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Master Curves of Viscoelastic Behavior in the Plastic Region of a Solid Polymer

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Synopsis

Stress relaxation and creep tests following strain ramps were made on Mylar, both above and below the yield stress. The ramp velocity was varied over a 40-fold range. All data exhibit nonlinear viscoelastic behavior. However, those obtained above the yield point, i.e., in the plastic region, could be reduced to single master curves for both the creep and the relaxation tests by means of a simple time shift factor. This factor is inversely proportional to the strain rate existing just prior to the test.

INTRODUCTION

It is well known that most, if not all, polymeric materials are viscoelastic and that, at sufficiently low stresses, the viscoelastic behavior is linear. Linearity implies that the mechanical behavior of the material can be predicted once a few material functions, the viscoelastic functions, have been experimentally determined.

Unfortunately, the linearity breaks down above a certain stress level which, for most polymeric solids, is well below the yield or fracture stress.[1-4] Thus, the design of structurally efficient items where the fracture or yield stress is approached or the analysis of plastic forming techniques where the yield stress is exceeded require a knowledge of the nonlinear viscoelastic behavior of the material.

In the nonlinear region, molecular mobilities and relaxation spectra become dependent upon stress and strain.[5-8] None of the simple rules of linear viscoelasticity apply, including those which allow collecting viscoelastic data taken under different conditions into master curves. It is not excluded, however, that simple rules, albeit different from those of linear viscoelasticity, can be found in the nonlinear region which permit construction of master curves of general use. A contribution in this direction is hopefully given in this paper.

Stress relaxation and creep data taken on Mylar, both above and below the yield stress, will be presented and discussed. The possibility of obtaining master curves will be throughly examined.

EXPERIMENTAL

Constant-velocity stress–strain, constant-force creep, and stress relaxation tests were performed at room temperature (about 25°C) by an Instron tensile

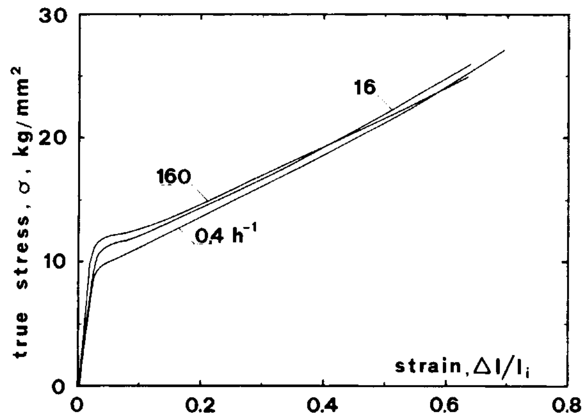

Fig. 1. True stress vs strain in constant velocity extensional tests at different values of initial deformation rate α_i.

testing machine. The material used was poly(ethylene terephthalate) in the form of 10-mil-thick biaxially oriented sheets (Mylar manufactured by du Pont).

The samples had a rectangular shape with a width of 1 cm and were cut all in the same direction from the sheet. The distance between the two Instron jaws at the beginning of each test was 6 cm. Because of the sample shape, a part of the material inside the jaws was effected by the deformation. However, a good reproducibility was found, probably because the jaws were pneumatically driven and the acting pressure was always the same. A large central portion of the test piece was photographically found to deform homogeneously throughout each test, and the deformation Δl_r of a reference zone 3 cm long resulted to a very good approximation proportional to the displacement Δl of the lower jaw. The ratio $\Delta l_r/\Delta l$ was found equal to 0.41. The lower jaw displacement Δl was then used to calculate deformations with respect to an initial equivalent length of the specimen $l_i = 7.3$ cm.

Comparison among tests made with samples of different widths showed that 1 cm was sufficient a width to neglect the hardening effect (due to the cutting of the sample) of the specimen edges.

RESULTS

The experimental results of load versus elongation were converted into true stress σ versus the strain $\Delta l/l_i$ and are reported in Figure 1. In order to convert the load into true stress, the assumption of constant density was made.

The stress–strain curves, reported in Figure 1, differ by the value of the initial deformation rate $\alpha_i = V/l_i$, where V is the velocity of the Instron crosshead. A change of α_i over a 400-fold range produces very small variations of the stress–strain curves. Also, the initial slope of the curves increases by 10% at most by increasing the velocity in the experimental range, approaching a value of about 500 kg/mm^2.

The creep data are reported in Figures 2 and 3. The samples were deformed with a constant velocity up to a fixed value of the force which was then held constant. The subsequent displacement Δl_c of the lower jaw was measured by

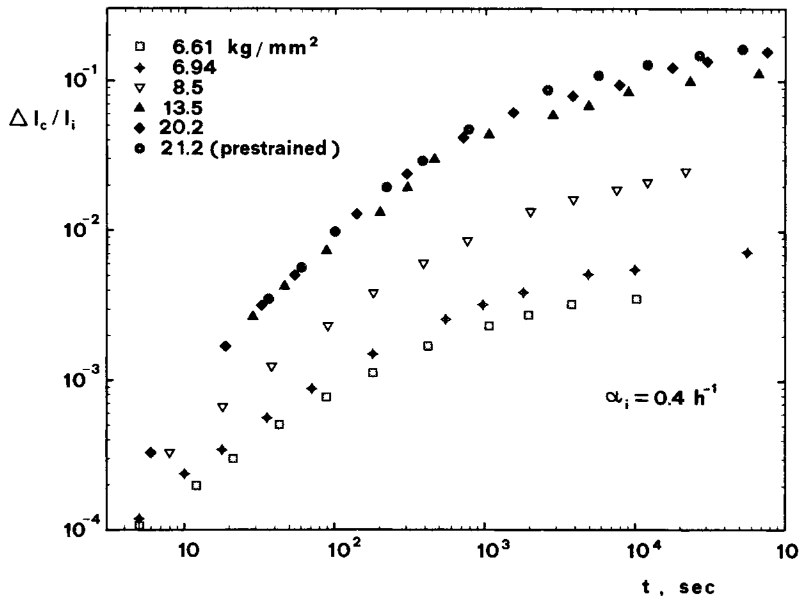

Fig. 2. Creep strain vs time for different values of initial creep stress σ_0. Initial creep stress is reached with constant velocity and initial deformation rate α_i = 0.4 h^{-1}.

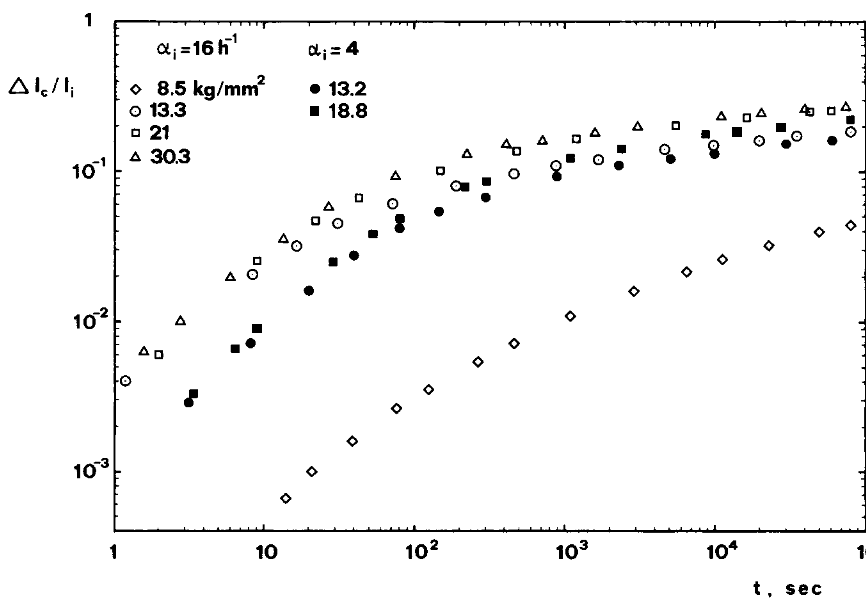

Fig. 3. Creep strain vs time for different values of initial creep stress σ_0 and of initial deformation rate α_i.

a transducer connected to the Instron crosshead. The data are plotted as $\Delta l_c/l_i$ versus time as measured since the force reached the fixed value. In Figure 2, the data refer to a value of α_i equal to 0.4 hr^{-1}. Larger values of α_i (4 and 16 hr^{-1}) are reported in Figure 3. It was not possible to further increase the deformation rate before the creep tests because at larger velocities the Instron cross head had

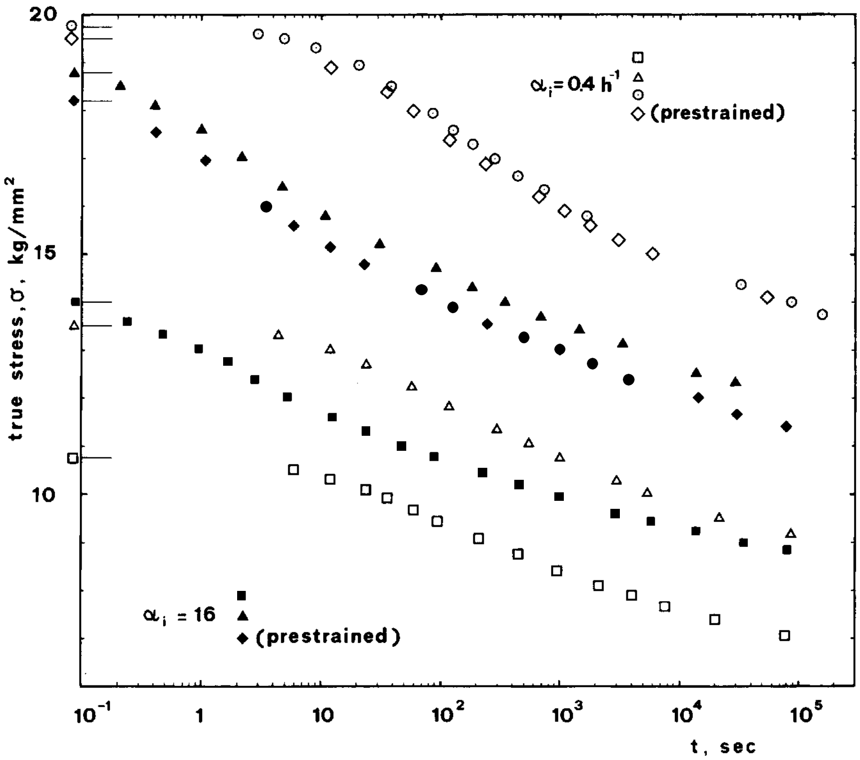

Fig. 4. True stress vs time in relaxation tests after strain ramps with different values of initial deformation rate α_i. The initial stress σ_0, always larger than the yield stress, is indicated by a short horizontal segment.

a small but significant reverse motion after the creep force had been reached. This effect was absent at lower deformation rates within the sensitivity of the transducer system with a recorder full scale equivalent to 1 mm displacement.

The parameter of Figure 2 is the tensile stress σ_0 at the end of the strain ramps which, of course, also represents the initial creep stress. The data of Figure 2 show that, while σ_0 has a large effect on the creep deformation when it is smaller than the yield stress, the creep behavior becomes essentially independent from the stress level provided σ_0 is larger than the yield stress. The latter feature is confirmed by data reported in Figure 3 for other values of α_i. Figures 2 and 3 show also that, when σ_0 exceeds the yield stress, larger values of α_i give rise to faster creep deformations, and at any given time the creep deformation is about directly proportional to the initial deformation rate α_i.

Also the stress relaxation tests were made after constant velocity strain ramps and starting from stresses both larger and smaller than the yield stress. The initial strain rates of the ramps were the same (0.4, 4, and 16 hr^{-1}) as for the creep tests; larger values were avoided for the same reasons. Figures 4 and 5 show that the amount of stress relaxation is large, especially when the initial stress σ_0 is larger than the yield stress. Also, similarly to the behavior observed for the creep tests, at larger values of α_i the stress relaxation occurs more rapidly. This behavior is found consistently for all values of σ_0 provided the yield stress has been

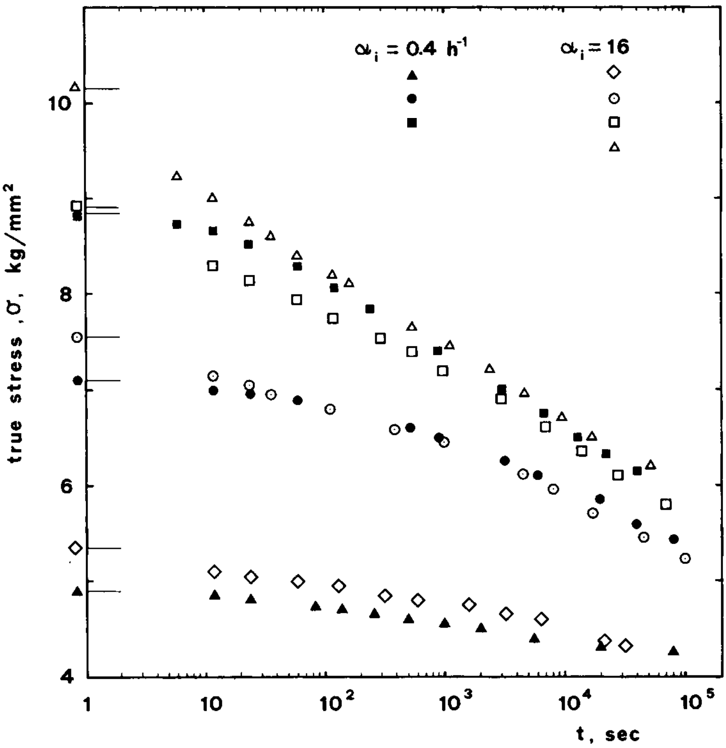

Fig. 5. True stress vs time in relaxation tests after strain ramps with different values of initial deformation rate α_i. For all curves, the initial stress σ_0 is smaller than the yield stress.

exceeded. Below the yield stress (see Fig. 5), the effect of α_i is much less pronounced and tends to disappear by decreasing the value of the initial stress, σ_0.

In Figures 2 and 4 are reported also some data relative to creep and stress relaxation tests made on prestrained samples. These samples were subjected to strain ramps (with the initial deformation rate α_i indicated in the figures) up to a strain $\Delta l/l_i = 0.2$. The motion of the Instron crosshead was then reversed and, after the stress was completely released, the samples were let to recovery for a period of time t_r. The recovery time t_r was varied with the initial deformation rate according to the following rule:

$$t_r \cdot \alpha_i = 4$$

About 35% of the deformation imposed was recovered by the material in all cases. After the recovery, the samples were again elongated with the same cross-head velocity of the previous strain ramp; and, after yielding, when the stress–strain curves of prestrained samples approached that of a virgin sample,[10] stress relaxation and creep tests were performed in the usual manner.

Both the stress relaxation and creep data of these tests are very close to those relative to "normal" tests for equal values of α_i and σ_0. It can thus be stated that the viscoelastic behavior of the material in the plastic region does not seem to depend on the previous deformation history but only on instantaneous values of deformation rate and, to the extent previously shown, of stress level.

Let us further extend this analysis. As the creep deformation at short times is inversely proportional to the "apparent viscosity" of the material defined as the ratio of the stress and the deformation rate, the data of Figures 2 and 3 suggest that (i) the "apparent viscosity" decreases steeply with stress up to the yield stress and has much smaller variations afterward; (ii) the "apparent viscosity" at stresses larger than the yield stress depend upon α_i and to a good approximation seems inversely proportional to it. These preliminary observations are also in good agreement with the stress relaxation data of Figures 4 and 5 provided the "relaxation time" is taken to be proportional to the "viscosity."

Because the amount of stress relaxation after the yield point, and thus the fraction of stress related to viscous elements during elongation, is very large, the fact that the stress–strain curves of Figure 1 show a substantial independence upon the velocity over a 400-fold range confirms that the "apparent viscosity" of the material is nearly inversely proportional to the deformation rate.

We shall now make use of the above observations in a more quantitative form in order to construct master curves of the viscoelastic behavior in the plastic region. We shall assume that relaxation times and viscosity change in a proportional way. We also need to choose in a more precise way the measures of the deformation and of the deformation rate.

SUPERPOSITION RULE IN THE PLASTIC REGION

The classical superposition principle brings creep or stress relaxation data obtained in different situations into unique curves by means of time shift factors. This powerful tool is generally used to account for changes in temperature, and the time shift factor is the inverse of some relaxation time, τ, obviously a function of temperature.

Let us assume that the "viscosity" and the "relaxation time" of the material in the plastic region of an elongational test are proportional to the inverse of the instantaneous deformation rate α. Let us indicate by α_0 the value of α just prior to the start of the viscoelastic tests, either creep or relaxation. The use of a reduced time $\bar{t} = t\alpha_0$ should then gather the stress relaxation and creep data into single curves, at least in the initial time range.

For the creep data, it seems reasonable to assume a measure of the deformation based on the sample length at the begining of the creep itself, l_0, rather than on the "initial" length l_i. Figure 6 reports all creep data (above the yield point) as $\epsilon \equiv \Delta l_c/l_0$ versus $\bar{t}$. It may be observed that a single master curve fits all the data, not only initially, but over the whole time range. It is worth noting that the master curve is obtained in terms of deformation ϵ and not of compliance, unlike the linear viscoelasticity case. However, one might argue that, if the viscous part of the stress could be sorted out, insofar as this stress might well be approximately constant, a compliance based on it would be proportional to the deformation.

Figure 7 reports all relaxation data (above the yield point) as σ/σ_0 versus $\bar{t}$. The fit into a single curve seems slightly less successful because, although curves corresponding to different α_0 values superimpose, some distance is observed between curves differing in the value of σ_0. This is related to the fact that the amount of stress relaxed increases more slowly than the initial stress σ_0. In order to have a good superposition on the complete $\bar{t}$ axis, one should probably refer only to that part of the stress which can relax and thus use the ratio $(\sigma - \sigma_\infty)/(\sigma_0$

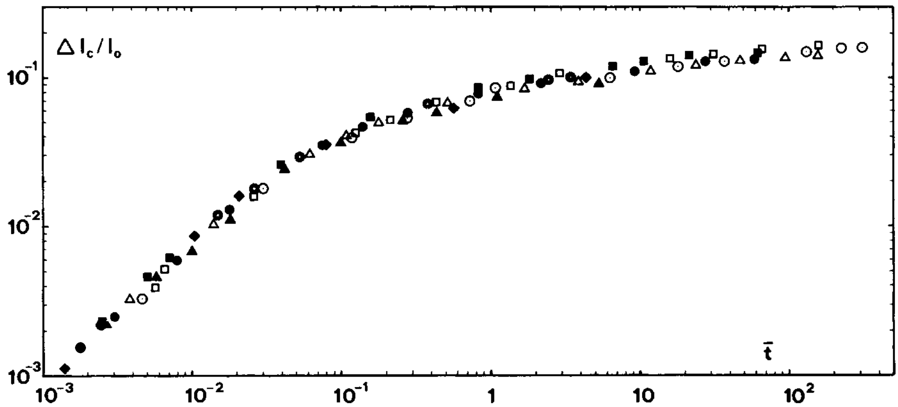

Fig. 6. Master curve for creep tests in plastic region. Modified creep strain $\epsilon = \Delta l_c/l_0$ vs reduced dimensionless time $\bar{t} = t\alpha_0$. Key to symbols same as for Figures 2 and 3.

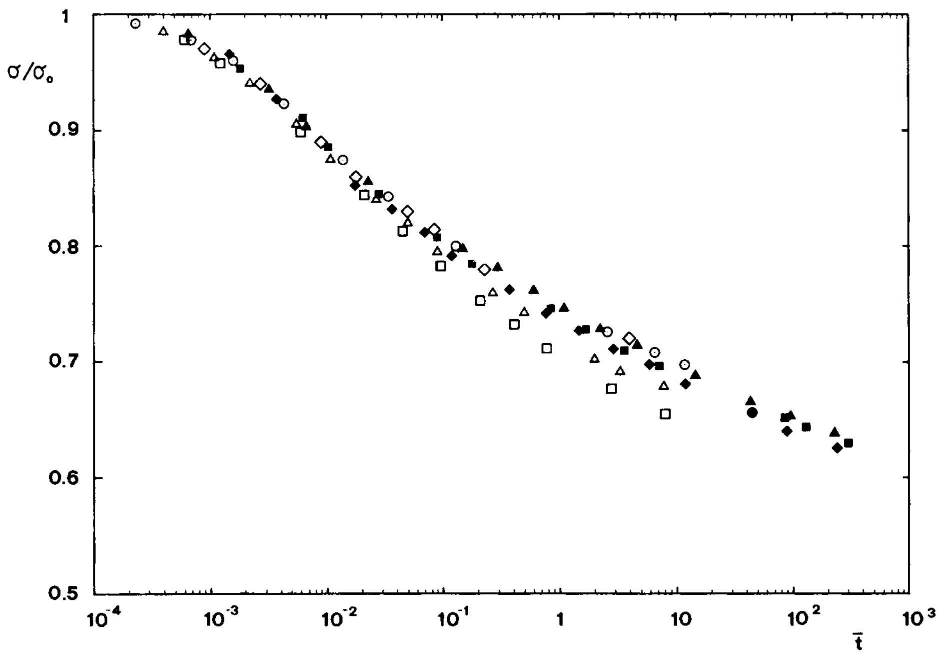

Fig. 7. Master curve for relaxation tests in plastic region. Normalized stress σ/σ_0 vs reduced dimensionless time $\bar{t} = t\alpha_0$. Key same as in Figure 4.

$- \sigma_\infty$), where σ_∞ is the asymptotic value of each stress-relaxation curve. The value of σ_∞cannot be experimentally determined because of the extremely long times involved. However, if one tentatively assumes that at $\bar{t} = 10$ the material has released 90% of the relaxable stress, σ_∞ can be determined, and the superposition becomes excellent.

CONCLUDING REMARKS

The simple superposition rules which seem to apply in the plastic region are hopefully not restricted to the case of Mylar which was here examined. Some indications of a wider applicability can already be found. In reference 9, the stress relaxation behavior of Lexan (a polycarbonate manufactured by General Electric) was determined, and an inverse dependence of the "relaxation time" upon deformation rate was observed.

It does not seem possible to find simple rules for the intermediate region which goes from the very low stresses, where linear viscoelasticity holds, to the stresses above the yield, where the rules proposed here seem to apply.

In fact, for the case of a creep experiment, following a strain ramp, one can write

$$\epsilon = f(t,\alpha_0,\sigma_0,G,\tau,\ \text{dimensionless parameters}) \tag{1}$$

where G,τ, and a suitable set of dimensionless parameters identify the material and α_0 and σ_0 uniquely determine the previous deformation history. G and τ are a characteristic modulus and time, respectively, while the dimensionless parameters can be related to the "shape" of the relaxation spectrum. For a given material, the shape of the spectrum is either fixed or a function of the history. Thus, for a given material, one has

$$\epsilon = f\left(\frac{t}{\tau},\ \tau\alpha_0,\ \frac{\sigma_0}{G}\right) \tag{2}$$

or, equivalently,

$$\epsilon = f(t\alpha_0,\tau\alpha_0,\sigma_0/G) \tag{2'}$$

Linear viscoelasticity represents a special case of eq. (2) in the form

$$\epsilon = \frac{\sigma_0}{G} f\left(\frac{t}{\tau}\right) \tag{3}$$

while "plastic" viscoelasticity is represented by a special case of eq. (2′):

$$\epsilon = f(t\alpha_0) \tag{4}$$

The creep data below the yield stress reported in Figure 2, which refers to only one value of the initial deformation rate, cannot be superimposed on each other by means of time shift factors changed arbitrarily with stress. This is true also if the same data are plotted in terms of compliance. It can then be argued that in eq. (2), apart from t/τ, also σ_0/G plays an independent role and more complex than in eq. (3).

As there is certainly an influence of α_0 on the creep behavior (see also Fig. 3), one has to conclude that in the transition region between linear and plastic viscoelasticity, i.e., for most data below the yield stress, all dimensionless groups of eq. (2) seem to play a significant role.

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