The application of blending law on linear viscoelastic properties of linear–star and star–star polymer blends

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Abstract

A quadratic binary blending law of the terminal relaxation spectra is used to predict the viscoelastic properties of star–star and linear–star polymer blends. The results are compared with the experimental data reported by Struglinski et al. Star polymers with long arms are assumed to dominate the relaxation behavior of the star–star polymer blends. In the linear–star polymer blends, star polymers are assumed to dominate the relaxation behavior. The ‘iso-relaxation time’ approach is proposed to represent the linear chain by an equivalent star chain for the linear–star polymer blends. The predicted viscoelastic properties agrees with the experimental observation very well. Also, the well known relation, $(J_e^o)_b \propto 1/\nu_2$ (ν_2 is the volume fraction of long-arm star chains), can be deduced from the binary blending law for the concentrated long-arm star chains entangled with much shorter chains. Furthermore, it also predicts that it would systematically depart from the relation, $(J_e^o)_b \propto 1/\nu_2$, when the molecular weight of shorter chain becomes closer to the molecular weight of long-arm chain. In the limit, $M_1/M_2 = 1$, the relation is switched to $(J_e^o)_b \propto \nu_2$. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The star polymers, because of the chain architecture of a central point and equal branches, exhibit quite different viscoelastic behaviors from the linear polymers [1–14]. In the past years, extensive work has been done theoretically and experimentally on the viscoelastic properties of the monodispersed star polymers [2–6]. Attention has primarily been focused on two steady shear flow properties of polymer solutions, the zero-shear viscosity (η_0) and steady-state recoverable compliance (J_e^o). The η_0 relates to the relaxation with long relaxation time of the polymer solution and the J_e^o

relates to the broadness of the relaxation time spectrum [15].

In the regime of low and moderate concentration that the Rouse–Ham theory applies, the zero-shear viscosity (η_0) and steady-state recoverable compliance (J_e^o) of the star polymers, are comparable to those of the linear polymers with the same radius of gyration as the star polymers. In other words, the η_0 and J_e^o of the star polymers are much lower than those of the linear polymers, with the same molecular weight.

On the other hand, in the regime of high concentration and high molecular weight that the entanglements are formed among polymer chains ($M_w > M_c$, M_c is the characteristic molecular weight), the η_0 and J_e^o of the star polymers are much greater than those of the linear polymers. For the star polymers, the η_0 increases exponentially with the increasing molecular weight of the arm, M_a . However, the η_0 of the linear

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polymers has a power law relation with the molecular weight, i.e., $\eta_0 \propto M^{3.5}$. It is surprising that the recoverable compliance, (J_e^0), is found to still can be described by Rouse–Ham theory which is suitable for the non-entangled systems. However, this does not mean that the Rouse–Ham mechanism is prevailing in the entangled star polymers [11]. From the terminal relaxation spectra of the entangled star polymers, one can find that it is different from and much broader than that of the linear polymers [6,7].

Therefore, the relations of η_0 and J_e^0 relaxation spectra, are quite different for the linear and star polymers in the entangled regime. From the recent theories based on the tube model [11–14], it has been suggested that there are two competing mechanisms of relaxation for the entangled linear polymers, reptation and constraint-release (CR) by tube renewal, while they are path-breathing (arm retraction) and CR for the entangled star polymers. The relations between these mechanisms are complicated and still needed to be studied.

Another important factor for the viscoelastic behavior of polymers is the molecular weight distribution (MWD). To study the effect of MWD on the viscoelastic behavior, polymer blends containing two narrow MWD polymers are studied extensively. Yoshida et al. [10–12] and Struglinski et al. [9] have prepared several series of linear–star and star–star polymer blends to examine the effect of chain architecture on relaxation behaviors and viscoelastic properties. In the ‘dilute blend’ [10], a dilute component (probe chain) with high molecular weight, M_2 , is added to the component (test component) with low molecular weight, M_1 ($M_2 \gg M_1 > M_c$). By investigating the motion of the probe chain, Yoshida et al. evaluated the mutual interaction of two components. They suggested that the behavior of the probe chain is essentially identical with that in its own monodispersed dilute system and practically controls the relaxation modes of the test component. In this research area, some studies have been done for linear–star and star–star polymer blends [13,14].

On the other hand, in the ‘concentrated blend’, the component with high molecular weight is large enough to form chain entanglements, not only with the other component, but also among themselves. On the contrary to the dilute blend, the studies are relatively few for the concentrated polymer blends.

Although, several mixing rules of linear viscoelastic behaviors for linear–star and star–star polymer blends have been proposed. However, a general and quantitative blending law for all blends is helpful to describe the viscoelastic behaviors. The purpose of this work is to propose a general blending law on relaxation spectra for the star–star and linear–star polymer blends. The compositional dependence of linear viscoelastic

properties is then derived and compared with the experimental results reported by Struglinski et al. [9].

2. Theoretical treatment

2.1. Star–star polymer blends

2.1.1. Binary blending law

For lack of entanglements in the dilute or low molecular weight systems, the relaxation spectrum $H(\tau)$ for a blend of two monodispersed polymer chains with molecular weight M_1 and M_2 can be simply represented by the Ninomiya blending law [10,15]:

$$H_b(\tau_b) = v_1 H_1\left(\frac{\tau_b}{\lambda_1}\right) + (1 - v_1) H_2\left(\frac{\tau_b}{\lambda_2}\right) \quad (1)$$

where the subscript ‘1’, ‘2’ and ‘b’ denote the polymer 1, polymer 2 and polymer blend, respectively; H the relaxation spectrum; τ_b the relaxation time of the blend; λ the shift factor; and v_1 the volume fraction of polymer 1.

In the concentrated and high molecular weight blends ($M_1, M_2 > M_c$), the entanglements are formed among the same species as well as the different species (i.e., ‘1-1’, ‘1-2’, ‘2-2’ entanglements are formed). Thus, the linear blending law is not suitable in such a system. The quadratic blending law proposed by Montfort [16] and Kurata [17] is accepted favorably. It has the form:

$$H_b(\tau_b) = v_1^2 H_1\left(\frac{\tau_b}{\lambda_1}\right) + (1 - v_1^2) H_2\left(\frac{\tau_b}{\lambda_2}\right) \quad (2)$$

When the above blending law is constituted simply by the entanglements, it is found that the $v_1^2 H_1(\tau_1)$ is provided by the ‘1-1’ chain contacts, $v_2^2 H_2(\tau_2)$ by the ‘2-2’ chain contacts and $2v_1 v_2 H_{12}(\tau_{12})$ by the ‘1-2’ chain contacts. In quadratic blending law, it is assumed that the shorter chain (polymer 2) is predominant. Therefore, the contribution of ‘1-2’ entanglement is replaced by $2v_1 v_2 H_2(\tau_2)$.

In an extreme interpretation, the relaxation of ‘1-2’ entanglements should cooperate the two-sided effect, the relaxation of the short chain is retarded by the long chain and the relaxation of the long chain is accelerated by the short chain at the same time [11]. For the linear–linear polymer blends, the relaxation of the short chain is weakly retarded by the long chain and the relaxation of the long chain is strongly accelerated by the short chain. Thus, the short chain is predominant.

However, this effect of blending can possibly be different for the star chains in the blend. The induced relaxation spectra for the polymer chains with different chain architecture can therefore be very different. For

lack of the study in this area, it is not known whether the short star chain or the long star chain predominated the relaxation behavior in the star–star polymer blends. In this study, we assume that the long star chain is predominant. Thus, the quadratic blending law [16,17], that the long star chain dominate the relaxation in the entangled star–star polymer blends, is used to simulate the relaxation spectra of blends with respect to its individual components.

Because the star chain with long arms is the dominant component, the subscript ‘2’ in Eq. (2) represent the long-arm star chain and ‘1’ represent the short-arm star chain. The v_1 is the volume fraction of the short-arm star chain.

2.1.2. Shift factors

The definitions of shift factors λ_1 and λ_2 are the factors by which the relaxation times $\tau_{1,b}$ and $\tau_{2,b}$ of the polymer ‘1’ and ‘2’ in the blend are altered relative to their values (τ_1 and τ_2) when the polymer is surrounded by others of its own kind [15].

$$\lambda_1 = \frac{\tau_{1,b}}{\tau_1}, \quad \lambda_2 = \frac{\tau_{2,b}}{\tau_2} \quad (3)$$

From the generalized proposed tube models of the monodispersed star polymer [2–6], the relaxation time of pure component is expressed as:

$$\tau_i \propto (\eta_0)_i M_i \quad (4)$$

$$(\eta_0)_i = A \exp\left(\frac{vM_i}{M_e}\right), \quad i = 1, 2 \text{ in this system} \quad (5)$$

where $(\eta_0)_i$ is the zero-shear viscosity of i th component, M_e is the molecular weight corresponding to entanglement spacing M_i is the arm molecular weight of i th component, and v is the constant. Parameter, ‘ A ’ depends on the molecular weight [3,18,19].

Whereas the relaxation time of each star component in the blend $\tau_{i,b}$ can be expressed as [15]:

$$\tau_{i,b} \propto (\eta_0)_b \frac{M_i^2}{\bar{M}_w} \quad (6)$$

where $\bar{M}_w = v_1 M_1 + v_2 M_2$ (average arm molecular weight of blend) and $(\eta_0)_b$ is the zero-shear viscosity of the blend. For the first trial to estimate the shift factor of each component, it is assumed that $(\eta_0)_b$ is expressed in the same form as in Eq. (5), i.e.,

$$(\eta_0)_b = A \exp\left(\frac{v'\bar{M}_w}{M_e}\right) \quad (7)$$

Then the shift factors, λ_1 and λ_2 in Eq. (3) could be derived as below:

$$\lambda_1 = \frac{\tau_{1,b}}{\tau_1} = \frac{(\eta_0)_b (M_1^2/\bar{M}_w)}{(\eta_0)_1 (M_1^2/M_1)} \quad (8a)$$

$$= \frac{\exp(v'\bar{M}_w/M_e)M_1}{\exp(v'M_1/M_e)\bar{M}_w} \quad (8b)$$

$$\lambda_2 = \frac{\tau_{2,b}}{\tau_2} = \frac{(\eta_0)_b (M_2^2/\bar{M}_w)}{(\eta_0)_1 (M_2^2/M_2)} \quad (9a)$$

$$\lambda_2 = \frac{\exp(v'\bar{M}_w/M_e)M_2}{\exp(v'M_2/M_e)\bar{M}_w} \quad (9b)$$

Since the parameter, A ’s in Eqs. (5) and (7) are dependent on molecular weight, Eqs. (8b) and (9b) are not quite accurate. However, Eqs. (8b) and (9b) are used to estimate the initial values of shift factors only. The refinement of shift factors is performed according to Eqs. (8a) and (9a).

2.1.3. Zero-shear viscosity

All the linear viscoelastic functions are theoretically interrelated. The zero-shear viscosity (η_0) , can be expressed as moments of the relaxation spectrum $H(\tau)$ [15]:

$$\eta_0 = \int_0^\infty H(\tau) d\tau \quad (10)$$

Similarly, in the polymer blends:

$$(\eta_0)_b = \int_0^\infty H_b(\tau_b) d\tau \quad (11)$$

If Eq. (2) holds in the concentrated blend, the zero-shear viscosity of the blend in terms of those of the individual pure components is given by

$$\begin{aligned} (\eta_0)_b &= \int_0^\infty H_b(\tau_b) d\tau = \\ &= \int_0^\infty [v_1^2 H_1(\tau_b/\lambda_1) + (1 - v_1^2) H_2(\tau_b/\lambda_2)] d\tau \\ &= v_1^2 \lambda_1 \int_0^\infty H_1(\tau_b/\lambda_1) d(\tau_b/\lambda_1) + (1 - v_1^2) \lambda_2 \\ &\quad \int_0^\infty H_2(\tau_b/\lambda_2) d(\tau_b/\lambda_2) \\ &= v_1^2 \lambda_1 (\eta_0)_1 + (1 - v_1^2) \lambda_2 (\eta_0)_2 \end{aligned} \quad (12)$$

There are few words to say about the calculation of $(\eta_0)_b$ and the shift factors. (1) They are calculated by iteration. (2) The shift factors are calculated from Eqs.

(8b) and (9b) first then the values of shift factors are substituted into Eq. (12) to obtain the $(\eta_0)_b$. (3) Because of the assumption made in Eq. (7), we must correct the shift factors calculated from Eqs. (8a) and (9a) by the new value of $(\eta_0)_b$, and the procedure is repeated until the $(\eta_0)_b$ closed to the experimental value.

Once the shift factors and zero-shear viscosity $(\eta_0)_b$ of individual components are known, the compositional dependence of zero-shear viscosity of blends can be obtained from Eq. (12).

2.1.4. Steady-state recoverable compliance

The steady-state recoverable compliance (J_e^o) can be expressed as the moments of the terminal relaxation spectrum $H(\tau)$ in the entangled regime ($M > M_c$), as well as the zero-shear viscosity [15]:

$$J_e^o = \frac{\int_0^\infty H(\tau) \tau d\tau}{\left[\int_0^\infty H(\tau) d\tau \right]^2} = \frac{1}{\eta_0^2} \int_0^\infty H(\tau) \tau d\tau \quad (13)$$

For the polymer blends,

$$(J_e^o)_b = \frac{1}{(\eta_0)_b^2} \int_0^\infty H_b(\tau_b) \tau_b d\tau_b \quad (14)$$

If Eq. (2) holds in the concentrated blend, the steady-state recoverable compliance of the blend in terms of the individual pure components is given by

$$(J_e^o)_b = \frac{1}{(\eta_0)_b^2} \int_0^\infty \left[v_1^2 H_1\left(\frac{\tau_b}{\lambda_1}\right) \tau_b d\tau_b + (1 - v_1^2) H_2\left(\frac{\tau_b}{\lambda_2}\right) \tau_b d\tau_b \right]$$

$$= \frac{1}{(\eta_0)_b^2} \left[v_1^2 \lambda_1^2 \int_0^\infty \tau_1 H_1(\tau_1) d\tau_1 + (1 - v_1^2) \lambda_2^2 \int_0^\infty \tau_2 H_2(\tau_2) d\tau_2 \right]$$

$$= \frac{1}{(\eta_0)_b^2} \left[v_1^2 \lambda_1^2 (J_e^o)_1 (\eta_0)_1^2 + (1 - v_1^2) \lambda_2^2 (J_e^o)_2 (\eta_0)_2^2 \right]$$

$$= v_1^2 \left[\frac{(\eta_0)_b M_1}{(\eta_0)_1 \bar{M}_w} \right]^2 \left[\frac{(\eta_0)_1}{(\eta_0)_b} \right]^2 (J_e^o)_1 + (1 - v_1^2) \\ \times \left[\frac{(\eta_0)_b M_2}{(\eta_0)_2 \bar{M}_w} \right]^2 \left[\frac{(\eta_0)_2}{(\eta_0)_b} \right]^2 (J_e^o)_2$$

$$= v_1^2 \left(\frac{M_1}{M_w} \right)^2 (J_e^o)_1 + (1 - v_1^2) \left(\frac{M_2}{M_w} \right)^2 (J_e^o)_2 \quad (15)$$

When $v_1 \rightarrow 0$ ($v_2 \rightarrow 1$), Eq. (15) can be simplified as:

$$(J_e^o)_b \approx (1 - v_1^2) \left(\frac{M_2}{M_w} \right)^2 (J_e^o)_2 \\ = (2v_2 - v_2^2) \left(\frac{1}{\frac{M_1}{M_2} + \left(1 - \frac{M_1}{M_2}\right)v_2} \right)^2 (J_e^o)_2 \\ = \frac{\frac{2}{v_2} - 1}{\left[\frac{M_1}{M_2} \frac{1}{v_2} + \left(1 - \frac{M_1}{M_2}\right) \right]^2} (J_e^o)_2 \\ = \frac{\frac{1 + v_1}{v_2}}{\left[\frac{M_1}{M_2} \frac{1}{v_2} + \left(1 - \frac{M_1}{M_2}\right) \right]^2} (J_e^o)_2 \\ \approx \frac{\frac{1}{v_2}}{\left[\frac{M_1}{M_2} \frac{1}{v_2} + \left(1 - \frac{M_1}{M_2}\right) \right]^2} (J_e^o)_2 \quad (16)$$

If $M_1/M_2 \ll 1$ then $(J_e^o)_b \propto \frac{1}{v_2}$. Thus, the mixing rule proposed here can predict the relation $(J_e^o)_b \propto \frac{1}{v_2}$ as it is observed in the experiment [9,11].

2.1.5. Dynamic moduli

In a similar way as the derivation of the recoverable compliance, the dynamic storage and loss moduli can also be expressed in terms of the moments of the terminal relaxation spectrum $H(\tau)$ in the entangled regime ($M > M_c$) [15]:

$$G' = \int_{-\infty}^\infty H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d \ln(\tau) \quad \text{and} \quad (17)$$

$$G'' = \int_{-\infty}^\infty H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d \ln(\tau)$$

Substitute Eq. (2) to Eq. (17), the dynamic storage and loss moduli of the blend in terms of the individual pure components are given by

$$(G')_b = \int_{-\infty}^\infty v_1^2 H_1(\tau_b / \lambda_1) \frac{\omega^2 \tau_b^2}{1 + \omega^2 \tau_b^2} d \ln \tau_b + \\ \int_{-\infty}^\infty (1 - v_1^2) H_2(\tau_b / \lambda_2) \frac{\omega^2 \tau_b^2}{1 + \omega^2 \tau_b^2} d \ln(\tau_b)$$

Table 1
Viscoelastic properties of pure-component polybutadiene [9]

Sample	$M \times 10^{-4}$	$J_e^o \times 10^7 \text{ cm}^2 \text{ dyne}^{-1}$	$\eta_0 \times 10^{-4} \text{ (25}^\circ\text{C, P)}$	$(M^*)^a \times 10^{-4}$
41L	3.68	1.78	1.35	4.07
105L	10.0	1.95	43.7	7.63
174L	16.8	1.82	295	9.65
75S	7.46	8.31	47.9	
127S	12.7	13.5	2750	

^a M^* obtained from ‘iso-relaxation time’ approach in this work

$$(\eta_0)M = (\eta_0)_{\text{star}} \cdot M^* = A \exp(M^*/B)M^*$$

where $B = 3M_e v' = 3 \times 1850/0.6 = 9250$; $A = 150.6$ (from 75S).

$$= v_1^2 \int_{-\infty}^{\infty} H_1(p) \frac{\lambda_1^2 \omega^2 p^2}{1 + \lambda_1^2 \omega^2 p^2} d \ln(p) + (1 - v_1^2) \int_{-\infty}^{\infty} H_2(q) \frac{\lambda_2^2 \omega^2 q^2}{1 + \lambda_2^2 \omega^2 q^2} d \ln(q)$$

where $p = \tau_b/\lambda_1$ and $q = \tau_b/\lambda_2$.

Furthermore,

$$\int_{-\infty}^{\infty} H_1(p) \frac{\lambda_1^2 \omega^2}{1 + \lambda_1^2 \omega^2 p^2} d \ln(p) = G_1'(\lambda_1 \omega)$$

and $\int_{-\infty}^{\infty} H_2(q) \frac{\lambda_2^2 \omega^2 q^2}{1 + \lambda_2^2 \omega^2 q^2} d \ln(q) = G_2'(\lambda_2 \omega)$

Thus,

$$(G')_b = v_1^2 G_1'(\lambda_1 \omega) + (1 - v_1^2) G_2'(\lambda_2 \omega) \quad (18)$$

Similarly, the loss modulus can be written as:

$$(G'')_b = \int_{-\infty}^{\infty} v_1^2 H_1(\tau_b/\lambda_1) \frac{\omega \tau_b}{1 + \omega^2 \tau_b^2} d \ln(\tau)_b + \int_{-\infty}^{\infty} (1 - v_1^2) H_2(\tau_b/\lambda_2) \frac{\omega \tau_b}{1 + \omega^2 \tau_b^2} d \ln(\tau)_b$$

$$= v_1^2 \int_{-\infty}^{\infty} H_1(p) \frac{\lambda_1 \omega p}{1 + \lambda_1^2 \omega^2 p^2} d \ln(p) + (1 - v_1^2) \int_{-\infty}^{\infty} H_2(q) \frac{\lambda_2 \omega q}{1 + \lambda_2^2 \omega^2 q^2} d \ln(q)$$

$$\int_{-\infty}^{\infty} H_1(p) \frac{\lambda_1 \omega p}{1 + \lambda_1^2 \omega^2 p^2} d \ln(p) = G_1''(\lambda_1 \omega)$$

and $\int_{-\infty}^{\infty} H_2(q) \frac{\lambda_2 \omega q}{1 + \lambda_2^2 \omega^2 q^2} d \ln(q) = G_2''(\lambda_2 \omega)$

Thus,

$$(G'')_b = v_1^2 G_1''(\lambda_1 \omega) + (1 - v_1^2) G_2''(\lambda_2 \omega) \quad (19)$$

2.2. Linear–star polymer blends

2.2.1. ‘Iso-relaxation time’ approach

There are two ways to treat the linear–star polymer blends. One way is that the star chain is treated as a linear chain and a linear–linear binary blending law is used. The other way is that the linear chain is treated as a star chain and a star–star binary blending law is used. Since the linear viscoelastic properties derived above is based on the star–star polymer blends, the latter will be used in this work. A linear chain can be treated as an equivalent star chain if the relaxation time of the linear chain is equal to that of the star-equivalent chain. Therefore, instead of the ‘iso-viscosity’ approach [9], we initiated the ‘iso-relaxation time’ approach to obtain the star-equivalent molecular weight M^* for the monodispersed linear chains of the blend. Thus,

$$(\eta_0)_{\text{linear}} M = (\eta_0)_{\text{star}} \cdot M^* = A \exp\left(\frac{v' M^*}{f M_e}\right) M^* \quad (20)$$

where $(\eta_0)_{\text{linear}}$, M are the viscosity and molecular weight of monodispersed linear component and M^* , f are the star-equivalent molecular weight and number of arms. Thus, a linear–star blend system can be theoretically represented by a star–star blend system with the Eq. (20). The linear chains will behave like their corresponding star-equivalent chains on the relaxation spectrum.

2.2.2. Binary blending law

For the linear–star polymer blends, the binary blending law can similarly be represented by Eq. (2) with the ‘iso-relaxation time’ approach. From the published experimental data, it is found that the volume fraction of the star polymer, predominantly determined the relaxation behavior [11–13]. Therefore, the subscripts ‘1’ and ‘2’ in the Eq. (2) represent the linear

Fig. 1. Zero-shear viscosity (η_0)₀ vs. volume fraction of 127S star-component (v_2) for the 75S/127S series of polybutadiene system. The filled points denote the experimental data and the solid line represents the predicted values.

and star components, respectively. As the star–star blends, the shift factors, zero-shear viscosity, steady-state recoverable compliance, and dynamic moduli at very low frequency of the linear–star polymer blends can be obtained from Eqs. (8a), (9a), (12), (15), (18) and (19).

3. Results and discussion

To evaluate the applicability of quadratic binary blending law to the star–star and linear–star polymer blends, the predicted results are compared with the experimental data reported by Struglinski et al. [9]. The data and discussion reported by Struglinski are detail enough to evaluate the quadratic binary blending law easily. The materials used in Ref. [9] are blends of nearly monodisperse linear and three-arm star polybutadienes. The viscoelastic properties of those materials are listed in Table 1. The fifth column of Table 1 is calculated according to the ‘iso-relaxation time’ approach. Five series of binary blends are prepared by Struglinski, four with linear and star components (the linear–star series, 41L/127S, 105L/127S, 174L/127S, 105L/75S) and one in which both components are stars (the star–star series 75S/127S). The notations have followed the Struglinski’s work. All blends are well entangled.

It is found that the determination of constants, A and v' of the Eq. (5) for the monodispersed star polymer, is very important. Theoretically, constants A and v' can be obtained from the data fitting, if there are enough data of the monodispersed star polymers. However, there are only two samples for the monodispersed star polybutadiene in the Ref. [9]. If we proceed directly from the data fitting, there could be many

Table 2
Shift factors for polymer blends

v_2	λ_1	λ_2
75S/127S Series		
0.05	1.16	0.034
0.1	1.35	0.040
0.2	1.82	0.054
0.3	2.47	0.073
0.5	4.69	0.14
0.7	11.40	0.34
0.85	19.07	0.57
41L/127S Series		
0.05	1.36	0.0021
0.1	1.59	0.0024
0.2	2.69	0.0041
0.3	4.77	0.0073
0.5	16.8	0.026
0.75	96.4	0.15
105L/127S Series		
0.05	1.16	0.031
0.1	1.36	0.036
0.15	1.59	0.042
0.2	1.86	0.049
0.3	2.56	0.068
0.5	5.04	0.133
0.75	12.81	0.34
174L/127S Series		
0.05	1.16	0.057
0.1	1.35	0.066
0.2	1.82	0.089
0.3	2.46	0.12
0.5	2.29	0.323
105L/75S Series		
0.05	1.02	0.911
0.1	1.04	0.928
0.2	1.07	0.957
0.3	1.10	0.981
0.5	1.13	1.01
0.7	1.15	1.02
0.8	1.14	1.02
0.9	1.13	1.01
0.95	1.13	1.01

errors. Therefore, instead of the data fitting from only two samples, the proposed value, $v' = 0.6$, for the monodispersed star polybutadiene and polystyrene are adopted [3,5,9]. Then the constant A can be obtained from one of two monodispersed star samples. In this study, we determine the constant A from the monodispersed star sample, 75S.

For the star–star polymer blend, the blend, 75S/127S, of polybutadiene is examined. The long-arm star chain component (127S) is assumed to dominate the relaxation behavior and the quadratic blending law is used to simulate the relaxation spectrum of the blend, with respect to its individual components. The results confirm that the assumption is correct. Also, the quad-

Fig. 2. Zero-shear viscosity $(\eta_0)_b$ vs. volume fraction of 75S star-component (v_2) for the 105L/75S series of polybutadiene system. The filled points denote the experimental data and the solid line represents the predicted values.

ratio blending law is examined with the assumption that the short-arm star chain is predominant. However, the results do not match the experimental data.

3.1. Shift factors

Recalled that in the evaluation of shift factors, we must correct the shift factors until the $(\eta_0)_b$ closed to the experimental value. The results for the star–star polymer blend are shown in Table 2 and Fig. 1. It was found that the differences between calculated values and experimental values are small enough, not more than four iterations. Therefore, correct shift factors can be obtained by iteration.

Fig. 3. Zero-shear viscosity $(\eta_0)_b$ vs. volume fraction of 127S star-component (v_2) for 41L/127S (●), 105L/127S (▲), and 174L/127S (■) series of polybutadiene system. The filled points denote the experimental data and the solid line represents the predicted values.

For the linear–star polymer blends, the ‘iso-relaxation time’ approach for the monodispersed linear chain component is adopted to obtain the corresponding star-equivalent chain. The results are shown in the fifth column of Table 1 for polybutadiene. Then the linear chain is treated as an equivalent star chain and the binary blending law is applied. When the M^* of the linear chain with the molecular weight of the star chain is compared, the star chain is the dominant component. Table 2 shows the results of trials on shift factors for linear–star polymer blends. As the star–star polymer blends, the differences between calculated and experimental values are no more smaller than four iterations (Figs. 2 and 3).

3.2. Zero-shear viscosity

The calculated values of $(\eta_0)_b$ of the 75S/127S blend from Eq. (12) and the experimental values are plotted in the Fig. 1. As the experimental data, it is found that the predicted zero-shear viscosity of the blend increased monotonically with the increasing of the volume fraction of 127S star components, v_2 . From Fig. 1, it is found that the predicted values can match the experimental values very well. Therefore, the assumption that the long-arm star chain is predominant in the star–star polymer blends is suitable in the binary blending law. This result is contrary to the entangled linear chain system which the short linear chain predominantly determines the relaxation behavior as shown by Montfort et al. [16] and Kurata [17]. This may be due to the strong effect of chain architecture that results in the different relaxation mechanisms between entangled linear and star polymers. Considering the tube model, [11–14] there are two competing mechanisms of relaxation for the entangled linear polymers, reptation and CR, while they are path-breathing (arm-retraction) and CR for the star polymers. These different relaxation mechanisms may result in the different binary blending laws for entangled linear–linear and star–star polymer blends.

Fig. 2 shows the comparative result of zero-shear viscosity between experimental data and theoretical prediction for the 105L/75S blend system. As pointed out by Graessley et al. [8,9], the component viscosity is nearly same for this blend and there is a weak maximum around $v_2 = 0.5$. The quadratic binary blending law also predicts that there is a weak maximum around $v_2 = 0.65$. The predicted zero-shear viscosity of the blends changes less than the experimental data across the composition range. The difference between the predicted values and experimental data is less than 15%. Fig. 3 shows the comparative results of zero-shear viscosity between experimental data and theoretical prediction for the 41L/127S, 105L/127S, and 174L/127S blends. As in the star–star blends, $(\eta_0)_b$ increases

Fig. 4. Recoverable compliance $(J_e^o)_b$ vs. the volume fraction of star-component (v_2) for 41L/127S (●), 105L/127S (■), 174L/127S (▲), 75S/127S (○), and 105L/75S (□) series of polybutadiene system. Points denote the experimental data and the solid line represents the predicted values.

monotonically with the increasing volume fraction of the star components and the predicted values fit the experimental data very well.

3.3. Steady-state recoverable compliance

The calculated and experimental results of the steady-state recoverable compliance, $(J_e^o)_b$ of the blends is showed in Fig. 4. For 75S/127S, 41L/127S, 105L/127S, and 174L/127S series, it is found that $(J_e^o)_b$ initially increases with the increasing volume fraction of long-arm star components, v_2 , then reaches a maximum and finally it decreases with the increasing volume fraction, v_2 . However, the recoverable compliance of the blend, 105L/75S, increased monotonically with the increasing volume fraction of the star components. The predicted values can fit the experimental data and predict the trend very well. It reconfirms that the quadratic binary blending law and the assumption that the long-arm star chain is predominant in the relaxation behavior of star–star polymer blends are reasonable.

Another interesting thing is the relation between the steady-state recoverable compliance, $(J_e^o)_b$, and the volume fraction of long-arm star polymer, v_2 , near $v_2 = 1$. Yoshida et al. [11] and Struglinski et al. [9] have pointed out that the steady-state recoverable compliance, $(J_e^o)_b$, of the linear–star and star–star blends containing concentrated long-arm star chains entangled with much shorter chains, is inversely proportional to the volume fraction of the long-arm star chain. This relation can be predicted from the mixing rule proposed in Section 2. Furthermore, it can be easily deduced that $(J_e^o)_b \propto v_2$ with $M_1/M_2 = 1$ from Eq. (16). The relation agrees with the experimental ob-

Fig. 5. Dynamic storage modulus for selected compositions of the 105L/127S series. Points denote the experimental data and the solid line represents the predicted values. $v_2 = 0.75$ (◆,◇), 0.5 (▼,▽), 0.3 (■,□), 0.2 (▲,△), and 0.1 (●,○)

servation very well. Struglinski et al. [9] pointed out that the steady-state recoverable compliance is proportional to the volume fraction of star chain for 105L/75S, where the star-equivalent molecular weight of 105L is nearly same as the molecular weight of star chain. Also, it can be proved from Eq. (16) that it will systematically depart from the relationship, $(J_e^o)_b \propto 1/v_2$, when the molecular weight of short-arm chain becomes closer to the molecular weight of long-arm chain. In Fig. 4, it is shown that the prediction of relation between $(J_e^o)_b$ and v_2 agrees with the experimental data very well.

Fig. 6. Dynamic loss modulus for selected compositions of the 105L/127S series. Points denote the experimental data and the solid line represents the predicted values. $v_2 = 0.75$ (◆,◇), 0.5 (▼,▽), 0.3 (■,□), 0.2 (▲,△), and 0.1 (●,○)

3.4. Dynamic moduli

In Ref. [9], the published experimental observation on the frequency dependence of storage and loss moduli are limited only to the 105L/127S series. Thus, only the dynamic moduli of the 105L/127S blend are predicted here. The values of dynamic storage and loss moduli of blends can be predicted from Eqs. (18) and (19) with known values of dynamic moduli of pure components. The results are shown in Figs. 5 and 6. The lines represent the calculated results of the linear–star polymer blends. The filled and open points represent the experimental data [9]. The experimental data at the high frequency side ($\log \omega > 1$) is so crowded that it is difficult to extract from original figure of Ref. [9]. However, the difference of dynamic moduli of star and linear polymers is very small in the high frequency region [9]. Thus, the mixing rule should predict the dynamic moduli quite well in this region. From Figs. 5 and 6, it was found that the predicted values can fit the experimental data very well.

4. Conclusion

In this work, a quadratic blending law on the relaxation spectra for the star–star and linear–star polymer blends is proposed. On the contrary to linear–linear blends, for the linear–star polymer blends, the star component is dominant and the long-arm star component is dominant for the star–star polymer blends. In addition, the ‘iso-relaxation time’ approach is proposed to obtain the ‘star-equivalent’ molecular weight, M^* , for the monodispersed linear component of blends.

Both the quadratic binary blending law and ‘iso-relaxation time’ approach can provide a generally excellent prediction on the compositional dependence of the zero-shear viscosity, steady-state recoverable compliance, and dynamic modulus for the entangled linear–star and star–star polybutadiene blends.

The trends that, $(J_e^o)_b$ initially increases with increasing volume fraction of star component (v_2) then reaches a maximum, $(G'_0)_b \propto \omega^2$ and $(G''_0)_b \propto \omega$, all can be predicted fairly well with the experimental observations.

The quadratic binary blending law can predict the

well known relationship, $(J_e^o)_b \propto 1/v_2$, near $v_2 = 1$. Furthermore, it predicts that it will systematically depart from the relationship, $(J_e^o)_b \propto 1/v_2$, when the molecular weight of short-arm chain (or star-equivalent chain) becomes closer to the molecular weight of long-arm chain. In the limit, $M_1/M_2 = 1$, the relationship is switched to $(J_e^o)_b \propto v_2$.

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