Structural Time Dependency in the Rheological Behavior of Molten Polymers

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Synopsis

In order to elucidate the role of reentanglement processes in the rheology of molten polymers, we have used the interrupted shear test and the reduction-in-shear-rate test to study a linear and a branched polyethylene at 170°C. A cone-plate rheometer was used, and shear rates were thus limited to values below 1 sec^{-1}. For both polymers, the characteristic time for reentanglement was found to be significantly greater than the time scales associated with the relaxation of shear and normal stresses after cessation of steady shear. This observation has important implications for the modelling of melt flow in plastics processes and the evaluation of constitutive equations.

INTRODUCTION

Concentrated polymeric liquids can exhibit certain time-dependent rheological phenomena which are in some respects similar to those observed in the case of concentrated suspensions of solid particles. In the case of suspensions, it is customary to interpret these phenomena in terms of a time-dependent structure. The most common situation is that in which the viscosity decreases with duration of shearing, and this type of behavior is called thixotropy. The recent review by Mewis[1] provides a thorough and thoughtful summary of what is known about this type of behavior. On the other hand, polymeric liquids are usually described as viscoelastic.

It is useful at this point to classify fluid behavior as follows:

(1) time-independent fluids (Newtonian fluid is special case), and (2) time-dependent fluids: (a) inelastic fluids with time-dependent structure (suspensions of solids in Newtonian fluids), (b) Viscoelastic fluids without time-dependent structure (dilute polymer solutions), and (c) Viscoelastic fluids with time-dependent structure (concentrated polymer solutions and melts or suspensions of solids in polymer solution). Rather than define these types of behavior in terms of the mathematical language of rational mechanics, we suggest the following phenomenological definitions as more useful in the present context.

First, we note that the inelastic fluid with time-dependent structure cannot store energy elastically, so that all work of deformation must be immediately dissipated. Stress relaxation after cessation of deformation is instantaneous, and no recoil will be observed if the deforming stress is suddenly removed. The fact that the stress is isotropic however, does not imply that the material is in its virgin or rest state, i.e., the state it would have if left undeformed for a long time.

Turning now to the case of the viscoelastic fluid without time-dependent structure, we note that elastic energy storage is possible so that retarded stress

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relaxation and elastic recoil can be exhibited.   Unlike the material with time-
dependent structure, however, if the material is incompressible the isotropy of
the stress implies that the material is in its rest state.

We are concerned here with materials in class 2c, which are viscoelastic but
also have time-dependent structure, and we address the following questions:

(1) What kinds of experiments are useful in elucidating the role of time-
dependent structure in the rheology of concentrated polymeric liquids?

(2) To what extent is it necessary to take structural time dependency explicitly
into account in understanding and modeling the behavior of these materials?

Addressing ourselves first to question (1), consider the stress growth experi-
ment in which the fluid, after having been allowed to stand at rest for a long
period of time, is suddenly subjected to a steady simple shear flow at a significant
shear rate.   Figure 1 shows the types of response observed in the shear stress for
a thixotropic suspension and a polymeric liquid at significant shear rates.

Both materials exhibit a stress overshoot, but the detailed behavior is clearly
different for the two materials.   Since the suspension cannot store energy, as
soon as we start to do shearing work on the material it must be immediately
dissipated.   Thus, the stress rises instantaneously and then decays, somewhat
because of the breakdown of structure caused by the shearing.   In the case of
the polymeric liquid, however, some energy can be stored so that an instantaneous
increase in stress is not necessary.   Ultimately, of course, the amount of stored
energy approaches an equilibrium level and there is a balance between shear work
and dissipation.

This article is concerned with the role of structural time dependency in the
behavior of polymeric liquids; we are interested in knowing how much can be
learned about this from the stress growth experiment.   For example, does the
presence of a stress overshoot imply structural time dependency?   The answer
to this question is clearly no, as such an overshoot can be observed in the case
of dilute solutions which have no structure.   In concentrated solutions and melts,
it is thought that some kind of structure is present, and this is often represented
as a temporary network, the junctions of which are entanglements rather than
chemical crosslinks.   There is however, no marked difference between the stress
overshoot generated by these materials and that characteristic of dilute solutions.
Thus, we conclude that stress growth is not a useful test for elucidating the role
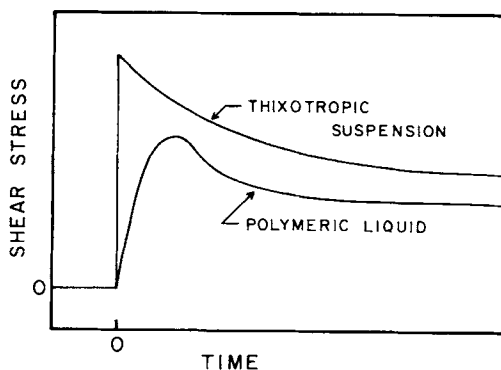of time-dependent structure in polymeric liquids.

Fig. 1. Stress growth curves for thixotropic fluid and viscoelastic fluid.

One interpretation of this result is that the rate of structure breakdown or disentanglement during deformation is of the same order as, or higher than, the rate of the viscoelastic relaxation processes. On the other hand, since the rebuilding of structure (reentanglement) is a thermal phenomenon requiring many segmental motions of the chain, it may occur at a rate considerably slower than that of the stress relaxation process. If this is the case, we might hope to see evidence of it in the long-term effects of previous deformation.

Hanson[2] and Maxwell and Plumeri[3] have demonstrated that shearing a molten thermoplastic at a high rate alters its response to further deformation that may occur a fairly long time later. Howells and Benbow[4] and Prichard and Wissbrun[5] found that, in the case of crystallizable polymers with long branches, many hours may be required for the material to recover its rest state structure after a period of intensive shearing. It would clearly be useful to study this phenomenon in such a way that well-defined characteristic times could be associated with the reentanglement process, and this article is concerned with two techniques for doing this: interrupted shear and reduction in shear rate.

INTERRUPTED SHEAR

The only rheological variable we can use to determine the state of an incompressible material is some anisotropic component of the stress, i.e., a shear stress or a normal stress difference. If we wish to follow the development of structure after the cessation of steady shear, once the stresses have relaxed they provide no further information as to the state of the material.

One solution to this problem is to restart the shear after various rest times and study the effect of the rest time on the stress growth curve. This technique has been used, for example, by Joye and Poehlein[6] to study clay suspensions and by Pohl and Gogos[7] to study molten polymers.

Stratton and Butcher[8] suggested a procedure for using the results of such an experiment to determine a characteristic time for reentanglement. In their studies of nondilute polymer solutions, they found that the stress overshoot was reduced by the previous shearing, i.e., that the maximum shear stress, τ_m, was a function of the rest time, t_r, for a given shear rate. For very long rest times, the maximum stress approaches an asymptotic value, $\tau_m(\infty)$, which can be associated with the behavior of material initially in its rest state, i.e., having its equilibrium structure. They took the peak height as a characteristic feature of the stress growth curve and represented this as a function of the rest time.

$$\tau_m = \tau_m(t_r, \dot\gamma) \tag{1}$$

The meaning of these quantities is illustrated in Figure 2.

In order to obtain a characteristic time for the reentanglement process, Stratton and Butcher[8] defined such a time, t_e, as the rest time for which

$$\tau_m(t_e, \dot\gamma) - \tau_s(\dot\gamma) = \left(1 - \frac{1}{e}\right)[\tau_m(\infty, \dot\gamma) - \tau_s(\dot\gamma)] \tag{2}$$

where

$$\tau_s = \eta\dot\gamma \tag{3}$$

This is an empirical definition not intended to imply that the reentanglement process is describable by a single exponential factor. They compared this
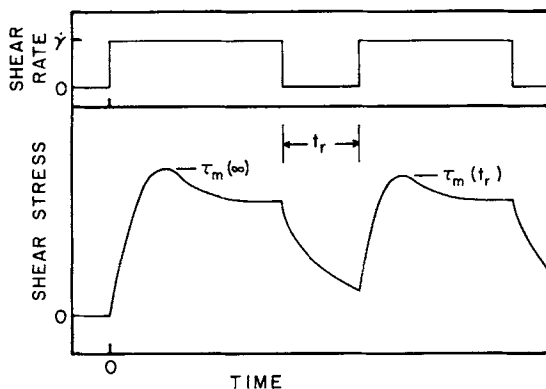
Fig. 2. Interrupted shear experiment.

reentanglement time with a relaxation time obtained by measuring the shear stress after cessation of simple shear. This relaxation time, t_d, is defined as the time at which the stress is $(1/e) \times \tau_s$.

$$\tau(t_d, \dot{\gamma}) = \tau_s(\dot{\gamma})/e = \eta\dot{\gamma}/e \qquad (4)$$

Stratton and Butcher found that when a log–log plot was made showing both $t_d(\dot{\gamma})$ and $t_e(\dot{\gamma})$, both sets of data fell near straight lines except at higher shear rates. Furthermore, the $t_e(\dot{\gamma})$ line was about a decade above the $t_d(\dot{\gamma})$ line implying that the characteristic time for reentanglement is an order of magnitude larger than the stress relaxation time applicable to the same shear rate.

We have used the interrupted shear technique to study a high-density polyethylene and have used the same procedure as Stratton and Butcher to interpret the data. The polymer, which we have designated as "resin 22," is Sclair 59C blow molding resin, manufactured by du Pont of Canada. It is a linear homopolymer with a density of 0.956, a melt index of 0.42, and a weight average molecular weight of 1.85×10^5. This resin has been studied previously by Utracki, Bakerdjian, and Kamal[9] and by Garcia-Rejon, Dealy, and Kamal,[10] the latter authors giving a rather complete rheological characterization of the material. The viscosity, first normal stress difference, dynamic viscosity, and storage modulus are shown in Figure 3, while the linear spectrum, calculated using Tschoegl's second approximation formula as given by Ferry,[11] is shown in Figure 4.

All the experiments described in this article were carried out at 170°C using a Rheometrics Mechanical Spectrometer, model 71C, of the type described by Macosko and Starita.[12] This is a general purpose rotational rheometer in which a variety of fixtures can be used. For the transient shear tests, cone and plate fixtures were used; the cone having an angle of 0.1 rad (5.73°) and a diam of 2.5 cm. Complete details of the experimental procedure are given in the thesis of Tsang.[13]

The maximum stress is plotted versus the logarithm of the rest time in Figure 5 at a shear rate of 0.104 sec^{-1}. From Figure 3, we see that this shear rate is well into the non-Newtonian region where significant disentanglement would be expected at steady state. The initial peak stress, $\tau_m(\infty)$, and the steady state stress, τ_s, are also shown in Figure 5, and we see that there is a marked stress overshoot.
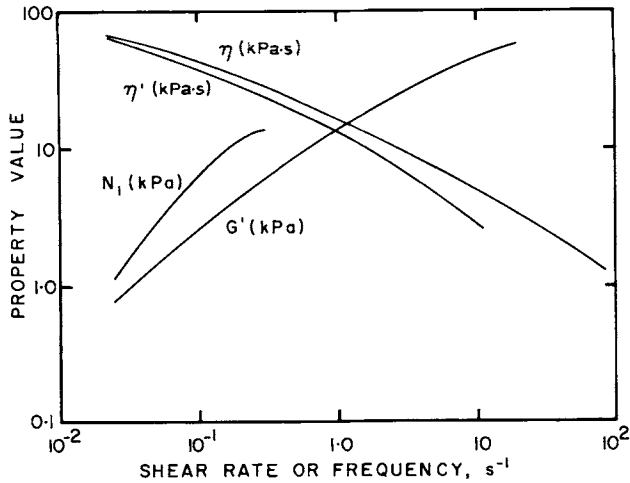
Fig. 3. Rheological properties of resin 22 at 170°C.

Using the Stratton and Butcher definition of t_e, as given by eq. (2), the reentanglement time was found to be 385 sec. From measurements of the relaxation of shear and normal stresses after cessation of steady shear, we also calculated a relaxation time for the shear stress, as per eq. (4), and another, t_n, for the first normal stress difference, defined as follows:

$$N_1^-(t_n, \dot{\gamma}) = N_1(\dot{\gamma})/e \tag{5}$$

The three relaxation times are compared below.

$$t_d = 3.6 \text{ sec}$$

$$t_n = 54 \text{ sec}$$

$$t_e = 385 \text{ sec}$$

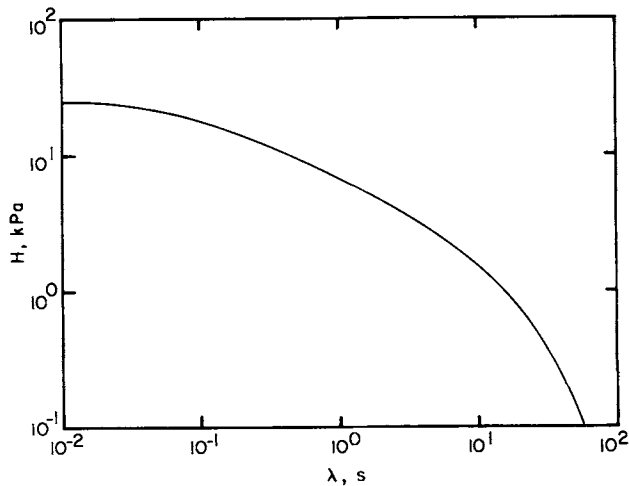We observe the well-known fact here that the normal stresses relax considerably

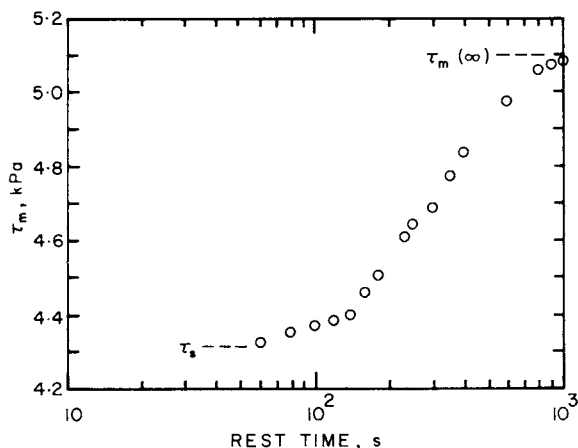Fig. 4. Relaxation spectrum for resin 22 at 170°C.

Fig. 5. Maximum stress vs. rest time for resin 22 at 170°C.

more slowly than the shear stress, but the reentanglement time is much greater even than the normal stress relaxation time. This result implies that the relaxation of the stresses to an isotropic state does not imply that the material has returned to its rest state. Thus, it is not a "viscoelastic fluid without time-dependent structure" as defined in the Introduction.

REDUCTION IN SHEAR RATE

The interrupted shear test is inconvenient because it involves a long sequence of operations to obtain a single value of reentanglement time. An alternative test is one in which the material is subjected to steady shear at a rate, $\dot{\gamma}_1$, until the stresses are steady, at which time the shear rate is reduced to a lower level, $\dot{\gamma}_2$. In this case, the reentanglement process can be monitored by measuring the stresses, as these do not relax to zero but to new steady-state values consistent with the equilibrium entanglement density corresponding to the second shear rate. The reduction in shear rate test has been used to study thixotropic suspensions by Joye and Poehlein,[6] but it does not appear to have been used to any great extent in the study of elastic liquids.

In the limiting case of linear viscoelasticity, the Boltzmann superposition principle can be used to show that the development of the stress in a reduction-in-shear-rate test is directly related to the stress growth function, $\eta^+(t)$, or the stress relaxation function, $\eta^-(t)$, for cessation of steady shear:

$$\tau(t) = \eta_0\dot{\gamma}_2 + (\dot{\gamma}_1 - \dot{\gamma}_2)\eta^-(t) \tag{6}$$

$$\tau(t) = \eta_0\dot{\gamma}_1 - (\dot{\gamma}_1 - \dot{\gamma}_2)\eta^+(t) \tag{7}$$

Similar expressions can be derived for the normal stress differences. These relationships show that within the limits of linear viscoelasticity, the stresses are monotonically decreasing functions of time.

However, in the case of nonlinear viscoelasticity, particularly when the material has time-dependent structure, an undershoot can occur, and the recovery of the stress from its minimum to a new steady state is a measure of the approach of the material to its equilibrium state consistent with the second shear rate. This type of behavior is illustrated in Figure 6.
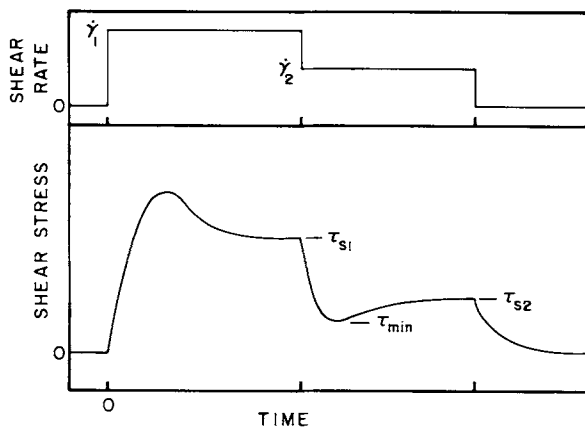
Fig. 6. Reduction in shear rate experiment.

In a manner analogous to that used to define t_c, we define a reentanglement time, t_E, which is a function of both $\dot{\gamma}_1$ and $\dot{\gamma}_2$. It is the value of the time which has elapsed since the reduction of shear rate at which the shear stress is given by

$$\tau(t_E) = \tau_{s2} - \frac{1}{e}(\tau_{s2} - \tau_{\min}) \tag{8}$$

where

$$\tau_{s2} = \eta(\dot{\gamma}_2)\dot{\gamma}_2$$

and $\tau_{\min}$ is the stress at the bottom of the undershoot. Of course, as $\dot{\gamma}_1$ approaches $\dot{\gamma}_2$, this reentanglement time must approach zero, and it is only cases in which $\dot{\gamma}_2$ is significantly less than $\dot{\gamma}_1$ that are of interest. The disadvantage of this experimental technique is that as $\dot{\gamma}_2$ becomes small, the stresses which are being measured also become small, and the values of t_E become less reliable.

Figure 7 shows t_E, t_d, and t_n plotted as functions of $\dot{\gamma}_2$ for a fixed value of $\dot{\gamma}_1$ (0.258 sec$^{-1)}$ for resin 22. The dashed curves show the expected behavior as $\dot{\gamma}_1$ approaches $\dot{\gamma}_2$, while at the lower values of $\dot{\gamma}_1$ we see that t_E is rising significantly above the two relaxation times.

Figure 8 shows a similar plot for a low-density polyethylene, "resin 10," which is DFDQ 4400 film resin made by Union Carbide, Canada, and studied previously by Tee and Dealy,[14] Dealy and Vu,[15] and Dealy, Garcia-Rejon, and Kamal,[16] the latter giving a rather complete rheological characterization of it. In this case, $\dot{\gamma}_1$ is 0.64 sec^{-1} and the general trends for this highly branched polymer are the same as in the case of the linear resin. Rokudai[17] found that long-term effects of previous shearing were much more pronounced for low-density than for high-density polyethylene. However, his experiments involved shearing in a Brabender Plasticorder so that the shear rates were much higher than those used in this study. It seems plausible that the difference in reentanglement time between the two materials would be more pronounced at high shear rates.
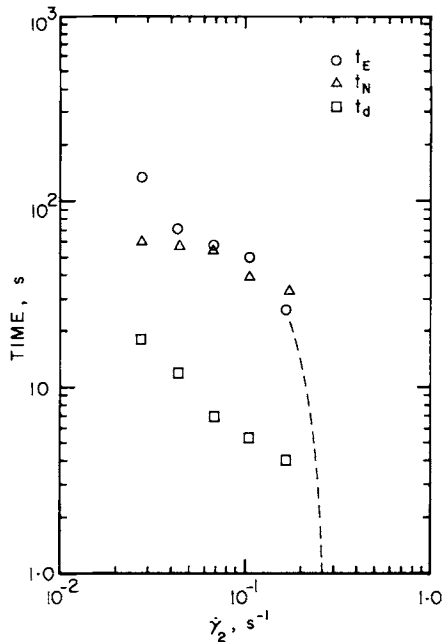
Fig. 7. Characteristic times t_E, t_d, and t_n as functions of $\dot{\gamma}_2$ with $\dot{\gamma}_1 = 0.258$ sec^{-1} for resin 22 at 170°C. t_d and t_n are based on eqs. (4) and (5) with $\dot{\gamma} = \dot{\gamma}_2$. Dashed line shows behavior expected for t_E when $\dot{\gamma}_2$ approaches $\dot{\gamma}_1$. O, t_E; $\triangle$, t_N; $\square$, t_d.

CONCLUSIONS

Two experimental techniques have been used to study the role of time-dependent structure in the response of molten polymers to transient shearing deformations. Interrupted shear yields a well-defined characteristic time for structure formation, but the experimental procedure is a lengthy one. In the reduction-in-shear-rate test, on the other hand, a single experiment yields a characteristic time for reentanglement. However, the lower the second shear rate, the poorer the precision of the results. Since it is desirable to have $\dot{\gamma}_2$ be substantially less than $\dot{\gamma}_1$, the restriction of rotational rheometers to low shear rates severely limits their usefulness for carrying out this test. Moreover, this restriction, which is associated with the inevitable radial accelerations occurring in all rotational rheometers, is currently a basic barrier to the study of viscoelastic liquids because there is no reliable alternative for the study of transient shearing tests.

Both a linear and a branched commercial polyethylene were found to have characteristic times for reentanglement which are significantly greater than times associated with stress relaxation processes. This observation has a number of important implications. For example, it tells us that properties measured using material which has been at rest in the melt state for a long time may be quite inappropriate for correlating the behavior of materials which have been subjected to periods of shearing even several minutes previously. Secondly, it is a warning that constitutive equations which incorporate the equivalence of rest state with isotropic stress will fail to accommodate long-term transient behavior.

This latter problem is sometimes circumvented by combining a traditional viscoelastic model with a kinetic expression which accounts explicitly for the
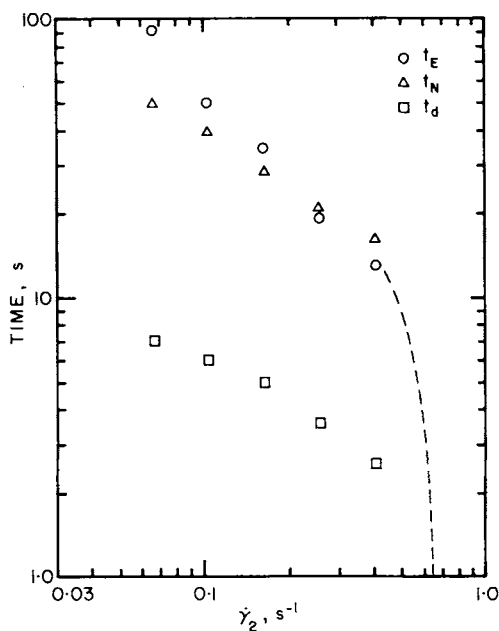
Fig. 8. Characteristic times t_E, t_d, and t_n as functions of $\dot\gamma_2$ with $\dot\gamma_1 = 0.64$ sec^{-1} for resin 10 at 170°C. t_d and t_n based on eqs. (4) and (5) with $\dot\gamma = \dot\gamma_2$. Dashed line shows behavior expected for t_E when $\dot\gamma_2$ approaches $\dot\gamma_1$. O, t_E; Δ, t_N; □, t_d.

time-dependent structure. Examples are the models proposed by Jachimiak, Song, and Brodkey,[18] Acierno, et al.,[19] and Soong and Shen.[20] It seems likely, in the light of our results, that in the simulation of flows involving strain histories in which reentanglement processes are likely to play a central role, models of this type would be useful.

In any event, it seems likely that experiments such as those used here would provide rather severe tests of constitutive equations for entangled polymeric liquids. Takahashi, Masuda, and Onogi[21] have, indeed, used the predicted responses to interrupted shear as a means of classifying a number of integral constitutive equations for viscoelastic fluids.

NOMENCLATURE

e	2.718
N_1	first normal stress difference in steady shear
N_1^-	normal stress relaxation function after cessation of steady shear
t_d	shear stress relaxation time defined by eq. (4)
t_e	reentanglement time defined by eq. (3)
t_E	reentanglement time defined by eq. (8)
t_n	normal stress relaxation time defined by eq. (5)
t_r	rest time in interrupted shear experiment
$\dot\gamma$	shear rate
$\dot\gamma_1$	first shear rate in reduction-in-shear-rate experiment
$\dot\gamma_2$	second shear rate in reduction-in-shear-rate experiment
η	viscosity
η_0	zero-shear viscosity
η^+	shear stress growth function, $\tau(t)/\dot\gamma$, at startup of simple shear

η^- shear stress relaxation function, $\tau(t)/\dot{\gamma}$, after cessation of simple shear
τ shear stress
τ_m maximum shear stress in stress growth experiment
τ_{min} minimum shear stress in reduction in shear rate experiment
τ_s steady-state shear stress
τ_{s2} steady-state shear stress for shear rate = $\dot{\gamma}_2$

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