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Rheological behaviour of metallocene catalysed high density polytheylene blends

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Dynamic and steady state flow measurements and shrinkage experiments have been carried out to investigate the influence of blend composition on viscous and elastic properties of a new type of polyolefin: high density polyethylenes of high and low molecular weight obtained via metallocene catalysts. The polyethylenes are characterized by narrow molecular weight distribution and absence of branching. A model based on the additivity of molecular weight and free volume has been used to fit the complex and steady state viscosities vs composition data, at constant frequency or shear rate, which show a large positive deviation from linearity. The single correlation between G' and G'' and the small effect of blend composition on dimensional stability correspond to the behaviour expected for a miscible blend. 'Sharkskin' and 'slip-stick' effects observed in extrusion process of the high molecular weight sample disappear for blends of 50% and higher content of low molecular weight polyethylene. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: metallocene catalysed polyethylene; rheology; blends; dynamic viscoelasticity; shrinkage)

INTRODUCTION

The main purpose of physical blending of polymers is to obtain new materials with an improved properties/processing/price relationship. Blending is a very usual common practice in the polyolefin area, for instance, blending polyethylenes of different degrees of branching has long been employed as a method to improve processability. On the other hand, the miscibility of polyolefin blends in the melt has been the subject of fundamental research, because although one expects the interactions between the repeat units to be similar, phase separation in the liquid state has been observed[1,2].

In a recent work we reported[3] dynamic and steady state rheological results of a new type of high density polyethylene prepared with metallocene catalysts. The main rheological features of these new polyethylenes (characterized by their low polydispersity and the total absence of short and long chain branching) are the high viscosity and the presence of 'sharkskin' and 'slip-stick' regimes at very low shear rates.

In this paper we present dynamic viscoelasticity and steady state viscosity results, as well as a study on the dimensional stability (shrinkage) of a series of blends of two linear metallocene-catalysed polyethylene of very different molecular weight. These experiments can give one insight, serving as a model, on the behaviour of polydisperse high density polyethylenes obtained via conventional Ziegler–Natta catalysts.

EXPERIMENTAL

Materials and blending

The materials were obtained following the method of Kaminsky *et al.*[4] using Cp_2ZrCl_2 as catalyst. The molecular parameters were measured by gel permeation chromatography (g.p.c.), and the level of branching by ^{13}C n.m.r. (*Table 1*).

The polymers were mixed for 5 min in a Mini-Max Molder CS-183 MMX at a temperature of 180°C and a piston-rotating velocity of 60 rpm. Previous to the preparation of the mixtures the polymers were stabilized by addition of Irganox 1001 to prevent the thermo-oxidative degradation process. The extrudates were pelletized for rheological testing.

Rheological measurements

The dynamic viscoelastic measurements were performed in a Carri-Med CSL-100 rheometer, with the parallel plate geometry. The steady state measurements were carried out in a Sieglaff–McKelvey capillary rheometer, using a capillary ratio $L/D = 25$.

Shrinkage measurements were accomplished in a silicone oil bath at 180°C, with the extrudate samples (filaments) obtained in the capillary rheometer at a shear stress of 0.16 MPa and a temperature of 160°C. The filaments were placed in the silicone oil bath and their lengths were measured as a function of time.

The strain recovery measured by means of this technique was studied in terms of:

$$\xi_r = \ln \frac{L_0}{L(t)} \tag{1}$$

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Table 1 Molecular and structural parameters of metallocene catalysed polyethylenes

Materials	M_w	M_w/M_n	Total CH_3/1000 C	[a]Branching
PE01	14 000	2.3	6.65	0.00
PE04	238 000	3.5	<0.4	0.00

[a] Branches given as CH_3/1000 C atoms

where L_0 is the initial length of the filaments and $L(t)$ the length at a time t.

RESULTS AND DISCUSSION

Dynamic viscoelasticity

Complex viscosity. In *Figure 1*, we present the complex viscosity, η^*, of PE01/PE04 blends at 190°C, as a function of frequency. With the exception of PE01 all the samples display similar non-Newtonian (shear thinning) behaviour. *Figure 2* shows the data of the complex viscosity at 0.01 Hz and 10 Hz (the two limits of the covered frequency range) plotted against the blend composition: a strong positive deviation from log-additivity rule can be noticed for both sets of data.

We have used three different models, compiled from literature, which foresee positive deviation in viscosity–composition plots: the kinetic network theory[5], the Christov *et al.* model[6] and the altered free volume state model[7]. Noting that none of them adjust satisfactorily our experimental data, we have developed a model which is based on the additivity of the molecular weight and the non-additivity of the free volume of the components.

As a starting point we consider that the viscosity depends on two factors: the molecular weight and the temperature. This latter has a direct relation with the free volume related to the specific volume of the material[8]. These dependences are expressed by:

$$\eta = A(M)\exp\left(\frac{1}{f}\right) \tag{2}$$

where $A(M)$ is the factor that includes the molecular weight effect and f is the fractional free volume. Therefore, the viscosity of a blend can be expressed as:

$$\eta_b = A_b(M)\exp\left(\frac{1}{f_b}\right) \tag{3}$$

Applying the molecular weight additivity to the factor $A_{b(M)}$ we obtain:

$$A_b(M) = \left(\sum_i \phi_i A_i(M)^{1/a}\right)^a \tag{4}$$

where a is the power law exponent of the equation $\eta \propto M_\omega^a$. A value of $a = 4.2$ was obtained in a previous work[3] for this type of polymers.

On the other hand we assume that the free volume of a polymer is altered by the presence of a second component. This change is given by the expression[7]:

$$f_b = \phi_1 f_1 + \phi_2 f_2 + K\phi_1\phi_2 \tag{5}$$

where K is a constant that describes the modifications of the free volume of the blends due to the mixing process, f_i is the free volume fraction of each blend component and ϕ_i the volume fractions of blend components.

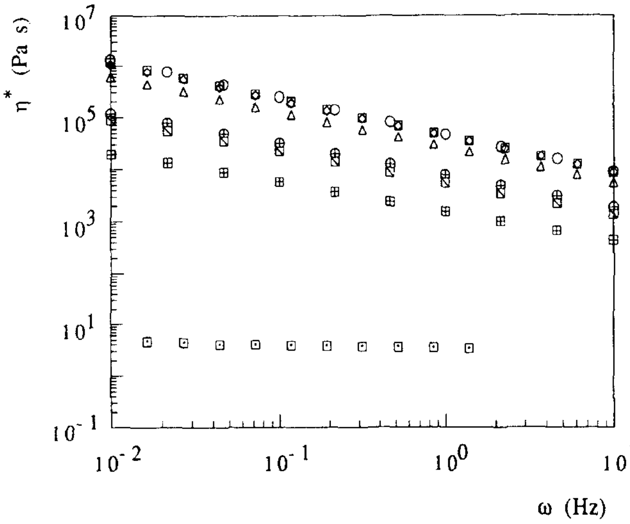

Figure 1 Complex viscosity, η^* vs frequency, ω, at 190°C for PE04, PE01 and their blends. ⊡, PE01; ⊞, 80/20; ⧅, 60/40; ⊕, 50/50; △, 40/60; ◇, 20/80; □, 10/90; ○, PE04

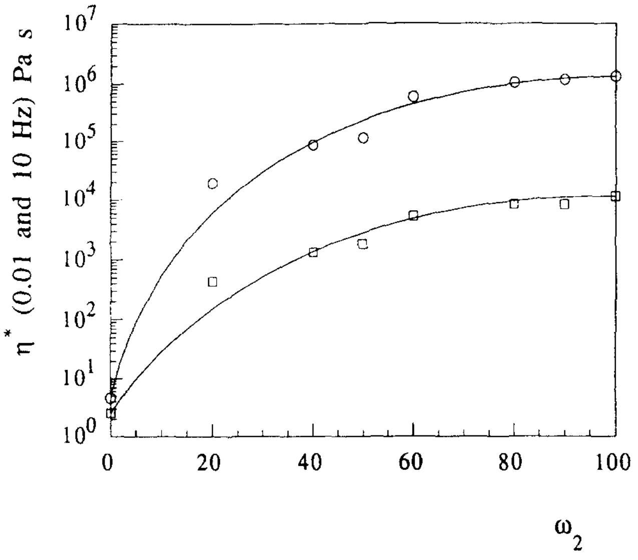

Figure 2 Complex viscosity of the blends at 190°C and (○) 0.01 Hz and (□) 10 Hz. Lines correspond to equation (6)

The equation for the viscosity is obtained by combining equations (3), (4) and (5):

$$\eta_b^* = \left(\sum_i \phi_i A_i(M)^{1/a}\right)^a \exp\frac{1}{\sum_i \phi_i f_i + \prod_i K\phi_i} \tag{6}$$

The values of $A_i(M)$ can be calculated from equation (2), applied to experimental data, if we know the free volume fractions, f_i. These volume fractions change with temperature as follows[9]:

$$f = f_g + \alpha_f(T - T_g) \tag{7}$$

where f_g and α_g can be expressed in terms of the well known

WLF coefficients, C_1^g and C_2^g:

$$f_g = \frac{1}{2.3C_1^g} \qquad (8)$$

$$\alpha_f = \frac{1}{2.3C_1^g C_2^g} \qquad (9)$$

The temperature dependence of viscosity is also expressed by the Fulcher equation[10]:

$$\mathrm{Log}\,\eta = A' + \frac{B'}{T - T_\infty} \qquad (10)$$

The WLF coefficients are related to the parameters of equation (10):

$$C_1^g = \frac{B'}{T_g - T_\infty} \qquad (11)$$

$$C_2^g = T_g - T_\infty \qquad (12)$$

In our case the best fits of viscosity experimental data are obtained using a value of $T_\infty = 0\mathrm{K}$, which transforms equation (10) into an Arrhenius type equation, where $B' = E_a/R$. Taking an activation energy of flow $E_a = 7\,\mathrm{kcal\,mol^{-1}}$[3] and the glass transition temperature for the polyethylene as $T_g = 200\mathrm{K}$, the value obtained for the free volume fractions by means of equation (7) is 0.058 at 190°C for neat materials. The best fits of equation (6) with the viscosity experimental results (*Figure 2*) are attained with a value of the parameter $K = 0.0125$. The smallest free volume fraction is obtained for the composition 50/50; there is a decrease of 5% with regard to that calculated for neat materials.

The blending rule expressed in equation (6) fits well the experimental data of all the frequencies considered in this work. This is a consequence of the fact that the effect of the frequency on the complex viscosity (slope of $\log\eta^* - \log\omega$ plots) does not practically change from one blend to the other. The molecular weight additivity rule of equation (4) is not therefore affected by the frequency, since we can assume that the parameter a, which accounts for the effect of molecular weight on viscosity, is not modified when small amplitude deformations are applied. In order to justify the good fit of equation (6) to the experimental data we have to remark that both metallocene catalysed materials, PE01 and PE04 have been obtained via the same polymerization process, and possess narrow molecular weight distribution and extraordinary linear structures. The fundamental difference between these samples is the average molecular weight (*Table 1*), thus they can be considered homologous materials or fractions of the same polymer with very different molecular weights.

Storage and loss moduli

Han and coworkers[11–15] established a thermorheological criterion to determine copolymers and blends homogeneity in the melt: the plots of G' vs G'' in the logarithmic scale give rise to temperature independent correlations in homopolymers and compatible blends in the molten state, but they are very sensitive to changes in heterogeneous systems morphology (inmiscible blends and copolymers with microphase separation) in the terminal zone of the mechanical spectrum. This means that when domain separation in the bulk takes place, the response is different for each temperature.

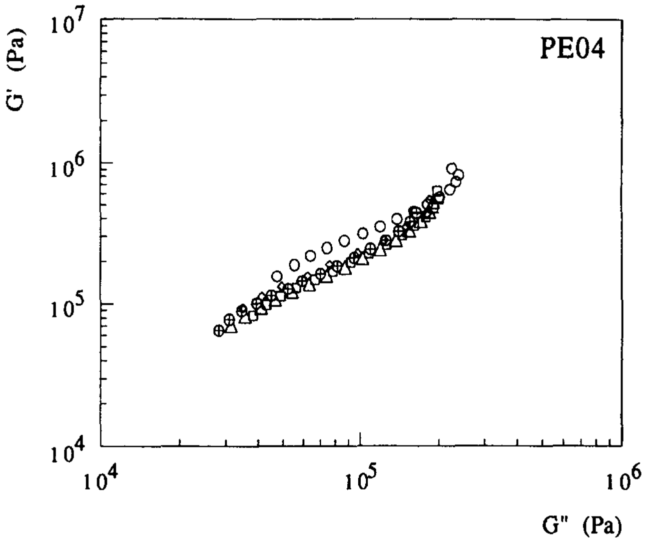

Figure 3 G' vs G'' for PE04 at different temperatures (°C). ○, 130; □, 150; ◇, 170; △, 190; ⊕, 210

In *Figure 3* data of G' are plotted against G'' for PE04 at various temperatures. Both functions are independent with respect to the temperature up above 130°C. At this temperature microphase crystalline domains can exist in the melt, keeping their identity during the experiment. Therefore, the viscous liquid is not a homogeneous mass, but a two phase system with microcrystals which have a great influence in the rheological properties of the material. We can assume that these microdomains have disappeared completely at temperatures above 140°C. This phenomenon is very important in olefin copolymers and other block copolymers[12,13,16] as well as in polymer blends[13–15]. In the case of copolymers the presence of microdomains is owing to the different structural chain segments, and depends on the composition of the copolymers and the method of copolymerization. In blends, the different structural characteristics of the components, as long chain branching (LCB), short chain branching (SCB), molecular weight distribution (MWD), chemical structure, concentration and method of preparation, are the main factors that may affect the morphology.

Figure 4 shows the plot of G' vs G'' for the blends. It can be seen that the data fit well to a single correlation for all the compositions. This means that, for a given value of G'', G' is constant for all compositions, a result which differs from that of multiphase systems which give rise to strong positive deviations in melt elasticity at about 50/50 compositions, due to storage mechanism of energy that take place by the event of interface phenomena[1,17–20].

Flow in a extrusion capillary rheometer

As we have pointed out in a previous work[3] metallocene catalysed polyethylenes with narrow MWDs and total absence of branching are difficult to process. These polymers show flow instabilities at very low shear rates in a temperature range of 160–190°C. In order to analyse the effect of blend composition of PE01/PE04 systems on the processability, and in particular on the flow instabilities, steady state rheological measurements were carried out in an extrusion

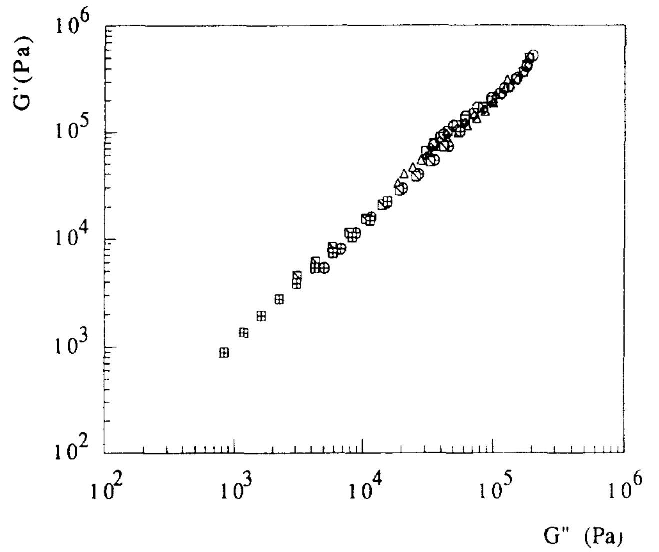

Figure 4 G' vs G'' for PE04 and its blends with PE01 at 190°C. Symbols as in *Figure 1*

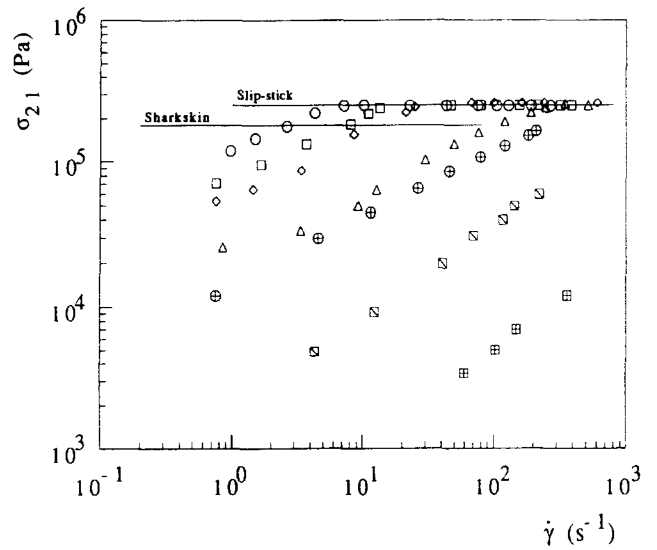

Figure 5 Flow curves for PE04 and its blends with PE01 at 160°C. Symbols as in *Figure 1*

capillary rheometer. The flow curves (shear stress vs shear rate) of the blends are shown in *Figure 5*. The samples with less than 50% of PE01 show 'sharkskin' and 'slip-stick' regimes for critical values of 0.18 and 0.25 MPa respectively. The critical shear rate for the 'sharkskin' effect, $\dot{\gamma}_c$, increases as the content in PE01 increases: this implies that the low molecular weight fraction improves the processability of the high molecular one. It is well known that in conventional polyethylenes of high molecular weight with broad MWDs, low molecular weight tails improve the processability of the polymer.

In *Figure 6* we show the compositional variation of steady state viscosities taken at $\dot{\gamma} = 1\,\mathrm{s}^{-1}$ and $\dot{\gamma} = 100\,\mathrm{s}^{-1}$. The values of the viscosity at $1\,\mathrm{s}^{-1}$ for the blends of low PE04 content were obtained by extrapolation. Since 'slip-stick' regime was observed for PE04, 90PE04/10PE01 and 80PE04/20PE01 samples at $100\,\mathrm{s}^{-1}$, we calculated the viscosity at this shear rate assuming the power law equation $\sigma_{21} = K\dot{\gamma}^n$.

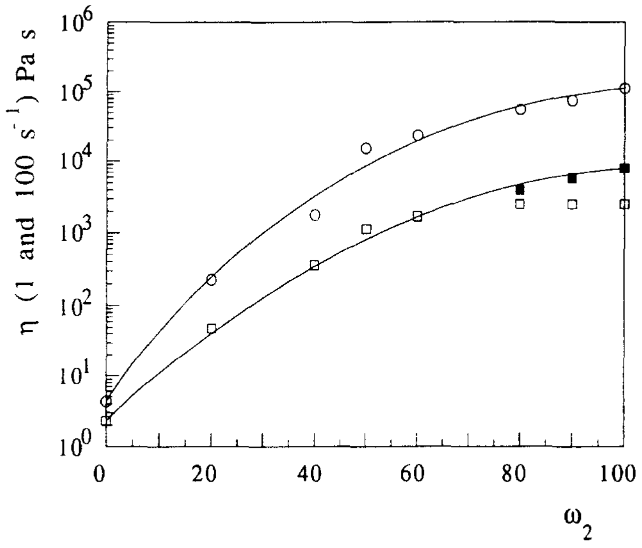

Figure 6 Compositional variation of steady state viscosity, η, taken at (○) $1\,\mathrm{s}^{-1}$, (□) $100\,\mathrm{s}^{-1}$ and (■) extrapolated values at $100\,\mathrm{s}^{-1}$ without 'slip-stick' effect. Lines correspond to our model (equation (6)) for $a = 3.6$ ($1\,\mathrm{s}^{-1}$) and $a = 2.7$ ($100\,\mathrm{s}^{-1}$). See text

Our experimental data fit well to the model expressed in equation (6) with adjustable parameter (a, f and k) values which differ with respect to those used to adjust complex viscosity data. The value of the interaction parameter $K = -0.0125$ is the same for both sets of data, but the free volume fractions, f_i, decrease by 20% and 4% for PE04 and PE01 respectively. These results may be due to the effect of the shear stress and the extent of deformation on free volume fractions. The values of a decrease as the output velocity increases, a result which reflects the decline of the molecular entanglement density when shear rate is increased in a steady state flow. This is in agreement with the theory of dynamics of entanglements proposed by Graessley[21] and with data found in linear polyethylenes which reveal that the slopes of $\log \eta$ *versus* $\log M_\omega$ plots decrease with increasing shear rate[22].

Shrinkage effect

Stretching of polymer filaments immersed in a hot silicone bath and melt spinning experiments are used to characterize the elongational behaviour of polymers. Substantial shrinkage of filaments has been observed (before stretching) in the former case, specially for polyolefin blends. This has lead some authors[23–26] to pay attention to dimensional stability measurements, which have given striking results such as extremely high values of the Hencky strain (equation (1)) for central compositions of two-phase LDPE/EVAc and PS/PMMA blends.

The shrinkage of filaments at high temperatures is the consequence of two processes[24]: the relaxation of internal chain orientations created during sample preparation and the influence of interfacial tension between the polymer and the silicone oil. The measured shrinkage, ξ_r, can be therefore expressed:

$$\xi_r = \xi_{re} + \xi_\alpha \qquad (13)$$

where ξ_{re} is the elastic response that takes place at very short times and ξ_a the response attributed to the interfacial tension between the material and the surrounding silicone oil.

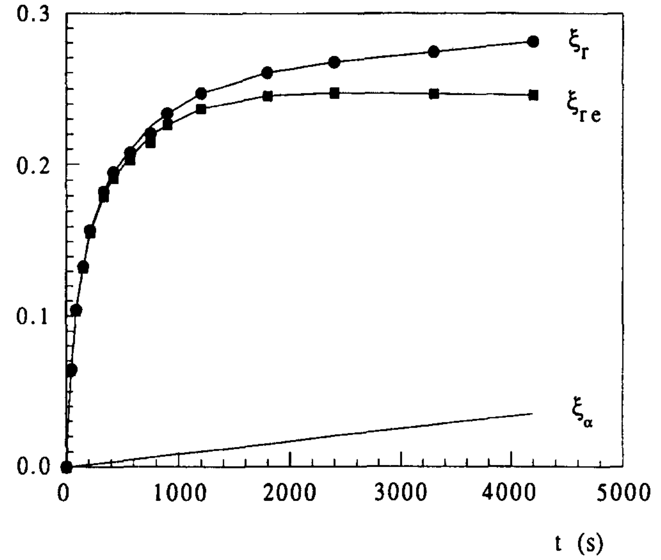

Figure 7 Shrinkage effect in PE04 at 180°C

Table 2 Elongational parameters of PE04 and one of its blends with PE01 at 180°C

Materials	$\dot{\xi}_\alpha$ (s^{-1})	ξ_{re}	η_E (Pa s)	η^* (Pa s)^a
PE04	0.84 10^{-5}	0.25	9.2 10^6	1.5 10^6
90PE04/10PE01	0.94 10^{-5}	0.22	7.9 10^6	1.3 10^6

^{a} The values of η^* have been obtained at 0.01 Hz and 180°C by time-temperature superposition method

Shrinkage measurements of PE04 are presented in *Figure 7*. The values of ξ_{re} have been calculated subtracting the linear part of the plot to the measured ξ_r. The slope of the linear part gives a value of $\dot{\xi}_\alpha$ the shrinkage velocity, that is considered as a measure of elongational strain rate, $\dot{\epsilon}$. If we know the interfacial tension between the material and the silicone oil, ν_{12}, we can calculate the elongational viscosity at the corresponding elongational rate, $\dot{\xi}_\alpha$[27]:

$$\eta_E = \frac{\nu_{12}}{\dot{\xi}_\alpha R} \tag{14}$$

where R is the radius at the beginning of the linear behaviour. We have taken a value of interfacial tension of $5 \times 10^{-2}\,\mathrm{N\,m^{-1}}$, given by Wu[28] for polyethylene/silicone oil system.

In *Table 2* are presented the values of $\dot{\xi}_\alpha$, ξ_{re} and η_E obtained for high molecular weight metallocene catalysed polyethylene and the 90PE04/10PE01 blend. The evaluated elongational viscosities are in the range of those found for high density polyethylenes of broad molecular weight distribution and similar molecular weight[29], and are six times higher than the corresponding shear complex viscosities taken at $\omega = 0.01$ Hz. Such a big difference is due to the fact that elongational viscosities are measured at very low elongational strain rates ($\dot{\epsilon} \sim 10^{-5}\,\mathrm{s^{-1}}$) which very likely correspond to the linear range, whereas shear complex viscosities are measured at a frequency of $\omega = 0.01$ Hz which, according to the results shown in *Figure 1*, is in the non-Newtonian (shear thinning) zone.

In *Figure 8* we report the behaviour of the metallocene catalysed high molecular weight polyethylene and its blends with low molecular weight material, PE01. Below compositions of 80% in PE04 the effect of interfacial tension is not noticed ($\dot{\epsilon} = 0$).

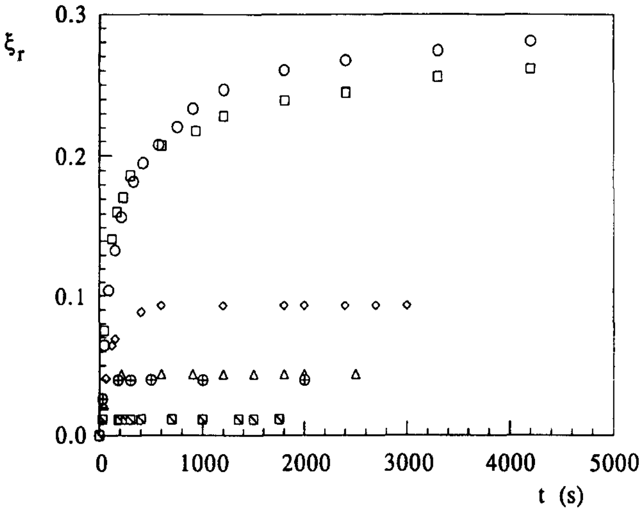

Figure 8 Shrinkage effect in PE04 and its blends at 180°C. Same symbols as in *Figure 1*

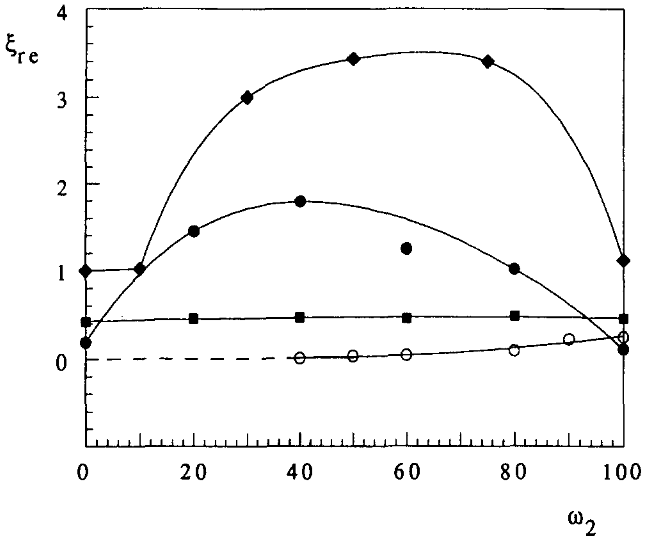

Figure 9 Elastic strain recovery values for literature and PE01/PE04 blends. $T = 180$°C. ◆, LDPE/PP[23]; ●, LDPE/PS[24]; ■, HDPE/HDPE[24]; ○, PE01/PE04 blends

Plots of ξ_{re} as a function of composition can be used to obtain indications of phase separation in polymer blends[24]. When an inmiscible mixture is extruded, the domains immersed in the continuous phase form microfibrils due to stretching or elongational flow in the converging zone[30,31]. This co-continuous fibrillar morphology with weak interfacial interactions causes a very large shrinkage effect in the extrudates.

The variation of ξ_{re} with PE01/PE04 blend composition is shown in *Figure 9*, which also includes data taken from literature for miscible and inmiscible blends. The two-phase LDPE/PS and LDPE/PP systems are characterized by their high values of strain at central compositions, which give rise to the observed large deviation from linearity. However, for presumable miscible HDPE/HDPE blends[24] the values of ξ_{re} remain unchanged for all compositions.

CONCLUSION

A strong positive deviation from log-additivity rule has been observed for compositional variation of the complex and steady state viscosities. The experimental data fit well to an equation based in a model which takes into account two effects: the additivity in the molecular weight of the components, and the changes in the free volume due to the mixing process and the interaction between the molecules.

A single correlation between storage modulus, G', and loss modulus, G'', show that microphases do not exist in the melt for any composition. This is seemingly confirmed by dimensional stability measurements which show no deviation in compositional variation of shrinkage values, a characteristic feature of miscible systems.

The high molecular weight metallocene catalysed polyethylene shows distortion in an extrusion process at very low shear rates. The critical shear rate for the appearance of flow instabilities increases with the content of low molecular weight polyethylene in the blend. Thus we can affirm that this material acts as a processing-aid for the high molecular weight polymer. In the composition range 60–100% of high molecular weight polyethylene the values of the critical shear stress for the onset of 'sharkskin' and 'slip-stick' effects are 0.18 and 0.25 MPa, respectively.

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