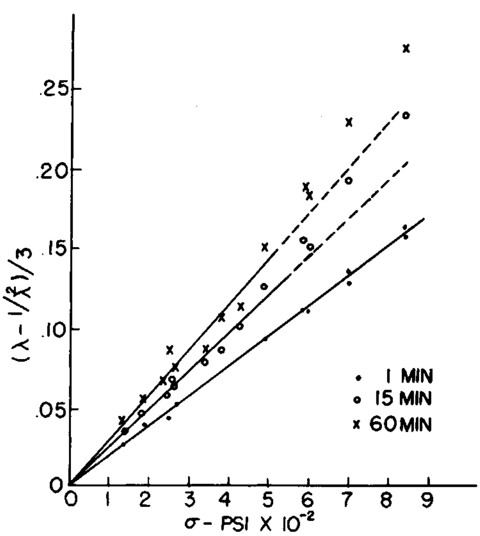

Fig. 5. Leaderman creep measure with $k_2 = 0$.

poly(vinyl chloride). These tests were run at extension ratios ranging from 1.09 to 1.59, and typical results are displayed in Figures 2 and 3 as a series of isochrones of $(\sigma/\lambda - 1/\lambda^2)$ versus $1/\lambda$. It can be seen from these figures that it is possible to identify a linear segment for $1/\lambda > 0.83$. Furthermore, the data for each isochrone can be fit reasonably well with straight lines which intersect the $1/\lambda$ axis at the single point. This means that the ratio of slope to intercept is constant for all isochrones, which satisfies the condition required by eq. (14). Thus, the relaxation tests would indicate that

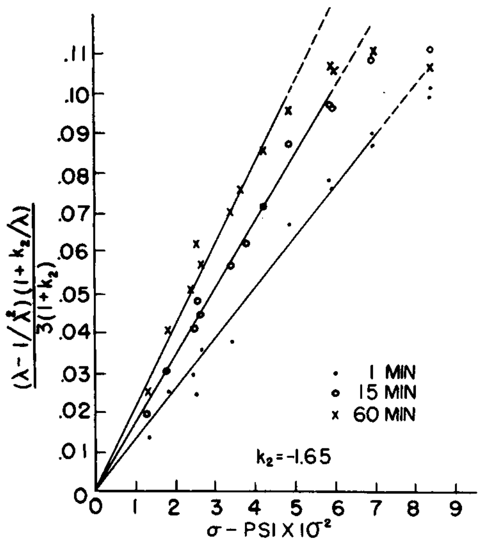

Fig. 6. Leaderman creep measure with $k_2 = -1.65$.

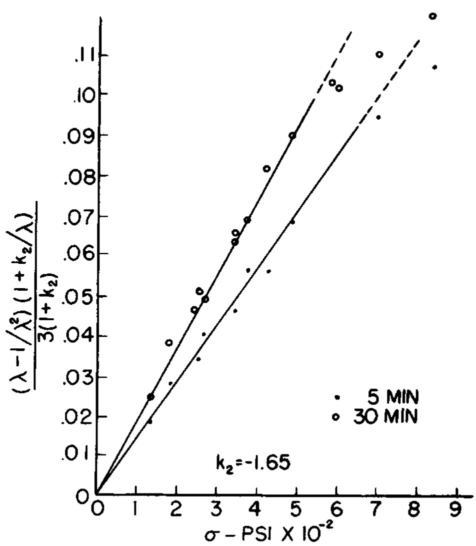

Fig. 7. Leaderman creep measure with $k_2 = -1.65$.

the Reed Plastic's stock plasticized PVC should obey the Leaderman creep relation for strains up to approximately 20%.

To further substantiate the applicability of the Leaderman theory, a series of nominal-stress creep tests were conducted for a range of loadings which resulted in strains from about 0.5% to 32%. The results of these tests are displayed in Figures 4 through 7 as a series of isochrones of the Leaderman creep measure

$$p(t) = \frac{(\lambda - 1/\lambda^2)\,(1 + k_2/\lambda)}{3(1 + k_2)} \tag{2a}$$

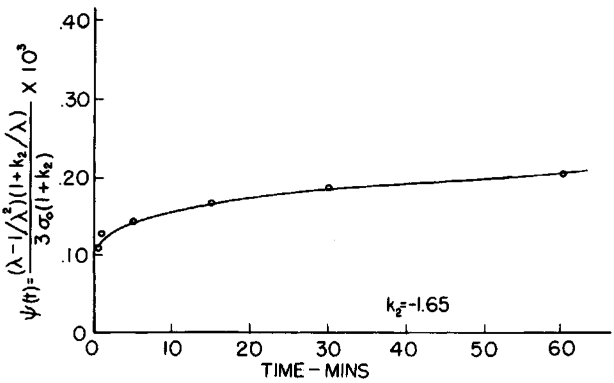

Fig. 8. Experimentally determined Leaderman creep function for commercial plasticized PVC.

plotted against nominal stress. In Figures 4 and 5 we have taken k_2 equal to zero, and it can be observed that the Leaderman measure linearizes the strain–stress isochrones up to an adjusted strain level of about 11%. (The strain data has been shifted to correct for a strain offset at zero load. This offset is believed to be due to experimental difficulty in obtaining accurate data in the very small strain range.) However, this choice for k_2 is not acceptable since it would lead to relaxation which would be meaningless. With this choice we can see from eq. (12) that the isochrones on a Mooney-Rivlin plot would degenerate to a single point. Moreover, there is really no choice possible for k_2 because, as we have already noted, the ratio of the slope to intercept of any isochrone on the Mooney-Rivlin plot must, in fact, be equal to k_2. Thus, k_2 can be uniquely determined from a series of uniaxial relaxation tests.

In the present study, the isochrones of Figures 2 and 3 lead to a value of k_2 equal to -1.65. Using this value for k_2 leads to the creep strain–stress isochrones shown in Figures 6 and 7. As can be observed from these graphs, our required value for k_2 does not lead to a larger linear range but simply causes the nonlinear range to change directions. If the choice for k_2 were free, it can be shown that the creep data could be linearized for strains up to 20%.

The Leaderman creep function $\psi(t)$ is now defined as the creep strain measure $p(t)$ divided by the nominal stress. The creep function can be found at each time by simply determining the slope of each isochrone from the strain–stress curves. These results are shown in Figure 8 for times up to 60 min.

To further substantiate our approach to the Leaderman theory, a comparison was made of the stress relaxation function found by inverting the Leaderman creep function with that found from the actual relaxation experiments. The method of inversion used was a numerical step-by-step procedure proposed by Hopkins and Hamming.[6] The measured Leader-

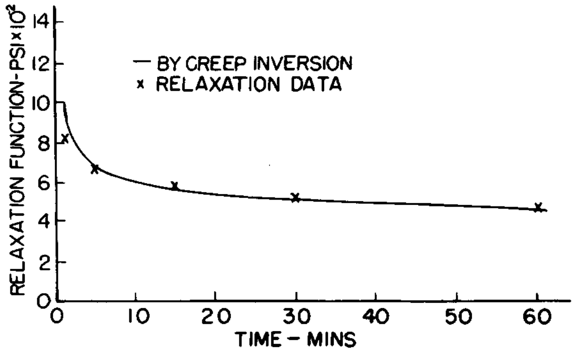

Fig. 9. Leaderman relaxation function for commercial plasticized PVC.

man relaxation function is found with the aid of eq. (12) and the experimental straight line isochrones of Figures 2 and 3. From eq. (12) we have

$$\frac{\sigma(t)}{\lambda^2 - 1/\lambda} = \frac{\phi^L(t)}{3(1+k_2)} + \frac{k_2\ \phi^L(t)}{3(1+k_2)}\frac{1}{\lambda} \tag{12}$$

so that the relaxation function for each time is determined from the intercept of the relaxation isochrone by taking

$$\underset{\text{measured}}{\phi^L(t)} = (\text{intercept})\ (3)\ (1 + k_2) \tag{15}$$

Figure 9 shows a comparison of the inverted Leaderman relaxation function and the measured function. It can be seen from this curve that remarkable agreement was found when one considers the various restrictions placed on the required material response. Of course, it should also be noted that some flexibility existed in the curve fitting of the data since no formal curve fitting procedure (such as least-squares error) was utilized. Thus, these curves were plotted with a knowledge of the desired results always in mind.

CONCLUSIONS

The experimental evidence in this study has indicated that it is possible to justify the empirical creep relation of Leaderman by utilizing the Lianis approximation to finite linear viscoelasticity. I should be noted, however, that this study was restricted to one-step uniaxial situations, and there is no guarantee that this approach would be applicable in more complex multistep experiments. We can merely comment that the empirical approach used by Leaderman leads to results which are also obtainable from a theory based on continuum concepts.

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