Studies of Relaxation Phenomena in Polymers.   I. The Use of Periodic Square and Triangular Stress Functions

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Synopsis

In order to evolve the methods of mechanical spectroscopy and find new methods of studying the rise of nonlinear viscoelasticity, periodic square and triangular stress functions have been used. A "new" viscoelastic function is defined, $\log J_2 = g\{\log J_1\}$, where J_1 and J_2 are the compliances at the time $(\zeta/2 + 2n\zeta)_{n\to\infty}$ for an odd, periodic, square function and an even, periodic, triangular function, respectively, with periods of 2ζ. The function shows characteristic shapes for viscoelastic spring and dashpot models. The interrelations between the complex compliance and J_1 and J_2 are developed; and since the sum of J_1 and J_2 at the time $\zeta/2$ agrees very well with the creep compliance at the same time, J_1 and J_2 can be used as an interrelation between complex compliance and creep compliance. Special equipment for measuring the compliances J_1 nd J_2 is described.

INTRODUCTION

When studying viscoelastic transition phenomena in polymers, "mechanical spectroscopy," i.e., the analysis of periodic or transient viscoelastic functions, is often used.

Usually, viscoelastic functions such as complex modulus, relaxation, or retardation spectra, etc. are studied, which by their definition are limited to linear viscoelastic behavior. The traditional mechanical spectroscopy is therefore limited to small stress–strains for which the behavior can be assumed to agree with Boltzmann's superposition principle.[1] Phenomenological and physical theories have been reviewed extensively for the linear viscoelastic behavior by Meares[2], Kubát,[3] Andrews[4] McCrum, Read, and Williams,[5] Tobolsky and Du Pré,[6] and Ferry,[7] etc.; and for nonlinear viscoelastic behavior by Ferry,[7] Ward,[8] Kubát,[3] and Yannas.[9,10] There is no point in recapitulating them here.

In spite of the very substantial theories by Halsey, White, and Eyring,[11] Rouse,[12] Bueche,[13] Zimm,[14] Kubát,[3] Andrews,[4] Tobolsky, Aklonis, and Du Pré,[6] and others, there is no theory at present which predicts in detail the behavior of polymers in the solid state; nor have any successful results been reported in the efforts to find general properties for the more frequently studied viscoelastic functions (e.g., Ferry,[7] and Ward[8]).

Although it would be expected that any particular transition mechanism, independent of the type of polymer, should give an identifying characteristic in the viscoelastic functions, it has not yet been possible to find any recognizable features of these characteristics. Thus, it is not possible to identify a particular transition mechanism only by studying the shapes of the commonly used viscoelastic functions, and therefore it has not been possible to use the traditional mechanical spectroscopy as an identification method for transition mechanisms in polymers.

At stress–strains which are so large that there is no longer any approximation to linear viscoelastic behavior, the same mechanisms as in the linear region will obviously appear; and, in addition, it is reasonable to expect that other mechanisms will arise. Besides, it is most likely that the "linear" mechanisms will alter. Thus, a shift in the main transition region toward shorter times is usual (e.g., Ender[15]) and is referred to shorter relaxation times due to the increase in the free volume.

In order to evolve the mechanical spectroscopy and find new methods of studying the rise of nonlinear viscoelasticity, a new viscoelastic function has been developed and is described in the following.

STRESS FUNCTIONS

A pair of stress functions has been chosen, with the period 2ζ,

$$\sigma_1(t) = \begin{cases} \sigma_0; & 2n\zeta < t < (2n + 1)\zeta \\ -\sigma_0; & (2n + 1)\zeta < t < (2n + 2)\zeta \end{cases} \tag{1}$$

representing an odd, square function, and

$$\sigma_2(t) = (-1)^n (2n + 1)\sigma_0 - (-1)^n \frac{2\sigma_0}{\zeta} t$$

$$n\zeta < t < (n + 1)\zeta \tag{2}$$

representing an even, triangular function where $n = 0,1,2,3 \ldots$ and the compliances J_1 and J_2, defined as

$$J_1 = \lim_{n\to\infty} \frac{\epsilon_1(\zeta/2 + 2n\zeta)}{\sigma_0}$$

and

$$J_2 = \lim_{n\to\infty} \frac{\epsilon_2(\zeta/2 + 2n\zeta)}{\sigma_0}$$

where ϵ_1 and ϵ_2, the strain responses of the stress functions σ_1 and σ_2, respectively, are studied. In most cases, a steady state for determination of J_1 and J_2 is approximately reached after only a few periods.

As seen in Figure 1 for a Kelvin model, the locations of ϵ_1, at the quarter periods, follow curves which are parallel to each other and to the relaxation curve. The distance between the ϵ_1 curves gives J_1.
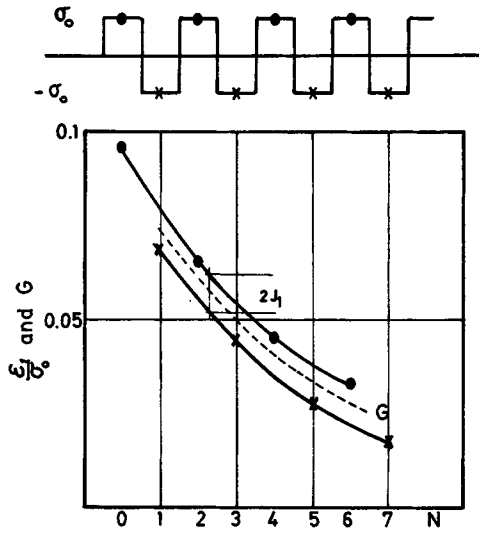
Fig. 1. Compliance $\epsilon_1/\sigma_0 = 1 - e^{-(2N+1)\alpha} - 2\sum_{n=0}^{N-1}(-1)^n(1 - e^{-(2n+1)\alpha})$, and relaxation modulus $G = 0.1e^{-(2N+1)\alpha}$, where $\alpha = \zeta/2\tau = 0.1$ for a Kelvin model.

APPLICATION TO LINEAR VISCOELASTIC SYSTEMS

The function $\sigma_2(t)$ gives a constant stress rate, and $\sigma_1(t)$ constitutes its time derivative. At the time $(\zeta/2 + 2n\zeta)_{n\to\infty}$, ϵ_1 will not include strain components which vary in direct proportion to the time, and ϵ_2 will not include strain components which are independent of time.

For an ideal-linear elastic system, $J_1 = J_{10} = $ const. and $J_2 = 0$; and for a linear viscous element, $J_1 = 0$ and $J_2 \sim \zeta$. A Kelvin model, characterized by the overall compliance J_e and the retardation time τ, gives the compliances

$$J_1(\zeta/2) = 2J_e\left\{\frac{1}{2} + \sum_{n=0}^{N_{odd}}(-1)^n\left(1 - e^{-(2n+1)\frac{\zeta}{2\tau}}\right)\right\} = f(\zeta) \qquad (3)$$

and

$$J_2(\zeta/2) = 2J_e\frac{2\tau}{\zeta}\left\{\frac{1}{2} + \sum_{n=0}^{N_{odd}}(-1)^n\left(1 - e^{-(2n+1)\frac{\zeta}{2\tau}}\right)\right\} = \frac{2\tau}{\zeta}\cdot f(\zeta) \qquad (4)$$

For long times, i.e., $\zeta \gg \tau$, $J_1 \to J_e$ and $J_2 \to 0$; and for short times, i.e., $\zeta \ll \tau$, $J_1 \sim \zeta$ and $J_2 \sim \zeta$. A three-element model containing an elastic element, J_{10}, connected in series with the Kelvin element will give $J_1 = f(\zeta) + J_{10}$, while J_2 remains unchanged.

It is of interest to notice that both J_1 and J_2 contain the same function $f(\zeta)$, and thus for the Kelvin model,
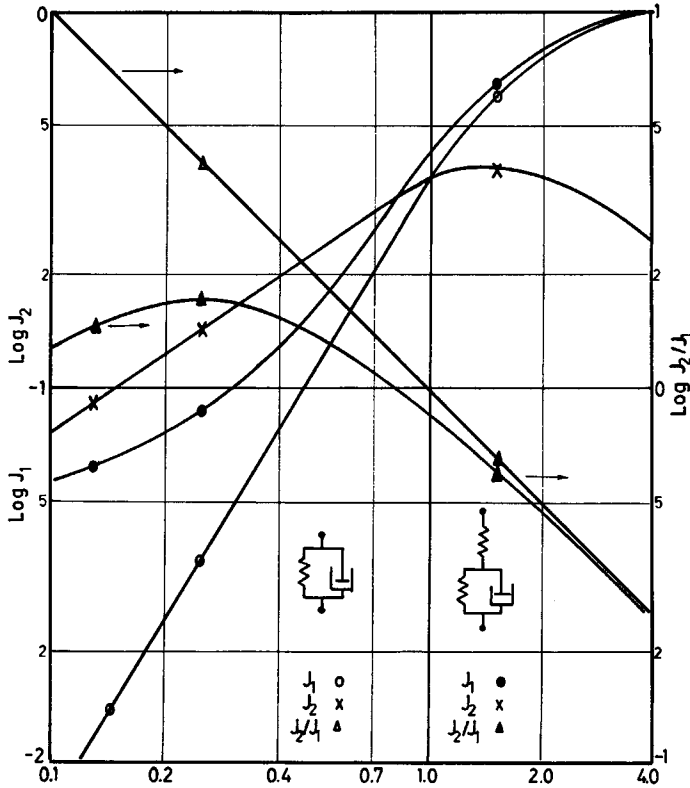
$$J_2/J_1 = 2\tau/\zeta \qquad (5)$$

Fig. 2. Functions J_1, J_2, and J_2/J_1 for a Kelvin element and a three-element model.

which is in complete agreement with the mechanical loss factor $\tan \delta = \omega\tau$ if $\omega = 2/\zeta$. J_1, J_2, and J_2/J_1 are shown in Figure 2 for the Kelvin and the three-element model treated above.

The correspondence between J_2/J_1 and J''/J' is also valid for the generalized Kelvin model.

Thus, J_2 can be looked upon as an expression for the loss mechanisms and J_1, as an expression for the storage mechanisms of the linear viscoelastic system.

This can also be seen from the determination of the compliances J_1 and J_2 by Fourier analysis (e.g., Tolstow[16]) from complex data. As σ_1 is an odd and σ_2 an even periodic function, J_1 and J_2 can be expressed in terms of the real, J', and imaginary, J'', parts of the complex compliance, respectively. Thus,

$$J_1(\zeta/2) = 4/\pi \sum_{n=0} (-1)^n \frac{1}{2n+1} J'_{2n+1} \qquad (6)$$

and

$$J_2(\zeta/2) = 8/\pi^2 \sum_{n=0} (-1)^n \frac{1}{(2n+1)^2} J''_{2n+1} \qquad (7)$$

where J'_{2n+1} and J''_{2n+1} are the real and imaginary parts of the complex compliance at the frequencies

$$f_{2n+1} = \frac{1}{(2n + 1)2\zeta}.$$

It should be noted that the Fourier series in eqs. (6) and (7) converge rapidly and that it is not often necessary to take into consideration more than the first four terms of J' and the two first terms of J''. Equations (6) and (7) then constitute the interrelation between the complex compliance and the compliance functions J_1 and J_2.

APPARATUS FOR MEASURING THE FUNCTIONS J_1 AND J_2

To be able to measure the functions J_1 and J_2, special equipment has been set up in which, besides the stress functions σ_1 and σ_2 in eqs. (1) and (2), sinusoidal stresses can also be applied.

In order to get a constant and controllable shearing stress, a short, thin-walled, cylindrical specimen is twisted to small angles. Figure 3 shows the apparatus schematically. The circular ends of the specimen, O, (diameter
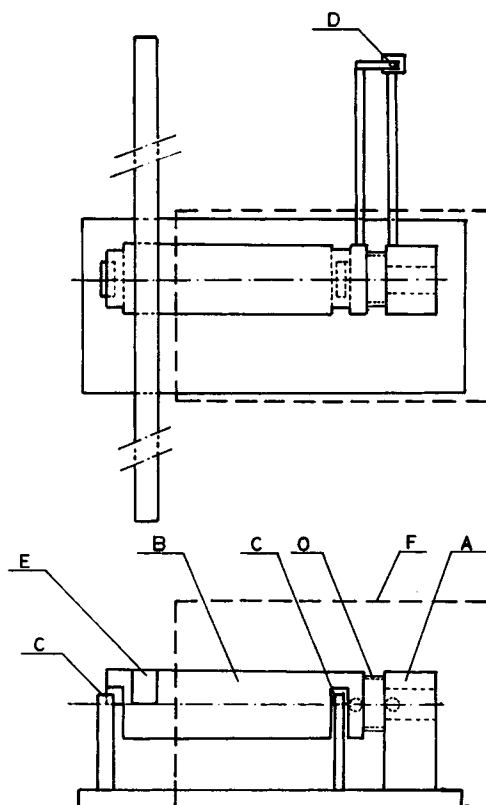

Fig. 3. Apparatus for measuring functions J_1 and J_2.

<50 mm, length, <40 mm) are glued to the fixed wall, A, and the balance, B. The balance is supported by two edges, C, with a distance between them of about 150 mm. The edges are carefully fixed in the centerline of the balance axes, and the level and the horizontal positions have been thoroughly adjusted until the plate, A, and the surface, B, of the balance are parallel to each other without divergence when the balance is revolved.

The torsion of the specimen is measured by the differential transformer, D, and is plotted by a recorder. To increase the sensitivity, to insulate the differential transformer thermally from the oven, and to get sufficient space between the transformer and neighboring metal surfaces, it has been fixed on a bar about 200 mm from the specimen.

An oven, F, is placed around the specimen, the main part of the balance, and round the fixed wall. This permits heating to about 150°C with the aid of internally circulating air and an external heating device. To obtain uniform heating, the specimen is separated from the surrounding hot air by a metal screen (not shown in Fig. 3), which is fixed to the wall, A. Within the specimen, a metal cylinder is fixed on the balance. Thus, the temperature of the specimen is determined mainly by the surrounding metal surfaces and is measured inside and outside the specimen. The friction of the balance is less than 10^{-2} pm.

At present, the equipment can be used for the measurement of torsion angles in the specimen less than tg $\phi \approx 5 \times 10^{-2}$ with an accuracy greater than $\pm$ tan $\phi \approx 10^{-6}$, which means shear strains less than 7.5% with an accuracy greater than $\pm 10^{-4}$% on as pecimen 10 mm long and 30 mm in diameter.

Because of the very small amount of friction at the balancing edges and the careful adjustment of their positions, torques above 5 pm can be used. The upper limit is set by the strength of the joints or of the specimen or by the angle of twist.

The stress function σ_1 is obtained by loading the arm E of the balance periodically, and the stress function σ_2 is obtained by moving a weight to and fro on the lever arm at a constant speed. The period, 2ζ, of the stress functions can be preset automatically at eight fixed values between 5×10^{-2} and 5×10^{-5} sec.

CALCULATION OF CREEP

From eqs. (3) and (4), it is seen that for the Kelvin model the sum of $J_1(\zeta/2)$ and $J_2(\zeta/2)$ approximately agrees with the creep compliance for the model $J(\zeta/2) = J_e(1 - e^{-\zeta/2\tau})$.

The divergence is

$$\Delta J = 2J_e \left\{ (1/2 + 2\tau/\zeta)(1 - e^{-\zeta/2\tau}) \right.$$

$$\left. + (1 + 2\tau/\zeta) \sum_{n=1}^{N_{odd}} (-1)^n (1 + e^{-(2n+1)\zeta/2\tau}) + 1/2(1 + 2\tau/\zeta) \right\} \quad (8)$$
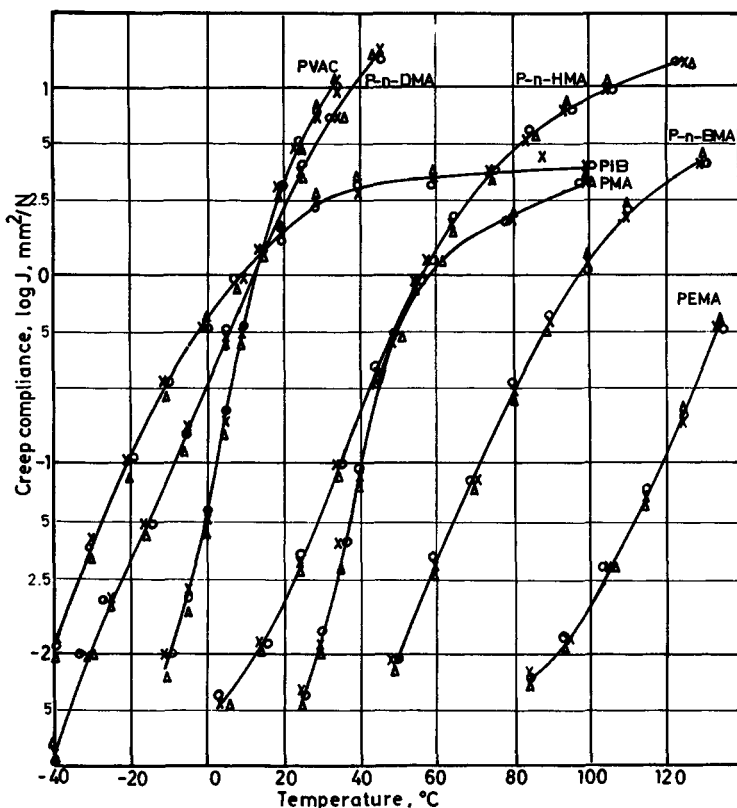
Fig. 4. Comparison between creep compliance at 2.5×10^{-3} sec, calculated in accordance with the methods of Ferry[17] (x), Schwarzl[18] (O), and Jansson (△). Dynamic data taken from PVAc,[20] PMA[21], PIB,[22] and PXMA.[23-27]

and it changes sign at $\zeta/2\tau \approx 0.7$. The maximum divergence appears at $\zeta/2\tau \approx 2$ where the logarithmic value is about 0.1. Thus, eqs. (6) and (7) can be used as an approximate method to determine creep from complex data.

In Figures 4 and 5, the creep compliance is compared, calculated from the complex compliance by methods of Ninomya and Ferry,[17] Struik and Schwarzl,[18] and from the sum of J_1 and J_2. The agreement between the three methods is very high.

In addition, Figure 6 shows the measured creep compliance compared with the sum of measured values of J_1 and J_2 for the polymers shown in Table I. In this case, too, the agreement is good. Both Ferry's and Schwarzl's methods agree well with the experimental data. Therefore, there is no direct need for new approximate methods. (The main part of the very extensive literature of relations between different viscoelastic functions has been reviewed by Ferry,[7] Ward,[8] Schwarzl,[19] and others.)

However, the agreement between the creep compliance and the sum of J_1 and J_2 shows an aspect of the physical meaning of the functions. With
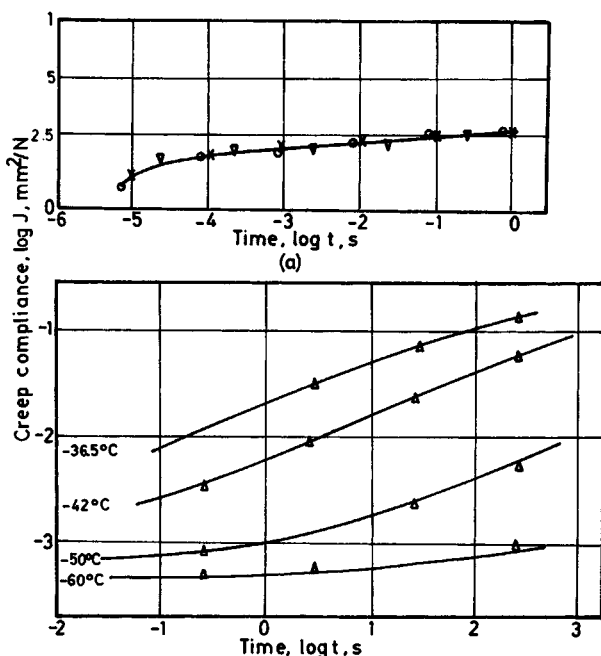
Fig. 5. Comparison between (a) creep compliance at 25°C for NR calculated in accordance with the methods of Ferry[17] ($\times$), Schwarzl,[18] (O) and Jansson ($\triangle$).   (b) Measured creep compliance and calculated in accordance with the method of Jansson ($\triangle$) for UR. Dynamic data taken from NR[28] and UR[18].

TABLE I
Polymers Studied by Direct Measurements

Polymer	Description
PVC-1	(R45 from KemaNord AB), $\bar{M}_w \approx 130,000$
PVC-5	(from KemaNord AB), R45 + 2% dioctyladipate (DOA)
PVAc	$\bar{M}_w \approx 55,000$

respect to what has been said above, J_1 and J_2 can therefore be looked upon as the storage and loss compliances of creep, respectively.

THE FUNCTION LOG J_2 = G$\{$LOG $J_1\}$

It is hardly probable that it will be possible to find more general properties of J_1 and J_2 as functions of time or temperature than those of the more frequently studied viscoelastic functions.

To eliminate the different influences of temperature or time characteristic for each particular polymer, the function $\log J_2 = g\{\log J_1\}$ is of interest, as well as the corresponding function in the complex plane, $\log J'' = h\{\log J''\}$.   For linear viscoelastic systems, it can be expected that these two functions will give similar results.   The latter function, however,
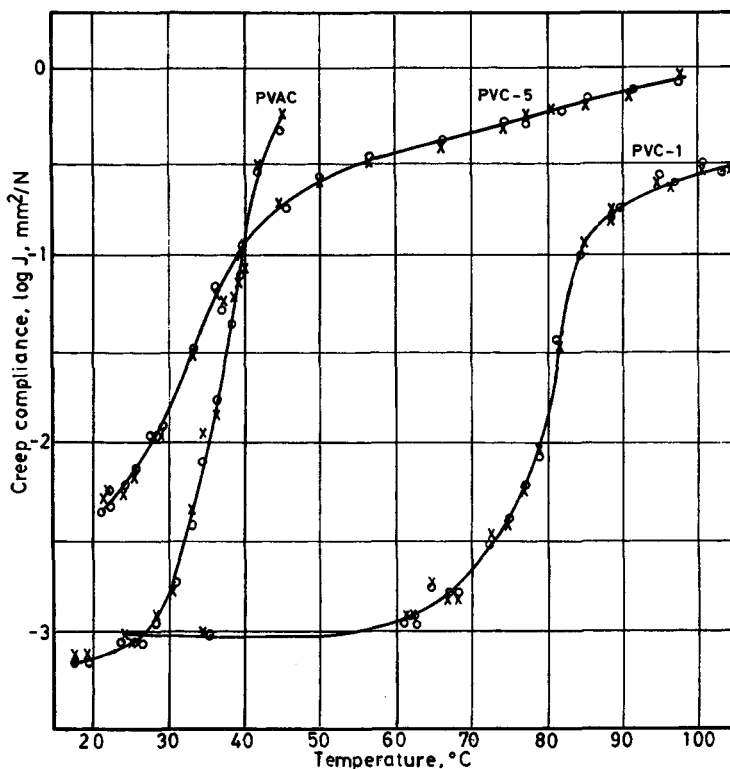
Fig. 6. Comparison between creep compliance and the sum of the functions J_1 and J_2 measured in the described apparatus: ($\times$) from direct measurements; ($\triangle$) from the sum of J_1 and J_2.   Materials described in Table I.

based on complex compliance, is limited to linear viscoelastic systems. The former does not have this limitation and has been used for studies partly of transition mechanisms in the linear viscoelastic region and partly of the rise of nonlinear viscoelasticity.

Figure 7 shows the characteristic shape of the function $\log J_2 = g\{\log J_1\}$ for a Burgers' four-element model with a pronounced plateau zone and a viscous flow which is visible only for times much longer than the retardation time.

In the "glassy" region, J_1 approaches a constant value J_{10} as J_2 moves toward zero.   The curve has a local maximum, and above this maximum, J_1 approaches a constant value and J_2 drops to zero in the "plateau" zone. The viscous flow, for this special model, is seen as an increase of J_2 for a constant J_1.

APPLICATION TO NONLINEAR VISCOELASTIC SYSTEMS

There is at present no representation of nonlinear viscoelasticity in polymers that gives an adequate description of the behavior and which
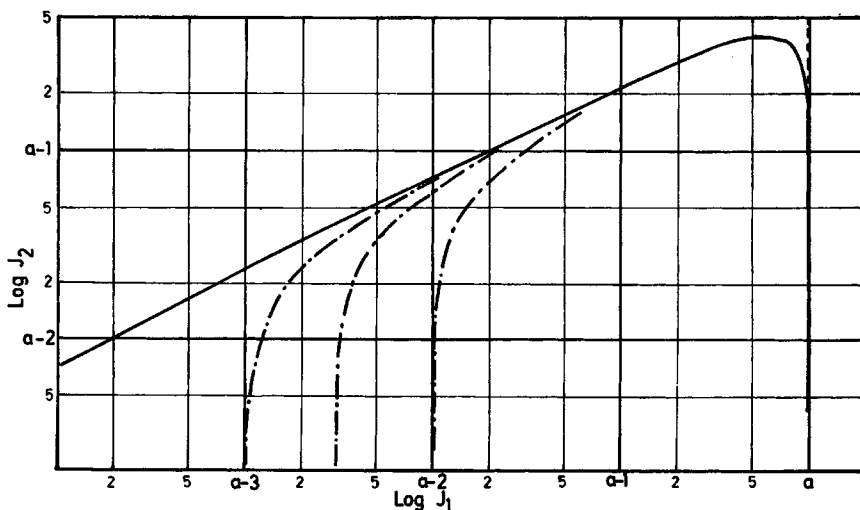
Fig. 7. Viscoelastic function $\log J_2 = g\{\log J_1\}$ for a Kelvin element (continuous line) and for three Bugers models with different stiffness in the hard elastic region (dotted-dashed lines). Dashed line represents the viscous flow of the Burgers models.

provides some physical insight into the origins of this behavior. From the viewpoint of material science, the problem can be given two different approaches[8]:

a. The Molecular Approach. It is suggested that the viscoelastic non-linearity is a consequence of some molecular mechanisms and the aim is to define them.

b. The Continuum-Mechanical Approach. Attempts are made to extend the formal description of linear viscoelasticity to the nonlinear region and form constitutive relations. The developed viscoelastic function can be expected to find applications in both fields.

The study of changes in the function during the rise of nonlinearity might give information about the molecular mechanisms, and the detailed study of the strain response during the two stress cycles might provide information about the most suitable phenomenologic model to be applied.

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