Viscoelastic Properties of Blends of Poly(Methyl Methacrylate)s

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ABSTRACT: The viscoelastic properties of molten blends of poly(methyl methacrylate)s having different molecular weights were measured, and several characteristic parameters resulting from these measurements were determined.

The Vogel temperature T_0 , plotted against the weight fraction of the high molecular-weight component, w_2 , has a minimum at about $w_2 = 0.2$, while the temperature coefficient of the fractional free volume, α_f , is almost constant in the entire range of w_2 . The steady-state compliance J_e^0 of the blends is inversely proportional to w_2^2 , when w_2 is near unity, but it decreases with decreasing w_2 after passing through a maximum at about $w_2 = 0.2$. At this point the higher molecular-weight component shows a shoulder rather than a clear peak on the molecular weight distribution curve for the blend.

The horizontal and vertical shift factors a_M and c_M obtained from the time-composition superposition proposed in our previous papers are respectively related to the interaction parameter λ_2 in the Ninomiya theory and to the steady-state compliance J_e^0 . Further, a_M is proportional to $\bar{M}^{1.2-2.5}$, and c_M to $\bar{M}^{-2.5--2.8}$, where $\bar{M}$ is the calculated weight-average molecular weight of the blend.

KEY WORDS Viscoelasticity / Poly(Methyl Methacrylate) / Blend /
Time-Composition Superposition / Steady-State Compliance / Vogel
Parameters / Molecular Weight Distribution /

In our previous papers¹⁻³ the rheological properties of blends of two components differing only in molecular weights were studied for several kinds of high polymers. It was found that the frequency dependence curves of the storage shear modulus G' and the loss modulus G'' in the terminal or flow zone for blends having different compositions can be superposed into respective master curves by appropriate horizontal and vertical shifts. The horizontal and vertical shift factors, a_M and c_M , depend not only on the composition but also on the difference in average molecular weights of the components. The logarithms of a_M and c_M are proportional to $\log(\eta_{02}/\eta_{0b})$, where η_{02} and η_{0b} are, respectively, the zero-shear viscosities of the high molecular-weight component and the blend.

On the other hand, it has been found in our

recent studies with narrow-distribution polystyrenes⁴ having molecular weights higher than the critical molecular weight M_C that the steady-state compliance J_e^0 is independent of molecular weight; in contrast J_e^0 for fractions of poly(methyl methacrylate)⁵ is proportional to molecular weight. Moreover, for blends of narrow-distribution polystyrenes J_e^0 is proportional to w_2^{-2} , when w_2 , the weight fraction of the high molecular-weight component, is close to unity.

In the present paper, the dynamic viscoelastic properties have been measured for two series of blends of poly(methyl methacrylate)s. The effect of blending on certain rheological parameters, such as the zero-shear viscosity, the steady-state compliance, the horizontal and vertical shift factors, a_M and c_M , and the parameters in the free volume theory, are discussed in connection with the composition of blends.

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EXPERIMENTAL

Materials

Poly(methyl methacrylate)s (PMMA) prepared by anionic and radical polymerizations were employed in this study. The weight-average molecular weight M_w , number-average molecular weight M_n and the ratio M_w/M_n of the PMMA samples are tabulated in Table I. The

Table I. The weight- and number-average molecular weights and their ratio for poly(methyl methacrylate) samples

Sample	M_w	M_n	M_w/M_n
702	174000	139000	1.25
910	52100	37500	1.39
MS	41000	—	—

samples 702 and 910 are the same as those used in the previous study, which were prepared by radical polymerization followed by subsequent fractionation. The other sample MS, on the other hand, was prepared by anionic polymerization using tetrahydrofuran as the solvent and sodium naphthalene as the initiator. The details of the characterization of these samples were described in the previous paper.⁵

To obtain the blends, a mixture of the two components was first dissolved in benzene by stirring. Then the solvent was removed either by freeze-drying or by evaporation from a thin film of the solution. These two methods for removing the solvent gave the same results for the rheological properties. The blends thus obtained were dried in a vacuum oven at 60°C. The sample codes, compositions and calculated

Table II. The weight fraction of high molecular-weight component (702), w_2 , and calculated weight-average molecular weight, $\bar{M}$, of the blend samples

(a) MB1 series (702—912)			(b) MB2 series (702—MS)		
Sample	w_2	$\bar{M}$	Sample	w_2	$\bar{M}$
MB180	0.800	150000	MB270	0.698	134000
MB160	0.600	125000	MB240	0.400	94300
MB140	0.400	101000	MB220	0.200	67700
MB123	0.231	80300	MB210	0.100	54300
MB110	0.101	64400			

weight-average molecular weights $\bar{M}$ of the blends used in this study are shown in Table II. $\bar{M}$ was calculated from the following equation

$$\bar{M} = w_1 M_1 + w_2 M_2 \quad (1)$$

where M_1 and M_2 are the weight-average molecular weights, and w_1 and w_2 are the weight fractions of the low and high molecular-weight components, respectively. The MB1 series are composed of the components 702 and 910, and the MB2 series of 702 and MS.

Measurements

Measurements of the viscoelastic properties were carried out by means of a concentric cylinder type rheometer⁶ which enabled us to measure the storage shear modulus G' and loss modulus G'' over wide ranges of frequencies and temperatures. The frequency dependence curves of G' and G'' measured at various temperatures were superposed on to their respective master curves by a horizontal shift only, according to the time-temperature superposition principle. The reference temperature was 220°C.

RESULTS AND DISCUSSION

Effect of Temperature and Free-Volume Parameters

The shift factors a_T obtained in the course of the time-temperature superposition for the low molecular-weight components 910 and MS are lower than those for the high molecular-weight component 702 at the same temperatures, though the molecular weights of all of these polymers exceed the critical molecular weight of entanglement coupling M_c . Such an unusual result has been reported and discussed in the previous paper.⁵

As is well-known,^{7,8} if the temperature dependence of viscoelastic functions obeys the WLF-type equation, the plots of $-(T - T_r)/\log a_T$ against temperature difference $(T - T_r)$ produce a straight line. From such plots the slopes and intercepts give certain parameters defined in the free-volume theory, such as the Vogel temperature T_0 and the temperature coefficient of the fractional free volume α_f .

The dependences of T_0 and α_f on the composition for the blend series MB1 and MB2 are shown in Figure 1. In this figure, α_f seems to

Figure 1. The Vogel parameters T_0 and α_f plotted against the weight fraction of the high molecular-weight component w_2 .

be independent of the composition, while T_0 for the blend series MB2 shows a minimum at around $w_2 = 0.2$. T_0 for MB1, on the other hand, increases gradually with increasing w_2 . The reason for the minimum in the T_0 curve is not yet clear, but it is noteworthy that the T_0 curve for diethyl phthalate solutions of PMMA also manifests a minimum at a concentration of about 20 %.

Frequency Dependence of Viscoelastic Functions

It has been found for some blends of narrow-distribution polystyrenes studied in the previous paper that the frequency dependence curves of G' manifest the "two-step" plateau³ in the rubbery zone. At the same time, the frequency dependence curves of G'' show two peaks corresponding to the two components in the blend samples. Such a "two-step" plateau suggests the existence of two or three groups of relaxation times associated with entanglement slippage in the binary blends of the narrow-distribution polymers.⁴

In Figures 2—5 are shown master curves of the storage shear modulus G' and loss modulus G'' for the MB1 and MB2 series. The G' curves in Figures 2 and 4 as well as the G'' curves in Figures 3 and 5 do not show the "two-step" plateau clearly, because the molecular weight distributions of PMMA employed in this study

Figure 2. Frequency dependences of G' for the MB1 series and the components, reduced to 220°C.

Figure 3. Frequency dependences of G'' for the MB1 series and the components, reduced to 220°C.

Figure 4. Frequency dependences of G' for the MB2 series and the components, reduced to 220°C.

Figure 5. Frequency dependences of G'' for the MB2 series and the components, reduced to 220°C.

are not as narrow as those used in the case of the polystyrenes.⁴ However, the frequency dependence curves of the viscoelastic functions, especially those for the blends containing small amounts of high molecular-weight component, show the "two-step" plateau. This seems to support our previous viewpoint⁴ that there are three groups of entanglement couplings in blends, each having a different set of relaxation times.

Zero-Shear Viscosity and Steady-State Compliance

The zero-shear viscosity η_0 and the steady-state compliance J_e^0 characteristic of the terminal zone are defined by the following equations

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (2)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{\eta_0^2 \omega^2} \quad (3)$$

In Figure 6, η_0 for various blends and their components is plotted logarithmically against the weight-average molecular weight $\bar{M}$ calculated by eq 1. The points for the blends fall on the straight lines which connect the two points for the pure components. The slopes of the straight lines are 5.0 and 4.0 for the MB1 and MB2 series, respectively. The latter value of 4.0 for MB1 seems to be reliable in that it compares well with the value for the radical PMMA studied in the previous paper, while the former value for MB2 is rather high. This can probably be attributed to the fact that the MB1 series contain MS obtained by anionic polymerization and that the anionic PMMA has somewhat lower η_0 as compared with the radical PMMA of the same molecular weight at the same temperature, as was described in the previous paper.⁵

In Figure 7 is shown the variation of the steady-state compliance J_e^0 with composition for the two blend series. It is evident from this figure that J_e^0 first increases markedly with decreasing w_2 and then decreases after passing through a maximum at about $w_2 = 0.2$. It can also be seen that at higher w_2 the slope of the linear portion of the J_e^0 curve is 2.0; and that the linear portion for MB2 continues longer than

Figure 6. Zero-shear viscosity η_0 of the blends and the components, logarithmically plotted against the calculated weight-average molecular weight $\bar{M}$ at 220°C.

Figure 7. Steady-state compliance J_e^0 of the blends and the components, logarithmically plotted against the weight fraction of the high molecular-weight component.

that for MB1, because the low molecular-weight component of the former is smaller than that of the latter. In the case of MB2, the $\log J_e^0$ vs. $\log w_2$ curve deviates from the straight line at $w_2 = 0.4$. It is very interesting to notice that when w_2 becomes less than this limiting value of 0.4, the high molecular-weight component in the blend cannot show a clear peak but rather only a shoulder on the molecular weight distribution curve, as is shown by the gel-permeation chromatogram in Figure 8.

Figure 8. Gel permeation chromatogram of MB2 series and the components.

Time-Composition Superposition of Viscoelastic Functions

The time-composition superposition principle proposed in the previous papers¹⁻³ can be expressed by

$$G_2^*(i\omega a_M) = G_b^*(i\omega) c_M \quad (4)$$

where $G^*(i\omega)$ is the complex shear modulus, and the subscripts 2 and b denote, respectively, the high molecular-weight component and the blend. a_M and c_M are the horizontal and vertical shift factors, respectively. From this equation, the following relation can be derived

$$\frac{c_M}{a_M} = \frac{\eta_{02}}{\eta_{0b}} \quad (5)$$

or

$$\log c_M - \log a_M = \log \frac{\eta_{02}}{\eta_{0b}} \quad (6)$$

where η_{02} and η_{0b} are the zero-shear viscosity for the high molecular-weight component and the blend, respectively. Furthermore, when we consider that the steady-state compliance does not depend on a_M , the ratio of the steady-state

compliance for the blend, J_{eb}^0 , to that for the high molecular-weight component, J_{e2}^0 , becomes equal to c_M :

$$\frac{J_{eb}^0}{J_{e2}^0} = c_M \quad (7)$$

Eq 4 and 7 show that the shift factors a_M and c_M represent the effect of blending on the very long relaxation times and the steady-state compliance, respectively. Also, a_M has the same meaning as the interaction parameter λ_2 in the Ninomiya theory for binary blends. In our early studies with binary blends of several kinds of polymers, it was found that $\log a_M$ is approximately proportional to $\log (\eta_{02}/\eta_{0b})$:

$$\log a_M = -B \log \frac{\eta_{02}}{\eta_{0b}} \quad (8)$$

with $B = 1.00, 0.46, 0.80$, and 0.80 for polyethylene,¹ polypropylene,⁹ polystyrene,¹⁰ and poly(methyl methacrylate),³ respectively. The other shift factor c_M , on the other hand, can be expressed as follows

$$\log c_M = C \log \frac{\eta_{02}}{\eta_{0b}} \quad (9)$$

with $C = 0.00, 0.55, 0.20$, and 0.20 for the above four materials. These experimental values clearly satisfy the condition:

Figure 9. Horizontal and vertical shift factors, a_M and c_M , obtained from the time-composition superposition, logarithmically plotted against η_{02}/η_{0b} .

$$B + C = 1 \quad (10)$$

This relation is obtained by substituting eq 8 and 9 into eq 6. These results suggest that a_M and c_M depend not only on the composition but also on the difference in molecular weight distribution of the two components. For binary blends, when molecular-weight distributions of the components are very broad or when average molecular weights of the components are close to each other, B is larger and C is smaller, as is the case with polyethylene.

In Figure 9, the shift factors a_M and c_M are logarithmically plotted against η_{02}/η_{0b} for the two blend series used in this study. The slopes B and C given in eq 4 and 5 are, respectively, 0.3 and 0.7 for MB1, and 0.5 and 0.5 for MB2 in the low η_{02}/η_{0b} region, where w_2 is near unity. Since the zero-shear viscosity of the blends η_{0b} is proportional to $\bar{M}^{4.0}$ and $\bar{M}^{5.0}$ for these series, a_M and c_M are, respectively, proportional to $\bar{M}^{1.2}$ and $\bar{M}^{2.8}$ for MB1, and $\bar{M}^{2.5}$ and $\bar{M}^{2.5}$ for MB2. This molecular weight dependence of c_M seems to compare well the variation

of J_e^0 with w_2 shown in Figure 7 when $\bar{M}$ is given by eq 1.

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