RELAXATION SPECTRA AND VISCOELASTIC PROPERTIES OF THE BINARY LINEAR FLEXIBLE POLYMERS

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Abstract—A binary blending law was proposed for a mixture which was composed of two narrowly distributed linear polymer fractions with different molecular weights and the high entanglement density. The relaxation spectrum was used to express the binary blending law and it was derived from the chain relaxation processes based on tube model theories as well as from the earlier observations on the viscoelasticity of linear polymers with bimodal molecular weight distribution. The proposed law showed good agreements with experimental data over a wide range of time or frequency for the viscoelastic properties such as shear stress relaxation modulus and dynamic moduli. It also showed good-fitted results for the compositional dependences of some viscoelastic constants such as zero-shear viscosity and recoverable compliance.

INTRODUCTION

General-purpose polymers have molecular weight distributions in general. The molecular weight distribution (MWD) has important effects on the rheological properties of polymeric liquids closely related to their processability. Hence, the MWD has been intensively and extensively studied for past two decades in the form of the theory or experiment to describe the viscoelasticity of the linear flexible polymers, but most works have been done for monodispersed polymer systems.

Molecular theories to explain the phenomenological observations for the entanglement effects of polymer concentrates have been proposed. Hansen et al. [1] proposed the extended Rouse model introducing concepts of elastic coupling and enhanced friction of Rouse beads which were represented as entanglement points, and simulated the rheological behavior of flexible polymers successfully. Based upon de Gennes' idea[2,3] of 'reptation', Doi and Edwards (DE)[4] suggested a tube model in which a primitive chain moves through a tube-like region formed by neighboring chains. After the appearance of DE's tube model theory, several additional concepts, such as the contour length fluctuation of reptating chain[5,6], constraint release due to the tube renewal process[6,7], etc. have been introduced. Yet there are still a few differences between the tube model theory and experi-

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mental results for zero-shear viscosity η_o, steady-state shear compliance J_e^o, and rubbery plateau modulus G_N^o.

Molecular weight distribution has been thought as a very important factor for the explanation of polydispersity effects on the viscoelasticity of flexible polymers. In this field of research the binary mixture composed of two narrowly distributed polymer fractions has been analyzed and used as one of the simplest model to describe the effects of polydispersity. In the case of small difference of molecular sizes between two components, terminal zone of relaxation spectrum becomes wide. But in the case of large difference, two rubbery plateau regions are observed. To describe the influence of the MWD of binary mixture and the compositional dependence of the viscoelastic properties, many blending laws have been suggested[4,8-13]. DE [4] proposed that the stress of a given system could be described as a summation of the contribution of each component. Monfort et al.[9] used DE's idea to examine the rheological behavior of binary as well as polydispersed systems.

Using phenomenological methods, many blending laws have been suggested for different blending ratios and molecular weights. Masuda et al.[10] reviewed several laws published previously, and discussed their applicabilities. They finally set up an advanced blending law, which was composed of the primary or secondary combinations of the relaxation spectrum $H_i(\tau_i)$ of each component. For the secondary combinations, the spectrum H_{ij} related to the entanglement between two different components was introduced for the first

time. Kurata[11] also considered a secondary combination derived approximately from DE's reptation theory. He showed that the component with shorter chain in the binary mixture acted like a simple solvent molecule. Introducing the diffusion mechanism according to the tube renewal process, Watanabe et al.[12] set up a blending law for the two cases of large and small differences in molecular size.

Kim and Chung[13-15] recently developed a new model for linear polydispersed polymer systems, called 'equivalent primitive chain model', emphasizing the importance of constraint release due to local tube renewal process. In this paper this model will be used to suggest a more advanced binary blending law in terms of relaxation spectrum $H(\tau)$. including the effects of reptation, contour length fluctuation, and constraint release.

BINARY BLENDING LAW

A binary mixture consists of the same linear polymer species but different molecular weights. The component with lower molecular weight(MW) is called as 1-chain component with MW M_1 and the higher MW component as 2-chain component with M_2. The largest relaxation times of 1-chain and 2-chain components are expressed as τ_1^{o} and τ_2^{o} respectively in the purely monodispersed state, and the relaxation times in a blended state are indicated as τ_1 and τ_2. It can be observed that τ_1 and τ_2 depend upon the composition for 2-chain (w_2) and the molecular weight ratio $R(=M_2/M_1)$. The following assumptions are made to establish the relaxation spectrum $H_B(\tau)$ in the binary system according to the molecular theories as well as the experimental results:

(1) The two component chains are well entangled each other with equal probability.

(2) The MW of each component is much larger than minimum molecular weight M_c for the entanglement effects on viscoelasticity, i.e., $M_2 > M_1 \gg M_c$.

(3) Each chain motion follows tube model theory. Each chain continuously moves by the reptation and the contour length fluctuation related to intramolecular mechanism even in the polydispersed state. The effect of constraint release related to intermolecular interaction is neglected for 1-chain.

(4) The relaxation spectrum $H_B(\tau)$ in the binary mixture is the summation of the contributions of each component:

$$H_B(\tau) = \sum_i w_i H_i(\tau) \tag{1}$$

This has the same meaning with the single-chain approximation[4], which means that the stress $\sigma(t)$ of a

concentrated polymer solution system is represented as the sum of the contributions of individual chain.

(5) As proved in tube model theory, the longest relaxation time during the Brownian motion is nearly equal to the longest relaxation time for the stress after a sudden deformation.

It is often possible to point out that $H_1(\tau)$ due to the contribution by 1-chain in the binary mixture is identical with the relaxation spectrum $H_1^{o}(\tau)$ for the purely monodispersed state of 1-chain. This is explained reasonably by the facts that 1-chain hardly suffers the constraint release of neighboring chains. Until τ_1^{o}, according to the assumption (4):

$$H_1(\tau) = H_1^{o}(\tau), \quad \tau_1 = \tau_1^{o} \tag{2}$$

The relaxation process of a 2-chain in the mixture show somewhat different behaviors from those in purely monodispersed state, for it is entangled with other 2-chain components as well as with 1-chain components. Thus $H_2(\tau)$ in eq.(1), the contribution of 2-chain in $H_B(\tau)$, is different from $H_2^{o}(\tau)$. This $H_2(\tau)$ is considered to have two independent modes of slip-links: one is '2-2 slip-link' between 2- and 2-chain and the other '2-1 slip-link' between 2- and 1-chain, where the slip-link corresponds to an entanglement point between two different chains. Hence, the relaxation process for each slip-link also becomes different to some extent. The relaxation spectrum may be written as follows:

$$H_2(\tau) = H_{12}(\tau; \tau_{12}) + H_{22}(\tau; \tau_{22}) \tag{3}$$

The first term in eq.(3) indicates the effect of tube renewal caused by the release of short chain(1-chain) in 2-1 slip-link and the second term represents the effect by the reptational motion inside the tube which maintained by the 2-2 slip-link. Therefore, it is possible to fix $\tau_{12} = \tau_1$ and $\tau_{22} = \tau_2$. Since $H_2(\tau)$ is affected by the release of 2-1 slip-link and 2-2 slip-link and the entanglement density, the following equations can be chosen reasonably.

$$H_{12}(\tau) = f_{12}(w_2) H_2^{o}(\tau/\lambda_{12}), \quad \lambda_{12} = \tau_{12}/\tau_2^{o} \tag{4}$$

$$H_{22}(\tau) = f_{22}(w_2) H_2^{o}(\tau/\lambda_{22}), \quad \lambda_{22} = \tau_{22}/\tau_2^{o} \tag{5}$$

Here λ_{ij} refers to the shifting factor for the relaxation time and $f_{ij}(w_2)$ is a weighting factor for the mixture composition and spectrum intensity (Fig. 1).
Thus, from the eqs.(1)-(5) the relaxation spectrum for the binary mixture is obtained in the following form:

$$H_B = w_1 H_1^{o}(\tau) + w_2 f_{12}(w_2) H_2^{o}(\tau/\lambda_{12})$$
$$+ w_2 f_{22}(w_2 f_{22}(w_2) H_2^{o}(\tau/\lambda_{22}) \tag{6}$$

We define here a characteristic variable $\nu(=1-M_1/M_2)$ which has a limiting value when $M_1/M_2 \to 0$. For the much higher $R(=M_2/M_1)$, i.e., $\nu \to 1$, the plateau mo-
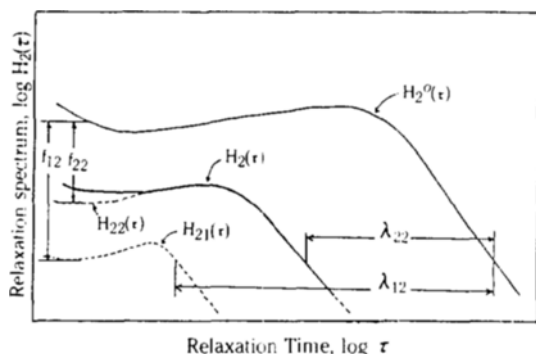
Fig. 1. Relaxation spectrum $H_2(\tau)$ attributed by the high MW 2-component chain.

dulus of 2-chain in low frequency zone may be represented as $w_2^2 G_N^o$ because 1-chain components act like a solvent molecule. And, $f_{12} + f_{22} = 1$ are required to be satisfied. On the other hand, when R approaches to monodispersed state ($\nu \to 0$), f_{22} becomes one and f_{12} is equal to zero because the effects of constraint release are neglected and it results in $H_B(\tau) = w_1 H_1^o(\tau) - w_2 H_2^o(\tau)$. Then it is possible to put $f_{12} = 1-w_2^\nu$ and $f_{22} = w_2^\nu$.

According to the theories of Graessley[6] and Klein[7], when 2-chain relaxes only by the constraint release of 1-chain, its characteristic time shall be

$$\tau_{12} = kN_2^2 \tau_1^o \qquad (7)$$

where $N_2(=M_2/M_e)$ is the number of entanglement in 2-chain and k a proportional constant ($k \ll 1$). This equation proves the dependences of τ_{12} on M_1 and M_2. According to the experimental results of Watanabe et al.[12], $\tau_{12} \propto M_2^2 M_1^{3.3.5}$. We get from this

$$\lambda_{12} = \tau_{12}/\tau_2^o = kN_2^2 (\tau_1^o/\tau_2^o)$$
$$\simeq kN_2^2 (M_1/M_2)^{3.4}. \qquad (8)$$

Since the longest relaxation time of 2-chain $\tau_2 (= \tau_{22})$ is equal to $w_2^\nu \tau_2^o$ [13-15],

$$\lambda_{22} = \tau_{22}/\tau_2^o = w_2^\nu \qquad (9)$$

Using eqs.(1)-(9), we can propose a binary blending law which would be a main equation in this paper:

$$H_B(\tau) = w_1 H_1^o(\tau) + w_2 (1-w_2^\nu) H_2^o(\tau/\lambda_{12})$$
$$+ w_2^{1+\nu} H_2^o(\tau/\lambda_{22}) \qquad (10)$$

Extending eq.(10) to the viscoelastic properties for a binary blended system[8], we can easily obtain the following results:

(a) Shear stress relaxation modulus:

$$G_B(t) = w_1 G_1(t) + w_2 (1-w_2^\nu) G_2(t/\lambda_{12})$$
$$+ w_2^{1+\nu} G_2(t/\lambda_{22}) \qquad (11)$$

(b) Storage modulus:

$$G_B'(\omega) = w_1 G_1'(\omega) + w_2 (1-w_2^\nu) G_2'(\omega \lambda_{12})$$
$$+ w_2^{1+\nu} G_2'(\omega \lambda_{22}) \qquad (12)$$

(c) Loss modulus:

$$G_B''(\omega) = w_1 G_1''(\omega) + w_2 (1-w_2^\nu) G_2''(\omega \lambda_{12})$$
$$+ w_2^{1-\nu} G_2''(\omega \lambda_{22}) \qquad (13)$$

(d) Zero-shear viscosity:

$$(\eta_0)_B = w_1 (\eta_0)_1 + kN_2^2 w_2 (1-w_2^\nu) (\eta_0)_1$$
$$+ w_2^{1+2\nu} (\eta_0)_2 \qquad (14)$$

(e) Steady-state compliance:

$$(J_e^o)_B = \{w_1 (\eta_0)_1^2 (J_e^o)_1 + k^2 N_2^4 w_2 (1-w_2^\nu)$$
$$(\eta_0)_1^2 (J_e^o)_2 + w_2^{1+3\nu} (\eta_0)_2^2 (J_e^o)_2\}/(\eta_0)_B^2 \qquad (15)$$

EXPERIMENT

The nearly monodisperse fractions used in this study are standard polystyrene polymers which were manufactured by Pressure Chemical Co. using the anionic polymerization method. Their MWs and poly-dispersity indices are shown in Table 1 with those of binary blended mixtures. In Table 1, samples used for viscoelastic measurement were designated in accordance with blend type. The first letters M and B represent standard fraction and binary blends, respectively. The number after M denotes the apparent MW of the fraction multiplied by 10^{-3}. For binary mixtures, the first number is the apparent MW of the lower MW component multiplied by 10^{-3} while the second number is that of the higher MW component multiplied by 10^{-3}. The two numbers are separated by slash (/). The last number following hyphen (-) is the weight fraction of the higher MW component, w_2.

In this study, Rheometrics Dynamic Spectrometer (RDS) with the parallel plate geometry was used to measure the shear stress relaxation modulus and dynamic modili both. All data were taken at several

Table 1. Molecular weights and polydispersity indices of polymer fractions and binary mixtures

Sample	M_n	M_w	M_w/M_n
M95	93,300	96,700	1.036
M400	372,000	401,000	1.078
M575	485,000	528,000	1.087
M900	828,000	919,000	1.109
B95/575-0.2	111,300	183,400	1.648
B95/575-0.4	137,900	270,200	1.960
B95/575-0.6	181,100	357,000	1.971
B400/900-0.4	478,900	607,400	1.268

temperatures from 140 to 270°C. The reference gap was set at 160°C, and during the measurement after the equilibration of sample temperature the fluctuation of the temperature was less than 1°C.

The relaxation modulus was measured in transient mode. The applied step shear strain was adjusted with test temperature to obtain the reasonable torque value during stress relaxation. Linear viscoelastic response was confirmed by measuring G(t) at different strain values with a range of 0.005-0.1 (sec^{-1}). The dynamic moduli were measured maintaining linear deformation regime which was verified by strain-sweep test at selected frequencies. In addition to this condition for the upper bound of strain amplitude, the reasonable range of torque values limits its lower bound. The moduli were obtained over the frequency range 0.1-100 (rad/ sec) in the rate-sweep mode with six points per decade.

RESULTS AND DISCUSSION

1. Relaxation Spectrum for Binary Mixtures

In Figs. 2 and 3, $H_B(\tau)$ for the mixture, $H_1^{o}(\tau)$ and $H_2^{o}(\tau)$ for the pure states are obtained from the experimental data[14] and denoted as dotted lines. The calculated $H_B(\tau)$ by the proposed law is denoted as solid line. It is shown that for both cases of higher R(e.g., $R \simeq 6$ for B95/575) and lower R(e.g., $R \simeq 2.3$ for B400/ 900) there are good agreements between solid line and dotted line over the wide range of relaxation time.

The longest relaxation time of 2-chain mixed with 1-chain is reduced by lowering w_2 and this reduction is represented as $\tau_{22} = w_2^{\nu}\, \tau_2^{o}$. Hence, it indicates that the intermolecular interactions in polydisperse polymer systems are strongly dependent on the effects of
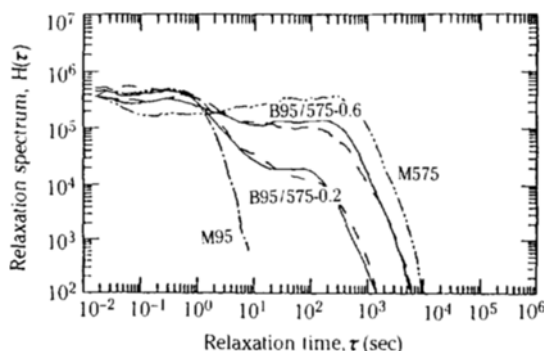
constraint release as well as reptational motion.

2. Some Viscoelastic Functions

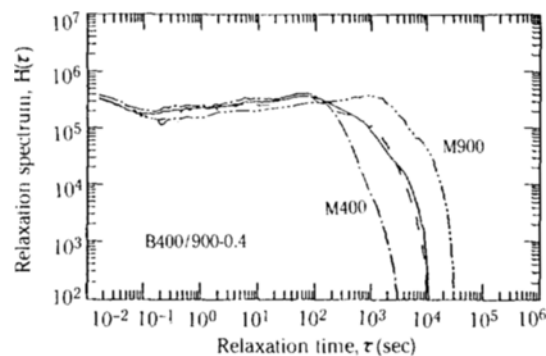By using eqs.(11)-(13), we can plot $G_B(t)$, $G_B'(\omega)$,

Fig. 3. Relaxation spectrum H(τ), dyne/cm², plotted against relaxation time τ.
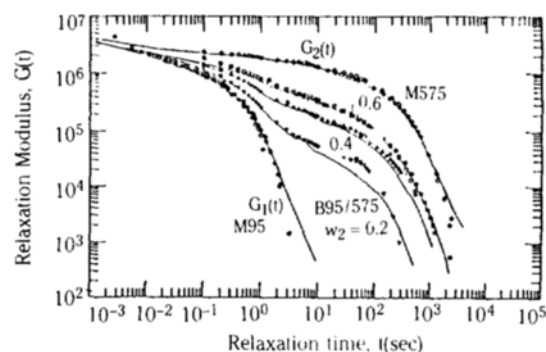See also caption to Fig. 2.

Fig. 4. Shear stress relaxation modulus G(t), dyne/cm², plotted against time t.
Symbols and lines denote experimental data and predicted values from $G_1(t)$ and $G_2(t)$, respectively.

Fig. 2. Relaxation spectrum H(τ) plotted against relaxation time τ.
Solid line denotes the proposed binary blending law for H(τ); dashed line for the blends; dash-dot lines for pure components.
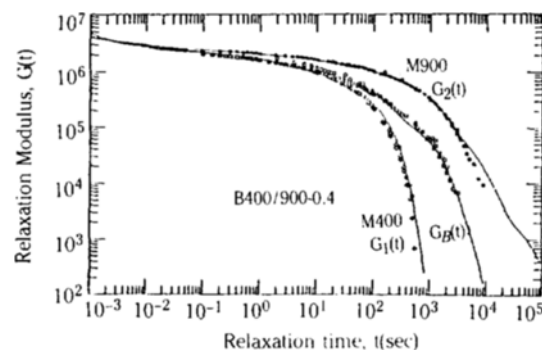

Fig. 5. Shear stress relaxation modulus G(t), dyne/cm², plotted against time t.
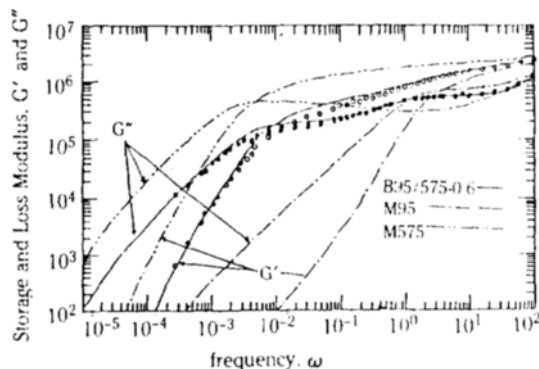See also caption to Fig. 4.

Fig. 6. Storage modulus G'(ω) and loss modulus G"(ω), dyne/cm², plotted against frequency ω.
Dash-dot lines denote G'(ω) for fraction data, solid line does G$_B$(ω); symbol denotes experimental data for binary blend.

Fig. 7. Storage modulus G'(ω) and loss modulus G"(ω), dyne/cm², plotted against frequency ω.
See also caption to Fig. 6.

and $G_B"(\omega)$ for given variables and compare with the experimental data. In Figs. 4 and 5, the comparisons of calculated curves (solid lines) with the experimental master curves (consisted of some symbols) are represented for stress relaxation modulus $G_B(t)$. Comparisons for dynamic moduli $G_B'(\omega)$ and $G_B"(\omega)$ are also shown in Figs. 6 and 7. As shown in these figures, the proposed blending law can be easily applied to those viscoelastic functions over the range of w_2, R, and time t or frequency ω. For the mixture of B95/575 particularly, two step plateau regions are obviously observed because the binary mixture has a large MW difference between two components. For the mixture with low R like B400/900, even the overlapping behavior between two plateau regions caused by the effect of low
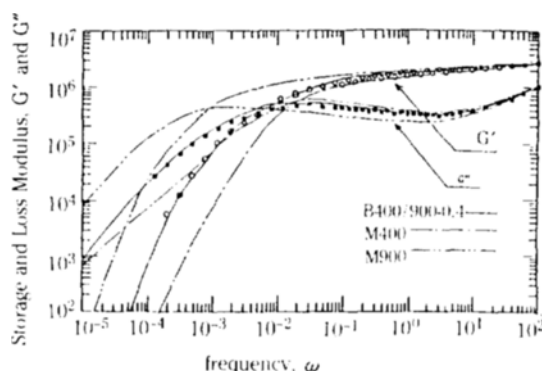
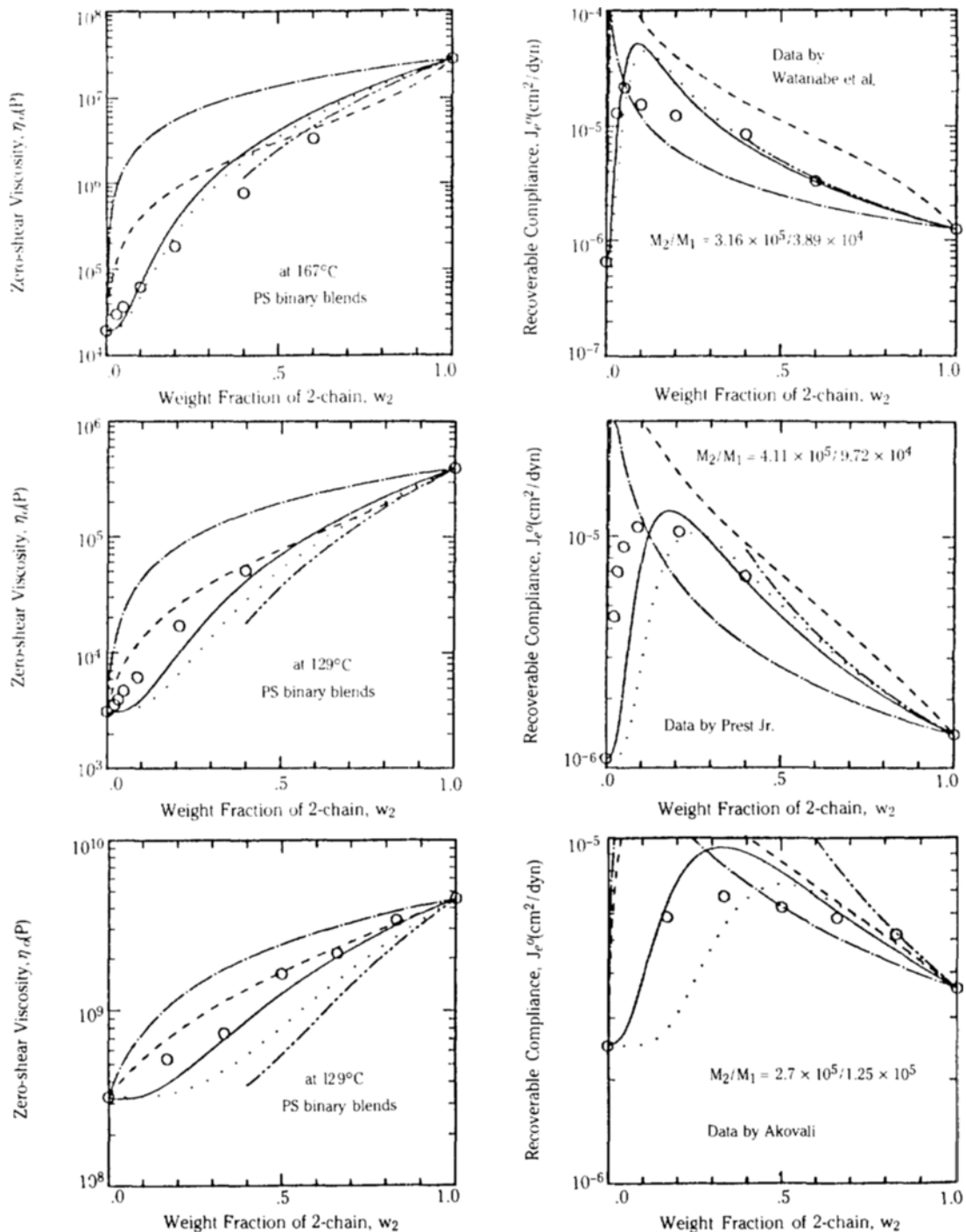blending ratio is well explicable with the presently suggested law.

3. Zero-shear Viscosity and Recoverable Compliance

Present blending law is compared with other laws which are also based on the tube model theory, and we include the experimental data to distinguish which law approaches better to the experimental data. Several blending laws for the viscoelastic constants such as zero-shear viscosity and recoverable compliance are summarized in Table 2.

Consequently, Fig. 8 shows the applicability of the proposed law for a wide range of blending ratio of $2.2 \leq R \leq 8.12$ and the comparison with other laws introduced in Table 2. The binary blending law by DE [4] overestimates the effects of blending for η_o. And for J_e^o, experimental data are seriously overestimated for

Table 2. A summary of binary blending laws for zero-shear viscosity and recoverable compliance

Proposer (s)	Formula		Remarks
Doi and Edwards[4]	$\eta_o = \sum_{i=1}^{2} w_i (\eta_o)_i$	(16)	Weight-basis additivity
	$(J_e^o) (\eta_o)^2 = \sum_{i=1}^{2} w_i (J_e^o)_i (\eta_o)_i^2$	(17)	rule
Schausberger et al.[16]	$\eta_o = \sum_{i=1}^{2} x_i (\eta_o)_i$	(18)	Molar-basis additivity
	$(J_e^o) (\eta_o)^2 = \sum_{i=1}^{2} x_i (J_e^o)_i (\eta_o)_i^2$	(19)	rule, considered for pure reptation within mean field
Watanabe et al.[12]	$\eta_o = w_2^{2+\beta} (\eta_o)_2$, with $\beta = 1.4$	(20)	For R$\geq$8 and $w_2 \geq 0.4$,
	$J_e^o = w_2^{-2} (J_e^o)_2$	(21)	included the effects of constraint release and contour length fluctuation
Masuda et al.[10]	Equal to eqs.(20) and (21), but $\beta = 1.5$		
Kurata[11]	$\eta_o = (1 - w_2^2) (\eta_o)_1 + w_2^2 (\eta_o)_2$	(22)	
	$(J_e^o) (\eta_o)^2 = (1 - w_2^2) (J_e^o)_1 (\eta_o)_1^2$ $+ w_2^4 (J_e^o)_2 (\eta_o)_2^2$	(23)	

Fig. 8. Zero-shear viscosity η_o **and steady-state shear compliance** J_e^o **plotted against weight fraction** w_2 **for undi-
luted polystyrene binary blends (a) with high blend ratio (data by Watanabe et al.[12]), (b) with intermedi-
ate blend ratio (data by Prest, Jr. [17]), and (c) with low blend ratio (data by Akovali [18]).**
Circles denote data. Curves denote predicted values; (———) presently proposed law; (—·—) blending law by DE; (———) by
Schausberger et al.; (········) by Kurata; (—··—··—) by Masuda et al.

the region of small w_2 while underestimated as $w_2 \to 1$. Those discrepancies may be caused by the neglect of constraint release effects in polydisperse polymer systems. As increasing the blend ratio, the differences between the presently proposed law and others are reduced. For much higher blend ratio, the proposed law reaches the limits of $\eta_o \propto w_2^3 (\eta_o)_2$ and $J_e'' \propto w_2^{-2}(J_e'')_2$, which correspond to those of eqs.(20)-(23). In other words, the higher the blending ratio becomes, the closer the proposed law approaches to the real data. For much lower blend ratio, the proposed law approaches to eqs.(16) and (17) by DE, but according to Fig. 8(c) for R = 2.16 some quantitative deviation exists between the proposed law and DE's equations, eqs.(16) and (17). Thus, it is wishful to remove the differences which occurred in comparisons with other laws. The discrepancies between the proposed law and experimental data for the region of very low w_2 is plausible, if the entanglement effects by the 2-1 slip-link and 1-1 slip-link, not by the 2-2 slip-link, would be considered.

As a whole, the proposed law may be considered as one of the best-fitted blending law because it proves that over the wide range of w_2 it enables η_o and J_e'' to approach to the experimental data successfully. The reason for this may be that the proposed binary blending law includes strongly the effects of constraint release based upon the tube model theory.

NOMENCLATURE

c	:	Polymer mass per unit volume
f_{ij}	:	Weighting factor
G_N^o	:	Rubbery plateau modulus
$G(t)$	:	Shear stress relaxation modulus
$G_B(t)$	:	Shear stress relaxation modulus for binary blend
$G_i(t)$	:	Shear stress relaxation modulus of i-th component chain in pure monodispersed state
$G'(\omega)$	:	Storage modulus
$G_B'(\omega)$	:	Storage modulus for binary blend
$G_i'(\omega)$	:	Storage modulus of i-th component in pure monodispersed state
$G''(\omega)$	:	Loss modulus
$G_B''(\omega)$	:	Loss modulus for binary blend
$G_i''(\omega)$	:	Loss modulus of i-th component in pure monodispersed state
$H(\tau)$	:	Relaxation spectrum; distribution of relaxation time
$H_B(\tau)$	:	Relaxation spectrum for binary blend
$H_i^o(\tau)$	:	Relaxation spectrum of i-th component in purely monodispersed state
$H_i(\tau)$	:	Relaxation spectrum of i-th component chain in blended state where the contour length fluctuation effect is included

J_e''	:	Steady-state shear compliance
$(J_e'')_B$	:	Steady-state shear compliance for binary blend
$(J_e'')_i$	:	Steady-state shear compliance of i-th component chain in pure monodispersed state
k	:	A proportional constant
M	:	Molecular weight
M_i	:	Molecular weight of i-th component chain
M_n	:	Number-average molecular weight
M_w	:	Weight-average molecular weight
N_i	:	Number of the primitive path steps for an i-th component chain equal to M_i/M_e
R	:	Binary blend ratio equal to M_2/M_1
t	:	Time
w_i	:	Weight fraction of i-th component chain
x_i	:	Mole fraction of i-th component chain

Greek Letters

η_o	:	Zero-shear viscosity
$(\eta_o)_B$	:	Zero-shear viscosity for binary blend
$(\eta_o)_i$	:	Zero-shear viscosity of i-th component chain in pure monodispersed state
λ_{ij}	:	Shifting factor
ν	:	Power index ($= 1-M_1/M_2$)
$\sigma(t)$	:	Deviatoric stress tensor
τ	:	Relaxation time
τ_i	:	Terminal relaxation time of i-th component chain in blended state where the contour length fluctuation effect is not included
τ_i^o	:	Terminal relaxation time of i-th component chain in monodispersed state where the contour length fluctuation effect is not included
ω	:	Frequency

Abbreviations

DE	:	Doi and Edwards
MW	:	Molecular weight
MWD	:	Molecular weight distribution

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