Analysis of the Flow Behavior of HDPE / LDPE Blends Using a Kinetic Network Model

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Synopsis

Theoretical predictions of the flow behavior of high and low-density polyethylene polymer blends have been obtained using the kinetic network model proposed by Williams et al. The results show that this model can be used even in the case of polydisperse components having similar relaxation spectra. Furthermore, in order to obtain meaningful predictions, the characterization of the complete system (blends and pure components) should be carried out on samples with the same thermomechanical history. Experimental data show that the shearing history influences the rheological properties of the pure homopolymers to a measurable and significant degree and that it has to be taken into account when these properties are used to predict the flow behavior of their blends.

INTRODUCTION

The blending of two or more polymers to produce materials with interesting properties is a very active area in the field of polymer processing. Certainly, polymer blends might be mixtures of chemically different elements and also multiphase systems with structure dependent on composition and blending.[1] In terms of their rheological behavior, polymer blends also show many varieties of response and in an attempt to understand this, a classification of polymer blends based on the deviation of the rheological properties from the mixing rule has been introduced.[2] Specifically this classification separates some systems into (1) positive deviation blends (PDB), that is, systems where the viscosity of the blend is higher than the viscosity of the pure components; (2) negative deviation blends, or systems with blend viscosity lower than their pure components; and (3) positive-negative deviation blends (PNDB), systems with blends viscosities lower or higher than the viscosity of the pure components depending on the blend composition.

Currently, the literature reports several attempts[3-13] to predict the rather complicated rheological behavior of polymer blends, but in general the equations proposed have been empirical or semiempirical and restricted only to a limited number of these systems.

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Williams et al.[14] have developed a molecular network model to describe the behavior of polydisperse systems in steady and transient flows and also the steady-state and transient properties of binary blends of monodisperse components in shear flow.[15] This kinetic network model takes into account only two mechanisms that affect the instantaneous structural state of the fluid via the loss and regeneration of entanglements between molecules. In the papers by Williams et al. the hypothesis is that, in the case of steady-state flow, the two molecular processes influencing the structural state of the fluid reach a balance. Hence, the total viscosity of the system can be expressed as the sum of the rate-dependent viscosity plus the additional resistance experienced as the chain segments slide by one another or interact with nearby solvent molecules. The usefulness of this model has been applied successfully to predict the viscosity versus shear rate curves of several binary systems from molecular information and rheological data of their monodisperse components.

Based on their results[14,15] we present in this work its straightforward implementation for the case of blends of polydisperse commercial-grade high- and low-density polyethylene (HDPE/LDPE), and also, we analyze the effect that mechanical treatment has on the predictive power of the model.

THEORETICAL BACKGROUND

Williams et al.[15] developed expressions for the zero shear rate viscosity of the binary blends, η_b^0 and for the non-Newtonian viscosity curves from the information of its pure components.

The zero shear rate viscosity of a binary blend is given in this model by

$$\eta_b^0 = \phi_1 w_1 \eta_1^0 + \phi_2 w_2 \eta_2^0 \tag{1}$$

where w_i is the weight fraction and ϕ_i is the composition-dependent coefficient of the i-th component that takes into account the existing intensified interaction. η_1^0 and η_2^0 are the zero shear rate viscosities of pure components, respectively.

For the blending rule of this model, it can be easily noticed that allowing ϕ_i to vary between 0 and 1, and also, since w_i ranges between zero and one, the values of η_b^0 higher or lower than the values of pure components are excluded from this relationship.

Within this model, the dynamics of long and short chains in the network are hypothesized by assuming that the characteristic relaxation time of the long chain in the blend is reduced from that of its pure state, whereas the relaxation time to the short component remains unaffected. In this way, for the high-molecular weight element (component one) we have:

$$\lambda_1 = \phi_1 \lambda_1^0 = w_1 \lambda_1^0 + w_2 \lambda_2^0 \tag{2}$$

where λ_i^0 denotes the relaxation times of the i-th component in the pure state and

$$\lambda_2 = \phi_2 \lambda_2^0 = \lambda_2^0 \quad \text{(with } \phi_2 = 1) \tag{3}$$

Besides, the terms $w_1\lambda_1^0$ and $w_2\lambda_2^0$ account for the intracomponent and intercomponent interactions in the blend, respectively.

The parameters ϕ_i are such that they show a composition dependence given by:

$$\phi_1 = w_1 + w_2\frac{\lambda_2^0}{\lambda_1^0} \tag{4}$$

and

$$\phi_2 = 1 \tag{5}$$

With the assumption of equilibrium between creation and destruction of entanglements, the model yields an expression for the viscosity of the pure components given as

$$\frac{\eta}{\eta^0} = \frac{1}{1 + b^0\dot{\gamma}^m} \tag{6}$$

where m and b^0 are parameters related to the rate of disappearance of entangled points and to a diffusional characteristic time involved in the creation of an entanglement, respectively. Furthermore, for a binary blend, Eq. (6) is modified into the following expression

$$\eta(\dot{\gamma}) = \frac{\phi_1 w_1 \eta_1^0}{1 + b_1^0\dot{\gamma}^m} + \frac{\phi_2 w_2 \eta_2^0}{1 + b_2^0\dot{\gamma}^m} \tag{7}$$

EXPERIMENTAL PROGRAM

High ($\rho = 0.956$ g/cm^3, MFI = 0.3) and low ($\rho = 0.920$ g/cm^3, MFI = 2) density polyethylenes manufactured by PEMEX (Mexico) were used throughout this study.

All the blends used in this work were made from the virgin polymers as given by the supplier without adding antioxidants nor stabilizers and were melt-blended in an internal mixer (Haake Rheomix 400) equipped with roller-type mixing heads using the following operating conditions: mixing speed = 50 rpm; mixing temperatures = 170, 190, and 210°C; mixing time = 20 min; compositions = 20, 50, and 80% (by weight). The pure components were also subjected to the same mixing process in order to have a set of pure resins with a similar shear and thermal history as their blends.

After removing the sheared and mixed samples from the mixer, part of them were remelted and disc-shaped. This treatment was necessary in order to measure their steady shear flow properties ($\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$) in a Rheometrics Mechanical Spectrometer with a cone and plate ($R = 2.5$ cm, $\theta_0 = 0.04$ rad). Shear rates were varied between 0.025 and 10 s^{-1} and fixed test temperature at 190°C.

RESULTS AND DISCUSSION

In this study we only analyze the effect of shear modification of the pure components and its consequences on the prediction of the blend viscosities
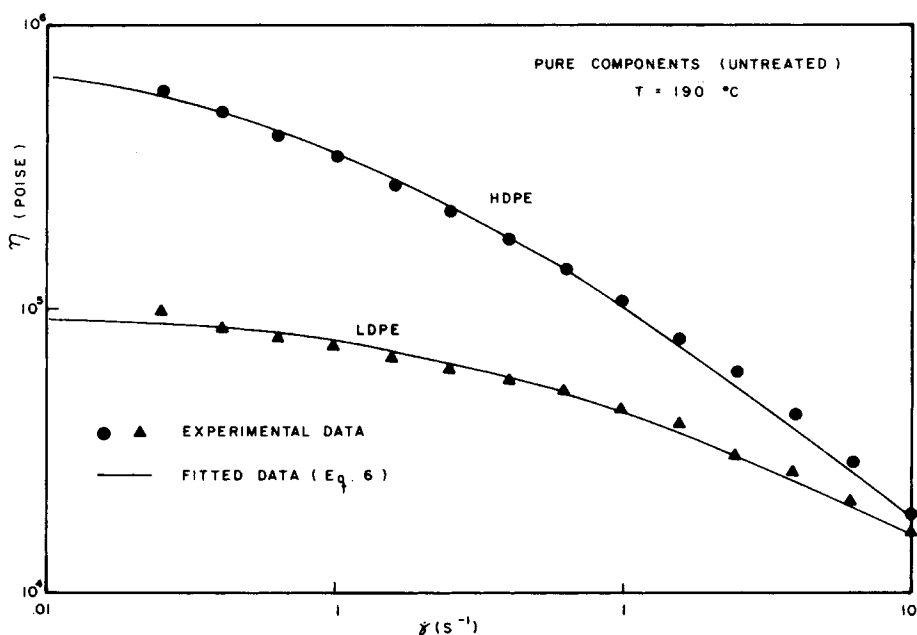
Fig. 1.   Viscosity vs. shear rate. Pure components (untreated).

using the model of Williams et al. The other effect which deals with the mixing temperature will be reported in a later publication.

Experimental data for $\eta(\dot{\gamma})$ as a function of $\dot{\gamma}$ for pure and unsheared HDPE and LDPE at 190°C are shown in Figure 1. Similarly, Figure 2 shows the $\eta(\dot{\gamma})$ versus $\dot{\gamma}$ for HDPE and LDPE resins after being sheared at 50 rpm and 190°C.

Comparison between Figures 1 and 2 shows evidence of shear modification in both materials. This evidence implies that in spite of the experimental technique (shearing the polymers, letting them solidify, melting them again to form the discs, a second solidification, and final remelting to take the measurement) the shear-induced effect in the materials survived many opportunities to relax during the remelting and resolidification treatments of the samples.

This shearing-induced modification in the rheological properties of melts and concentrated solutions has been documented and explained in terms of the significant modifications of the intermolecular interactions induced through the extra entanglements generated by the shearing forces.[16,17]

Furthermore, it has been phenomenologically substantiated that, in some cases, the mechanical perturbations of a polymer induced through shearing, modify the melt viscosity and elasticity through minor changes in its molecular weight distribution or chemical structure.[18,19] Also, in a case similar to ours, it was also found that shearing virgin LDPE yielded a drop in fluidity and a rise in melt elasticity. In addition to this effect, direct measurement of melt viscosity in a cone and plate rheometer also indicated an increase in the melt viscosity after being recuperated from several cycles of processing[20] or simply, in an analogous test, a considerable decrease in the melt flow index.[21]
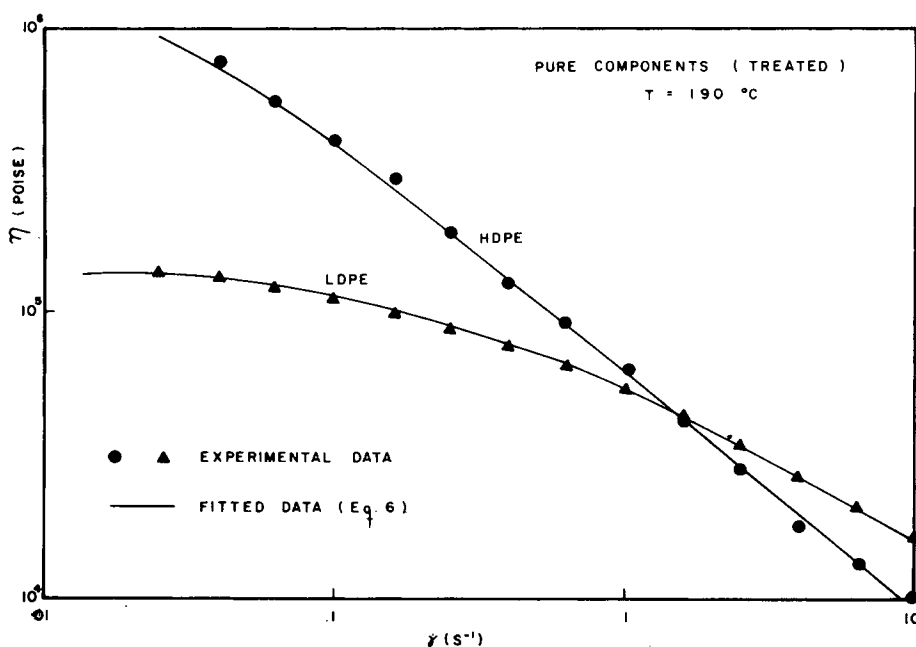
Fig. 2.   Viscosity vs. shear rate. Pure components (treated).

Analogously, for the case of HDPE, a decrease has been reported in the melt index (or alternatively an increase in apparent viscosity) when samples with no previous shear history were melted and subjected to shear mixing.[22-26]

All these evidences show that shear-induced changes in the melt rheological properties is a well documented phenomenon and that the shearing history indeed influences the polymer flow properties to a measurable and significant degree. In our case, which included the effect on HDPE and LDPE, it was found that particularly the same thermomechanical treatment had a more profound effect on the HDPE.

With this evidence and quantitative information, we pursued the main goal of the paper: the implementation of the Williams et al. equation for binary systems with the same reference state or uniform thermomechanical history.

The solid lines of Figures 1 and 2 were fitted using Eq. (6) and a nonlinear least-squares numerical scheme. The results of this computation are summarized in Table I.

TABLE I
Parameters in Eq. (6)

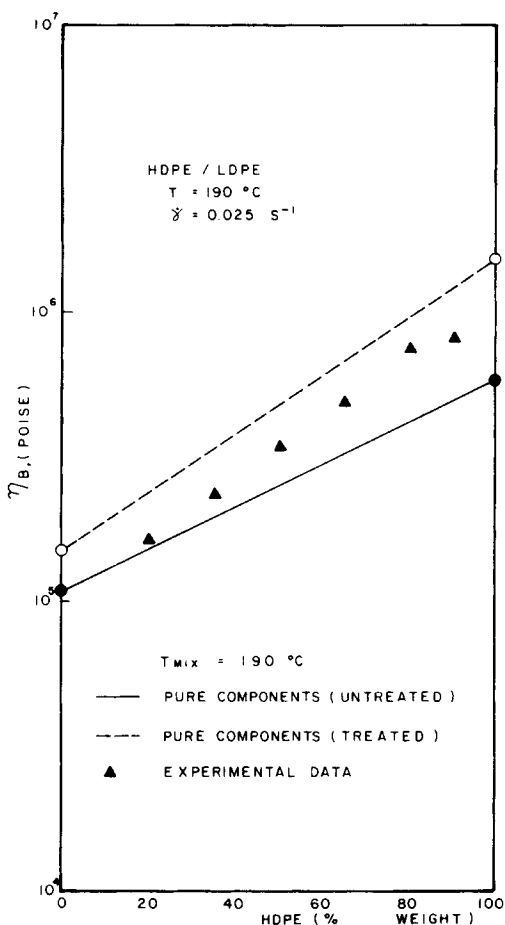|	Pure		Shear modified	
	HDPE	LDPE	HDPE	LDPE
η_0 (poise)	7.5×10^5	1×10^5	7×10^6	1.6×10^5
b^0	6.5	1.27	70	1.9
m	0.78	0.6	0.8	0.7

Fig. 3. Viscosity as a function of HDPE composition.

Figure 3 shows the variation of η_B ($\dot{\gamma} = 0.025$ s^{-1}) with composition. It has been assumed that this shear rate is sufficiently low so that the viscosity values approximately correspond to η_B^0. This assumption is more approximate for the case of LDPE and the blends with low HDPE content.

The lines shown in Figure 3 correspond to the mixing rule established when there is no intensified intercomponent interaction between the pure components (additivity rule). The solid line joins the pure component low shear viscosities measured as received from the supplier; the dashed line joins the pure component low shear viscosities measured after being sheared under the same conditions as the blends. If the experimental data for the blends are analyzed with respect to the pure components behavior we face two situations: (1) If the virgin pure components are taken as reference the blends show an anomalous positive deviation behavior characterized by large viscosity values (larger than both pure components) at high HDPE content (> 80% by weight); and (2) on the other hand, when taking the sheared pure components as reference, the behavior of the blends falls in the negative deviation category.

These results create the need of posing the following question: When using a model to predict the flow behavior of polymer blends (from pure component viscosities), what reference state should be used for the pure components flow curve?

It seems reasonable that on all systems involved in the characterization (i.e., pure components and blends), the same thermomechanical work should be applied in order to make a meaningful prediction. We believe that if we ignore this fact it can lead to an erroneous interpretation of the experimental data. In our case, Williams' model cannot predict blend viscosities if virgin pure components are taken as reference and in an indirect way this result highlights the importance of the blending procedure.[27]

To explore an answer to the above question, in the following paragraphs we will restrict ourselves to the case of fitting the Williams et al. model to a set of HDPE/LDPE blends taking as reference the shear modified pure components.

The prediction of the viscosity of the blends at a given shear rate can be obtained from Eq. (7); it involves also the calculation of ϕ_1 values using the equation

$$\phi_1 = w_1 + w_2 \left(\frac{\lambda_2^0}{\lambda_1^0} \right) \tag{10}$$

Following Graessley's work,[28] the parameters in Williams' model can be expressed empirically as $b \sim \eta^0$ so that $\lambda \sim (\eta^0)^{1/m}$. Therefore, Eq. (10) can be written as

$$\phi = w_1 + w_2 \left(\frac{b_2^0}{b_1^0} \right)^{1/m} \tag{11}$$

Evaluation of ϕ_1 from Eq. (11) requires the knowledge of b_1^0, b_2^0, and m for the pure components. In the case of polydisperse pure components, the fitting of the respective $\eta(\dot\gamma)$ curve results in different values of both b_i^0 and m_i. It should be mentioned that the m_i parameters found in this work (see Table I) are smaller (but of the same order of magnitude) than the values reported for several monodisperse polymer melts.[29] Furthermore, in the case of systems with large low shear viscosity differences, Eq. (11) predicts values of ϕ_1 almost independent of the m parameter. In the system under present study, (η_2^0/η_1^0) < 0.1, the values of ϕ_1 calculated using the two m values differed less than 5%.

The theoretical values of ϕ_1 obtained from Eq. (11) (under the assumptions outlined above) are shown in Table II and compared with the values obtained directly from Eq. (1) and the experimentally determined η_b^0 at a given composition. These results can be interpreted as follows:

It has been shown that in the system under study the theoretical prediction of ϕ_1 is basically a function of a ratio of single relaxation times (case of monodisperse pure components). A polydisperse system is characterized by a spectrum of relaxation times and the first moment of this spectrum of relaxation times is defined as the zero-shear viscosity. Two systems with

TABLE II
Comparison of ϕ_1 Values

	ϕ_1	
w (% by weight)	Experimental [Eq. (1)]	Theoretical [Eq. (11)]
0.2	0.19	0.23
0.5	0.46	0.52
0.8	0.74	0.81

similar relaxation time spectra would produce first moment ratios comparable to the single relaxation times ratio of monodisperse systems.

The assumption is validated by the results of the relaxation spectra for high and low density polyethylene calculated as proposed by Ferry[30] (Fig. 4).

Finally, Figures 5–7 show the comparison between the prediction and experimentally determined flow curves. The full lines represent the upper and lower bounds predicted by Eq. (7) when using both m values corresponding to each pure component. Better agreement was found particularly at low HDPE content. When the content is high, however, agreement with experiments is apparent when $m = 0.8$, corresponding to the m value of HDPE. To explain this fact, attention is given to molecular characteristics: LDPE presents a more branched structure with long lateral groups. On the other hand, smaller lateral branches and a more linear structure are found in HDPE.[31] The theoretical predictions presented here are better applied to flexible macro-molecules (polystyrene, for instance) where the appearance of rigid linear like structures in the polymer network is scarce. In this context, LDPE follows
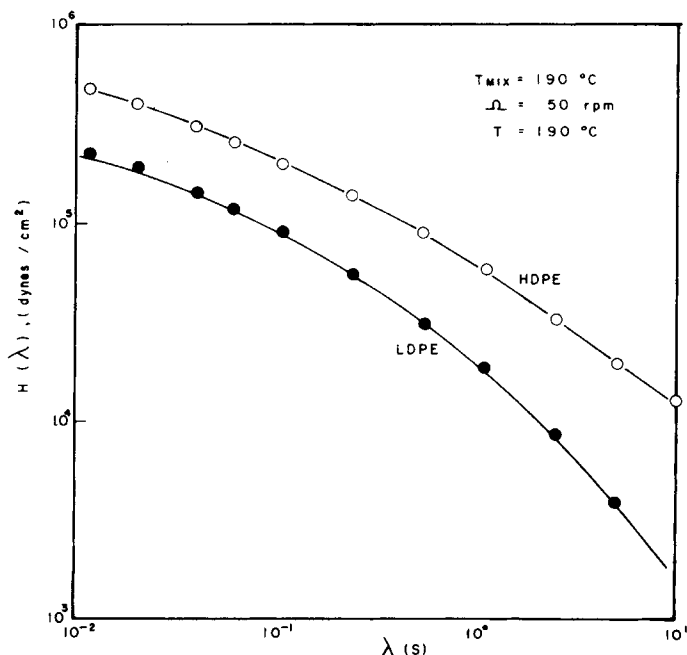

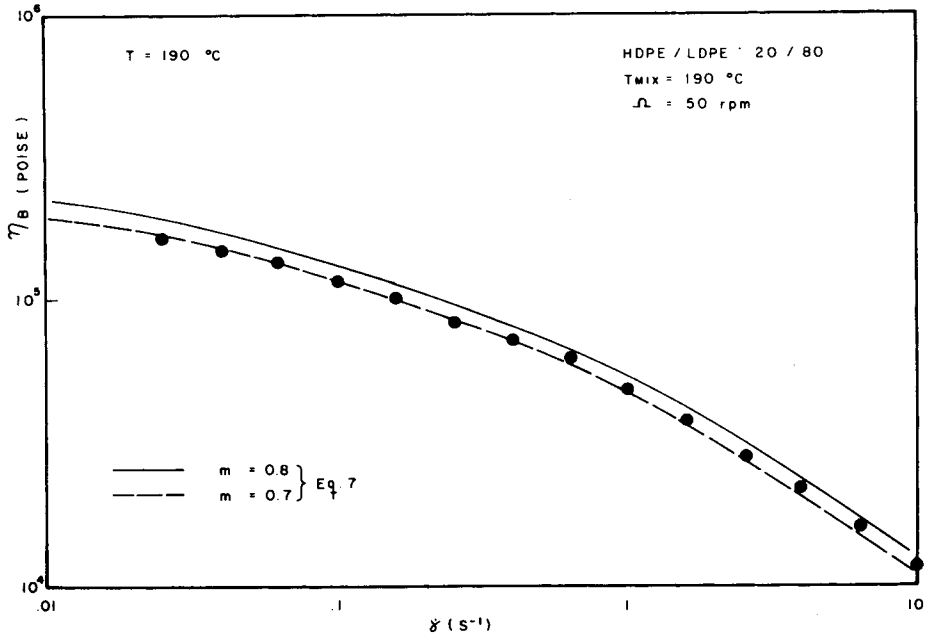Fig. 4.   Relaxation spectra (treated pure components).

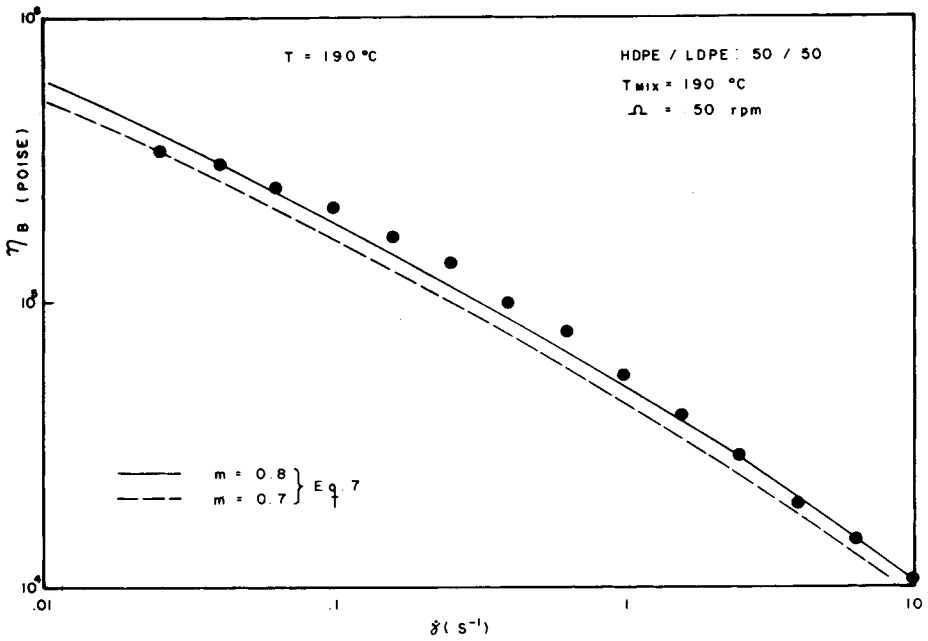Fig. 5.   Viscosity vs. shear rate. Blend: 20% HDPE.

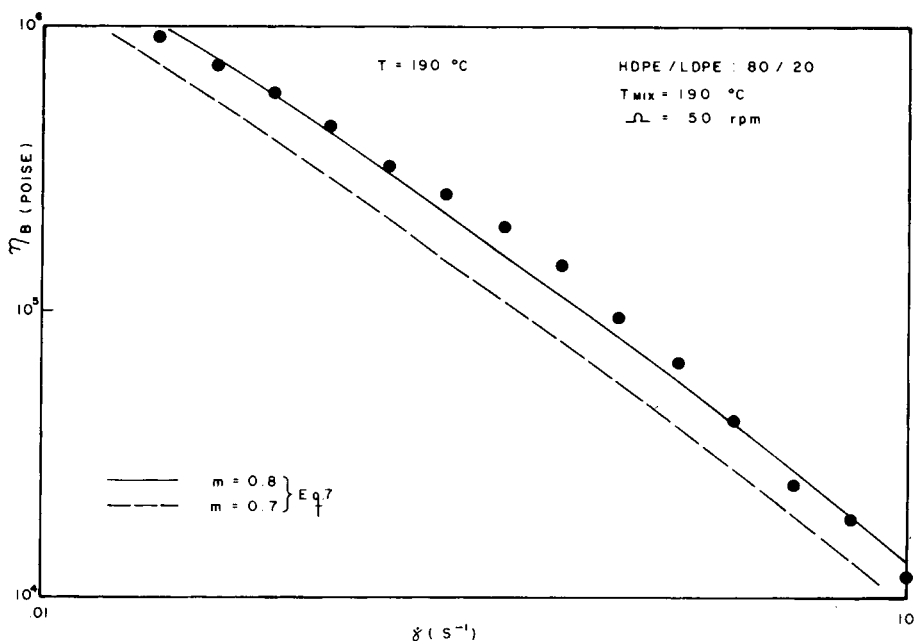Fig. 6.   Viscosity vs. shear rate. Blend: 50% HDPE.

Fig. 7.   Viscosity vs. shear rate. Blend: 80% HDPE.

this theory better than HDPE. Moreover, this explains why at higher content of HDPE, data tends to deviate from theoretical predictions. Similarly, when the proportion of this material in the blend is higher (more than 50%), a strong influence on the viscosity properties of the blend is observed. Indeed, HDPE is more affected than LDPE by thermomechanical work, as is shown in Figures 1 and 2. Ram and Getz[20] have pointed out that the increase in viscosity in polyethylene can be associated with the initiation of microgels and recombination of polymer chains by free radicals. To substantiate this point, they measured an actual increase in intrinsic viscosity and in the higher modes of the molecular weight distribution.

Complementarily, Czlonkowska and Raszczuk[32] have reported the effect of the viscoelastic properties of polydimethylvinylsiloxanes (PDMVS). They found a noteworthy change between the viscoelastic properties η' and G' of PDMVS samples containing microgels and those free of microgel samples. These changes showed, for the samples with microgels, a similar trend of increasing the dynamic viscosity and the storage modulus and a stronger shear rate dependence in comparison to the microgel-free samples. Their study[32] also documented the fact that the considerable effect of small amounts of microgels on the values of the dynamic viscosity and the storage modulus at low frequencies was similar to the effect of high molecular weight fractions. Therefore, the existence of a correlation between the viscoelasticity of polymers and their microgel content can be associated with the characteristic changes in mild differences in molecular weight averages and also with the width of the molecular weight distribution of the polymer.

The relevance of the works of Ram and Getz[20] and Czlonkowska and Raszczuk[32] for our present problem is such that these papers allow us to give a plausible explanation for the behavior of HDPE as portrayed in Figure 2.

It can be noticed from our figure that HDPE for low shear rates verified an initial increase of viscosity, but at higher shear rates it showed a further decrease in comparison with the untreated sample. An explanation of such an effect lies in the qualitative changes involved in the increment of the molecular weight and its consequent change in the width of its distribution. Hence, the trend shown by HDPE in Figure 2 correlates very well with the presence of microgels and their important effect on the viscoelastic properties. Nevertheless, this is a significant effect that deserves a careful and quantitative explanation, but, this is beyond the scope of this paper. However, it is being explored and will be presented in a forthcoming publication.

CONCLUSIONS

The results presented in this work suggest that the model derived by Williams et al. can be used to predict the behavior of polydisperse polymer blends when the spectra of relaxation times of the pure components are similar.

Since the blending process involves mixing in the molten state, the rheological characterization of the complete system, blends and pure components, should be carried out on samples that have been subjected to the same thermomechanical history.

Further questions still remain to be solved, for example: as a result of the changes in the physical properties portrayed here for the homopolymers and their blends in the molten state, what kind of changes can be induced in their solid state and their morphology?

Furthermore, for these multicomponent systems, what are the durability of these alterations originated during shearing and their dependence with their source of origin?

Hence, this paper shows evidence of shear modification of virgin polymers and its effects. In addition, it also portrays a relevant case of the implementation of a constitutive equation for blends, which capacity of description can be improved by utilizing systems that underwent the same thermomechanical work. Therefore, a noteworthy point to consider is that the reliability of structure–property correlations may also be questionable, unless the property part of the correlation is knowledgeably interpreted.

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