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Effect of Molecular Weight Distribution on Viscoelastic Properties of Polymers. 2. Terminal Relaxation Time and Steady-State Compliance[†]

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ABSTRACT: The mole-basis blending law for the relaxation spectrum, $H(\tau) = \sum_i x_i H_i(\tau/\lambda_i)$, is presented, which gives better predictions of the terminal viscoelastic properties of polymer blends in the entangled state than does the weight-basis blending law. x_i is the mole fraction of the ith component, $H_i(\tau)$ the relaxation spectrum of the individual pure component i, and λ_i the shift factor of the time scale. The theoretical basis of this law is studied with partial success in the light of the tube model theory by Doi and Edwards. It has been reconfirmed that the lower molecular weight polymers in a binary blend behave like simple solvent molecules against the motion of the higher molecular weight polymers after the disengagement time of the former polymers elapsed.

Introduction

Doi and Edwards[1-3] have recently derived a rheological constitutive equation for highly entangled polymers from the primitive chain model and suggested that, for a mixture of a certain number of components, the memory function $\mu(t)$ involved in the constitutive equation obeys the weight-basis additivity[2]

$$\mu(t) = \sum_i w_i \mu_i(t) \qquad (1)$$

Here, w_i is the weight fraction of the ith component polymer in the mixture and $\mu_i(t)$ is the memory function of the polymer i in the individual pure state. The effect of polydispersity on the steady-state compliance J_e can be estimated from the Doi–Edwards constitutive equation with eq 1 as[4]

$$J_e = C(M_{z+2}M_{z+3}M_{z+4})/(M_w M_z M_{z+1}) \qquad (2)$$

where M's are the average molecular weights of indicated orders and C is a function of the polymer mass per unit volume, ρ, only. Thus J_e is independent of molecular weight for a monodisperse polymer but strongly dependent on the distribution of molecular weight. These are in accord with experiments, at least qualitatively.

Closer inspection, however, reveals a marked discrepancy between the theoretical prediction (2) and the experimental results. For example, let us consider the case in which the molecular weight distribution is represented by the logarithmic-normal distribution. Then we can rewrite eq 2 as

$$J_e = C(M_z/M_w)^9 \qquad (3)$$

with the aid of the well-known relations

$$M_w/M_n = M_z/M_w = M_{z+1}/M_z = M_{z+2}/M_{z+1} = \ldots \qquad (4)$$

On the other hand, the experimental data obtained by various investigators since Leaderman and associates[5,6] are fairly well represented by the empirical equation of Mills[7,8]

$$J_e = C(M_z/M_w)^{3.7} \qquad (5)$$

or by the empirical equation of Agarwal[9]

$$J_e = C(M_z M_{z+1})/(M_n M_w) \qquad (6)$$

The latter equation reduces to $J_e = C(M_z/M_w)^4$ for the logarithmic-normal distribution. Thus the two equations (5) and (6) give practically the same prediction not only for the case of binary blends but also for the continuous broad distribution.

The purpose of this paper is to bridge the existing gap between theory and experiment as exemplified by eq 3 and 5 and to afford a better understanding of the effect of molecular weight distribution on the terminal-zone behavior of highly entangled systems.

Phenomenological Linear-Blending Laws

We start with the classical linear blending law of Ninomiya[10] for a mixture of two monodisperse polymers with molecular weights M_1 and M_2, which may be written as

$$H(\tau) = w_1 H_1(\tau/\lambda_1) + w_2 H_2(\tau/\lambda_2) \qquad (7)$$

Here, $H(\tau)$ is the relaxation spectrum of the mixture, $H_1(\tau)$ and $H_2(\tau)$ are those of the individual pure components, and w_1 and w_2 are the weight fractions. The quantity λ_i (i =

[†] This paper is dedicated to Professor Walter H. Stockmayer on his 70th birthday.

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1 and 2) is the shift factor by which all the relaxation times of a molecule of component i in the mixture are increased relative to their values in the pure state. In this paper, we put $M_2 > M_1$; hence $\lambda_1 > 1$ and $\lambda_2 < 1$.

We assume that the viscosity η_i and the steady-state compliance J_{ei} of the pure component i are related to the molecular weight M_i as

$$\eta_i = \int_0^\infty H_i(\tau)\,\mathrm{d}\tau = AM_i^3 \tag{8}$$

$$\theta_i = \int_0^\infty \tau H_i(\tau)\,\mathrm{d}\tau = BM_i^6 \tag{9}$$

$$J_{ei} = \theta_i/\eta_i^2 = C \tag{10}$$

where A, B, and C are functions of the polymer mass per unit volume, ρ. Substitution of these expressions for H_i into eq 7 yields

$$\eta = \int_0^\infty H(\tau)\,\mathrm{d}\tau = A(w_1\lambda_1 M_1^3 + w_2\lambda_2 M_2^3) \tag{11}$$

$$\theta = \int_0^\infty \tau H(\tau)\,\mathrm{d}\tau = B(w_1\lambda_1^2 M_1^6 + w_2\lambda_2^2 M_2^6) \tag{12}$$

If λ_i is assumed to be

$$\lambda_i = (M_w/M_i)^2 \qquad (i = 1, 2) \tag{13}$$

we obtain

$$\eta = AM_w^3 \tag{14a}$$

$$\theta = BM_w^5 M_z \tag{14b}$$

and

$$J_e = \theta/\eta^2 = C(M_z/M_w) \tag{15}$$

On the other hand, if λ_i is assumed to be

$$\lambda_i = M_w/M_i \tag{16}$$

we obtain

$$\eta = AM_w^2 M_z \tag{17a}$$

$$\theta = BM_w^3 M_z M_{z+1} M_{z+2} \tag{17b}$$

and

$$J_e = C(M_{z+1}M_{z+2})/(M_w M_z) \tag{18}$$

The predictions of eq 15 and 18 are compared with the experimental results of Mills and Nevin[11] in Figure 1, which were obtained for mixtures of two narrow-distribution polystyrenes with $M_{1w} = 8.68 \times 10^4$ and $M_{1w}/M_{1n} = 1.15$ and with $M_{2w} = 5.00 \times 10^5$ and $M_{1w}/M_{1n} = 1.18$. Since the entanglement spacing M_e of this polymer is about 2.0×10^4, the mixtures are in a fully entangled state over the entire range of w_2. The circles in the figure represent the experimental values of J_e, the dotted line represents the prediction of eq 15, and the dash–dot line represents the prediction of eq 18. Equation 15 underestimates the polydispersity effect over the entire range of w_2, and eq 18 underestimates the effect at high values of w_2, though it predicts the peak height almost correctly.

A refinement of the situation can be based on the mole-basis additivity

$$H(\tau) = x_1 H_1(\tau/\lambda_1) + x_2 H_2(\tau/\lambda_2) \tag{19}$$

where x_i represents the mole fraction of component i in the blend. This equation if combined with eq 16 leads to

$$\eta = AM_n M_w^2 \tag{20}$$

and to the Agarwal equation (6) of J_e. The prediction of eq 6 is also shown in Figure 1 by the solid line.

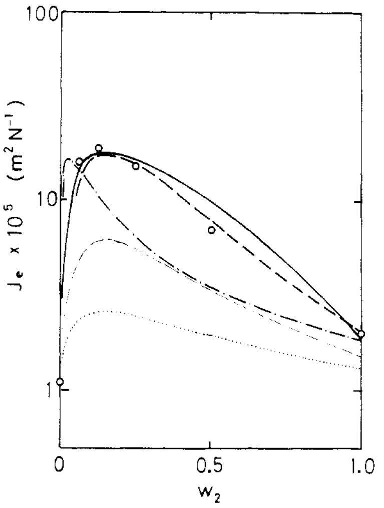

Figure 1. Steady-state compliance J_e plotted against the weight fraction of high molecular weight component w_2 for binary blends of undiluted polystyrenes ($M_1 = 8.68 \times 10^4$ and $M_2 = 5.00 \times 10^5$). Circles denote the experimental values of Mills et al.;[11] solid line, eq 6; thick dashed line, eq 47; thin dashed line, eq 45; dash–dot line, eq 18; dotted line, eq 15.

We have employed so far a set of equations (8), (9), and (10) as the basis of analysis, because these equations are compatible with the Doi–Edwards theory for a monodisperse polymer and are convenient for later use in molecular theoretical discussions. On the other hand, it has been established experimentally for narrow-distribution polymers that the molecular weight dependences of η_i, θ_i, and J_{ei} obey

$$\eta_i = AM_i^{3.5} \tag{21a}$$

$$\theta_i = BM_i^7 \tag{21b}$$

and

$$J_{ei} = C \tag{21c}$$

rather than eq 8–10. The weight-basis equation (7), if combined with eq 21, yields

$$\lambda_i = (M_w/M_i)^{2.5} \tag{22a}$$

$$\eta = AM_w^{3.5} \tag{22b}$$

and

$$J_e = C(M_z/M_w) \tag{22c}$$

while the mole-basis equation (19) yields

$$\lambda_i = (M_w/M_i)^{1.5} \tag{23a}$$

$$\eta = AM_n M_w^{2.5} \tag{23b}$$

and

$$J_e = C(M_z M_{z+1})/(M_n M_w) \tag{23c}$$

The η-equation (22b) has been repeatedly confirmed by various investigators. However, it is also true that the η vs. M relation has been often expressed in terms of the viscosity-average molecular weight M_v as $\eta = AM_v^{3.5}$. Since M_v is somewhere between M_n and M_w, the viscosity equation (23b) seems as acceptable as in (22b). Experimental discrimination between these two equations may not be an easy task.[27] Thus in view of the predicted behavior of J_e and also of λ_2, which will be shown later, we conclude that the mole-basis blending law, eq 19, is the best choice among various forms of linear-blending law.

Primitive Chain Model for Polydisperse Systems

In the primitive chain model, each polymer chain moves independently in the mean field imposed by the other chains. The mean field is represented by a tube with a uniform diameter a and an arc length L. The center path of the tube is called the primitive chain, which represents the large-scale configuration, both static and dynamic, of the real chain confined in the tube. Thus, the primitive chain is essentially a freely jointed chain of steps with length a and its mean square end-to-end length is given by La. The same quantity is also expressed as N_0b^2 in terms of the effective bond length b and the number of skeletal atoms of the real chain, N_0. Hence we have

$$L/a = N_0(b/a)^2 \tag{24}$$

As the quantity L/a represents the number of entanglements per molecule, we can also put

$$L/a = M/M_e \tag{25}$$

where M is the molecular weight of the polymer and M_e is the entanglement spacing. Our recent experiments[12] on polystyrene solutions have indicated that

$$\rho M_e = 2 \times 10^4 \text{ g cm}^{-3}, \qquad \rho \geq 0.3 \text{ g cm}^{-3} \tag{26a}$$

$$\rho^{1.4}M_e = 1.23 \times 10^4 \text{ (g cm}^{-3})^{1.4}, \qquad \rho \leq 0.3 \text{ g cm}^{-3} \tag{26b}$$

Thus we obtain

$$a^2 = (N_0b^2)(M_e/M) \propto \rho^{-\nu}M^0 \tag{27}$$

with

$$\nu = 1.0 \quad \text{in the concentrated region} \tag{28a}$$

$$\nu = 1.4 \quad \text{in the semidilute region} \tag{28b}$$

The similar dependence of a on ρ and M has been suggested theoretically.[13]

According to Doi and Edwards,[1] the stress-relaxation modulus $G(t)$ after a sudden small shear deformation is given for a monodisperse polymer by

$$G(t) = (1/5)G_0\mu(t) \tag{29}$$

where

$$G_0 = 3cRT(L/a) = 3\rho RT/M_e \tag{30}$$

$$\mu(t) = \sum_{p\,\text{odd}} (8/p^2\pi^2) \exp(-tp^2/T_d) \tag{31}$$

Here, c is the polymer mole in unit volume, ρ the polymer mass in unit volume, R the gas constant, T the absolute temperature, and L the arc length of the primitive chain. The disengagement time T_d is given as

$$T_d = L^2/D\pi^2 \tag{32a}$$

$$D = kT/N_0\zeta_0 \tag{32b}$$

where D is the curvilinear diffusion coefficient and ζ_0 is the friction coefficient per skeletal atom of the polymer chain. Using the independent alignment approximation, Doi and Edwards[2] have derived a rheological constitutive equation which, for example, yields the following equation for the zero-shear-rate viscosity:

$$\eta = (1/5)G_0 \sum_{p\,\text{odd}} (8/p^4\pi^2)T_d = (\pi^2/60)G_0T_d \tag{33}$$

Extension of these treatments of a monodisperse polymer to a polydisperse polymer is straightforward, provided that the entanglement spacing M_e is not affected by blending different molecular weight polymers at a given total polymer mass, $\rho = \sum_i \rho_i$, in unit volume. Under the condition, eq 29 can be rewritten as

$$G(t) = (1/5)\sum_i G_{0i}\mu_i(t) \tag{34}$$

where

$$G_{0i} = 3c_iRT(L_i/a) = 3\rho_iRT/M_e = w_iG_0 \tag{35}$$

The combination of eq 34 with eq 35 gives eq 1.

In the process of stress relaxation following a sudden deformation, polymer chains of lower molecular weight component 1 in a binary blend recovery their equilibrium conformations after the disengagement time T_{d1} elapsed, and thereafter the polymer chains 1 become ineffective in restricting polymer chains of the other component 2 within the deformed tube. In other words, the reptation of the higher molecular weight polymers 2 occurs within the tube imposed by the polymers 2 only. Under the circumstances, the tube parameters applicable to the polymers 2 are given as

$$L_2/a_2 = w_2^{\nu}(M_2/M_e) \tag{36}$$

$$a_2^2 = w_2^{-\nu}(N_0b^2)(M_e/M_2) \tag{37}$$

where M_e represents the entanglement spacing given by eq 26 and ν the index given by eq 28. Combining eq 36 with eq 37 to get L_2 and substituting it into eq 32, we obtain

$$\lambda_2 = w_2^{\nu} \tag{38}$$

Expression 35 for the intensity factor G_{02} is also modified as

$$G_{02} = w_2^{1+\nu}G_0 \tag{39}$$

Since $\lambda_1 = 1$ in the above treatment, we get

$$\mu(t) = (1 - w_2^{1+\nu})\mu_1(t) + w_2^{1+\nu}\mu_2(t/\lambda_2) \tag{40}$$

instead of eq 1. The relaxation spectrum $H(\tau)$ for highly entangled systems with $\nu = 1$ is then obtained as

$$H(\tau) = (1 - w_2^2)H_1(\tau) + w_2^2H_2(\tau/\lambda_2) \tag{41}$$

If $M_2 \gg M_1$, we can put

$$w_2 \doteq M_w/M_2 \tag{42a}$$

$$x_2 \doteq w_2(M_n/M_2) \tag{42b}$$

over a fairly wide range of composition that $M_1/M_2 \ll [w_2/(1 - w_2)] \ll M_2/M_1$. Hence, we get eq 16 for λ_2 and

$$w_2^2 \doteq x_2(M_w/M_n) \tag{43}$$

Thus the tube-model blending law, eq 41, can be put in a closely related form to the mole-basis linear-blending law, eq 19, though cannot be identified with it.

Discussion

The strong dependence of J_e on the polydispersity is also derivable from the so-called high-order blending law as shown in the previous paper.[14] For example, the quadratic law proposed by Boque et al.[15] has the form

$$H(\tau) = w_1^2H_1(\tau/\lambda_1) + 2w_1w_2H_{12}(\tau/\lambda_{12}) + w_2^2H_2(\tau/\lambda_2) \tag{44}$$

and yields

$$\lambda_i = (M_w/M_i)^{1.5} \tag{45a}$$

$$\eta = AM_w^{3.5} \tag{45b}$$

and

$$J_e = C(M_z/M_w)^2 \tag{45c}$$

with the aid of some assumptions on H_{12} and λ_{12}. The cubic-power law has the form

$$H(\tau) = w_1^3 H_1(\tau/\lambda_1) + 3w_1^2 w_2 H_{112}(\tau/\lambda_{112}) + 3w_1 w_2^2 H_{122}(\tau/\lambda_{122}) + w_2^3 H_2(\tau/\lambda_2) \quad (46)$$

and yields

$$\lambda_i = (M_w/M_i)^{0.5} \quad (47a)$$

$$\eta = AM_w^{3.5} \quad (47b)$$

and

$$J_e = C(M_z/M_w)^3 \quad (47c)$$

The second term in eq 41 is the same as the last term in eq 44, and it predicts J_e to be proportional to w_2^{-2} in the range $w_2 \gg w_1$ of binary blends or to ρ^{-2} in concentrated solutions of a monodisperse polymer. The cubic-power equation (46) predicts J_e to be proportional to w_2^{-3} or ρ^{-3}. Both the inverse-square and -cubic dependences of J_e on w_2 or ρ have been found experimentally,[16-22] though the former has been more widely accepted.

The prediction of J_e by eq 45 and 47 is compared with the experimental data of Mills and Nevin in Figure 1. Equation 45 underestimates the polydispersity effect, whereas eq 47 predicts it almost correctly. However, the terminal shift factor $\lambda_2 = (M_w/M_2)^{1.5}$ in eq 45 is more favorably compared with the experimental data[20,28] than is the factor $\lambda_2 = (M_w/M_2)^{0.5}$ in eq 45. Thus under the prerequisite that the viscosity is written as $\eta = AM_w^{3.5}$ in terms of M_w alone, we cannot incorporate two large polydispersity effects on J_e and λ_2 into a simple additive form of $H(\tau)$. For the purpose, it seems unavoidable to relax the prerequisite for η, as exemplified by eq 23 for the mole-basis additivity of $H(\tau)$.

The introduction of the symmetrical cross terms into the high-order blending laws as is done in eq 44 and 46 is also a necessary procedure to get the viscosity equation expressed in terms of M_w only. However, this makes the spectrum $H(\tau)$ diffusive, yielding a structureless curve for the dynamic or relaxation modulus, in contrast to the established experimental results.[19,21,23] In this respect, the two-term form of eq 41 seems superior to the three-term form of eq 45, and the former again leads to a more complicated viscosity equation than the latter. The blending laws with asymmetric form have been suggested theoretically by Graessley[24,29] and empirically by Prest.[25]

In conclusion, I present here two new blending law, eq 19 and 41, both being slightly in conflict with the widely accepted viscosity law, $\eta = AM_w^{3.5}$. There is still the unsettled question concerning the role of shorter chains in the formation of the tube field against the movement of longer chains. In an extreme interpretation, the short chains 1 are expected to fully cooperate with the long chains 2 for supporting the tube wall till the reorganization time T_R, apparently proportional to M_1^5, is attained.[26] The tube diameter a remains unchanged after the disengagement time T_{d1} for the short chains elapsed. In the other extreme, we expect the shorter chains to behave like solvents in the terminal region of time around T_{d2}, as has been pointed out by Masuda et al.[19] The present analysis has been developed along the latter interpretation.

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