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Influence of Long Chain Branching on the Elongational Behaviour of Different Polyethylenes and Their Blends

F. P. La Mantia[1]*, A. Valenza[1], and D. Acierno[2]

[1] Istituto di Ingegneria Chimica, University of Palermo, Viale delle Scienze, I-90128 Palermo, Italy

[2] Istituto di Ingegneria Chimico-Alimentare, University of Salerno, I-84100 Salerno, Italy

ABSTRACT

Elongational data on a series of polyethylenes with different structure and on their blends are presented in order to correlate the extensional behaviour with the long chain branching degree.

The results show that the strain hardening effect increases with the number of branch points; the troutonian value is reached when the branching index is larger than 0.6.

Empirical correlations between elongational viscosity and branching index are also presented.

INTRODUCTION

Extensional flow of molten polymers has to be considered a very important topic both from a fundamental point of view and for its implications in many technological process.

As for the first point of view, the response of molten polymers to an extensional flow is strongly different depending on the molecular structure.

It is well known, in fact, the strain hardening behaviour (1-7) of the low density polyethylene, as opposed to the almost troutonian behaviour of the linear low density and high density polyethylene (6,8-12).

Although it seems well assessed that this peculiar behaviour occurs at low stretching rates when the number of long chain branching is very high, a quantitative study of the effect of the long chain branching on the extensional behaviour of the polyethylene has not been made.

Aim of this work is to present extensional data on a number of polyethylene samples with different structure and on their blends in order to correlate the extensional behaviour at low streching rate with the long chain branching degree.

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* To whom offprint requests should be sent

EXPERIMENTAL

The materials employed were three commercial samples of low density polyethylene (LD), linear low density polyethylene (LL) and high density polyethylene (HD).

Their main physico-chemical characteristics, weight average molecular weight, $\overline{M}_w$, molecular weight distribution, β , and long chain branching index, g, are reported in Table I.

Table I

Physico-chemical characteristics of the homopolymers

Sample code	$\overline{M}_w \cdot 10^{-3}$	β	g
HD	113	4.1	0.98
LL	110	3.5	0.93
LD	220	6.9	0.094

The blends were prepared by melt mixing the homopolymers in a Plasticorder Brabender at 210°C at 20 rpm for about 15 min. The pure polymers were also subjected to the same procedure.

The blends composition and their characteristics are reported in Table II where the weight fraction, φ , is relative to the low density polyethylene.

Table II

Physico-chemical characteristics of the polymer blends

	HD/LD					
φ , %	25	50	70	75	90	
$\overline{M}_w \cdot 10^{-3}$	140	166	188	193	205	
β	4.5	5.6	6.1	6.3	6.8	
g	0.76	0.54	0.36	0.31	0.18	
	LL/LD					
φ , %	25	50	65	75	85	95
$\overline{M}_w \cdot 10^{-3}$	138	165	181	193	203	215
β	4.3	5.1	5.7	6.1	6.3	6.9
g	0.73	0.52	0.39	0.31	0.22	0.14

The weight average molecular weight and the number average molecular weight of the blends were evaluated through the relations:

$$\overline{M}_w = \varphi \overline{M}_{w_1} + (1-\varphi)\overline{M}_{w_2} \quad 1)$$

$$1/\overline{M}_n = \varphi/\overline{M}_{n_1} + (1-\varphi)/\overline{M}_{n_2} \quad 2)$$

Also the long chain branching index has been evaluated through an additive rule. For the homopolymers, the long chain branching index, g, is:

$$g^{0.5} = \frac{[\eta_{br}]}{[\eta_l]} \quad 3)$$

where $[\eta_{br}]$ is the intrinsic viscosity of the polyethylene sample and $[\eta_l]$ that of the linear sample with the same molecular weight.

The samples to be used in the elongational experiments have been prepared by a low rate extrusion in a piston-type extruder at 210 °C; before the tests they were remelted in hot silicon oil to allow for some shrinkage and after solidification their diameters were measured.

The apparatus employed for the tests, already described (7, 12), it allows to perform elongational experiments at constant elongational rate by wounding up the sample at a constant rotational speed. The temperature was 180 °C and the stretching rate $\dot{\Gamma} = 10^{-2}\ s^{-1}$ for all the runs.

Newtonian viscosities have been obtained at the same temperature by means of a rotational viscometer , Rheotron (Brabender).

RESULTS AND DISCUSSION

The transient elongational viscosity curves for all the samples are reported in Figs 1 and 2.

The high density and the linear low density polyethylene show a linear behaviour and, at this stretching rate, the troutonian value, $3\ \eta_0$, is achieved. Similar behaviour is shown by the HD and LL rich blends.

On the contrary the LD sample and the LD rich samples show a

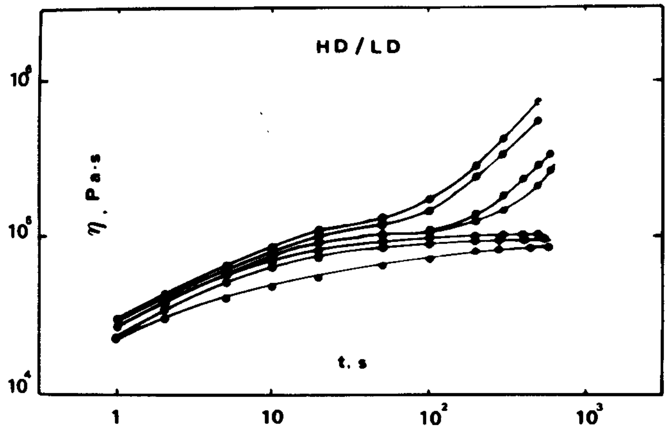

Fig. 1 Elongational viscosity curves at $\dot{\Gamma} = 10^{-2}\ s^{-1}$ for the system HD/LD. From top to bottom the LD content is: 100, 90, 75, 70, 50, 25 and 0 %.

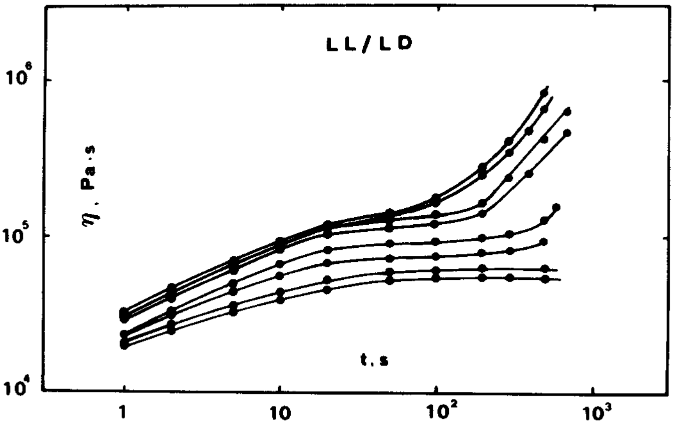

Fig. 2 Elongational viscosity curves at $\dot{\Gamma} = 10^{-2}\ s^{-1}$ for the system LL/LD. From top to bottom the LD content is: 100, 95, 85, 75, 65, 50, 25 and 0 %.

remarkable strain hardening effect, also at this low elongational gradient.

A moderate strain hardening is shown by the blends with intermediate compositions.

This features can be explained with the dilution effect on the average long chain branching degree undergone by thy LD sample in the blends.

In order to quantitatively evaluate the influence of the long chain branching on the elongational behaviour of the polyethylenes, the dimensionless viscosity has been plotted against the long chain branching index, see Fig. 3, at fixed values of the deformation.

The dimensionless viscosity is the viscosity at a given value of the deformation, Γ , divided by its troutonian value

$$\bar{\eta} = \frac{\eta_\Gamma}{3\,\eta_0} \qquad 4)$$

where η_0 is, of course , the newtonian viscosity, reported in Fig. 4 for the two systems as a function of the LD content.

It is well evident that when the g value is greater than 0.6 the elongational viscosity approaches the troutonian value, whatever is the deformation, at least at this streching rate.

Decreasing the g value, and then increasing the long chain branching number, the elongational viscosity rises with respect to the troutonian value and increases more and more with the deformation. This occurs, of course, because the strain hardening is more and more significant increasing the branching and the stretching deformation.

More quantitatively, by recalling that the branching index is related to the weight average number of branching points, per molecule, n , through the equation (13)

$$g = \frac{6}{n_w}\left[\frac{1}{2}\,\frac{(2+n_w)^{0.5}}{n_w^{0.5}}\ln\frac{(2+n_w)^{0.5}+n_w^{0.5}}{(2+n_w)^{0.5}-n_w^{0.5}} - 1\right] \qquad 5)$$

one may say that, under these experimental conditions, at least six branch points per molecule are necessary to induce a significant increase of the elongational viscosity with respect to the troutonian value.

Moreover an empirical correlation has been found between the dimensionless viscosity and the g value. From Fig. 2, we have

$$\bar{\eta} = a \cdot g^{b} \qquad 6)$$

where a and b depend on the deformation:

$$a = 1.17 \cdot \Gamma^{-0.208} \qquad 7)$$

$$b = 0.145 \cdot \Gamma^{1.11} \qquad 8)$$

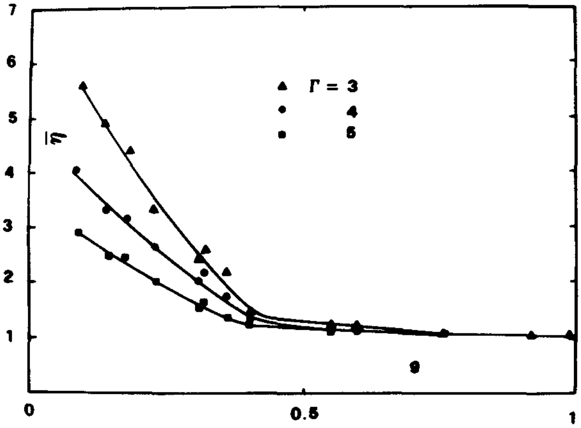

Fig. 3 Dimensionless elongational viscosity vs the branching index.

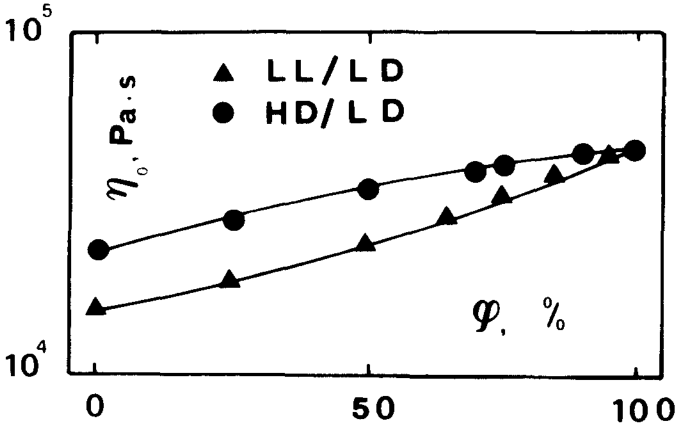

Fig. 4 Newtonian viscosity vs LD content.

From the relations 6-8 and with the newtonian viscosity, it is then possible to construct the elongational curves, at $\dot{\Gamma} = 10^{-2}$ s^{-1}, for all the polyethylenes.

Of course the numerical constants of the equations 7 and 8 depend, on its turn, not only on the experimental conditions (temperature and stretching rate) but also on the molecular weight and molecular weight distribution.

And in fact, as already found (12), both M_w and β can influence the elongational behaviour of the polyethylene at fixed number of branch points. In this case however the value of M_w and β of the homopolymers are not too different and in particular M_w and β are very similar when one considers only the samples with g values less than 0.6 which are the more significant in this work.

A further study on the effect of M_w and β is however necessary and at present in progress in our laboratories.

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