On a Blending Law for Two-Component Blends of Narrow-Distribution Polystyrene Components

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Synopsis

A model, which has previously been described for relating rheological behavior in highly polydisperse polymers to molecular structure, is shown to lead to a unique blending law. Unlike previously published polynomial blending laws in the open literature, no adjustable parameters or shift factors are necessary. The blending law suggested by the model is of the form

$$H(\tau) = W_1[W_1(H_1)^{1/(a-1)} + W_2(H_2/\phi)^{1/(a-1)}]^{(a-1)}$$
$$+ W_2[W_2(H_2)^{1/(a-1)} + W_1(H_1\phi)^{1/(a-1)}]^{(a-1)}$$

where ϕ is defined by the molecular weights of the components and the relaxation time, τ. Good agreement between predictions of this blending law and experimental results from the literature are demonstrated. This good agreement between the experimental results for blends of narrow molecular weight distribution samples and the predictions of blending law gives further credence to the previously reported relationships to describe the effects of polydispersity on the rheological behavior. However, because of the complexity of the blending law in terms of the relaxation spectra, it is concluded that the description in terms of molecular weight is simpler and perhaps more fundamental.

INTRODUCTION

In order to account for the rheological behavior of polydisperse samples of commercial interest, a number of researchers[1-5] have investigated the more simple case of two-component blends of essentially monodisperse materials of differing molecular weight. From these studies were obtained blending laws ranging from linear to cubic; the ultimate goal being the description of highly polydisperse samples. Most, if not all, these blending laws involved empirical shift factors, in order to fit the data.

More recently a somewhat different approach to the description of the rheological behavior of high-molecular weight polymeric materials has been put forth.[6-11] This approach emphasized the relationships of rheological behavior directly to molecular structure, primarily to molecular weight distribution in polydisperse samples of polyethylene and polystyrene. The present communication will demonstrate the form of the blending law for two-component blends of essentially monodisperse materials, and compare predictions of this blending law with experimental data in the open literature. The blending law obtained will contain no empirical shift factors or adjustable parameters. Consequently, the fit to the experimental data on the blends will be taken as a rigorous test of the phenomenological ideas

developed for highly polydisperse samples, which used the somewhat un-
reliable technique of gel permeation chromatography to correlate with rheo-
logical data.

MODEL DEVELOPMENT

The fundamental assumption for this model is that the effect of shear
rate is to progressively cut off the relaxation spectrum with shear rate. The
longest resulting relaxation time at a given shear rate and temperature
will be denoted $\tau_c(\dot{\gamma})$, and it will be taken to represent the longest relaxation
time associated with a molecule of molecular weight, M_c. The relationship
between τ_c and M_c will be assumed to be of the form[12]

$$\tau_c = \alpha(M_c)^a \tag{1}$$

where a is the exponent in the zero shear rate-molecular weight relation-
ship.

$$\eta_0 = K(\overline{M}_w)^a \tag{2}$$

Implications of these ideas are schematically represented in Figure 1. Since
essentially monodisperse samples differ most in their terminal zones, Figure
1 suggests that the two samples represented will be rheologically indistin-
guishable at the shear rate represented. Amplifying on this point, the vis-
cosity from linear viscoelasticity theory and our assumption on the effect
of shear rate can be represented by

$$\eta(\dot{\gamma}) = \int_0^{\tau c(\gamma)} H d\tau \tag{3}$$

Therefore, at shear rates where the relaxation spectra of a series of essen-
tially monodisperse samples are truncated, the viscosities should be equiv-
alent. Similar results for η as a function of $\dot{\gamma}$ to the schematic representation
in Figure 1 are indeed found[13] for very narrow MWD polystyrene materials,
where all molecular weight species undergoing non-Newtonian flow at a
given shear rate have the same viscosity. Results similar to the schematic
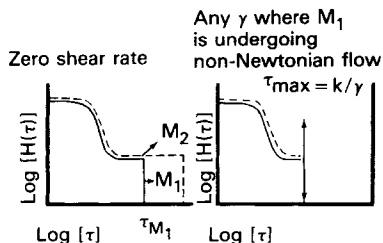representation in Figure 2 are found[2] for narrow fractions.

Fig. 1.   Schematic reprsentations of the effects of steady shearing on the relaxation spectrum
for two monodisperse materials of molecular weight M_1 and M_2, where $M_2 > M_2$.
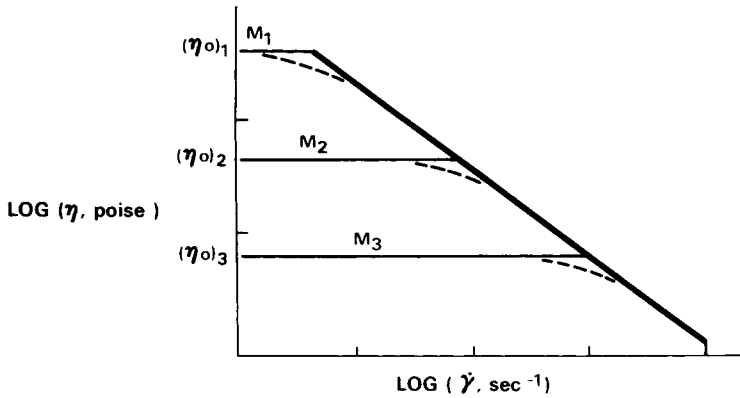
Fig. 2. Schematic showing effects of shear rate on the viscosity for essentially monodisperse samples of molecular weights M_1, M_2, and M_3 where $M_3 < M_2 < M_1$.

Assuming a similar truncation takes place in polydisperse samples as a function of shear rate, we are led to the following description of viscosity.

$$\eta(\dot{\gamma}) = K(\overline{M}_w{}^*)^a \tag{4}$$

where $\overline{M}_w = \sum_{i=1}^{c-1} W_i M_i + M_c A$ and $A = \sum_{i=c}^{\infty} W_i$

From Equations (1), (3), and (4), we can calculate[7] $H(\tau)$ as a function of molecular weight distribution as

$$H(\tau_c) = \frac{K}{\alpha}\left(\frac{\overline{M}_w{}^*}{M_c}\right)^{(a-1)} A \tag{5}$$

Equation (5) has been used[7] to calculate the relaxation spectrum directly from the molecular weight distribution (MWD). Comparisons of calculations and experimental results for a broad MWD polyethyelene (Fig. 3) and a narrow MWD polystyrene material (Fig. 4) show good agreement between experiment and theory, considering the limitations in the determinations of the MWD.

A blending law for two narrow MWD components can be derived from
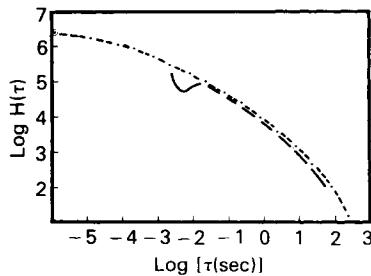

Fig. 3. Comparison of predictions (−•−) with experimental data (− −)for a broad MWD polyethylene.
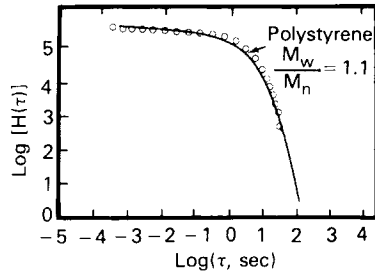
Fig. 4. Comparison of the relaxation spectrum, predicted from Eq. (5) (○) and molecular weight, with that experimentally determined (—) for a narrow MWD polystyrene[1] having $\overline{M}_w$ = 411,000 and $\overline{M}_w/\overline{M}_n$ < 1.1.

Eq. (5). Later predictions based on this blending law will be compared to experimental data. From Eq. (5)

$$H_1(\tau_c) = \frac{K}{\alpha}\left(\frac{M_1{}^*}{M_c}\right)^{(a-1)} A_1 \tag{6}$$

and

$$H_2(\tau_c) = \frac{K}{\alpha}\left(\frac{M_2{}^*}{M_c}\right)^{(a-1)} A_2 \tag{7}$$

We also note that $M^{\cdot}{}_w = M_1 \cdot W_1 + M_2 \cdot W_2$ and $A = A_1 W_1 + A_2 W_2$ where W_1 and W_2 represent the weight fractions of the components of the blend.

From Eqs. (5), (6), and (7) we arrive at

$$H = W_1\left[W_1(H_1)^{1/(a-1)} + W_2\left(H_2\frac{A_1}{A_2}\right)^{1/(a-1)}\right]^{(a-1)}$$
$$+ W_2\left[W_2(H_2)^{1/(a-1)} + W_1\left(H_1\frac{A_2}{A_1}\right)^{1/(a-1)}\right]^{(a-1)} \tag{8}$$

RESULTS AND DISCUSSION

The form of the blending law represented in Eq. (8) does not resemble any of the linear or higher order polynomial blending laws given by Ferry.[14] The form of Eq. (8) is, however, not particularly useful, since it contains the "A" terms, which for each sample in the blend represent the weight fraction of species having molecular weights greater than τ_c for each component. If the assumption of log-normal distributions and polydispersities of 1.1 are made from the components, it can be shown that over most of the range of τ

$$\frac{A_2}{A_1} = \exp\left[1.1\,(M)^2\left(\frac{1}{M_1{}^2} - \frac{1}{M_2{}^2}\right)\right] \tag{9}$$

We will also assume a in Eq. (8) is equal to 3.4 and $\tau = aM^{3.4}$, where α has previously[9] been evaluated to be 2.73×10^{-19}. Consequently, a more usable form of Eq. (8) is

$$H(\tau) = W_1 \left[W_1(H_1)^{1/2.4} + W_2(H_2/\phi)^{1/2.4} \right]^{2.4}$$
$$+ W_2 \left[W_2(H_2)^{1/2.4} + W_1(H_1\phi)^{1/2.4} \right]^{2.4}$$

where

$$\phi = \exp\left[9.15 \times 10^{10} \left(\left(\frac{1}{M_1}\right)^2 - \left(\frac{1}{M_2}\right)^2 \right)(\tau)^{0.59} \right] \qquad (10)$$

Comparison of predictions of Eq. (10) with the experimental data of Prest[1] for polystyrene blends is given in Figure 5. This agreement appears quite good.

Perhaps a more rigorous test of the blending law, particularly of the terminal relaxation spectrum, is to compare predictions of steady-state compliance. In principle, one should be able to simply use Eq. (8) and the usual[15] linear viscoelastic expression for the steady shear compliance, J_e°, to obtain J_e° for the blend, where J_e° is given by

$$J_e^0 = \int_0^\infty H\tau d\tau /(\eta_o)^2 \qquad (11)$$

In order to perform the integration as indicated in Eq. 11, some simplifications are necessary to Eq. (8). The simplifications are discussed further in the Appendix, where the terms involving the ratios of "A"'s are those involving approximations. The simplified result is

$$J_e^\circ = W_1 \left(\frac{M_1}{W_1M_1 + W_2M_2}\right)^{6.8} J_1^\circ \left[W_1 + W_2\left(\frac{M_2}{M_1}\right)^{2.1} \right]^{2.4}$$
$$+ W_2 \left(\frac{M_2}{W_1M_1 + W_2M_2}\right)^{6.8} J_2^\circ \left[W_2 + W_1\left(\frac{M_1}{M_2}\right)^{2.1} \right]^{2.4} \qquad (12)$$

where the component 2 has the higher molecular weight and a is taken as equal to 3.4.

Comparison of predictions in Eq. (12) with published experimental data of Akovali[16] and Mills and Nevin[17] is made in Figures 6 and 7.

This agreement appears to be quite remarkable, in view of the lack of adjustable empirical shift parameters.[14] Equation (12) contains no adjustable parameters, and the only empirical parameter that has been used is the empirical zero shear-$\overline{M}_w$ exponent, taken to be equal to 3.4. While an effective blending law, in terms of the relaxation spectra or rheological
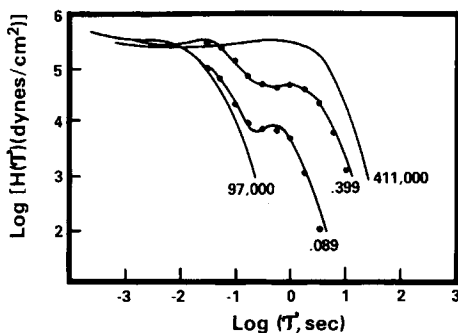
Fig. 5. Comparison of blending law predictions [Eq. (10)] with the experimental data of Prest[1] for blends of narrow MWD polystyrenes having molecular weights of 411,000 and 97,000. Predictions are the solid circles and the solid lines are the data of Prest. The two blends are for 0.089% and 0.399% of the higher molecular weight component as indicated.

properties of the components, has been demonstrated, it would appear that a more simple blending law for multicomponent blends or polydisperse samples is obtained in terms of molecular weights; this is the form as given in Eq. (5).

The proposed blending law given here appears to resemble the expression given by Montfort, et al.,[15] in that these authors also suggest a weighted sum of the pure component properties raised to fractional powers. However, closer inspection reveals some interesting differences. Montfort expresses the blend in terms of $G^*(\omega)$ and $\eta^*(\omega)$ instead of $H(\tau)$ as done here. Comparison of the two results is not easily made, since the exact integration of Eq. (8), using the usual linear viscoelastic relationships is not feasible. However, an approximate comparison can be made using η^*, if one accepts the approximate correspondence of η^* and η for $\omega = \dot{\gamma}$. Equation (4) with $a = 3.4$ suggests that

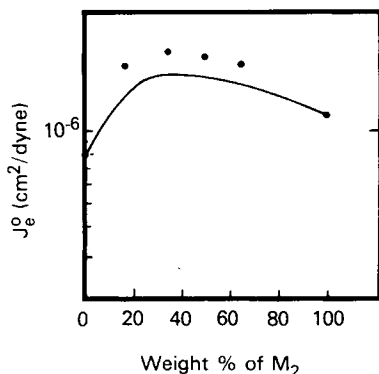$$(\eta_b)^{1/3.4} = (1 - \phi)(\eta_1)^{1/3.4} + \phi(\eta_2)^{1/3.4}, \tag{13}$$

Weight % of M_2

Fig. 6. Comparison of predictions of Eq. (12) (solid line) with experimental data[15] for a blend of narrow MWD polystyrene having $\overline{M_w}$'s of 125,000 and 267,000.
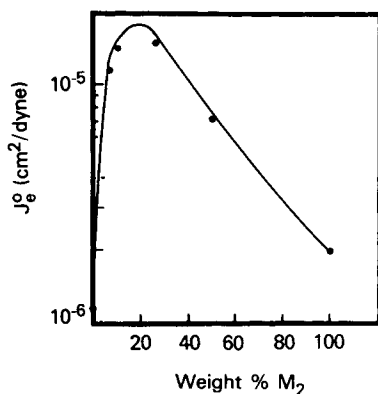
Fig. 7. Comparison of predictions of Eq. (12) (solid line) with experimental data[16] for a blend of narrow MWD polystyrene having $\overline{M}_w$'s of 500,000 and 87,000.

which is valid at any shear rate. From the assumption that $\eta(\dot{\gamma}) \simeq \eta^*(\omega)$ for $\omega = \dot{\gamma}$, one obtains

$$(\eta_b{}^*)^{1/3.4} = (1 - \phi)(\eta_1{}^*)^{1/3.4} + \phi(\eta_2{}^*)^{1/3.4} \tag{14}$$

Montfort et al.,[5] however, only obtain this result in the limit $\omega \rightarrow 0$. Otherwise they obtain

$$(\eta_b{}^*)^{1/3.4} = (1 - \alpha)(\eta_1{}^*)^{1/p} + \alpha(\eta_2{}^*)^{1/p} \tag{15}$$

such the p was found to be approximately 10 and α was a function of ϕ, the ratio of the molecular weights of the components, and the parameter p. Therefore, while Eq. (14) is based on an approximate relationship between η^* and η, the apparent differences in Eqs. (14) and (15) suggest some fundamental differences. One additional difference is the adjustable parameter p used by Montfort et al., whereas the present blending law contains no adjustable parameters; the parameters a and α, the zero shear viscosity molecular weight exponent and the constant between τ and M, in Eq. (10) are well defined from experiments on either individual component, and are not adjustable in the blending law relationship.

CONCLUSIONS

A model previously developed to relate rheological behavior for polydisperse samples directly to molecular structure is shown to lead to a unique blending law. Unlike most published blending laws, the one presented here contains no empirical shift parameters. Remarkable agreement, in that no adjustable parameters are involved in the current blending law, is obtained between experimental data for the relaxation spectra and steady-shear elastic compliance of two-component blends of narrow molecular weight polystyrene and predictions of the blending law presented here. This good agreement for blends of narrow MWD materials is taken as lending credence to the model previously put forth for highly polydisperse samples, and

suggests that it is capable of describing the effects of polydispersity on rheology for samples ranging from essentially monodisperse blends to highly polydisperse samples of commercial interest. Because of the complexity of these blending laws, it is concluded that the description of blends in terms of molecular weight is simpler and more fundamental than blending laws involving the relaxation spectrum.

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APPENDIX

Simplified Version of the Blending Law that is Suitable for Integration

Integration of Eq. (10) to give the steady-shear compliance for the blend in terms of the components does not seem feasible without simplification. For a log normal MWD having a polydispersity of 1.1, the following relationship is a good approximation.

$$A_2 \alpha (H)^{0.51} \tag{A.1}$$

for the long-time relaxation part of the relaxation spectrum. Eq. (8) therefore becomes

$$H = W_1[W_1(H_1)^{1/2.4} + W_2(H_2)^{.49}(H_1)^{0.51})^{1/2.4}]^{2.4}$$
$$+ W_2[W_2(H_2)^{1/2.4} + W_1((H_2)^{0.49}(H_1)^{0.51})^{1/2.4}]^{2.4} \tag{A.2}$$

In order to facilitate the integration, a relationship is needed between H_1 and H_2 at the terminal relaxation end at the same τ For the log normal MWD the following approximate relationship can be used for the terminal relaxations.

$$H_2(\tau)^{3.03} \tag{A.3}$$

or

$$\mathrm{H}_1 = H_2(\tau_1/\tau_2)^{3.03} \tag{A.4}$$

or

$$H_1 = H_2(M_1/M_2)^{3.03\ (3.4)} \tag{A.5}$$

This relationship, together with Eq. (A.2) and Eq. 11 of the text allows us to integrate and obtain Eq. (12) of the text.