Effect of Blending on the Rheological Properties of Polystyrene

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Synopsis

Experimental non-Newtonian viscosity, primary normal stress difference, complex viscosity, and shear stress relaxation were taken for highly fractionated polystyrene in Aroclor 1248 (a chlorinated biphenyl) as well as for blends differing in molecular weight and concentration. The data are described by three parameters: a zero-shear rate value, the slope of the log–log plots in the high shear rate region, and a time constant defined as the inverse of the shear rate at the intersection of the low and high shear rate asymptotes. For the functions measured, the low shear rate region is characterized by a dependence on M_w and the high shear rate region by a dependence on M_n. Implications to polymer processing are discussed.

INTRODUCTION

Improvement of products in the market and the production of new polymers with special properties are two tasks which face industry today. Blending offers one possible route to achieve these goals.[1-5] Little effort outside of industry has been put forth to define the effects of blending on polymer properties, especially the rheological properties. Zabusky and Heitmiller[1] investigated the effect of blending on the stress cracking resistance of polyethylene. Recently, Han and co-workers[2] have investigated the effects of blending incompatible polymers on viscometric properties. The purpose of this work is to determine the effect of blending polystyrenes of different molecular characteristics on the viscometric properties.

The polystyrenes used in this work are fractionated with narrow to moderate distributions (1.06 to 1.69). The solvent is Aroclor 1248, a chlorinated biphenyl and a "good solvent" for polystyrene. Major limitations of this work are three: a linear polymer, a narrow range of concentration (2.5%–7.5% by weight) and molecular weight ($M_w = 411,000$ to $1,800,000$), and a limited range of shear rates (<20 sec^{-1}).

EXPERIMENTAL

Apparatus

All data were taken on a Weissenberg (R16) Rheogoniometer at 25°C following procedures described elsewhere.[6-10] In the course of this study, a

check was made to determine the reliability of the measurements by comparing data taken on the rheogoniometer with that taken on a different type instrument (a coaxial cylinder) in another research laboratory. Viscosity and primary normal stress data were taken on a mixture of PIB in a PIB of different molecular weight by Vale and Pritchard in Manchester, England.[11,12] All data agreed well over the shear rate range common to both instruments.[10]

Materials

The polystyrene (density 1.06 g/cc)[6] was prepared by Pressure Chemical Company of Pittsburgh, and Table I gives the molecular characteristics. The solvent was Aroclor 1248 (density 1.44 g/cc)[6] made by Monsanto. Solution densities are given in Table II. This particular polymer was chosen because, at the initiation of this work, polystyrene was the only well-characterized polymer available in sufficient quantities to pursue the objective. . In the course of this work, the author discovered from original fractionation data provided by Pressure Chemical that the correct M_n for the 1,800,000 polymer was lower than specified which increased M_w/M_n from 1.2 to 1.69.

TABLE I
Molecular Weight of Polystyrene

Nominal mol. wt.	M_w	M_n	M_w/M_n
411,000	394,000	372,000	1.06
860,000	862,000	750,000	1.15
1,800,000	1,906,000	1,128,000	1.69

TABLE II
Solution Properties[a]

Concentration, wt-%	ρ Solution, g/cc	c Polymer, g/cc
2.5	1.427	0.0357
5	1.415	0.0707
7.5	1.402	0.1052

[a] Additivity of volumes is assumed.

RESULTS

Method of Presentation

The simplest method of describing the flow of high polymers in industrial applications has been through the use of equations such as the power law and the Ellis models. These equations express the relationship between η and $\dot{\gamma}$ empirically in terms of constants which are related to the asymptotes and the characteristic shear stress or shear rates. The method of presentation here follows the same type of procedure although it does not depend on any particular model.
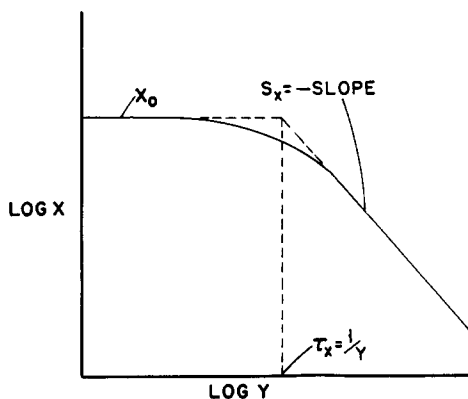
Fig. 1. Nomenclature for material parameters. The curve $X(Y)$ may be any of the following: $\eta(\dot{\gamma})$, $\theta(\dot{\gamma})$, $\eta'(\omega)$, $\eta''(\omega)/\omega$, $|\eta^*(\omega)|$.

Three general parameters have been chosen to describe the curve shown in Figure 1. These parameters are: (1) the zero-shear asymptote or value, (2) the negative of the slope of the curve in the power law region, and (3) the reciprocal of the shear rate (or frequency) at which the low and the high shear rate (or frequency) asymptotes intersect. The latter parameter, a time constant, may be thought of as a characteristic value indicative of the onset of non-Newtonian behavior.

Alternatively, the description of the behavior of these solutions could have been through the use of constitutive equations and/or molecular theories. Generally, however, constitutive equations are difficult to apply in industrial applications, although they are valuable as a means of predicting processing behavior, and constitutive equation parameters have to be redetermined for each new equation. Molecular theories do not apply to blends[10] but are usually restricted to simplifying assumptions such as $c \to 0$ and $M_w/M_n = 1$.

The results below are applicable to both single-component and two-component solutions when c, M_w, and M_n are replaced by

$$c_{\text{blend}} = v_1 c_1 + v_2 c_2 \tag{1}$$

$$M_{w_{\text{blend}}} = w_1 M_{w_1} + w_2 M_{w_2} \tag{2}$$

$$M_{n_{\text{blend}}} = \frac{1}{w_1/M_{n_1} + w_2/M_{n_2}} \tag{3}$$

where v_1 and w_1 are the volume and weight fractions of component 1. Table III gives the blending ratios and the molecular characteristics of the blends. The concentration range covered was 2.5% to 7.5% by weight. Below this range it was difficult to get the power law region of the viscosity and normal stress curves, and above this concentration range it was difficult to get the zero-shear rate region on the rheogoniometer.[6] Another limitation was the range of shear rates which could be covered without

TABLE III
Blend Molecular Weights

Blend	M_w	M_n	M_w/M_n
411,000/1,800,000			
3:1	772,000	447,000	1.73
1:1	1,150,000	559,500	2.06
1:3	1,528,000	748,000	2.04
411,000/860,000			
3:1	511,000	425,600	1.20
1:1	628,000	497,300	1.26
1:3	745,000	598,000	1.25
860,000/1,800,000			
3:1	1,123,000	818,600	1.37
1:1	1,384,000	901,000	1.54
1:3	1,645,000	1,002,000	1.64

complications due to inertial forces. Above approximately 20 sec^{-1}, the fluid would leave the gap for the more concentrated higher molecular weight solutions.

Data are presented both in graphic and empiric forms. The empiric relations are intended mainly to show the functional relationships between the viscometric parameters and the polymer properties. The correlations are good only over the range of concentration and molecular weights studied.

Viscosity

Figure 2 shows the viscosity curves for three blends and their components, typical of the viscosity data in this work. Designation of single-component solutions, e.g., 5-860-48, is by three numbers giving the concentration, the nominal molecular weight, and the Aroclor 1248. Designation of blends, e.g., 5-860-3/5-411-1, is by six numbers giving the concentra-
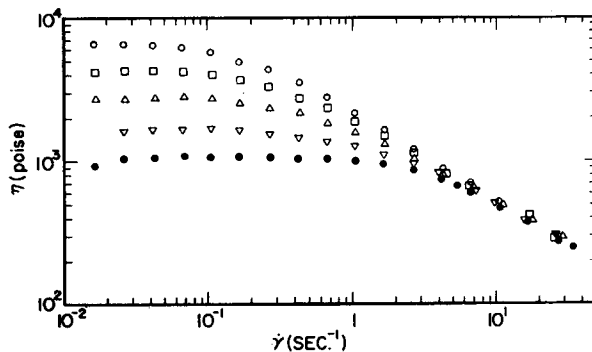

Fig. 2. Non-Newtonian viscosity curves for three blends and their components:
($\bullet$) 5-860-48; ($\triangledown$) 5-860-3/5-1800-1; ($\triangle$) 5-860-1/5-1800-1; ($\square$) 5-1800-3/5-860-1;
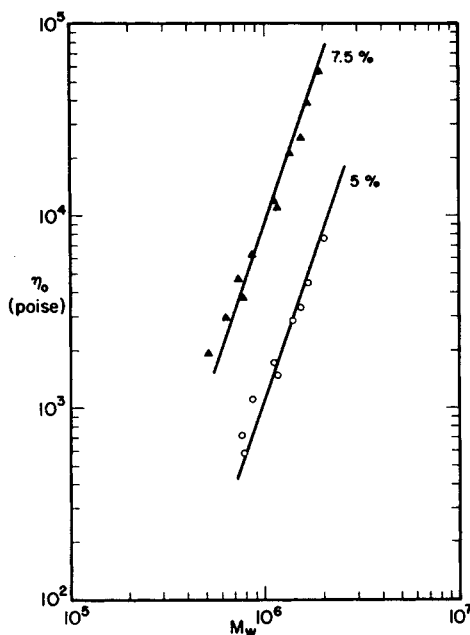($\bigcirc$) 5-1800-48.

Fig. 3. Zero-shear rate viscosity as a function of c and M_w for blends and one-component systems: (O) 5%; (▲) 7.5%.

tion, the nominal molecular weight and the parts by weight of that component in solution.

Equations (4) to (6) and Figures 3 to 5 express the relationship between the three viscosity parameters and c, M_w, and M_n:

$$\eta_0 = 1.27 \times 10^{-9} c^{5.27} M_w{}^3 \tag{4}$$

$$\tau_\eta = 4.0 \times 10^{-16} c^{3.77} M_w{}^{3.3} \tag{5}$$

$$S_\eta = 0.63 \log(c M_n) - 2.46. \tag{6}$$

Literature values for the exponent in eq. (4) are 3.3; the slightly lower value of 3 may be due to inaccuracies in the molecular weight determination discussed previously. Note in Figure 4 that the time constants as defined here for blends fall on the same line with those of the single-solute solutions, unlike the results of Graessley and co-workers[13] who find a different behavior for τ_R (the time constant from Graessley's theory[14,15]) for single- and two-component solutions. Note also in eq. (6) that the slope at high $\dot{\gamma}$ depends on M_n, whereas η_0 depends on M_w. Similar results have been reported by Ballman and Simon.[16]

Figure 6 and eq. (7) express the relationship between η_0 for the blend and η_0 for the components. A similar relation was observed by Onogi and co-workers[17] for melts. The expression

$$\log \eta_{0\text{blend}} \cong w_1 \log \eta_{0_1} + w_2 \log \eta_{0_2} \tag{7}$$

is only an approximation and becomes poorer as the difference between the molecular weights of the components increases.

The importance of the expressions (4) to (7) is their relative simplicity. With them it is thus possible to express the η–$\dot{\gamma}$ relationship of blends from the components.   Blends of incompatible polymers. will not show such simple relationships.[2]
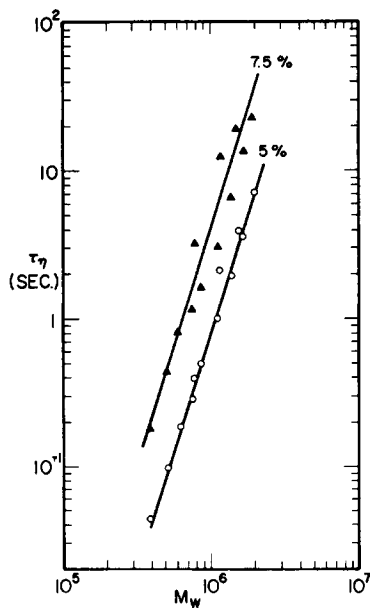

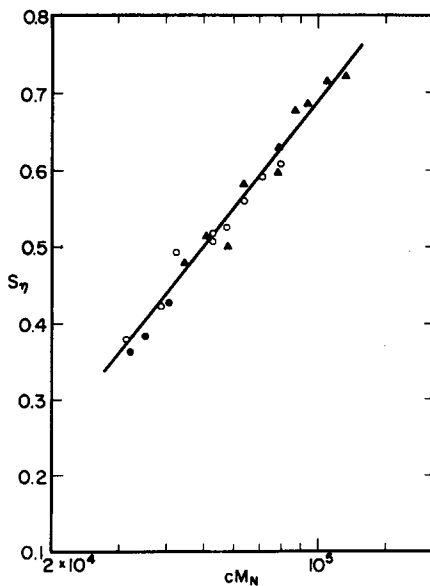Fig. 4. τ_η as a function of c and M_w for blends and one-component systems: (O) 5%;   (▲) 7.5%.

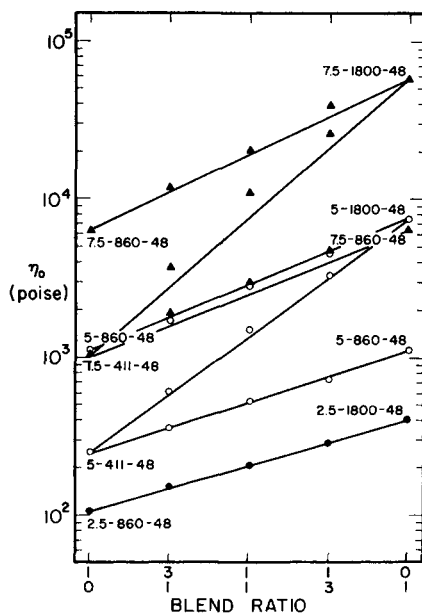Fig. 5. S_η as a function of (cM_n) for blends and one-component systems: (●) 2.5%;   (O) 5%;   (▲) 7.5%.

Fig. 6. η_0 as a function of blend ratio: (●) 2.5%; (○) 5.0%; (▲) 7.5%.

Primary Normal Stress Difference Coefficient

Figure 7 shows the θ data for three blends and their components, typical of all θ data taken. Equation (8) and Figure 8 express the relationship between S_θ and c and M_n.

$$S_\theta = 5.54 \times 10^{-6} \, cM_n + 0.69. \tag{8}$$

The rheogoniometer was not sensitive enough to determine θ_0 and hence τ_θ. It was found possible, however, to relate $\theta(\dot{\gamma})$ at constant $\dot{\gamma}$ to c and M, much in the same manner as other investigators have described $\eta|_\tau$ or $\eta|_{\dot{\gamma}}$.[18] Figures 9 to 11 present the results. Again the feature is simplicity of relationships. Note also that the slope in the high $\dot{\gamma}$ region is a function of M_n, as was S_η.

Small-Amplitude Sinusoidal Shearing

Figure 1 also applies to the functions $|\eta^*|$ and η''/ω from small-amplitude sinusoidal shearing. The function $|\eta^*|(\omega)$ is the same as the function $\eta(\dot{\gamma})$[17,20,21] for the solutions and also for the blends; therefore, the results for $\eta(c, M_w, M_n)$ apply to $|\eta^*|$.

The function $(\eta''/\omega)_0$, like θ_0, could not be determined on the rheogoniometer for the solutions used. The parameter $S_{\eta''/\omega}$ as a function of c and M_n is given in eq. (9). Note again that the slope depends on M_n as was the case for S_η and S_θ:

$$S_{\eta''/\omega} = 1.33 \log (c^{0.387}M_n) - 5.76. \tag{9}$$
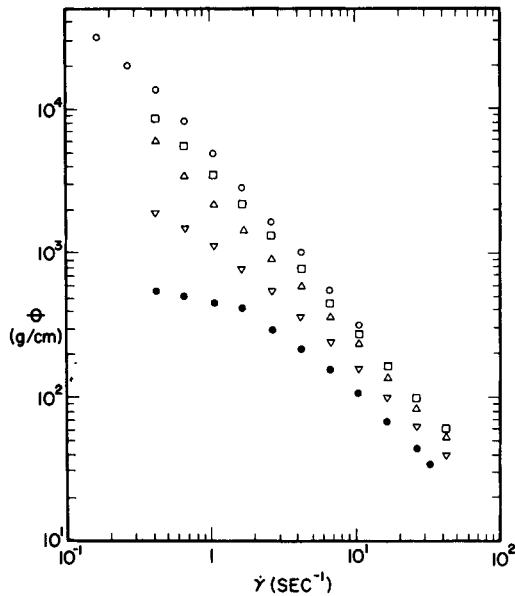
This is also shown in Figure 12.

Fig. 7. θ for three blends and their components: (●) 5-860-48; (▽) 5-860-3/5-1800-1; (△) 5-860-1/5-1800-1; (□) 5-1800-3/5-860-1; (○) 5-1800-48.
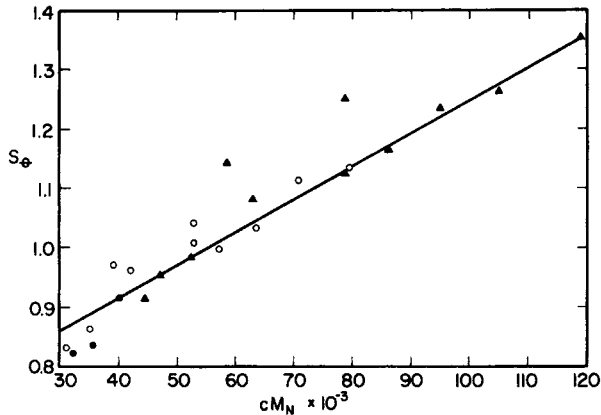

Fig. 8. S_θ as a function of (cM_n) for blends and one-component systems: (●) 2.5%; (○) 5%; (▲) 7.5%.

Shear Stress Relaxation

Figures 13 and 14 show the transient shear stress behavior of the blends and their components. The function $\bar{\eta}(\dot{\gamma}_0, t)$ represents the shear stress relaxation following cessation of steady simple shearing. The degree of stress relaxation depends on the largest molecule, with the smaller molecule acting as a diluent. The relationship of blending to the transient behavior is not as simple as that of the steady-state viscometric properties. This is probably due to different kinds of entanglements as suggested by Ferry.[19]
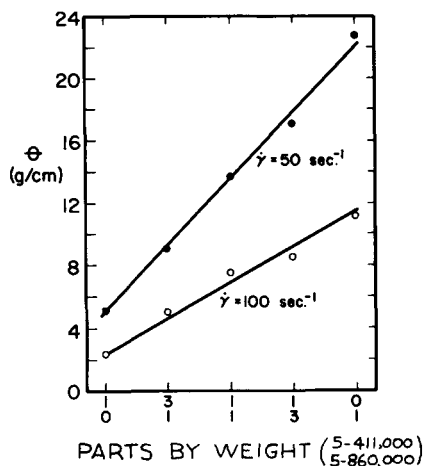
Fig. 9. θ at constant $\dot{\gamma}$ as a function of blend ratio for 5-411-48 and 5-860-48: ($\bullet$) $\dot{\gamma}$ = 50 sec^{-1}; (O) $\dot{\gamma}$ = 100 sec^{-1}.
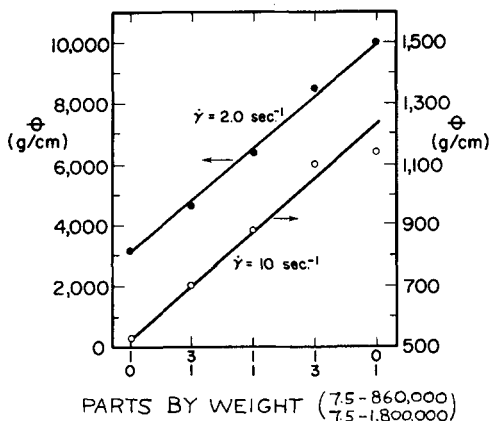

Fig. 10. θ at constant $\dot{\gamma}$ as a function of blend ratio for 7.5% –860,000 (ref. 2) and 7.5%—1,800,000.

POLYMER PROCESSING

Effect of Blending

This work has shown how the viscometric properties of blends can be predicted from the component properties. Within the experimental limitations listed in this paper, the blends behave viscometrically as a single-solute system. The zero-shear rate region is controlled by M_w and the power law region, by M_n. Tables IV and V show the effect on viscometric properties of holding M_w or M_n constant and varying M_w/M_n. Both M_w and M_n must be specified to predict the complete flow curve. Since processing conditions generally cover a wide range of shear rates, processibil-
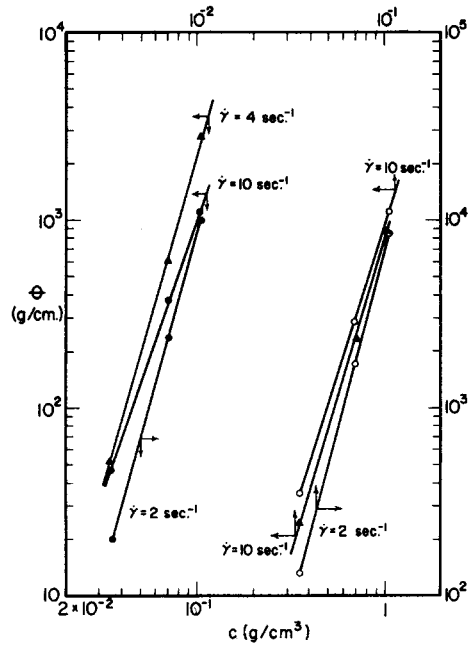
Fig. 11. θ at constant $\dot{\gamma}$ and M_w as a function of c: ($\bullet$) 2.5%, 5%, 7.5% —1,800,000; ($\bigcirc$) 2.5%, 5%, 7.5%—1,800,000 (3 parts)/860,000 (1 part); ($\blacktriangle$) 2.5%, 5%, 7.5%— 1,800,000 (1 part)/860,000 (1 part).
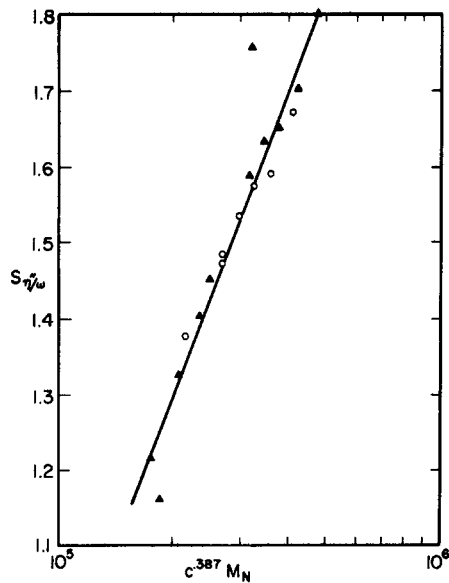
Fig. 12. $S_{\eta''/\omega}$ as a function of $(c^{0.387}M_n)$ for blends and one-component solutions: ($\bigcirc$) 5%; ($\blacktriangle$) 7.5%.

TABLE IV
Viscometric Parameters at Constant M_w with Varying M_n (7.5%)

Solution	η_0	τ_η	S_η	$\left.\dfrac{p_{11} -}{p_{22}}\right\|_{\dot{\gamma}=1\,\text{sec}}$	S_θ	M_w	M_n
411-1/1800-1	11,000	12.5 (5.5)[a]	0.47	9,100	1.14	1,150,000	559,500
860-3/1800-1	11,800	3.1 (5.5)[a]	0.68	10,300	1.16	1,123,000	818,600
411-3/1800-1	3,700	3.2 (1.5)[a]	0.37	3,600	0.95	772,000	447,000
411-1/860-3	4,600	1.2	0.58	3,500	1.08	745,000	600,000

[a] Values from eq. (5).

TABLE V
Viscometric Parameters at Constant M_n with Varying M_w (7.5%)

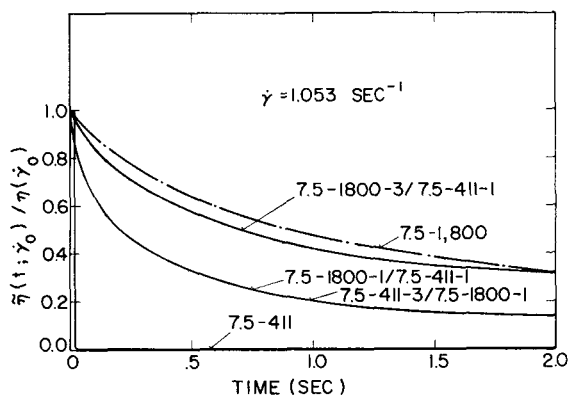| Solution	η_0	τ_η	S_η	$\left.\dfrac{p_{11} -}{p_{22}}\right\|_{\dot{\gamma}=1\,\text{sec}}$	S_θ	M_w	M_n
860	6,400	1.6	0.64	6,500	1.13	862,000	750,000
411-1/1800-3	25,400	19.2	0.60	17,300	1.25	1,528,000	748,000
411-3/1800-1	3,700	3.2	0.37	3,600	0.95	772,000	447,000
411-3/860-1	1,900	0.45	0.48	990	0.92	511,000	426,000

Fig. 13. $\bar{\eta}(t;\dot{\gamma}_0)/\bar{\eta}(\dot{\gamma}_0)$ for three blends and their components at $\dot{\gamma} = 1.05$ sec^{-1}.
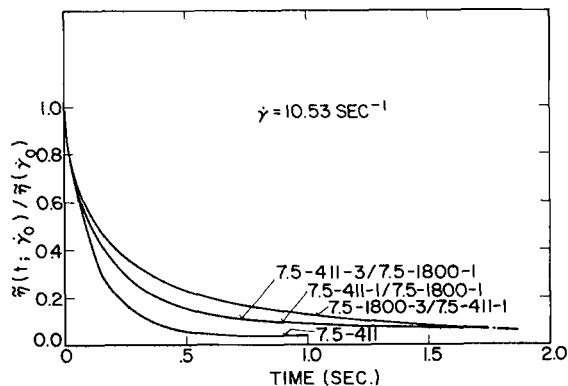

Fig. 14. $\bar{\eta}(t;\dot{\gamma}_0)/\bar{\eta}(\dot{\gamma}_0)$ for three blends and their components at $\dot{\gamma} = 10.5$ sec^{-1}.

ity can be changed by blending to alter the zero-shear rate viscosity, the power law slope, or the time constant (i.e., a measure of the viscoelastic response to flow changes) if these changes are not detrimental to final product properties. The difference of behavior in the two regions also suggests methods for quality control.

Mechanism

The number of entanglements is governed by M_n in the high $\dot{\gamma}$-region where M_n is a measure of the probability or frequency of entanglements. The effect of adding a low molecular weight component to a system is the altering of the type of entanglement present as has been suggested by Ferry.[19] The shearing action for the 411,000 polymer does not produce much of a change from a Newtonian fluid (low S_η value), indicating that the rate of breakage is slightly greater than the rate of entanglements. For the 1,800,000 polymer, the value of S_η is much greater, indicating a high rate of breakage of entanglements. The 411,000 molecule can be pictured as rotating in the shearing field, thus only slightly reducing its probability of forming entanglements. The 1,800,000 molecule can be pictured as parallelizing with the shearing direction, thus greatly reducing its rate of reformation. The addition of 411,000 to 1,800,000 thus leads to a mixture of entanglement types.[19] It should be noted that none of the solutions in this study degraded, and flow curves could be repeated from low $\dot{\gamma}$ to high and back to low $\dot{\gamma}$.

SUMMARY

Simple methods may be used to predict the non-Newtonian flow properties of blends from the properties of the components under the restrictive nature of the materials used. The three parameters η_0, τ, and S are shown to describe the polymer systems well for both blends and single-component solutions. The zero-shear rate parameters depend on M_w, while the power law region depends on M_n. Implications to polymer processing have been discussed.

FUTURE WORK

There are many areas of study which could be pursued from this work. Wider ranges of concentration and molecular weight and the effect of branching could be studied. As other well-characterized polymers become available in sufficient quantities, this work could be repeated. Three-component blends and blends of different types of polymers also offer topics for future study.

Molecular theories for polydisperse polymers are lacking due to the complexity of describing a variable M_w/M_n. However, it seems possible that by choosing experiments carefully to provide clues as to the nature of entanglements, a molecular theory such as that presented by Lodge[12] could

be developed by prescribing various rates of breakage and formation of entanglements.

Nomenclature

c	polymer concentration, g/cm^3
M	molecular weight
M_n	number-average molecular weight
M_w	weight-average molecular weight
$p_{11} - p_{22}$	primary normal stress difference for viscometric flow $v_1 = v_1(x_2)$ (notation and sign convention of Lodge)
S_η	slope of log viscosity versus log shear rate in high shear rate region
$S_{\eta'}$	slope of log dynamic viscosity versus log frequency in high-frequency region
$S_{\eta''/\omega}$	slope of log η''/ω versus log frequency in the high-frequency region
S_θ	slope of log θ versus log shear rate in high shear rate region
v_i	volume fraction of ith component
w_i	weight fraction of ith component
$\dot{\gamma} = \dfrac{dv_x}{dy}$	shear rate, cone-and-plate system, $= \Omega/\beta$, sec^{-1}
η	non-Newtonian viscosity, poise
η_0	zero-shear rate viscosity
η'	dynamic viscosity
η''	imaginary part of complex viscosity
$\lvert\eta^*\rvert = \sqrt{\eta'^2 + \eta''^2}$	magnitude of complex viscosity
η''/ω_0	zero-frequency value of η''/ω
$\tilde{\eta}(t;\dot{\gamma}_0)$	shear stress relaxation function
θ	primary normal stress difference coefficient ($= p_{11} - p_{22}/\dot{\gamma}^2$), g/cm
θ_0	zero-shear rate primary normal stress difference function
τ_η	viscosity curve time constant, see Fig. 1
$\tau_{\eta'}$	dynamic viscosity curve time constant, see Fig. 1
$\tau_{\eta''/\omega}$	η''/ω curve time constant, see Fig. 1
τ_θ	θ curve time constant, see Fig. 1
ω	frequency of oscillation, rad/sec

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