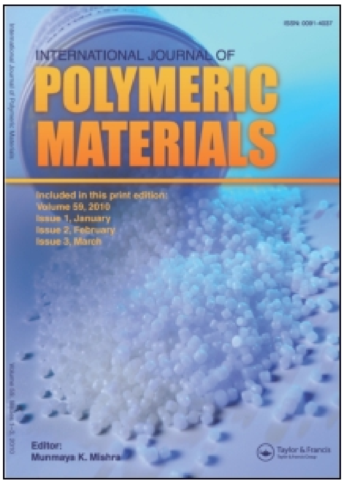

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On the Relaxation Rate in the Primary Transition Region of Amorphous Polymers

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It is known that the stress relaxation behaviour of solids is largely independent of their structure. This similarity is expressed as $F \approx 0.1\sigma_0^*$, where F is the maximum slope of the relaxation curve in a stress ln(time)-diagram and σ_0^* the initial effective stress of the experiment. This relation is found to be valid in temperature regions where no transitions occur; it is not expected to hold in the primary transition region of amorphous polymers. With reference to the theory of a damped Debye lattice, it is shown that the maximum value of F/σ_0^* is *ca.* 0.28 in this region. It is further pointed out that F/σ_0^* varies with temperature in a way reminiscent of that of the mechanical loss factor. The predictions are in agreement with experimental facts.

INTRODUCTION

Similarities in the flow behaviour of solids with different structures have been pointed out and discussed by several authors.[1–4] For stress relaxation it has been found that the maximum slope (F) of a relaxation curve in a $\sigma(\ln t)$-diagram is related to the initial effective stress (σ_0^*) as

$$F = -\left(\frac{\partial \sigma}{\partial \ln t}\right)_{\max} = (0.1 \pm 0.01)\sigma_0^* \qquad (1)$$

where σ denotes the stress and t the time. The effective stress σ^* is the difference between the stress acting on the sample and the internal stress, σ_i, the latter being equal to the equilibrium stress as $t \rightarrow \infty$. The normalization of the relaxation curves with regard to σ_i is crucial, as the regularity expressed by Eq. (1) otherwise may be entirely obscured by material-dependent factors.

Equation (1) has been found to be valid for a large number of materials, including metals and polymers.[3,4] It is also supported by numerous data relating to the kinetics of physical ageing of polymers and other solids.[2] Relaxation measurements on amorphous polymers in the vicinity of the glass transition temperature, however, appear to produce F/σ_0^* values higher than those required by Eq. (1), indicating that this equation applies only at temperatures that are not in the vicinity of a transition region.

Implications of Eq. (1) when interpreted in terms of the theory of stress aided activation and the theory of relaxation time spectra have been reported earlier.[5,6] In this note we discuss the behaviour of F/σ_0^* in the glass transition region in terms of the theory based on a damped Debye lattice.[7] It may be true that this theory has largely been abandoned, but it still appears to possess certain merits in the discussion of the flow mechanisms of amorphous polymers in the glass transition (T_g) region. In this region, F/σ_0^* theoretically takes a maximum value of approximately 0.28, corresponding to the three-dimensional case of the damped Debye lattice.

THE MAXIMUM VALUE OF F/σ_0^*

In terms of the theory of linear viscoelasticity, Eq. (1) formally corresponds to the familiar box distribution of relaxation times, $H(\tau)$, the dimensions of the box being given by the numerical factor in Eq. (1). In the vicinity of thermal transitions, however, the shape of the τ-spectrum will change.

Although the molecular processes responsible for the flow behaviour in the T_g-region (the primary flow region) may not yet be fully understood.[7] $H(\tau)$ is usually assumed to be of the wedge-type, i.e.,

$$H(\tau) = K\tau^{-m} \tag{2}$$

where K and m are constants. For a linear polymer chain (the one-dimensional case), the exponent m is 1/2.[9–11] In a two- and three-dimensional lattice the exponent takes on the values 2/2 and 3/2, respectively.

The relaxation modulus, $E_r(t)$, in the primary transition region can approximately be written as[8]

$$E_r(t) = E_1(1+t/\tau)^{-m}+E_2 \tag{3}$$

where E_1 is the glassy modulus, E_2 the rubbery plateau modulus, τ a constant, and m could be related to the dimensions of the damped Debye lattice as above. The exponent m, which is the maximum value of the negative slope of E *v*. log t in the transition region, is sometimes called the steepness index.[12] The value of this index and the general applicability of the damped Debye lattice concept have been evaluated and discussed for some polymers, in particular plasticized and substituted polystyrenes[12,13] and plasticized poly(methyl methacrylate).[14]

Equation (3) can also be derived from the power law for stress relaxation,

$$\dot{\sigma} = -B(\sigma^*)^n \tag{4}$$

where

$$n = 1 + \frac{1}{m}. \tag{5}$$

Equation (4) has been extensively used in solid mechanics;[15,16] it relies on observations of the stress dependence of the velocity of moving dislocations, which obey a similar power law.[17] During recent years, there has been an increasing interest in applying Eq. (4) to creep and other flow processes in polymers.[18]

From Eq. (4) the maximum slope (F) of the relaxation curve in a $\sigma(\ln t)$-diagrams is related to the initial stress as[19]

$$F = n^{-(n/n-1)}\sigma_0^*. \tag{6}$$

In the primary transition region, polystyrene represents the extreme case with the steepness index close to 3/2 (which corresponds to $n = 1.67$). The one-dimensional case (steepness index 1/2) corresponds to an n-value of 3. The F/σ_0^*-ratio would then take on the following values

$$F/\sigma_0^* \approx 0.28 \quad \text{(three-dimensional damped lattice)}$$

$$F/\sigma_0^* \approx 0.19 \quad \text{(one-dimensional damped lattice).} \tag{7}$$

In terms of the theory of the damped Debye lattice, the value of 0.28 thus represents the maximum value which the ratio F/σ_0^* can take on in the glass transition region.

In Figure 1 stress relaxation curves corresponding to Eq. (3) with steepness indexes of 1/2 and 3/2 are shown together with a relaxation curve obeying Eq. (1).

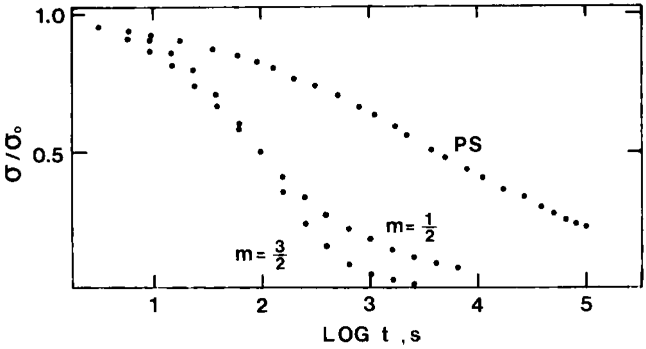

FIGURE 1 Stress relaxation curves according to Eq. (3) with $m = 3/2$ and $m = 1/2$, respectively, and an experimental curve (polystyrene at 60°C) conforming to Eq. (1).

A semi-empirical equation similar to Eqs. (3) and (4) is often used to describe the time dependence of the relaxation modulus in the primary transition region.[20] The relaxation modulus corresponds to a modified wedge distribution of relaxation times, and is given by

$$E_r(t) = \frac{(E_1E_2)^{1/2}}{\left[\frac{t}{\tau} + \left(\frac{E_2}{E_1}\right)^{1/2m}\right]^m} + E_2 \tag{8}$$

where E_1, E_2, τ and m have the same meaning as in Eq. (3). If $E_1 \gg E_2$, the F/σ_0-ratio is obtained as

$$\frac{F}{\sigma_0} = \left(\frac{m}{m+1}\right)^{m+1} \tag{9}$$

which is equivalent to Eq. (6) with $n = 1 + 1/m$.

Tobolsky[20] has listed m-values for a number of polymers; Table I gives the corresponding F/σ_0-values (obtained with Eq. (9)). This table also includes values of F/σ_0 for some other polymers calculated from experiments reported in the literature.

In the "viscous" region, i.e., beyond the rubbery plateau, the ultimate relaxation behaviour is determined by a single relaxation time (cf. Procedure X[20]) and the F/σ_0 ratio is then

$$F/\sigma_0 = 0.37 \qquad \text{(Maxwell-model)}. \tag{10}$$

TABLE I

F/σ_0-values, according to Eq. (9), for some polymers in the T_g-region

Polymer	F/σ_0	Ref.
Poly(methyl methacrylate)	0.19	20
Poly(methyl methacrylate)	0.19	21
60/40 Butadiene/styrene polymer	0.19	20
50/50 Butadiene/styrene polymer	0.20	20
30/70 Butadiene/styrene polymer	0.20	20
Polyisobutylene	0.23	20
Natural rubber (not vulcanized)	0.26	20
Natural rubber (vulcanized)	0.26	20
Poly(vinyl chloride)	0.21	7
Poly(ethylene terephthalate)	0.24	7
Polycarbonate	0.26	7
Polystyrene	0.28	7
Polypropylene (atactic)	0.20	22
Poly(vinyl acetate)	0.27	23
Butadiene-acrylonitrile vulcanisate	0.23	24

THE RELATION BETWEEN THE F/σ_0^*-RATIO AND THE MECHANICAL LOSS FACTOR

For sufficiently broad τ-distributions, the mechanical loss tangent (tan δ) is approximately related to the slope of the stress relaxation curve as

$$\tan \delta = \frac{\pi}{2} \frac{d \ln E_r(t)}{d \ln t} = \frac{\pi}{2} p \tag{11}$$

where $E_r(t)$ is the relaxation modulus and p is the negative slope of the $\ln E_r(t) - \ln t$ curve.[25]

This relation is derived for rather small values of the slope of the relaxation curve in an $\ln \sigma - \ln t$ diagram, but the experimental agreement with the equation is surprisingly good even at somewhat larger slopes.[18,25] From Eqs. (9) and (11) a qualitative relation between the F/σ_0^*-ratio and tan δ can be obtained i.e., a marked increase in damping corresponds to an increase in F/σ_0^* (or in the slope p).

SCHEMATIC TEMPERATURE DEPENDENCE OF F/σ_0^*

In the T_g-region, the stress relaxation curves are approximately straight lines when plotted in a $\ln E_r(t) - \ln t$ diagram. The slope of these lines increases from a rather low value at temperatures somewhat below the glass transition temperature to a maximum value in the transition region, i.e. the slope p approaches the steepness index, and then decreases again as the rubbery plateau is approached. The maximum slope is given by the steepness index. Since F/σ_0^* increases monotonically with the slope of the $\ln E_r(t) - \ln t$ curves, it is obvious that a maximum will be obtained when F/σ_0^* is plotted *v.* temperature; the curve obtained is reminiscent of a damping curve (tan δ *v.* T, cf. Eq. (11)). The maximum value of F/σ_0^* would then occur at a temperature associated with the glass transition temperature.

For higher temperatures F/σ_0^* decreases since the relaxation rate diminishes close to the rubbery plateau. For polyisobutylene, Eq. (1) is obeyed again in the rubbery region.[5] Whether this is true in general or not is presently under study. At still higher temperatures the F/σ_0^*-ratio should increase again due to viscous flow (cf. Eq. (10)), thus approaching the Maxwellian behaviour.

Figure 2 schematically illustrates the general temperature dependence of the F/σ_0^*-ratio for amorphous polymers. This behaviour has partly been experimentally confirmed for poly(vinyl chloride) plasticized with various amounts of dioctyl phthalate.[26]

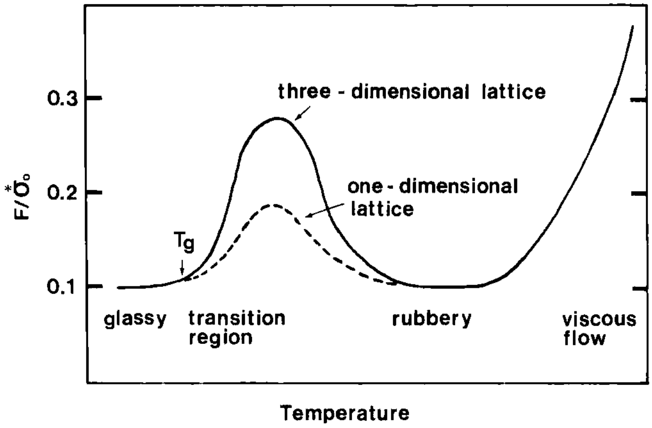

FIGURE 2 Variation of F/σ_0^* with temperature (in principle) for an amorphous polymer.

CONCLUSIONS

The results arrived at above can be summarized as follows.

1) In the absence of major structural changes, the ratio of F/σ_0^* attains the value of 0.1 for a large number of material irrespective of their structure. In the glass transition region of amorphous polymer, F/σ_0^* increases to the maximum value of 0.28 which, formally, corresponds to a three-dimensional damped Debye lattice.

2) With regard to the glass transition, the ratio of F/σ_0^* is expected to vary with temperature in a way similar to that of the mechanical loss tangent i.e., to display a maximum value close to the glass transition temperature. In principle, it might be possible to observe secondary mechanical transitions using the temperature dependence of the F/σ_0^*-ratio and also the glass transition temperature of semi-crystalline polymers.

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