# Influence of molecular weight distribution on viscoelastic constants of polymer melts in the terminal zone. New blending law and comparison with experimental data

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*(Received 9 January 1987; revised 17 March 1987; accepted 23 March 1987)*

A new blending law for the viscoelastic constants of polymer melts in the terminal zone is proposed on the basis of the well known power law for viscosity ($\eta_0 \sim M_w^a$) and a simple assumption of the dependence of the weight-average relaxation time on molecular weight distribution. This blending law reduces to the modified Rouse model if the exponent $a$ takes the value of 3. The recoverable compliance of binary blends can be calculated as a function of zero-shear viscosities and recoverable compliances of their components and of parameter $a$. Measurements have been carried out on binary blends of nearly monodisperse PS melts. For these results as well as for various experimental data from the literature, satisfactory agreement between calculated and experimental values of the recoverable compliance has been observed. The blending law is extended to polymer melts with continuous molecular weight distribution.

**(Keywords: linear viscoelasticity; polymer melt rheology; steady-state recoverable compliance; zero-shear viscosity; weight-average relaxation time; molecular weight distribution)**

## THEORETICAL BACKGROUND

The linear viscoelastic properties of narrow-molecular weight distribution (*MWD*) polymer melts have long been widely studied. It has been found that above a critical molecular weight $M_c$ the zero-shear viscosity of such a melt is given by:

$$\eta_0 = KM^a \tag{1}$$

where $a$ is approximately 3.4, $K$ is a constant and $M$ is the weight-average molecular weight[1].

On the other hand, the zero-shear recoverable compliance $J_e^0$ is independent of molecular weight when $M$ is higher than a critical molecular weight $M_c'$.

The values of $M_c$ and $M_c'$ are related to $M_e$, the average molecular weight between entanglements by the following approximate relations: $M_c \simeq 2M_e$ and $M_c' \simeq 3M_c = 6M_e$.

The product of the viscoelastic constants in the terminal zone defines a characteristic time $\tau_w$, the weight-average relaxation time[2]:

$$\tau_w = \eta_0 J_e^0 \tag{2}$$

Experimentally, both $\eta_0$ and $J_e^0$ can be obtained from the dynamic moduli $G''$ and $G'$ at low frequencies[1]:

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{3}$$

$$J_e^0 = \lim_{\omega \to 0} \frac{G'(\omega)}{G''(\omega)^2} \tag{4}$$

However, industrial polymers are always polydisperse, so that the influence of polydispersity on linear viscoelastic properties has been the subject of numerous studies.

In order to investigate the influence of polydispersity, blends of two monodisperse polymers may be used in preference to broad *MWD* polymers, since the *MWD* for these systems is relatively simple and can be well controlled.

For a blend of two monodisperse polymers with molecular weights $M_1$ and $M_2$, the following average molecular weights can be easily calculated:

$$M_n = \frac{1}{\dfrac{\phi_1}{M_1} + \dfrac{\phi_2}{M_2}} \tag{5}$$

$$M_w = \phi_1 M_1 + \phi_2 M_2 \tag{6}$$

$$M_z = \frac{\phi_1 M_1^2 + \phi_2 M_2^2}{\phi_1 M_1 + \phi_2 M_2} \tag{7}$$

$$M_{z+1} = \frac{\phi_1 M_1^3 + \phi_2 M_2^3}{\phi_1 M_1^2 + \phi_2 M_2^2} \tag{8}$$

where $\phi_i$ and $M_i$ are respectively the volume fraction (identical here with weight fraction) and the molecular weight of component $i$.

It is well known that if $M_2 > M_1 > M_c$ the zero-shear viscosity of binary blends or polymers with continuous *MWD*, varies as a constant power of the weight-average molecular weight $M_w$, and is otherwise independent of molecular weight distribution[1,3,4]. The same value of the exponent as that for monodisperse polymers is found.

0032-3861/87/091577-06$03.00

Therefore:

$$\eta_{0b}=KM_w^a \tag{9}$$

Or, using equations (1) and (6):

$$\eta_{0b}=(\Sigma\phi_i\eta_{0i}^{1/a})^a \tag{10}$$

where $\eta_{0b}$ is the zero-shear viscosity of the blend and $\eta_{0i}$ the zero-shear viscosity of component $i$.

Contrary to zero-shear viscosity, it is found that zero-shear recoverable compliance $J_e^0$ is very sensitive to *MWD*, especially at the tail of the distribution at high molecular weights. It has been observed that the $J_{eb}^0$ values for blends are always higher than the $J_e^0$ value for monodisperse samples, and that for binary blends $J_{eb}^0$ goes through a maximum when plotted against relative concentration of components.

Various blending laws relating $J_{eb}^0$ and *MWD* have been proposed; they take the general form[2]:

$$J_{eb}^0=J_e^0 P \tag{11}$$

where $J_e^0$ is the recoverable compliance for monodisperse samples with $M>M_c'$, and $P$ is a factor taking into account the effect of polydispersity and depending on the model being considered.

The quadratic blending law of Bogue[5] can be written as:

$$J_{eb}^0=J_e^0\left(\frac{M_z}{M_w}\right)^2 \tag{12}$$

A similar law has been proposed by Mills[6]:

$$J_{eb}^0=J_e^0\left(\frac{M_z}{M_w}\right)^{3.7} \tag{13}$$

Whereas Aggarwal suggested[7]:

$$J_{eb}^0=J_e^0\frac{M_zM_{z+1}}{M_nM_w} \tag{14}$$

According to Montfort *et al.*[8], the recoverable compliance of a binary blend is given by:

$$J_{eb}^0=\frac{(1-\theta)\eta_{01}J_{e1}^0+\theta\eta_{02}J_{e2}^0}{\eta_{0b}} \tag{15}$$

where

$$\theta=\frac{R^{(3.4/p)}}{R^{(3.4/p)}-1}\times\frac{(1-\phi_2+R\phi_2)^{(3.4/p)}-1}{(1-\phi_2+R\phi_2)^{(3.4/p)}} \tag{16}$$

$R$ is the ratio of molecular weights $M_2/M_1$ and $p$ is an adjustable parameter.

The same authors also proposed the following relation[9]:

$$J_{eb}^0=\frac{\phi_1^2J_{e1}^0\tau_1^2+(1-\phi_1^2)J_{e2}^0\tau_2^2}{(\phi_1^2\tau_1+(1-\phi_1)^2\tau_2)^2} \tag{17}$$

Finally, the modified Rouse model gives[1,2]:

$$J_{eb}^0=J_e^0\frac{M_zM_{z+1}}{M_w^2} \tag{18}$$

Recently, some blending laws[10–12] on the basis of the tube model[13,14] and others including some adjustable parameters[15,16] have been developed.

If the above listed equations are compared with the experimental data, it is found that they are all able to fit certain results, but that none of them fit entirely satisfactorily.

## NEW BLENDING LAW

In a linear viscoelastic steady shear flow (when the shear stress is small) the recoverable deformation takes the form:

$$\gamma_R=J_e^0\sigma=J_e^0\eta_0\dot{\gamma}=\tau_w\dot{\gamma} \tag{19}$$

It can be considered that the recoverable deformation originates from the orientation of the molecular chains in the melt. If we assume that the weight-average relaxation time is related to the effective life-time of the entanglements, equation (19) can be understood in terms of the orientation of a chain depending on the effective life-time of the entanglements and on the applied strain rate.

Let us now consider the variation of $\gamma_R$ with *MWD* in two different cases:

(a) If the strain rate is held constant, recoverable strain increases if the relaxation time $\tau_w$ (or molecular weight) increases.

(b) If stress is now held constant, strain rate will depend on viscosity since $\sigma=\eta_0\dot{\gamma}$.

For monodisperse polymers, we know[1,2] that both $\eta_0$ and $\tau_w$ are proportional to $M^a$. Therefore:

$$\gamma_R=\tau_w\frac{\sigma}{\eta_0}\sim\sigma \tag{20}$$

showing that, at constant stress, the recoverable strain of monodisperse samples does not depend on molecular weight (which means to say that the recoverable compliance is independent of molecular weight).

If the same constant stress is now applied to a blend of two monodisperse polymers of molecular weights $M_1$ and $M_2$, the recoverable deformation is higher for the blend than for the two components (cf. the maximum in the $J_e^0$ *versus* blend composition curve).

Since $\eta_0$ varies with $M_w^a$ for blends as well as for monodisperse samples, the increase in $\gamma_R$ necessarily originates from the variation of entanglement life-time $\tau_w$ with blend composition. The relationship between $\tau_w$ and *MWD* must be different from that for monodisperse components ($\tau_w\sim M^a$) which would lead to a *MWD*-independent value of $J_e^0$.

We postulate the following expression for the relaxation time $\tau_{wb}$ of a blend:

$$\tau_{wb}=\Sigma\phi_i\tau_{wi} \tag{21}$$

with $\tau_{wi}=\eta_{0i}J_{ei}^0$ being the relaxation times of the components. As will be shown below, this simple assumption based on relaxation times actually leads to the expected dependence of $J_e^0$ on *MWD*.

Equation (2), which is the definition of the weight-average relaxation time, holds for blends as well as for monodisperse samples. Therefore:

$$J_{\mathrm{eb}}^0=\frac{\tau_{\mathrm{wb}}}{\eta_{0\mathrm{b}}} \qquad (22)$$

Equation (22) is then rewritten for a binary blend according to equations (10) and (21):

$$J_{\mathrm{eb}}^0=\frac{\eta_{01}J_{\mathrm{e}1}^0+(\eta_{02}J_{\mathrm{e}2}^0-\eta_{01}J_{\mathrm{e}1}^0)\phi_2}{[\eta_{01}{}^{1/a}+(\eta_{02}{}^{1/a}-\eta_{01}{}^{1/a})\phi_2]^a} \qquad (23)$$

It should be noted that equations (21) and (23) can also be used for blends of two polydisperse components. Moreover, all parameters appearing in equation (23) can be determined experimentally.

The blending law can of course be generalized to blends with more than two components and to polymers with a continuous *MWD*:

$$J_{\mathrm{eb}}^0=\frac{\Sigma\phi_i\tau_{\mathrm{w}i}}{(\Sigma\phi_i\eta_{0i}{}^{1/a})^a}=J_{\mathrm{e}}^0\frac{\Sigma\phi_i M_i^a}{(\Sigma\phi_i M_i)^a} \qquad (24)$$

If an '*a*-average' molecular weight $M_a$ is introduced:

$$M_a=\frac{\Sigma\phi_i M_i^a}{\Sigma\phi_i M_i^3} \qquad (25)$$

the recoverable compliance can be written as a function of $M_{\mathrm{w}}$, $M_z$, $M_{z+1}$ and $M_a$:

$$J_{\mathrm{eb}}^0=J_{\mathrm{e}}^0\frac{M_a M_{z+1} M_z}{M_{\mathrm{w}}^{a-1}} \qquad (26)$$

It is interesting to note that if $a=3$, equation (26) is equivalent to equation (19) which is derived from the modified Rouse model.

If one defines $Q_x$ as a moment of the molecular weight distribution function:

$$Q_x=\int M^x\phi(M)\mathrm{d}M \qquad (27)$$

the above derived blending law amounts to:

$$J_{\mathrm{eb}}^0=J_{\mathrm{e}}^0\frac{Q_a}{Q_1^a} \qquad (28)$$

Whereas the modified Rouse model gives:

$$J_{\mathrm{eb}}^0=J_{\mathrm{e}}^0\frac{Q_3}{Q_1^3} \qquad (29)$$

If one takes $p=3.4$ in equation (16) (note that Montfort *et al.* found $p=10\pm1$ for PS[8]), Montfort's law (equation (15)) becomes[17]:

$$J_{\mathrm{eb}}^0=J_{\mathrm{e}}^0\frac{Q_{4.4}}{Q_1^{4.4}} \qquad (30)$$

It is clear that the results predicted by the blending law derived in this paper lie between that of the modified Rouse model and that of Montfort's equation.

## EXPERIMENTAL

The samples investigated in this study are narrow *MWD* polystyrenes (prepared by anionic polymerization) and binary blends of these polymers. For the blends, solutions of the components in benzene (10 wt%) were prepared and thoroughly mixed for 24 h. The solvent was then removed by freeze-drying. The characteristics of these samples are listed in *Table 1*.

The storage modulus $G'$ and the loss modulus $G''$ have been measured in a cone and plate geometry with a Rheometrics mechanical spectrometer (RMS-605) over a temperature range from 120°C to 220°C. The frequency varied from $10^{-2}$ to $10^2$ rad/s with strain amplitudes lying between 2% and 10% depending on frequency and temperature in order to obtain both sufficient values of torque and strain-independent values of the moduli (linear viscoelastic behaviour).

Master curves have been plotted at 140°C for all samples. Zero-shear viscosity and recoverable compliance have been obtained according to equations (3) and (4) from the dynamic moduli in the terminal zone. $\mathrm{Log}(\eta_0)$ data are plotted vs. $\log(M_{\mathrm{w}})$ in *Figure 1* showing that the following relation holds to a good approximation:

$$\eta_0=KM_{\mathrm{w}}^{3.6}$$

with a satisfactory agreement with the well-known power law being obtained.

## COMPARISON OF BLENDING LAW WITH EXPERIMENTAL RESULTS

In *Figure 2*, the recoverable compliance of the blends investigated in this study is compared with the values predicted by equation (23), and a close agreement is observed.

The curves in *Figure 3* are related to data of Prest[18] for binary PDMS blends which can also be fitted fairly well by equation (23). In *Figures 4* and *5*, we have plotted the experimental results of Montfort[9], Marin[19], Akovali[20], Prest and Porter[21] and Mills and Nevin[22] for binary polystyrene blends.

A good agreement with the blending law proposed here is found for the results of Montfort, Marin and Akovali. The data of Mills and Nevin lie above, those of Prest and Porter below the values of $J_{\mathrm{eb}}^0$ calculated according to equation (23). Since the deviations between calculated

**Table 1** Characteristics of S611–S567 blends

| Sample PS | $M_{\mathrm{w}}$ (g/mol) | $M_{\mathrm{w}}/M_{\mathrm{n}}$ | $\eta_0$ (Poise) | $J_{\mathrm{e}}^0$ (cm$^2$/dyne) |
|---|---|---|---|---|
| S611 | 120000 | 1.1 | $1.99\times10^7$ | $0.83\times10^{-6}$ |
| 5% S567 | 163000 | 1.3 | $5.25\times10^7$ | $27\times10^{-6}$ |
| 10% S567 | 205000 | 1.56 | $14.8\times10^7$ | $43\times10^{-6}$ |
| 20% S567 | 290000 | 1.99 | $45.9\times10^7$ | $31\times10^{-6}$ |
| 40% S567 | 460000 | 2.49 | $316\times10^7$ | $8.5\times10^{-6}$ |
| 60% S567 | 630000 | 2.46 | $820\times10^7$ | $4.3\times10^{-6}$ |
| S567 | 970000 | 1.19 | $3550\times10^7$ | $1.6\times10^{-6}$ |

and experimental data are sometimes positive and sometimes negative, we can conclude a satisfactory overall agreement. It should be pointed out that, for each different polymer, the corresponding value of parameter $a$ has been taken in the above calculations. For example, $a$ was taken as 3.59 for the PDMS blends of Prest, and 3.4 for the PS blends of Prest and Porter.

Another method of checking a blending law for the recoverable compliance is to plot the values of $J_{eb}^0$ as a function of the quantity $Q_a/Q_1^a$ as suggested by equation (28).

For binary blends, $M_a$ can be calculated according to the following relation:

$$M_a=\frac{\phi_1 M_1^a+\phi_2 M_2^a}{\phi_1 M_1^3+\phi_2 M_2^3}$$

In *Figure 6*, $\log(J_{eb}^0)$ is plotted vs. $\log(Q_a/Q_1{}^a)$ for

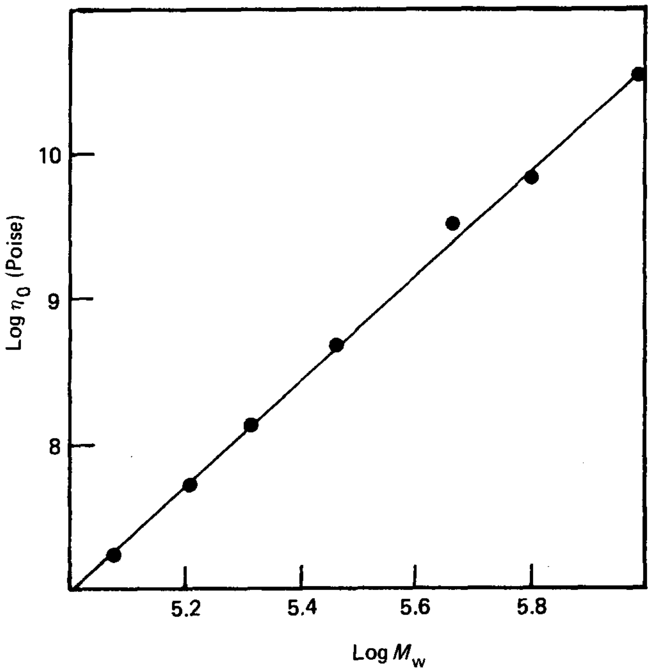

**Figure 1** Zero-shear viscosity as a function of weight-average molecular weight for S611-S567 blends at 140°C

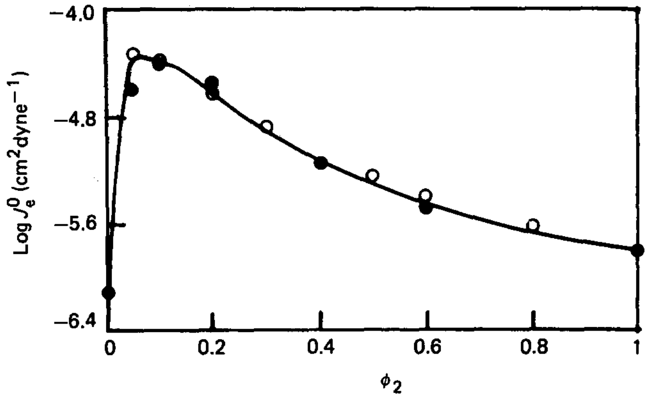

**Figure 2** Steady-state recoverable compliance *versus* volume fraction of S567 for S611–S567 blends at 140°C (●) experimental data, (○) values calculated from equation (23)

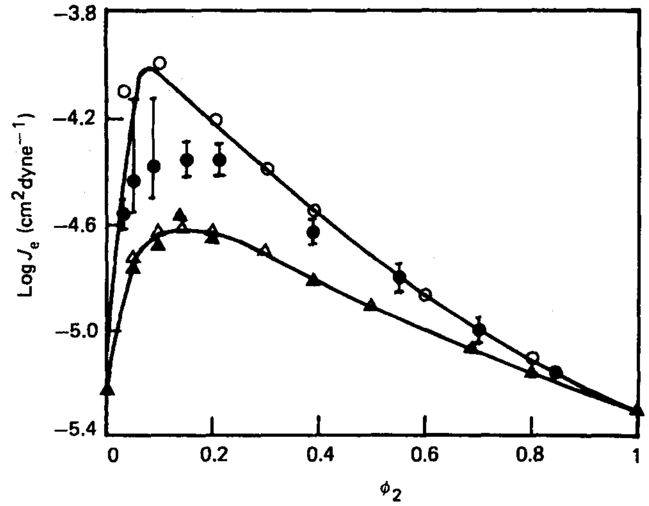

**Figure 3** Recoverable compliance *versus* volume fraction of high molecular weight component for PDMS blends (ref. 18). (●, ▲) experimental data, (○, △) values calculated from equation (24)

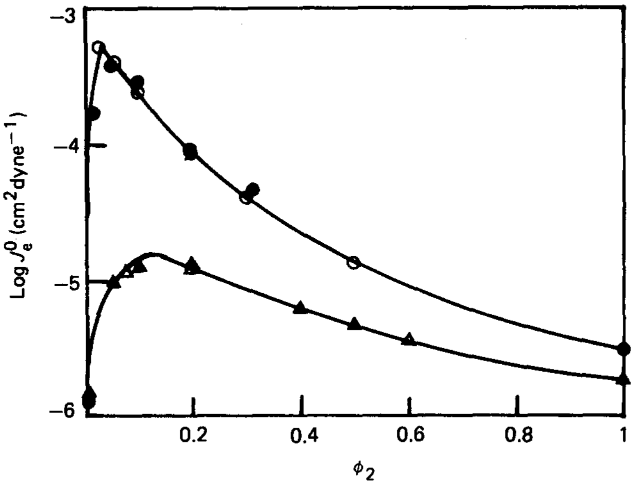

**Figure 4** Recoverable compliance *versus* volume fraction of high molecular weight component for PS blends (refs. 9, 19). (●, ▲) experimental data, (○, △) calculated values

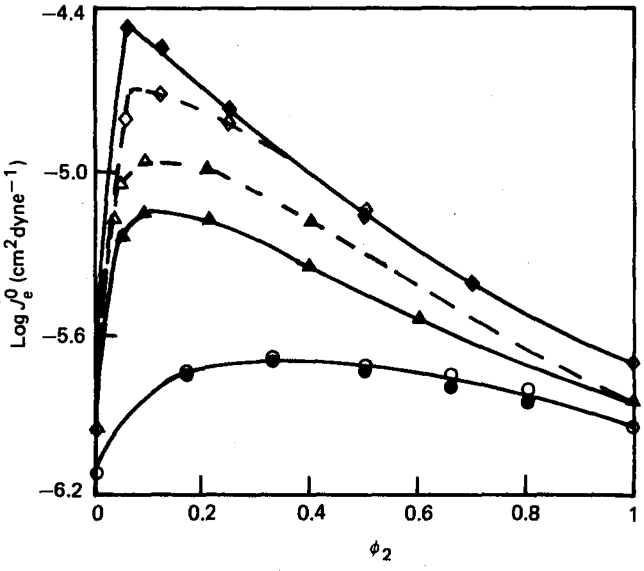

**Figure 5** Recoverable compliance *versus* volume fraction of high molecular weight component for PS blends (refs. 20, 21, 22). (◇, △, ○) experimental data, (◆, ▲, ●) calculated values

Graessley's data on polybutadiene blends. *Figure 7* shows the same plot relative to the data of Montfort[9], Marin[19], Prest[18], Mills[22], Orbon[23] and for the data from this study. The slope obtained on those plots lies between 1.04 for the polystyrene blends and 1.2 for the polybutadiene blends. These values are close to the expected value of 1.

All characteristics of the samples analysed here are summarized in *Table 2*.

Finally, for binary blends one can calculate the concentration of the high molecular weight component $\phi_{2m}$ for which $J^0_{eb}$ goes through a maximum by differentiating equation (23) with respect to $\phi_2$. If one takes $J^0_{e1}=J^0_{e2}$ and $\eta_{0i}=KM_i^a$, $\phi_{2m}$ can be written as a function of $R=M_2/M_1$ and $a$:

$$\phi_{2m}=\frac{(R^a-1)-a(R-1)}{(R-1)(R^a-1)(a-1)} \qquad (31)$$

In *Table 3*, values of $\phi_{2m}$ for binary blends of polybutadiene and polystyrene, as determined from the experimental results of different laboratories, have been listed together with values calculated according to equation (31). Clearly, the agreement here is satisfactory.

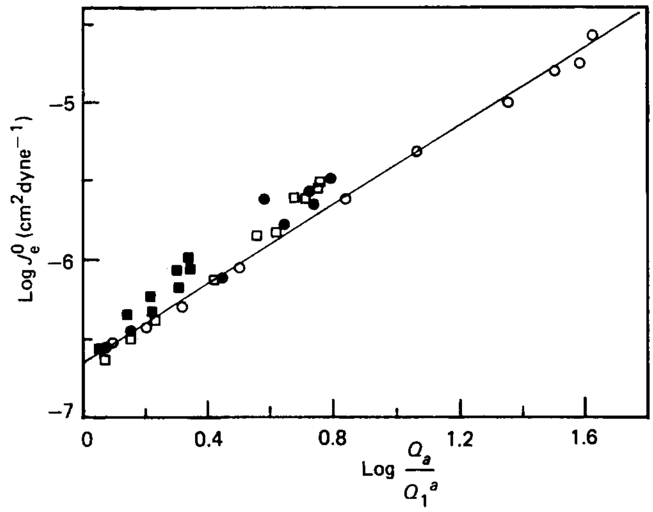

**Figure 6** Recoverable compliance as a function of $Q_a/Q_1{}^a$ for four series of PB blends (ref. 17). (○) $M_w=41\,000/M_w=435\,000$, (●) $M_w=98\,000/M_w=435\,000$, (■) $M_w=174\,000/M_w=435\,000$, (□) $M_w=41\,000/M_w=174\,000$

Furthermore, Graessley[17] recently found that the following relationship between $\phi_{2m}$ and $R$ is generally verified:

$$1+(R-1)\phi_{2m}=1.35 \quad \text{for} \quad 2.5<R<10.7$$

If this quantity is calculated according to equation (31), one finds:

$$1+(R-1)\phi_{2m}=1+\frac{(R^a-1)-a(R-1)}{(R^a-1)(a-1)}$$

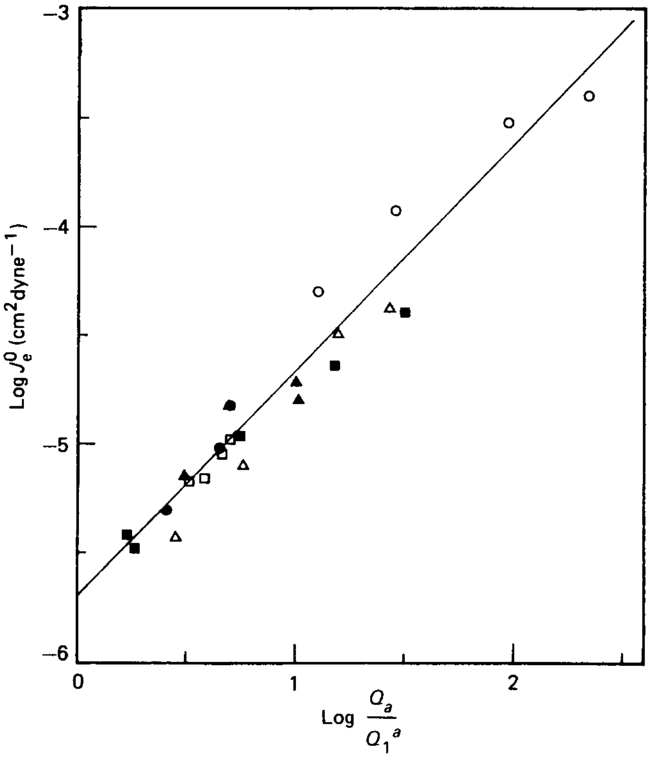

**Figure 7** Recoverable compliance as a function of $Q_a/Q_1{}^a$ for PS blends. (○) ref. 9, (●) ref. 19, (□) ref. 21, (▲) ref. 22, (■) ref. 23, (△) this study

**Table 2** Characteristics of blends investigated (results from different laboratories). (a) ref. 18, (b) ref. 19, (c) ref. 9, (d) ref. 21, (e) ref. 22, (f) ref. 20, (g) ref. 23

| Ref. | Sample | Temperature (°C) | $a$ | $R$ | $M_w$ (g/mol) | $\eta_0$ (Poise) | $J_e^0$ (cm$^2$/dyne) |
|---|---|---|---|---|---|---|---|
| a | PDMS | 25 | 3.59 | 7.08 | 113000 | $1\times10^3$ | $8.3\times10^{-6}$ |
| | | | | | 800000 | $1.15\times10^6$ | $5\times10^{-6}$ |
| | | | | 3.65 | 219000 | $1.1\times10^4$ | $5.9\times10^{-6}$ |
| | | | | | 800000 | $1.15\times10^6$ | $5\times10^{-6}$ |
| b | PS | 160 | 3.4 | 4.19 | 160000 | $1.6\times10^6$ | $1.4\times10^{-6}$ |
| | | | | | 670000 | $2.9\times10^8$ | $1.8\times10^{-6}$ |
| c | PS | 160 | 3.4 | 27 | 100000 | $5.75\times10^5$ | $1.26\times10^{-6}$ |
| | | | | | 2700000 | $15.9\times10^9$ | $3.16\times10^{-6}$ |
| d | PS | 192 | 3.41 | 4.23 | 97200 | $1\times10^4$ | $1.1\times10^{-6}$ |
| | | | | | 411000 | $1.25\times10^6$ | $1.4\times10^{-6}$ |
| e | PS | 190 | 3.57 | 5.8 | 86800 | $5\times10^3$ | $1.1\times10^{-6}$ |
| | | | | | 500000 | $4.2\times10^6$ | $2\times10^{-6}$ |
| f | PS | 129 | 3.75 | 2.14 | 125000 | $3.27\times10^8$ | $1.14\times10^{-6}$ |
| | | | | | 267000 | $4.53\times10^9$ | $0.79\times10^{-6}$ |
| g | PS | | 3.4 | 29.6 | 20000 | | |
| | | | | | 592000 | | |

**Table 3** Experimental and calculated values of $\phi_{2m}$ (according to equation (31))

| Sample | $M_{w1}$ (g/mol) | $M_{w2}$ (g/mol) | $R$ | $a$ | $\phi_{2m}$ (exp.) | $\phi_{2m}$ (calc.) | Ref. |
|---|---|---|---|---|---|---|---|
| PDMS | 219000 | 800000 | 3.65 | 3.59 | 0.14 | 0.13 | 18 |
| | 113000 | 800000 | 7.1 | 3.59 | 0.07 | 0.06 | |
| PB | 174000 | 435000 | 2.5 | 3.4 | 0.15 | 0.21 | 17 |
| | 41000 | 174000 | 4.3 | 3.4 | 0.10 | 0.12 | |
| | 98000 | 435000 | 4.5 | 3.4 | 0.10 | 0.11 | |
| | 41000 | 435000 | 10.7 | 3.4 | 0.05 | 0.04 | |
| PS | 173000 | 316000 | 1.8 | 3.5 | 0.30 | 0.29 | 25 |
| | 125000 | 267000 | 2.1 | 3.75 | 0.30 | 0.26 | 20 |
| | 46900 | 167000 | 3.6 | 3.7 | $<0.20$ | 0.14 | 24 |
| | 88600 | 316000 | 3.6 | 3.5 | 0.10 | 0.14 | 25 |
| | 111000 | 400000 | 3.6 | 3.4 | 0.13 | 0.14 | 8 |
| | 160000 | 670000 | 4.2 | 3.4 | 0.15 | 0.12 | 19 |
| | 97200 | 411000 | 4.2 | 3.4 | 0.10 | 0.12 | 21 |
| | 86800 | 500000 | 5.8 | 3.57 | 0.10 | 0.08 | 22 |
| | 41600 | 316000 | 7.6 | 3.5 | 0.05 | 0.06 | 25 |
| | 120000 | 972000 | 8.1 | 3.6 | 0.06 | 0.05 | [a] |
| | 100000 | 2700000 | 27 | 3.4 | 0.05 | 0.02 | 9 |

[a] This study

With $a=3.4$:

$$1+(R-1)\phi_{2m}=1.32 \qquad \text{if } R=2.5$$

$$1+(R-1)\phi_{2m}=1.41 \qquad \text{if } R=15$$

It is clear that the blending law proposed in this study is in agreement with Graessley's relation.

## CONCLUSIONS

It is shown in this study that a simple assumption based on the *MWD* dependence of weight-average relaxation times, leads to a blending law for the recoverable compliance which is able to fit most experimental data of the literature to a good approximation. No adjustable parameter appears in this blending law, which requires only knowledge of exponent $a$ in the power law relating viscosity and weight-average molecular weight. If one looks for a molecular significance of equation (19), the weight-average relaxation time $\tau_w$ should be thought of as an average life-time of entanglements of a chain. Blending law equation (21) then indicates that, in blends or in polymer melts with continuous *MWD*, the average life-time of entanglements $\tau_{wb}$ can be calculated as the weight-average of the entanglement life-times of the components:

$$\tau_{wb}=\int \tau_w(M)\phi(M)\mathrm{d}M$$

A better understanding of the physical meaning of this assumption in terms of a molecular model is, however, still necessary.

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