

Influence of polydispersity on the viscoelastic properties of linear polydimethylsiloxanes and their binary blends

J.A. Ressia, M.A. Villar, E.M. Vallés*

Planta Piloto de Ingeniería Química, UNS-CONICET, CC 717, 8000 Bahía Blanca, Argentina

Received 30 November 1998; received in revised form 24 May 1999; accepted 10 January 2000

Abstract

Linear polydimethylsiloxanes of relatively narrow molecular weight distribution (MWD) were synthesized by anionic polymerization and characterized by different techniques. Binary blends were also prepared with some of the synthesized polymers. Linear viscoelastic parameters, such as storage (G') and loss (G'') moduli, were obtained at different temperatures as functions of frequency (ω). The time–temperature superposition principle was applied in order to increase the frequency range measured. Zero-shear rate viscosity (η_0), steady-state recoverable compliance (J_e^0) and zero-shear rate first normal stress coefficient ($\Psi_{1,0}$) were calculated from the data corresponding to the terminal relaxation zone. The molecular weight dependence of those parameters shows a good agreement with classical models and previously reported results, although J_e^0 and $\Psi_{1,0}$ are strongly affected by polydispersity. Different polydispersity factors were applied in order to fit the experimental values of the viscoelastic properties with the theory. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polydimethylsiloxane; Polydispersity; Steady-state viscoelastic properties

1. Introduction

Steady-state rheological properties of molten polymers are generally characterized by the zero-shear viscosity, η_0 , the steady-state recoverable compliance, J_e^0 , and the zero-shear rate first normal stress coefficient, $\Psi_{1,0}$. When plotted against the weight average molecular weight, M_w , zero-shear rate viscosity measurements for linear polymer systems clearly show two regions [1,2]. They can be represented as follows:

$$\eta_0 = KM_w^a \quad (1)$$

where K is a constant for each polymer and temperature; $1 \leq a \leq 2.5$ below a certain molecular weight, namely the viscosity critical molecular weight, M_c , and $a \cong 3.4$ – 3.7 above M_c [2,3]. $M_c \cong 2M_e$, where M_e is the average molecular weight between entanglements.

For monodisperse linear polymers the steady-state recoverable compliance increases linearly with M_w below its critical molecular weight, $M_c' \cong 2 - 3M_c$, and becomes independent of M_w at molecular weights above M_c' [2,3].

The zero-shear rate first normal stress coefficient, $\Psi_{1,0}$,

can be expressed as [2]:

$$\Psi_{1,0} = 2\eta_0^2 J_e^0 \quad (2)$$

Thus, for monodisperse linear polymers with $M_w > M_c'$, the following relationship is expected [2]:

$$\Psi_{1,0} \propto M_w^{2a} \quad (3)$$

However, these steady-state properties are affected by the molecular weight distribution, MWD. In particular the steady-state recoverable compliance is strongly influenced by polydispersity. Then, for polydisperse systems, a proper way to present the viscoelastic properties must include a *polydispersity factor*, in order to account for the changes between the values corresponding to mono and polydisperse polymers with the same M_w . Thus, zero-shear rate viscosity and steady-state recoverable compliance for polydisperse molten polymers should be written as:

$$\eta_0 = \eta_{0,M} P_\eta = KM_w^a P_\eta \quad (4)$$

$$J_e^0 = J_{e,M}^0 P_J \quad (5)$$

where $\eta_{0,M}$ and $J_{e,M}^0$ represent the steady-state values for the analogous monodisperse polymers and P_η and P_J are the polydispersity factors for η_0 and J_e^0 , respectively. These factors are usually functions of the MWD, as it will be shown later.

* Corresponding author. Tel.: + 54-291-4861700; fax: + 54-291-4861600.

E-mail address: valles@plapiqui.edu.ar (E.M. Vallés).

Table 1
Number and weight average molecular weight and polydispersity of the synthesized and commercial linear polydimethylsiloxanes obtained by SEC

Polymer	$M_n \times 10^{-4}$ SEC	$M_w \times 10^{-4}$ SEC	M_w/M_n SEC	$M_n \times 10^{-4}$ FTIR	$M_n \times 10^{-4}$ MO	$M_w \times 10^{-4}$ LALLS
LM1	1.04	1.25	1.20	1.36		1.40
LM2	1.68	2.19	1.30	1.56		1.94
LM3	2.16	2.36	1.09	2.56		
LM4 ^a	2.22	2.43	1.09	2.12		2.69
LM5	2.47	3.05	1.23	3.32		
LM6 ^a	4.38	4.70	1.07	4.63		5.24
LM7 ^a	4.86	5.55	1.14	4.70		
LM8	8.81	9.23	1.05		9.75	10.00
LM9 ^a	8.83	9.97	1.13			10.11
LM10 ^a	8.96	11.11	1.24	9.66		12.87
LM11	13.63	16.83	1.24		15.50	18.30
LM12	17.26	25.29	1.47		17.30	25.00
LM13	22.47	26.94	1.20		20.20	29.50
LM14	27.39	31.43	1.15			
LB1	1.17	1.47	1.26	1.07		1.37
LB2 ^a	2.75	3.12	1.13	3.24		4.40
PD1	4.15	6.44	1.55			
PD2	5.18	8.37	1.62			
PD3	10.11	14.47	1.43			
PD4	10.89	25.09	2.30			
PD5	33.18	50.57	1.52			

^a Villar et al. [12].

From Eqs. (2)–(5), one can obtain the expression for the zero-shear rate first normal stress coefficient for polydisperse linear polymers with $M_w > M'_c$:

$$\Psi_{1,0} = 2(\eta_{0,M} P_\eta)^2 J_{e,M}^0 P_J \propto M_w^{2a} P_\eta^2 P_J \quad (6)$$

J_e^0 is strongly influenced by polydispersity and P_J values may be large, even for polymers with relatively narrow MWD. In contrast, viscosity is not seriously affected by polydispersity and P_η is always close to unity. Since $\Psi_{1,0}$ depends on P_J , it is also affected by polydispersity.

In this paper we report results on the rheological behavior of relatively narrow MWD linear PDMS in the molten state, some of their binary blends and a series of commercial polymers. Then, we analyze the influence of MWD on the viscoelastic properties, taking into account several polydispersity factors previously reported [1,4–11].

2. Experimental

2.1. Synthesis and molecular characterization

Linear polydimethylsiloxanes (PDMS) with relatively narrow molecular weight distribution were synthesized by anionic polymerization. The monomer used was hexamethylcyclotrisiloxane (D₃) (Petrarch Systems, Inc.). The reactions were initiated by *n*-butyl lithium (Alfa Ventron, 2.1 M in hexane) and carried out in glass reactors under vacuum in order to avoid the presence of non-desirable moieties such as H₂O, O₂ or CO₂. Previously distilled and dried *n*-hexane and tetrahydrofuran (THF) were used as solvent and solvating agent. Vinylidimethylchlorosilane

(Petrarch Systems, Inc.) was utilized as termination agent to introduce one or two terminal functional groups in the linear PDMS chain.

Table 1 shows all the linear polymers obtained. The nomenclature utilized was the following: polymers labeled as LM are linear monofunctional PDMS, those named as LB are linear difunctional PDMS and those identified as PD are commercial (Petrarch Systems, Inc.) polydisperse PDMS. Some of these polymers were synthesized and characterized in a previous work [12]. Monofunctional PDMS were obtained using *n*-hexane as solvent and difunctional PDMS were obtained with THF as solvent for the initiation step and also for the reaction [12]. Four sets of binary blends were prepared by mixing the highest M_w synthesized polymer (LM14) with polymers LM8, LM9, LM11 and LM13 at concentrations ranging from 5 to 75 wt% of polymer LM14.

All the polymers and blends were characterized using Size Exclusion Chromatography (SEC) in a Waters Model 440 Liquid Chromatograph at room temperature. Toluene was used as mobile phase at a flow rate of 1 ml/min. A set of four μ -Styragel columns (500, 10³, 10⁴ and 10⁶) was employed. Number and weight average molecular weights (M_n and M_w) of the linear polymers were obtained by calibrating the SEC with narrow MWD polystyrene (PS) standards (Press Chem. Corp.). Benoit universal calibration [13] was used and the Mark–Houwink constants for PDMS and PS in toluene at 20°C were obtained from the literature [14]. The adopted values were $K = 4.16 \times 10^{-3}$ and $\alpha = 0.788$ for PS and $K = 2.43 \times 10^{-3}$ and $\alpha = 0.84$ for PDMS. The resulting molecular weights are shown in Table 1. The elution chromatograms show that blends B1 and B2 present

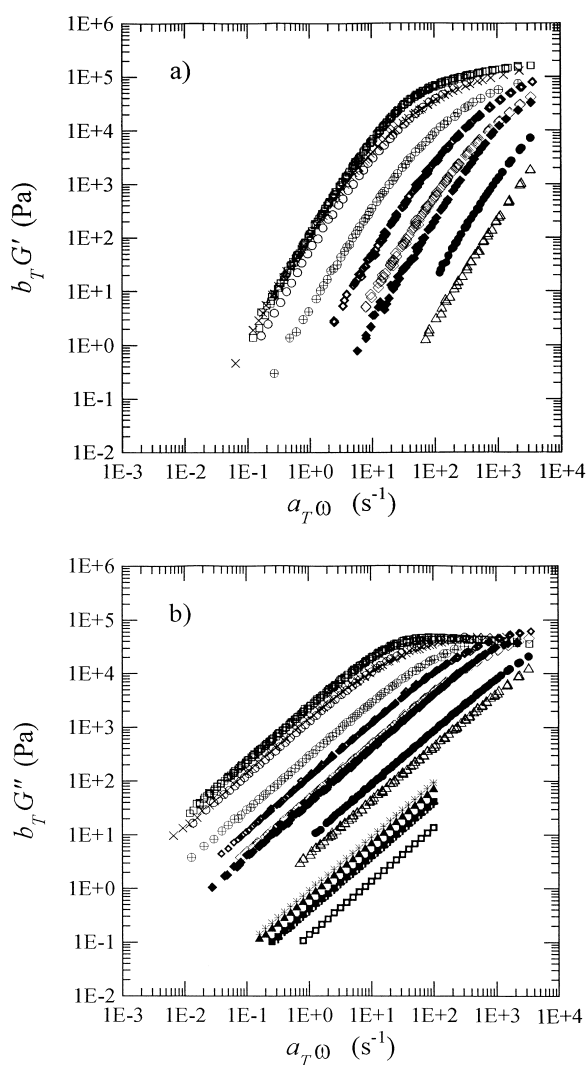


Fig. 1. (a) Elastic modulus (G') and (b) loss modulus (G'') as functions of frequency (ω) at 20°C for the anionic synthesized PDMS. Symbols: (□) LM1; (+) LM2; (■) LM3; (▲) LM4; (*) LM5; (△) LM6; (●) LM7; (◆) LM8; (◇) LM9; (◊) LM10; (⊕) LM11; (×) LM12; (○) LM13; (□) LM14.

clear bimodal distribution curves, while B3 and B4 do not. In previous works [12,15] we used a different set of Mark–Houwink constants for SEC characterization of some of the synthesized polymers and blends. However, in this work we preferred the set shown above, which led to slightly lower (about 8%) PDMS molecular weights.

Number average molecular weights of most of the synthesized PDMS were also obtained by Infrared Spectroscopy (FTIR) and Membrane Osmometry (MO). A Low-angle Laser Light Scattering (LALLS) photometer (Chromatrix KMX-6) was utilized to determine the weight average molecular weight of most of the polymers. Experimental conditions can be found in previous work [12]. Results for these measurements are also shown in Table 1.

2.2. Rheological measurements

The rheological characterization of the linear PDMS and the blends was carried out in a Rheometrics Dynamics Analyzer RDA-II at temperatures ranging from -40 to 150°C . Shear flow was obtained by dynamic tests using 25 mm diameter parallel plates. Strain-sweep tests were performed for the different samples at predetermined temperatures, several frequencies, ω , and various strains in order to determine the operable strain range for achieving linear viscoelasticity. The storage (elastic) modulus, G' , and the loss (viscous) modulus, G'' , were measured for frequencies ranging from 0.05 to 500 s^{-1} . Master curves for G' and G'' were obtained using the time–temperature superposition principle [2] at 20°C as reference temperature. With this procedure the range of measured frequencies was increased by almost two decades.

3. Results and discussion

The IRIS software [16] was used to obtain the master curves at 20°C for G' and G'' for all the polymers and blends. Fig. 1a and b shows the plots of G' and G'' as functions of the shear frequency for all the synthesized polymers. Fig. 2a and b shows the moduli for the five commercial PDMS analyzed. Expected values of 2 and 1 for the G' and G'' slopes at the terminal relaxation zone [2] were obtained for all the polymers except for the PD5. In this case the slope of the elastic modulus at low frequencies was found to be 1.83.

For the polymers LM1 to LM5, LB1 and LB2 we were not able to measure the elastic modulus (G') because the low molecular weight polymers have low viscosity and elasticity. For the time–temperature superposition, two shift factors were obtained: the frequency shift factor, a_T , and the modulus shift factor, b_T . Then it is possible to obtain a single master curve by plotting $b_T G'$ and $b_T G''$ versus $a_T \omega$ for each polymer. Two typical relationships often used to explain the dependence of a_T with temperature were analyzed: an Arrhenius type dependency [2,17], and the Williams, Landel and Ferry equation (WLF) [17]. For the set of polymers analyzed, a value of 2050.5 K was found for $\Delta\tilde{H}_a/R$, where $\Delta\tilde{H}_a$ is the flow activation energy for the Arrhenius expression and the WLF equation constants were found to be: $c_1^0 = 2.31$ and $c_2^0 = 223.8\text{ K}$. Both the activation energy and c_1^0 and c_2^0 constants are in good agreement with reported values for molten PDMS [2].

The zero-shear rate viscosity, η_0 , the zero-shear rate first normal stress coefficient, $\Psi_{1,0}$, and the steady-state recoverable compliance, J_e^0 , can be calculated from linear viscoelastic properties [2].

Zero-shear rate viscosity values as a function of weight average molecular weight are shown in Fig. 3. The plot presents the two expected regions [2,3]: at low molecular weights (Newtonian viscosity or non-entangling region,

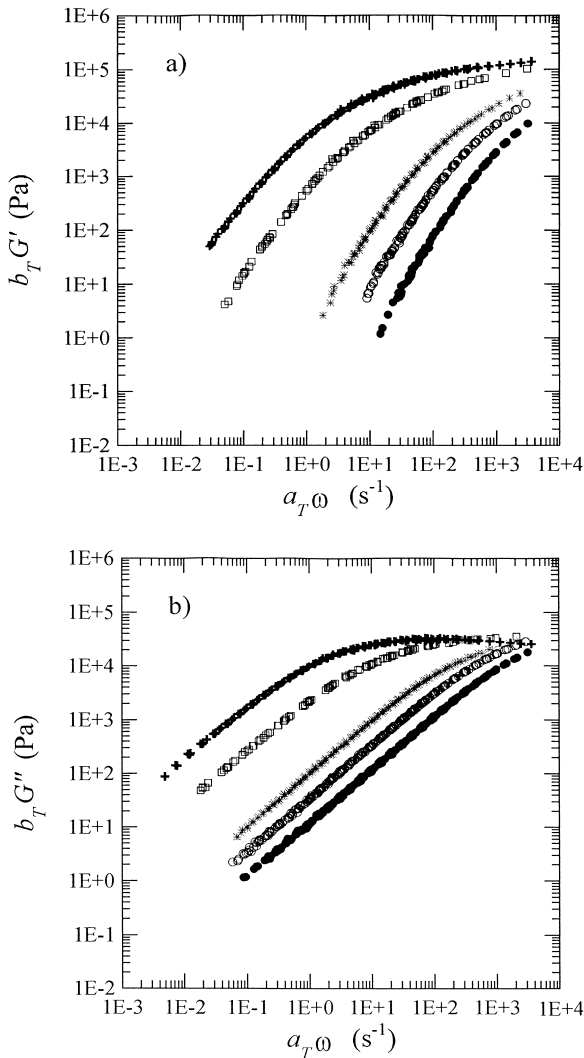


Fig. 2. (a) Elastic modulus (G') and (b) loss modulus (G'') as functions of frequency (ω) at 20°C for the commercial PDMS (Petrarch Systems, Inc.). Symbols: (●) PD1; (○) PD2; (*) PD3; (□) PD4; (+) PD5.

$M_w \leq 23,000$) η_0 increases with $M_w^{1.70}$, while at higher molecular weights (molecular entanglement region, $M_w \geq 31,000$) η_0 increases with $M_w^{3.44}$, in good agreement with experimental results extracted from the literature [2–4].

An important feature is the effect of polydispersity on the viscoelastic properties of the polymers. Polydispersity affects considerably the J_e^0 values of the polymers, even for materials with polydispersities as narrow as $M_w/M_n \cong 1.1$. The steady-state recoverable compliance of the polydisperse PDMS is evidently not constant in the region where $M_w > M_c^l$ and the values obtained are higher than those corresponding to a monodisperse polydimethylsiloxane (Fig. 4) [2,4]. Polydispersity also affects significantly the $\Psi_{1,0}$ values.

In order to take into account the polydispersity effect, several authors [4–11,18–28] have proposed the use of a polydispersity factor, which affects the predicted value of the corresponding viscoelastic property. Thus, Eqs. (4)–(6)

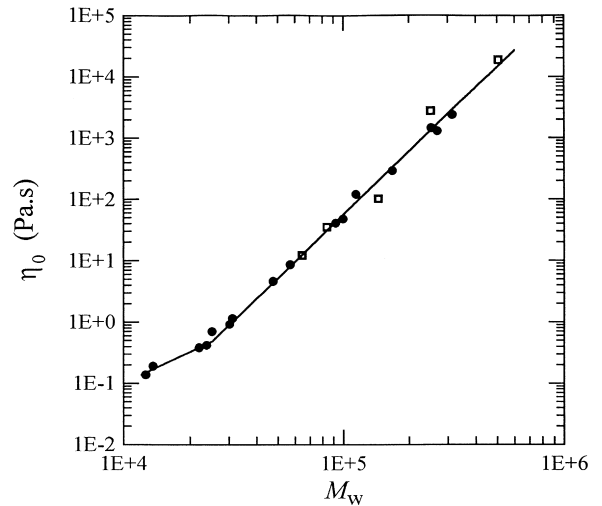


Fig. 3. Zero-shear rate viscosity (η_0) as a function of the weight average molecular weight (M_w) at 20°C for the synthesized and commercial PDMS. Symbols: (●) synthesized PDMS; (□) commercial PDMS.

must be considered. The factors P_η and P_J are functions of the MWD and they are generally defined in terms of the moments of the MWD:

$$Q_j = \sum_{i=1}^{\infty} M_i^j \omega_i \tag{7}$$

Here Q_j represents the moment of order j of the distribution and ω_i is the weight fraction of the macromolecules with molecular weight M_i .

In order to test which of the polydispersity factors are more suitable to correct the measured rheological properties we analyzed some of the models proposed in the literature. The experimental values of η_0 , J_e^0 and $\Psi_{1,0}$, and the

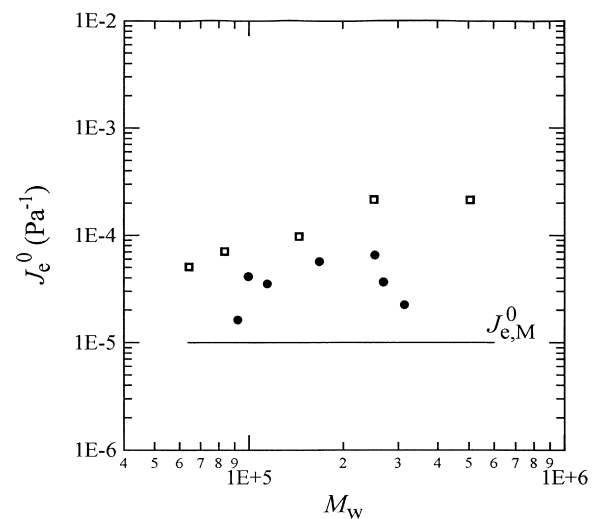


Fig. 4. Steady-state recoverable compliance (J_e^0) as a function of the weight average molecular weight (M_w) at 20°C for the synthesized and commercial PDMS. Symbols are the same as in Fig. 3. Solid line: $J_{e,M}^0$ value for a monodisperse linear PDMS at 20°C above M_c^l [2,4].

Table 2
Models for the viscosity (P_η) and recoverable compliance (P_J) polydispersity factors

Model	Equation	Obtained from
<i>Models for P_η</i>		
Malkin et al. [5]	$P_\eta = \left(\frac{M_z}{M_w}\right)^{1.5} = \left(\frac{Q_2}{Q_1^2}\right)^{1.5}$	Binary blends of linear polybutadienes
Doi and Edwards [9,22]	$P_\eta = \left(\frac{M_z M_{z+1}}{M_w^2}\right)^{3.41/3} = \left(\frac{Q_3}{Q_1^3}\right)^{3.41/3}$	The theory of Doi and Edwards [9], adjusted to give the experimentally observed viscosity power [22]
Anderssen and Mead [11]	$P_\eta = \left(\frac{M_w}{M_n}\right)^c = (Q_1 Q_{-1})^c$	A theoretical derivation based on previously reported works
<i>Models for P_J</i>		
Mills [4]	$P_J = \left(\frac{M_z}{M_w}\right)^{3.7} = \left(\frac{Q_2}{Q_1^2}\right)^{3.7}$	Molten polydisperse PDMS, PS and PE and fractions of them $M_w > 70,000$
Modified Rouse [1,2]	$P_J = \frac{M_z M_{z+1}}{M_w^2} = \frac{Q_3}{Q_1^3}$	A modification of the Rouse model [1,2]
Doi and Edwards [9]	$P_J = \frac{M_{z+2} M_{z+3} M_{z+4}}{M_w M_z M_{z+1}} = \frac{Q_6}{Q_3^2}$	The theory of Doi and Edwards [9]
Montfort et al. [6,7,10,22,24]	$P_J = \frac{Q_{4.4}}{Q_1^{4.4}}$	Binary blends of linear PS fractions, with $\eta_0 \propto M_w^{3.4}$ [22]
Agarwal [8]	$P_J = \frac{M_z M_{z+1}}{M_n M_w} = \frac{Q_3 Q_{-1}}{Q_1^2}$	Binary blend data of different PS systems from literature
Zang et al. [24]	$P_J = \frac{Q_a}{Q_1^a}$	Binary blends of narrow MWD PS, with $\eta_0 \propto M_w^a$

calculated values obtained from the models listed in Table 2 were compared in the region above M'_c .

The anionic PDMS with narrow MWD, their binary blends and the commercial PDMS were used in the experiments. The four sets of blends that were prepared contain the same high- M_w polymer (LM14) and a low- M_w polymer, either LM8, LM9, LM11 or LM13, at different concentrations: 5, 10, 17, 25, 50 and 75 wt% of LM14. Table 3 shows P_η and P_J values for the prepared blends calculated from some of the models presented in Table 2.

Fig. 5 shows the experimental η_0 values for the synthesized and commercial polymers, as well as the prepared blends, as functions of the M_w . Also, the values obtained by correcting the experimental data with the different models enumerated in Table 2 are shown. In order to appreciate better the individual fits to the various models, η_0 values were arbitrarily shifted for each model by multiplying η_0 by a factor A , as labeled in Fig. 5. Eq. (4) with $P_\eta = (M_w/M_n)^{0.5}$ fits with a straight line of slope 3.41 and gives a low dispersion of the experimental data. If no polydispersity factor is taken into consideration, i.e. $P_\eta = 1$, the

crude experimental values present higher deviations from the straight line and give a high value of 3.63 for the slope. When the models of Malkin et al. and Doi and Edwards are used to adjust the data, slopes of 3.33 and 3.21 are obtained and the results also present a higher dispersion. Table 4 presents the values of K and a obtained from the regression of the experimental results when they are adjusted by the polydispersity factor as η_0/P_η for the different models.

From all the models analyzed, that proposed by Anderssen and Mead [11] with $c = 0.5$ gives the best fit for the viscosity values. This exponent was previously reported for polydisperse samples and fractions of high density polyethylene [18]. So, the best representation for all the samples analyzed can be expressed as:

$$\eta_0 \text{ (Pa s)} = 4.51 \times 10^{-16} M_w^{3.41} (Q_1 Q_{-1})^{0.5} \quad (8)$$

The expression is valid for the region $M_w \geq 64,000$.

Although not presented here, the molecular weights of all the blends obtained from SEC were found to be in good agreement with the typical expressions used to calculate the average molecular weights for blends of two

Table 3
Polydispersity factors for η_0 (P_η) and J_c^0 (P_J) of the prepared blends

Blends	Low M_w component	$M_{w,H}/M_{w,L}$ ^a	ω_H ^b (%)	P_η ^c	P_J ^d		
					DE	Montfort	Eq. (16)
B1	LM8	3.41	0	1.02	1.80	1.53	1.42
			5	1.09	12.21	13.07	8.95
			10	1.09	11.65	12.62	8.70
			17.5	1.14	12.41	19.09	12.75
			25	1.18	12.23	19.91	13.29
			50	1.25	7.22	10.89	7.90
			75	1.21	4.50	5.30	4.20
B2	LM9	3.15	0	1.06	2.55	2.37	2.08
			5	1.18	8.18	11.58	8.27
			10	1.17	9.31	12.62	8.87
			17.5	1.20	8.07	12.33	8.79
			25	1.24	8.34	13.31	9.42
			50	1.26	4.22	6.50	5.10
			75	1.21	3.44	4.00	3.30
B3	LM11	1.87	0	1.11	4.59	4.62	3.69
			5	1.14	5.01	5.55	4.34
			10	1.13	4.75	5.10	4.03
			17.5	1.15	5.40	5.93	4.59
			25	1.16	5.43	5.87	4.55
			50	1.16	4.20	4.51	3.63
			75	1.13	3.41	3.24	2.72
B4	LM13	1.17	0	1.10	4.48	4.18	3.36
			5	1.12	4.97	4.70	3.72
			10	1.13	4.81	4.58	3.64
			17.5	1.13	5.92	5.35	4.14
			25	1.14	6.05	5.40	4.18
			50	1.13	5.37	4.50	3.56
			75	1.10	4.39	3.54	2.89
	LM14			1.07	3.51	2.80	2.37

^a $M_{w,H}$ and $M_{w,L}$ are the weight average molecular weight of the higher (LM14) and lower molecular weight polymer in the blend, respectively, obtained by SEC.

^b ω_H is the weight fraction of polymer LM14 and $\omega_H = 0$ corresponds to the pure low M_w component.

^c P_η calculated from the Anderssen and Mead model with $c = 0.5$.

^d P_J calculated from the Doi and Edwards (DE) and Montfort et al. models and from Eq. (16) with $b = 4.08$.

monodisperse polymers [24], i.e.

$$\frac{1}{M_{n,B}} = \frac{\omega_H}{M_{n,H}} + \frac{\omega_L}{M_{n,L}} \quad (9)$$

and

$$M_{w,B} = \omega_H M_{w,H} + \omega_L M_{w,L} \quad (10)$$

Here ω_i is the weight fraction of polymer i and the subscripts H and L represent the higher and lower molecular weight polymers and B denotes the blend. This fact implies that for blends made of polymers with $M_w/M_n < 1.24$ (as the ones presented in this work), Eqs. (9) and (10) accurately adjust the number and weight average molecular weights of the blends. Then, from Eqs. (1) and (10) a mixing rule for the viscosity can be obtained [22]:

$$\eta_{0,B} = \left(\omega_H \eta_{0,H}^{1/a} + \omega_L \eta_{0,L}^{1/a} \right)^a \quad (11)$$

If polydispersity factors are taken into account, Eq. (11) is rewritten as:

$$\eta_{0,B} = P_{\eta,B} \left(\omega_H \left(\frac{\eta_{0,H}}{P_{\eta,H}} \right)^{1/a} + \omega_L \left(\frac{\eta_{0,L}}{P_{\eta,L}} \right)^{1/a} \right)^a \quad (12)$$

where $P_{\eta,H}$ and $P_{\eta,L}$ are the viscosity polydispersity factors for the higher (H) and lower (L) molecular weight component in the blend and $P_{\eta,B}$ is the polydispersity factor of the blend.

Fig. 6 shows the zero-shear rate viscosity of the four sets of blends calculated by Eq. (12), with $a = 3.41$, as functions of the weight fraction of the higher molecular weight polymer in the blend (ω_H). The fit with the experimental values is good and adjusts very well the evolution of the blends. We found that there is not substantial difference between the fits given by Eqs. (11) and (12) for the polymers that we include

Table 4
Constants for the P_η adjustments and regression analysis from the models

Model for P_η	η_0 (Pa s) = $K M_w^a P_\eta$		Statistics of power law ^a	
	$K \times 10^{16}$	a	r^2	$\hat{\sigma}^2$
Experimental ($P_\eta = 1$)	0.375	3.62	0.983	0.046
Malkin et al.	13.85	3.33	0.989	0.024
Doi and Edwards	60.53	3.21	0.952	0.102
Anderssen and Mead ($c = 0.5$)	4.51	3.41	0.998	0.005

^a r^2 is the coefficient of determination and $\hat{\sigma}^2$ is the estimate of the variance.

in this study. But Eq. (12) seems to be a more adequate way to express the viscosity of a blend when its components are not really monodisperse.

In the case of the steady-state recoverable compliance for $M_w > M'_c$, Eq. (5) can be written as:

$$J_e^0/P_J = J_{e,M}^0 = \text{constant} \quad (13)$$

Therefore, if the proposed models for P_J give an adequate correction of the experimental data, by plotting J_e^0/P_J against P_J , a horizontal straight line should be obtained. The models of Doi and Edwards and Montfort et al. adjust fairly well Eq. (13) for the polymers and blends analyzed. The other models for P_J do not give a very good agreement with Eq. (13). Their J_e^0/P_J values are higher than previously reported data for PDMS ($J_{e,M}^0 \cong 10^{-5} \text{ Pa}^{-1}$) [2,4]. Table 5 shows the average deviations of each P_J model from the $J_{e,M}^0$ expected value.

Table 5
Steady-state recoverable compliance average values and average dispersion errors from the expected value ($J_{e,M}^0 \cong 10^{-5} \text{ Pa}^{-1}$) for the analyzed models

Model for P_J	J_e^0 average value (Pa^{-1})	Average error (%)
Experimental ($P_J = 1$)	6.45×10^{-5}	480
Mills	1.98×10^{-5}	98
Modified Rouse	2.58×10^{-5}	158
Doi and Edwards	1.07×10^{-5}	41
Montfort et al.	9.09×10^{-6}	38
Agarwal	1.85×10^{-5}	85
Zang et al.	1.74×10^{-5}	25
$P_J = Q_{4.08}/Q_1^{4.08}$	10^{-5a}	16

^a Proposed from experimental observations for monodisperse linear PDMS at 20°C [2,4].

From the $J_{e,M}^0$ values obtained for the Doi and Edwards and Montfort et al. models for P_J , J_e^0 for $M_w \geq 64,000$ can be expressed as:

$$J_e^0 (\text{Pa}^{-1}) = 1.07 \times 10^{-5} \frac{Q_6}{Q_3^2} \quad (14)$$

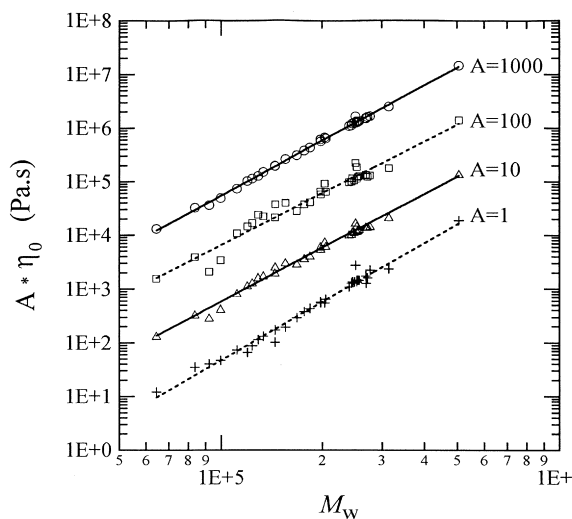


Fig. 5. Zero-shear rate viscosity (η_0) multiplied by an arbitrary constant A as a function of the weight average molecular weight (M_w) at 20°C for the individual PDMS and blends. Symbols: (+) experimental values (i.e.: $P_\eta = 1$), $A = 1$. (Δ) Malkin et al. model, $A = 10$. (\square) Doi and Edwards theory, $A = 100$. (\circ) Anderssen and Mead model with $c = 0.5$ (i.e.: $P_\eta = (M_w/M_n)^{0.5}$), $A = 100$. Lines: fits for experimental values (slope 3.62), Malkin et al. model (slope 3.33), Doi and Edwards theory (slope 3.21) and Anderssen and Mead model with $c = 0.5$ (slope 3.41).

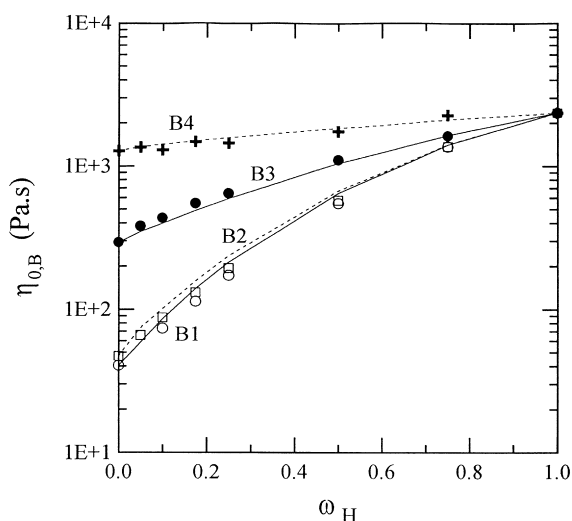


Fig. 6. Zero-shear rate viscosity (η_0) as a function of the weight fraction of the highest M_w polymer in the blend (ω_H) for the four sets of blends analyzed. Symbols: (\circ) blends B1; (\square) blends B2; (\bullet) blends B3; (+) blends B4. Lines: fits for the mixing rule of the blends (Eq. (12)), as labeled.

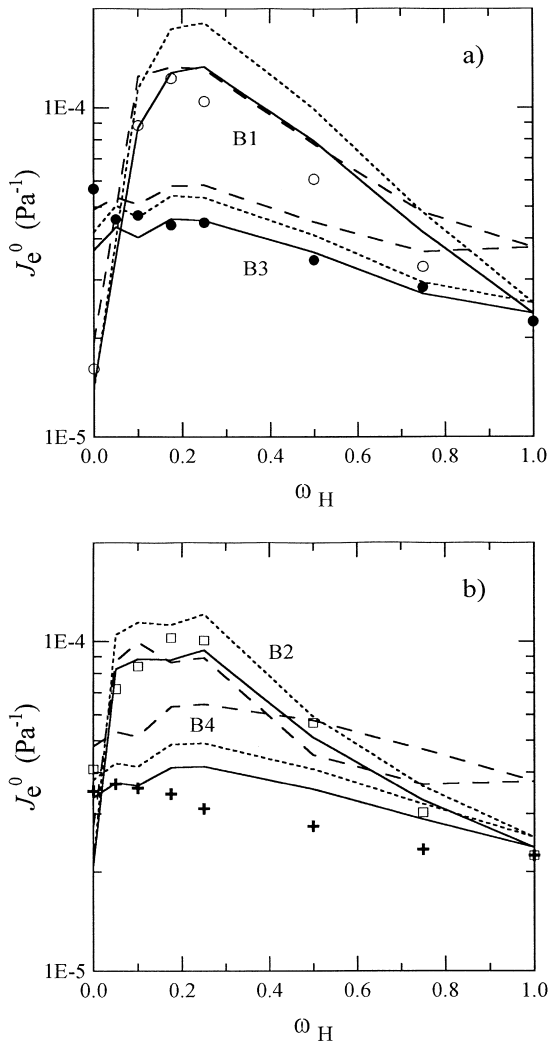


Fig. 7. Steady-state recoverable compliance (J_e^0) as a function of the weight fraction of the highest M_w polymer in the blend (ω_H) for: (a) blends B1 and B3; (b) blends B2 and B4. Symbols are the same as in Fig. 6. Solid lines: fits for Eq. (18), as labeled. Dashed lines: fits for the Doi and Edwards theory (Eq. (14)), as labeled. Dotted lines: fits for the Montfort et al. model (Eq. (15)), as labeled.

for the Doi and Edwards model, and

$$J_e^0 (\text{Pa}^{-1}) = 9.09 \times 10^{-6} \frac{Q_{4.4}}{Q_1^{4.4}} \quad (15)$$

for the Montfort et al. model.

These $J_{e,M}^0$ values of 1.07×10^{-5} and $9.09 \times 10^{-6} \text{ Pa}^{-1}$ obtained from Eqs. (14) and (15) are in good agreement with those previously reported for linear monodisperse PDMS at 20°C [2,4].

It is suitable to remark that the expression of the Montfort et al. polydispersity factor presented here is obtained from a mixing rule similar to Eq. (11) [6,7,10]. In this case, the mixing rule includes an adjustable parameter p . Struglinski and Graessley [22] and Zang et al. [24] proposed $p = 3.4$ (the exponent of the viscosity power law with molecular

weight). With this choice of parameter p , the equation for P_J from Montfort et al. model presented in Table 2 is achieved [22,24].

In view of the analogy of the expressions for P_J from the modified Rouse, Montfort et al. and Zang et al. models shown in Table 2, we decided to adjust our experimental data using an expression similar to those models. Thus, we proposed

$$P_J = \frac{Q_b}{Q_1^b} \quad (16)$$

where b is an adjustable parameter. Then, we calculate the b values for each linear PDMS and blend in order to assure:

$$J_e^0 (\text{Pa}^{-1}) = 10^{-5} \frac{Q_b}{Q_1^b} \quad (17)$$

since 10^{-5} Pa^{-1} is the J_e^0 expected value for a monodisperse linear PDMS at 20°C [2,4]. This $J_{e,M}^0$ value is shown as a straight horizontal line in Fig. 4 in order to visualize the enhancement of J_e^0 with polydispersity.

The average value of b to fit the data from all the analyzed polymers was $b = 4.08$, so the general expression for the fit of the experimental J_e^0 data is:

$$J_e^0 (\text{Pa}^{-1}) = 10^{-5} \frac{Q_{4.08}}{Q_1^{4.08}} \quad (18)$$

The obtained b value lies between the values proposed by Zang et al. ($b \equiv a = 3.41$) and by Montfort et al. ($b \equiv 4.4$).

It is also interesting to note that the anionic synthesized polymers LM8 and LM14 with lower polydispersity ($M_w/M_n \leq 1.15$) presented J_e^0 values that were closer to the constant value expected for “monodisperse” polymers.

Fig. 7a and b shows the fits of Eqs. (14), (15) and (18) to the experimental values of J_e^0 for the four sets of blends prepared. Blends with bimodal distribution (B1 and B2) show a maximum on the J_e^0 values at contents of high M_w polymer of approximately 15–20 wt%. The polydispersity factors calculated by the analyzed models reach values as large as 10 or 20 in some cases (Table 3), and considerably affect the J_e^0 values. Thus, a small fraction of a high M_w polymer can enhance the J_e^0 value of a lower M_w polymer with narrow MWD in one order of magnitude, as can be seen in Fig. 7a and b for blends B1 and B2. However, the models overestimate the recoverable compliance for some of the blends. This fact may be due to the high-order moments considered by these models when MWD of the blends are relatively narrow ($M_w/M_n < 1.35$).

We are able now to obtain an expression for the zero-shear rate first normal stress coefficient, $\Psi_{1,0}$, taking into account the effect of polydispersity. From Eqs. (6), (8), (14), (15) and (18), $\Psi_{1,0}$ for $M_w \geq 64,000$ can be expressed, as:

$$\Psi_{1,0} (\text{Pa s}^2) = 4.07 \times 10^{-36} M_w^{6.82} \frac{Q_{4.08} Q_{-1}}{Q_1^{3.08}} \quad (19)$$

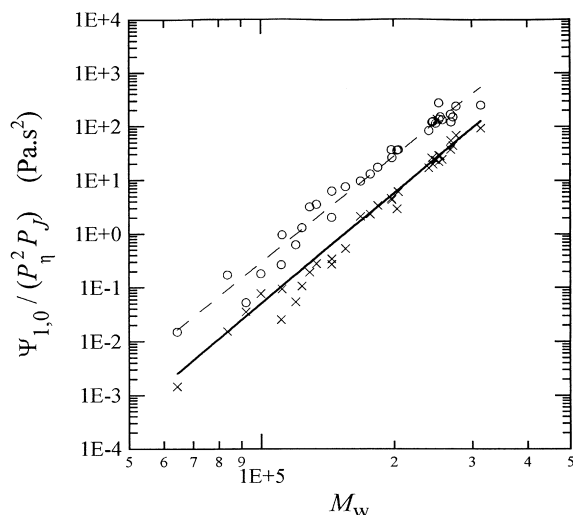


Fig. 8. $\Psi_{1,0}/(P_\eta^2 P_J)$ as a function of the weight average molecular weight (M_w) for the individual PDMS and blends, where $P_\eta^2 = M_w/M_n$. Symbols: (x) proposed model (Eq. (19)); (o) experimental values of $\Psi_{1,0}$ (i.e.: $P_\eta^2 P_J = 1$). Solid line: fit for Eq. (19) (slope: 6.82). Dashed line: fit for experimental values (slope: 6.56).

when P_J is given by Eq. (16) with $b = 4.08$,

$$\Psi_{1,0} \text{ (Pa s}^2\text{)} = 4.35 \times 10^{-36} M_w^{6.82} \frac{Q_6 Q_1 Q_{-1}}{Q_3^2} \quad (20)$$

for the Doi and Edwards model, and

$$\Psi_{1,0} \text{ (Pa s}^2\text{)} = 3.69 \times 10^{-36} M_w^{6.82} \frac{Q_{4.4} Q_{-1}}{Q_1^{3.4}} \quad (21)$$

for the Montfort et al. model. Fig. 8 shows the experimental values and the fit of Eq. (19) for the polymers studied.

The crude experimental $\Psi_{1,0}$ values obtained without any correction for polydispersity also adjust with a power of M_w , but two considerations should be made. First, the slope of the adjustment is slightly smaller than the theoretical value, 6.56 instead of 6.82; and second, the experimental values are almost one order of magnitude higher than those reported for “monodisperse” polymers [2,4].

4. Conclusions

The time–temperature superposition principle was applied for several linear polydimethylsiloxanes and binary blends of them. The values obtained for the shift factors are in excellent agreement with previously reported ones [2]. Slopes for G' and G'' in the terminal relaxation zone are coincident with the theoretical values of 2 and 1, respectively.

At molecular weights below a critical value, η_0 of the linear PDMS increases with $M_w^{1.70}$. On the other hand, for M_w higher than the corresponding critical value, η_0 increases with $M_w^{3.44}$, according to previous observations [2,3,5]. But a weak influence of MWD on the η_0 values for the polymers analyzed here was also observed. For the linear PDMS analyzed and the binary blends, amongst

different polydispersity factors studied, $P_\eta = (M_w/M_n)^{0.5}$ achieved the best fit to experimental values. This result was previously observed in the literature [11,18].

However, J_e^0 values are not independent of molecular weight for M_w greater than M'_c if no polydispersity factor is considered. Besides, this value may be considerably higher than the expected ones for essentially monodisperse polymers. The enhancement of J_e^0 is about one order of magnitude for polymers with $M_w/M_n \cong 1.5$.

We analyzed different models for the polydispersity factor which affects the J_e^0 values. Those obtained from the Doi and Edwards theory [9] and the Montfort et al. mixing rule [6,7,10] gave a constant value for J_e^0 , in very good agreement with previous observations in the literature [2,4].

We also proposed a new expression for P_J which arises from the similitude amongst different models presented in the literature. This expression is given by Eq. (16) with an adjustable parameter b . The best fit for all the polymers analyzed was found using $b = 4.08$, which lies between the limits given by the Modified Rouse model (where $b = 3$) and the Montfort et al. model ($b = 4.4$) (see Table 2).

Similar results were obtained for $\Psi_{1,0}$, which corrected values taking into account the MWD effect were one order of magnitude lower than the crude experimental ones.

Acknowledgements

We express our gratitude to the National Research Council (CONICET) and the Universidad Nacional del Sur (UNS) of Argentina who supported this work.

References

- [1] Graessley WW. Adv Polym Sci 1974;16:1.
- [2] Ferry JD. Viscoelastic properties of polymers. 3rd ed. New York: Wiley, 1980.
- [3] Pearson DS. Rubber Chem Technol 1987;60:439.
- [4] Mills J. Eur Polym J 1969;5:675.
- [5] Malkin AYa, Blinova NK, Vinogradov GV, Zabugina MP, Sabsai OYu, Shalganova VC, Kirchevskaya IYu, Shatalov VP. Eur Polym J 1974;10:445.
- [6] Montfort JP, Marin G, Arman J, Monge Ph. Polymers 1978;19:277.
- [7] Montfort JP, Marin G, Arman J, Monge Ph. Rheol Acta 1979;18:623.
- [8] Agarwal PK. Macromolecules 1979;12:342.
- [9] Doi M, Edwards SF. The theory of polymer dynamics. Oxford: Clarendon Press, 1986.
- [10] Montfort JP, Marin G, Monge Ph. Macromolecules 1986;19:1979.
- [11] Anderssen RS, Mead DW. J Non Newtonian Fluid Mech 1998;76:299.
- [12] Villar MA, Bibbó MA, Vallés EM. J Macromol Sci-Pure Appl Chem A 1992;29:391.
- [13] Grubisic Z, Rempp P, Benoit H. J Polym Sci: Part C: Polym Lett 1967;5:753.
- [14] Brandrup J, Immergut E. Polymer handbook. New York: Wiley, 1975.
- [15] Peirotti MB, Deiber JA, Ressa JA, Villar MA, Vallés EM. Rheol Acta 1998;37:449.
- [16] Baumgaertel M, Soskey PR, Winter HH. IRIS: innovative rheological

- interface software, Chem Engng Dept, University of Massachusetts at Amherst, 1990.
- [17] Bird RB, Armstrong RC, Hassager O. Dynamics of polymeric liquids. 2nd ed, vol. 1. New York: Wiley, 1987.
- [18] Locati G, Gargani L. J Polym Sci, Polym Lett Ed 1973;11:95.
- [19] Kurata M, Osaki K, Einaga Y, Sugie T. J Polym Sci, Polym Phys Ed 1974;12:849.
- [20] Graessley WW. J Polym Sci, Polym Phys Ed 1980;18:27.
- [21] Kurata M. Macromolecules 1984;17:895.
- [22] Struglinski MJ, Graessley WW. Macromolecules 1985;18:2630.
- [23] Graessley WW, Struglinski MJ. Macromolecules 1986;19:1754.
- [24] Zang YH, Muller R, Froelich D. Polymer 1987;28:1577.
- [25] Kim HY, Chung IJ. J Polym Sci: Part B: Polym Phys 1987;25:2039.
- [26] Han ChD. J Appl Polym Sci 1988;35:167.
- [27] Tsenoglou Ch. Macromolecules 1991;24:1762.
- [28] Cassagnau P, Montfort JP, Marin G, Monge Ph. Rheol Acta 1993;32:156.