

Constitutive equation and damping function for entangled polymers

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Abstract

The tube model theory of entangled polymer presumes that the polymer chain holds its equilibrium contour length under certain conditions of flow; at times longer than a certain characteristic time, τ_k , in the stress relaxation process following any flow history; in steady flow of rates smaller than τ_k^{-1} ; etc. Rheological phenomena associated with this presumption are discussed.

1. Introduction

The K-BKZ constitutive model is notable for its wide applicability and good prospect in view of the molecular picture among the constitutive models for entangled polymers (Larson, 1988). Here we refer to the model as a single-integral memory fluid with a strain-dependent memory kernel. The full description of the equation for any one material is not very simple since the model includes at least two independent strain tensors and two memory functions. One can work out some simplified equation to fit the data for shear and uniaxial elongation, for example, but cannot be sure whether it is applicable to other types of deformation. In this respect the model is still being developed.

The model is simple for shear deformation as far as the shear stress, σ and the first normal stress difference, N_1 , is concerned. This is because the corresponding components have simple forms for any choice of allowable strain tensors. The study of shear deformation is not suitable for the general development of the constitutive model. On the other hand, one can investigate the detailed variation of the memory function with molecular parameters like molecular weight through the study of shear deformation. The shear and normal stresses can be written as follows.

$$\sigma(t) = \int_{-\infty}^t m(t-t', |\gamma_{tr}|) \gamma_{tr} dt' \quad (1)$$

$$N_1(t) = \int_{-\infty}^t m(t-t', |\gamma_{tr}|) \gamma_{tr}^2 dt' \quad (2)$$

$$m(t, \gamma) = -\frac{\partial G(t, \gamma)}{\partial t} \quad (3)$$

Here γ_{tr} is the magnitude of shear applied in the period from t to t' and $m(t, \gamma)$ is the memory function for shear deformation. The function $G(t, \gamma)$ is the shear relaxation

modulus or the ratio of the shear stress to the magnitude of shear, γ , at time t after a constant shear is applied to the material. This function represents most of the rheological behavior in shear deformation and σ and N_1 for any flow history can be derived from the data of $G(t, \gamma)$.

One of the important features of $G(t, \gamma)$ for entangled polymers (Osaki, 1993) is that it can be factorized into functions of time, t and strain, γ , at sufficiently long times; longer than τ_k , say.

$$G(t, \gamma) = G(t) h(\gamma) \quad (t > \tau_k) \quad (4)$$

Here $G(t)$ is the linear relaxation modulus, i. e., the relaxation modulus at the limit of $\gamma = 0$. The function $h(\gamma)$ is called the damping function and represents the strain dependence of the relaxation modulus. The separability is a good approximation over relatively wide time ranges for polymers with wide molecular weight distributions, specifically for commercial polymers. The separability simplified the formula of constitutive equation and was extensively utilized for rheological calculations (Larson, 1988).

In spite of the early results indicating that the separability is valid only at long times (Einaga *et al.*, 1993; Fukuda *et al.*, 1975), it is sometimes described as a basic and general property of entangled polymers even at short times. I can agree with the author of a textbook in engineering application not writing too rigorous definitions for a certain feature provided that the readers use the description only for the specific application. I cannot agree with the reader if he or she raises the failure of separability as a proof of wall slip, for example. Another extreme attitude in recent studies is to claim that the separability is completely wrong until at very long times, say the time comparable to the longest relaxation time of the material, based on delicate theories or on the data taken with extremely high precision. This statement should be valid for a complex material like polymer; for example, a synthetic "monodisperse polymer"

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is composed of molecules with various molecular weights. On the other hand, the separability is a fact at an allowable level, though not unanimous, of approximation and may possibly give clue to the deeper understanding of entanglement.

Here we revisit the separability and investigate its implication in some rheological functions.

2. Standard damping function and separability criterion

A remarkable property of the damping function, $h(\gamma)$, is that it is approximately a universal function of the magnitude of shear, γ , for linear polymers with not too wide molecular weight distributions (Osaki, 1993). The behavior at relatively low strain was close to the prediction of a corotational constitutive model and thus suggested that the origin of the damping was geometrical, in contrast with specific intermolecular interaction like stickiness among chains, even at the early stage of the study (Fukuda *et al.*, 1975).

The tube model theory of entanglement by Doi and Edwards revealed the origin of the damping (Doi and Edwards, 1986). According to the theory, the entanglement points move in proportion to the instantaneous macroscopic deformation of the material and accordingly the entangled chain stretches and orients to the direction of deformation. When the deformation is large, the stretched chain shrinks rather rapidly passing through the entangled points so that some of the entanglements, located close to the chain ends, are lost. Also the tension of the chain decreases in this process. However, the orientation remains unchanged so that some small stress remains. The stress then relaxes in the same manner as that in small deformations. In summary, at large deformation, the modulus decreases rather rapidly to some extent, namely by a factor

h , and then decreases in proportion to $G(t)$ at longer times. The characteristic time τ_k in Fig. 1 would represent the end of the shrink process. It is easily seen that the damping function for entangled star-branched polymer should agree with that of linear chains (Doi and Edwards, 1986). This prediction was experimentally confirmed (Osaki *et al.*, 1990). The model cannot be applied without large modifications to polymers with two or more branch points.

The molecular picture as well as the experimental observation, like Fig. 1, involves a characteristic time as a criterion of separability. In the tube model theory it is the equilibration time of the fluctuation of chain density in the tube, or the equilibration time of the chain contour length. The process could be modeled with a Rouse model confined in a tube and the characteristic time can be derived as (Doi, 1980)

$$\tau_R = A_R M^2 \quad (5)$$

Here A_R is a parameter representing the frictional property of segment and may vary with the chemical structure of molecule, the concentration, and the temperature. It is independent of the molecular weight, M , or the entanglement molecular weight, M_e . In investigating the properties of characteristic times like τ_R and τ_k , it is convenient to work with the ratios, τ_1/τ_R and τ_1/τ_k , to avoid the effect of the segmental friction. The maximum relaxation time, τ_1 , can be written as

$$\tau_1 = A M_e^2 \left(\frac{M}{M_e} \right)^{3.5} \quad (6)$$

where A is a parameter similar to A_R . Eq. (6) describing the experimental result cannot be derived from the original Doi-Edwards theory but from a modified version involving the effect of finite chain length (Milner and McLeish, 1998).

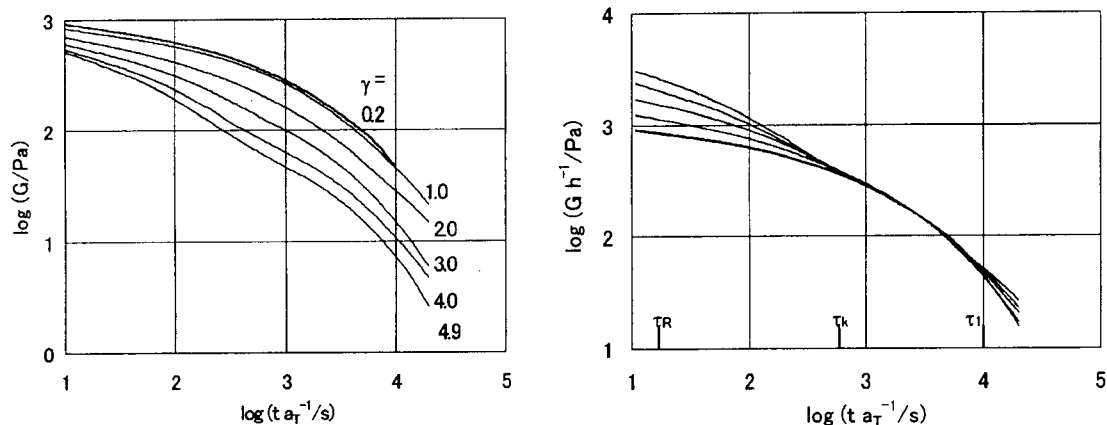


Fig. 1. Shear relaxation modulus, $G(t, \gamma)$, for polystyrene in tricresyl phosphate; $M = 5.48 \times 10^6$ and $c = 0.1 \text{ g cm}^{-3}$. Data were taken at 40°C and reduced to 0°C . $\gamma = 0.2, 1, 2, 3, 4$, and 4.9 from top to bottom (left panel). Curves of $G(t, \gamma)$ shifted vertically by factor h . $G(t, \gamma)$ can be separated as eq. (4) at times longer than a certain time, τ_k (right panel).

The characteristic time determined for some polystyrene solutions could be related with the maximum relaxation time through (Osaki *et al.* 1982),

$$\frac{\tau_1}{\tau_k} = 0.124 \left(\frac{M}{M_e} \right)^{1.5} \quad (7)$$

Equation (7) is consistent with eq. (5) and (6) if τ_k is proportional to τ_R . In the earlier paper, we proposed that τ_k would be about $5\tau_R$ based on some subtle handling of the relaxation spectra.

Since the earlier data were taken for solutions in polychlorinated biphenyl, now prohibited material, we have to start over with other solvents for more extensive study including good data for small deformation. Fortunately, the τ_k values for such solutions taken with an automated fancy apparatus were close enough to those estimated with eq. (7); see Fig. 3. This result may imply that the separability criterion defined earlier for data with a hand driven apparatus with relatively low precision can still be applied.

3. Rouse-like relaxation of entangled polymers

In the meantime we have made some progress in interpretation of the relaxation spectra at small deformations (Inoue and Osaki, 1996). Birefringence measurements carried out in the process of dynamic mechanical measurements revealed that a portion of stress in the glass-to-rubber transition zone is of entropic origin and is associated with the relaxation spectrum like that of the Rouse model; i.e., the power law spectrum proportional to $\tau^{-1/2}$. Such a concept was actually stated by Ferry as the contribution to stress of the chain strand shorter than the entanglement strand (Ferry, 1980). It was adopted also by Doi as the chain motion of relatively short scales within the tube (Doi, 1980). Usually the Rouse-like spectrum is not easy to detect in the mechanical spectrum of polymer melts because it is buried in the large contribution of the glassy stress in the transition zone (Inoue and Osaki, 1996). Birefringence data are required for the analysis. However,

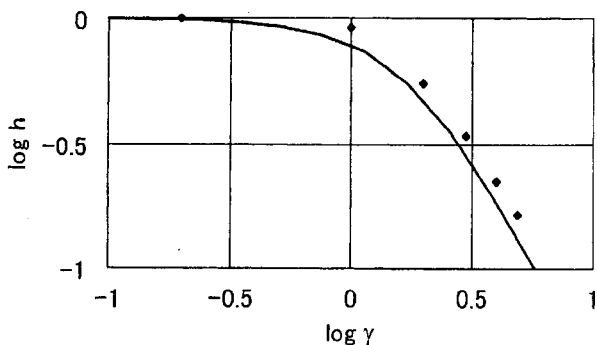


Fig. 2. Damping function, $h(\gamma)$, for the data of Fig. 1. Curve represents Doi-Edwards prediction without independent alignment assumption.

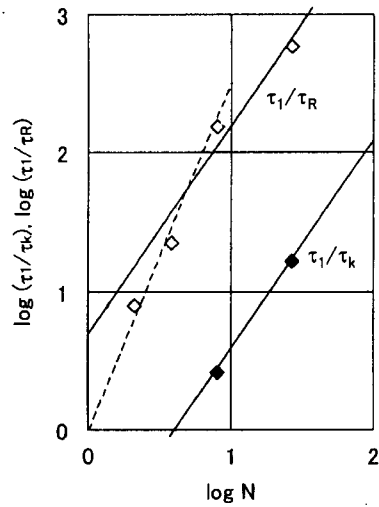


Fig. 3. Characteristic time τ_k and τ_R for polystyrene solutions. Line for τ_k indicates earlier results, eq. (7). Line for τ_R corresponds to a relation $\tau_k = 30\tau_R$. Dashed line indicates a possible variation of τ_1/τ_R at low N .

the glassy component is more affected by dilution than the Rouse contribution is and it becomes relatively small for solutions as seen below.

Fig. 4 gives the complex modulus of the polystyrene solution referred to in Figs. 1 and 2. The measured result can be written as

$$G'(\omega) + iG''(\omega) = \sum_p \frac{G_p i \omega \tau_p}{1 + i \omega \tau_p} \quad (8)$$

The set of parameters G_p and τ_p are shown in Fig. 4. The xs represent the "entanglement" portion of the spectrum and the dots represent the "Rouse" portion. The longest relax-

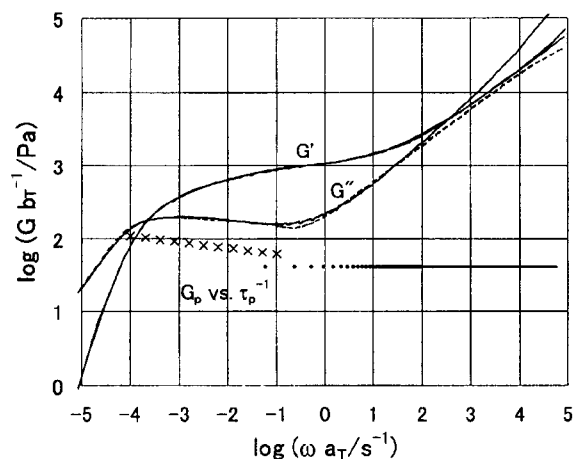


Fig. 4. Complex modulus of polystyrene in tricresyl phosphate; $M = 5.48 \times 10^6$ and $c = 0.1 \text{ g cm}^{-3}$. Thick curves represent data taken at various temperatures and reduced to 0°C . Vertical shift factor, b_T , was approximately proportional to absolute temperature, T . Thin curves represent results of fitting using the relaxation spectrum indicated by xs and dots.

ation times for these portions are regarded as τ_i and τ_R , respectively. The G_p values for the Rouse portion was assumed to be equal to $G_R = cRT/M$. Those for the entanglement portion were determined by curve fitting.

The ratio τ_i/τ_R for the sample of Fig. 4, together with those for a few other samples, is shown in Fig. 3. In contrast with the earlier guess, eq. (7), the ratio is far much larger than the ratio τ_i/τ_k . The result for large N may be described as

$$\tau_k = 30\tau_R \quad (N \gg 1) \quad (9)$$

In the earlier study the factor was guessed as about 5 instead of 30. The discrepancy came from the overestimate of τ_R due to the earlier assumption that τ_i/τ_R would be about 1 at $N = 1$ and the ratio would increase as $N^{1.5}$. The present result revealed that the increase was much stronger at low N , approximately like $N^{2.5}$. Thus the earlier result underestimated τ_i/τ_R at high N .

The present observation is consistent with the known result (Graessley, 1974) that at low N (but larger than 2), the steady shear compliance, J_e , is proportional to the molecular weight, M , while the viscosity, η , is proportional to $M^{3.5}$. Since the maximum relaxation time is approximately proportional to $J_e M^{3.5}$, it may well vary like $N^{4.5}$ at relatively low N .

4. The characteristic times and steady shear flow

4.1. Comparison of Two Characteristic Times, τ_R and τ_k

The characteristic time τ_k is much larger than τ_R . Suppose the former represents the completion of the process associated with the latter as assumed in the Doi theory for the shrink process. Considering the procedure of producing the lower panel of Fig. 1. and the precision of measurement, one may say that τ_k is of the order of $5\tau_R$. The result represented by eq. (9) may imply that the "shrink process" that completes at τ_k is associated with a characteristic time longer than τ_R and accordingly the Doi theory for the shrink process (Doi, 1980) does not correspond to the real process of stress relaxation. The proportionality of eq. (9) seems to indicate the importance of the single chain shrink process as assumed by Doi. The process may be retarded for some unknown reason.

4.2. The Separation Time, τ_k

The characteristic time τ_k defines the time over which the shear relaxation modulus is separable. In view of the tube model theory and our interpretation, the characteristic time τ_k represents the completion of the chain contour length equilibrium. The original Doi-Edwards theory is supposed to be applicable for the rate of shear less than τ_k^{-1} and for times longer than τ_k in any stress relaxation process. In view of the phenomenological model, the single-integral

memory fluid model with strain-dependent memory function seems to have a wider range of applicability than such ranges as defined with the parameter τ_k as seen later.

Suppose the characteristic time τ_k represents the completion of the chain contour length equilibrium. Then the stress cannot be very high at time τ_k in the relaxation process at a fixed shape after any strain history. When the chain contour length is equilibrated, the stress is written as

$$\sigma = G_N \langle \mathbf{u}\mathbf{u} \rangle - p\mathbf{I} \quad (10)$$

Here the quantity with bracket represents the average of the diadic tensor of tangent vector, \mathbf{u} , of tube segment and G_N is the entanglement modulus. The largest possible principal value the tensor is unity and the smallest possible is zero so that the principal values of the deviatoric stress tensor, σ_p , at time τ_k does not exceed G_N . In an earlier paper (Osaki and Kurata, 1980), we wrote it should not exceed $3G_N$ but G_N is more reasonable.

For the same reason, σ_p should not exceed G_N in the steady shear flow at the rate of shear τ_k^{-1} .

$$\sigma_p < G_N \text{ at } \tau_k \text{ time in relaxation; at rate } \tau_k^{-1} \text{ in steady shear} \quad (11)$$

If the orientation is high, i.e., N_1 is much higher than σ , then σ_p should be close to G_N .

An example of relation (10) is given in Fig. 5. The value in steady shear of rate τ_k^{-1} is slightly lower than G_N . Also the value in the relaxation process at $t = \tau_k$ approaches the same value at high rate of shear. Some other data in steady shear gave similar results as seen in Figure 6.

4.3. The Rouse Relaxation time, τ_R

As seen in Fig. 1, the relaxation modulus, $G(t, \gamma)$, at high

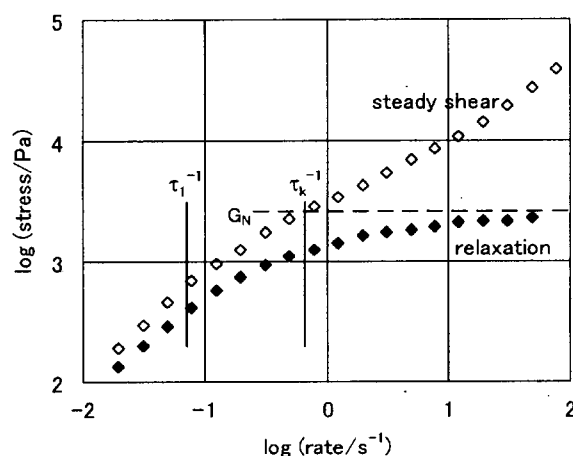


Fig. 5. The highest principal stress in steady shear and at time τ_k in the relaxation process after cessation of steady shear. Data by Crawley (1976) for polystyrene in tricresyl phosphate; $M = 1.8 \times 10^6$, $c = 0.138 \text{ g cm}^{-3}$, 25°C .

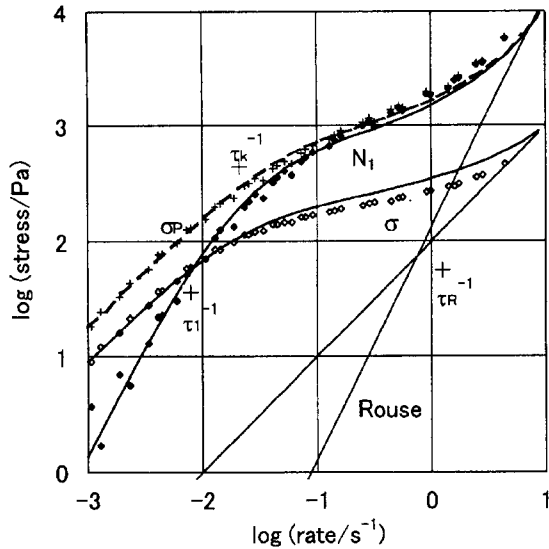


Fig. 6. Shear stress, σ , the first normal stress difference, N_1 , and principal stress, σ_p , in steady shear flow of polystyrene in tricresyl phosphate; $M = 5.48 \times 10^6$ and $c = 0.07 \text{ g cm}^{-3}$. Marks represent data taken at various temperatures and reduced to 0°C . Curves represent prediction of K-BKZ model with memory function obtained from $G(t, \gamma)$. Strain dependence at various times was precisely taken into account. Thin lines represent contribution from the Rouse spectrum similar to one shown by dots in Fig. 4. Big crosses show (τ_1^{-1}, G_1) , (τ_k^{-1}, G_N) , and (τ_R, G_R) , from left.

strain decreases much around the time $t = \tau_R$. Thus τ_R is likely to be related to the shrink process even if it is not the longest time of the process. What else phenomena could we find concerning this characteristic time?

For highly entangled systems, the Rouse relaxation time, τ_R , is very small compared with other times like τ_1 or τ_k . The rate of steady shear as high as τ_R^{-1} is usually not attainable. Fig. 6 shows some stress components in steady shear flow for a system with relatively low degree of entanglement, $N = 7$. It is seen that the curves of $\log(\text{stress})$ vs. $\log(\text{rate})$ exhibit inflection points at the rate approximately equal to τ_R^{-1} . A K-BKZ model calculation seems to indicate that the inflection, or the sharp upturn of stresses at rates higher than , is due to the relaxation modes of Rouse spectrum such as shown by dots in Fig. 4. The Rouse model without any damping predicts that

$$\sigma = \frac{\pi^2}{6} G_R \tau_R \dot{\gamma} \quad (12)$$

$$N_1 = \frac{\pi^4}{45} G_R \tau_R^2 \dot{\gamma}^2 \quad (13)$$

where $G_R = cRT/M$. These are shown with thin lines in Fig. 6.

The assumption that the Rouse modes are not affected by the magnitude of strain is consistent with the data of $G(t, \gamma)$. The present result may indicate that the Rouse modes support the stress of stretched chains at high rates of strain where the shrink process is not allowed.

5. Concluding remarks

The separability criterion of the shear relaxation modulus, $G(t, \gamma)$, for entangled polymers gives a characteristic time, τ_k , which is much larger than but is probably related to the Rouse relaxation time, τ_R . These parameters are reasonably related to some features of stress in steady shear flow.

The same type of study may possibly present some clue in the rheology of branched polymers, where the K-BKZ model seems to be acquiring credits in some experiments (Kasehagen and Macosko, 1998) while a completely different molecular theory is making a rapid progress (Inkson *et al.*, 1999).

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