

Modification of Rheological Properties of Branched Polyethylenes by a Thermomechanical Treatment

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Abstract. Shear refinement has been studied in four LDPE, which have been molecularly and rheologically characterized. They have been subjected to a pre-shearing in a cone-and-plate rheometer, and the decrease of viscosity, associated with the disentanglement of macromolecules, has been analyzed as a function of different mechanical parameters: shear rate, strain, stress, specific energy. It appears that disentanglement mechanisms are complex and cannot be explained by a unique molecular parameter, e.g., the molar mass between entanglements.

Keywords: Low-density polyethylene, molecular structure, entanglements, rheology, shear refinement.

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INTRODUCTION

Shear refinement refers to the modification of rheological properties of a polymer by a thermomechanical treatment applied in the melt. This phenomenon is usually interpreted in terms of modification of entanglements [1].

Low-density polyethylenes (LDPE) have a complex molecular structure, characterized by the presence of long-chain branching, which depends on the type of reactor (tubular or autoclave) and on the polymerization conditions. Because of their molecular architecture, the rheological properties of LDPE are very sensitive to a pre-shear: generally, it induces moderate decrease of viscosity [2-5], decrease of extrudate swell [2, 3, 5, 6], and substantial variations of elongation properties (e.g., decrease of melt strength [7]).

It is the reason why these polymers have been chosen here for an in-depth analysis of shear refinement in terms of progressive disentanglement of macromolecules. The variations of viscosity due to pre-shearing will be used to follow the modifications of entanglements. The objective of this work is to study the criteria for the onset of disentanglement in a cone-and-plate geometry, to highlight the complexity of the phenomena involved, and to show that a too simplistic approach is totally unsatisfactory to account for experimental observations.

MATERIALS

Molecular Characterization

Four commercial LDPE produced by free-radical polymerization have been considered in this work. They are labeled A, B, C and D, in order of increasing viscosity. B and C are obtained by a tubular process, A and D by an autoclave process. The molecular characteristics of these polymers are gathered in Table 1: average molar masses (M_n , M_w , M_z), polydispersity indices (M_w/M_n , M_z/M_w), short-chain branching *SCB* and long-chain branching *LCB*. According to this table, polymer A has the highest number of long branches and the lowest number of short ones. Conversely, in polymer B, long-chain branching is the least frequent, and short-chain branching the most important. C and D are close together. Thus, autoclave polymerization enhances the formation of long branches, whereas tubular polymerization favors short-chain branching, but to a lesser extent

TABLE 1. Molecular characteristics of the four LDPE.

Material	M_n (kg/mol)	M_w (kg/mol)	M_z (kg/mol)	M_w/M_n (-)	M_z/M_w (-)	SCB (/1000 C)	LCB (/1000 C)
A autoclave	14.40	106.5	532.5	7.4	5.0	11	2.4
B tubular	15.55	111.6	1 182.96	7.5	10.6	15	0.6
C tubular	13.40	70	210	7.8	3.0	12	1.4
D autoclave	12.25	95	242.25	5.2	2.5	14	1.6

Rheological Characterization

Classical steady-state and oscillatory shear measurements were performed on a cone-and-plate rheometer (ARES, Rheometrics). The zero-shear viscosity η_0 of the four polymers was measured (Table 2). In a classical way, the molar mass between entanglements M_e was calculated from the plateau modulus G_N^0 . The latter was determined from the maximum of G'' vs. frequency according to the method of Oser and Marvin [8]. As shown in Table 2, the values of the plateau modulus (from 0.42 to 0.68 MPa) are low with respect to those reported for linear PE (from 1.6 to 2.7 MPa). Consequently, the masses between entanglements are higher than the one currently admitted for linear PE (1800 g/mol). The number of entanglements per macromolecule N_e can be then calculated.

To summarize, materials A to D rank by increasing viscosity. A has the most important amount of long-chain branching, and B the least. A and B are more entangled than C and D.

TABLE 2. Rheological characteristics at 140 °C and number of entanglements per molecule.

PEBD	η_0 (Pa.s)	G_N^0 (MPa)	M_e (g/mol)	N_e (-)
A	25 000	0.68	3924	27
B	65 000	0.42	6346	18
C	180 000	0.44	6112	11
D	200 000	0.43	6112	16

EFFECT OF SHEAR FLOW ON RHEOLOGICAL BEHAVIOR

Experimental Protocol

Measurements were done at 160°C in a cone-and-plate geometry. Stabilized specimens were first annealed at 160 °C during 7200 s to obtain a fully entangled material. They were then subjected to a constant shear rate. The variations of viscosity with time, deduced from torque measurements, allow us to distinguish the different phases of flow (Figure 1):

- establishment of stress: viscosity first increases, passes through a maximum and then decreases;
- stabilization, associated with a steady state and characterized by a viscosity plateau. The viscosity at the plateau will be taken as the initial viscosity $\eta(0)$;
- decrease of viscosity, attributed to disentanglement.

To describe the effect of shear rate on the initial viscosity, the viscosity values are divided by $\eta(0)$ and the time evolution of the normalized viscosity $\eta/\eta(0)$ will be considered in the following.

Comparison of the Different Materials

For each experiment, we can determine the time t_0 when the viscosity begins to decrease (onset of disentanglement, see Figure 1), and calculate the corresponding strain: $\gamma_0 = \dot{\gamma}_0 t_0$. From the initial viscosity $\eta(0)$, one can also calculate the stress σ_0 applied to the material, $\sigma_0 = \eta(0)\dot{\gamma}_0$, and the specific energy received by it before the viscosity decreases: $SE_0 = \sigma_0 \dot{\gamma}_0 t_0 = \sigma_0 \gamma_0$.

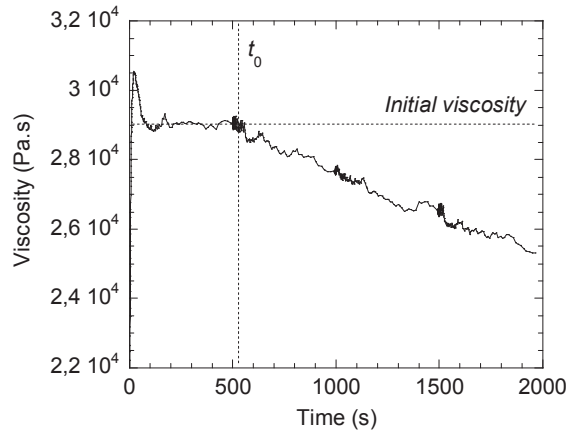
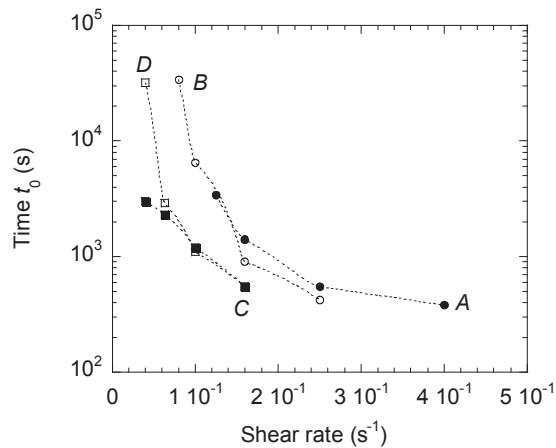


FIGURE 1. Time variation of viscosity for a shear rate of 0.16 s^{-1} during a time of 2000 s (Polymer D, 160°C).

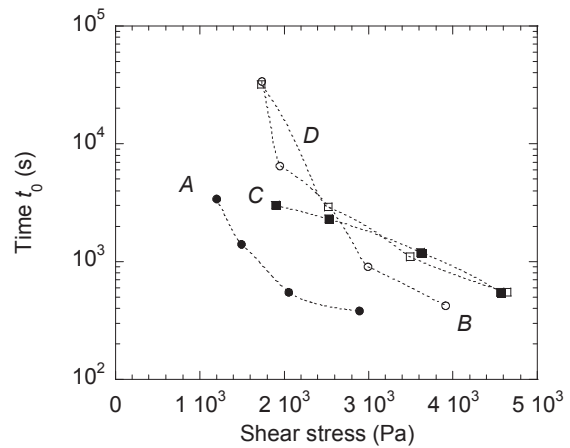
Figure 2a shows the evolution of t_0 as a function of shear rate for the four LDPE. In all cases, this time decreases very rapidly at low shear rates and then tends to stabilize. A and B exhibit similar behaviors, as well as C and D. At a given shear rate, the materials ranking is the following: $D \approx C < B \approx A$. Let us recall that A and B are more entangled than C and D.

As the materials have very different viscosities, a same shear rate induces very different stresses. If we now plot t_0 as a function of the shear stress, a different ranking is obtained (Figure 2b): $A < B \approx D \approx C$.

In Figure 2c, t_0 is plotted as a function of specific energy. Except for those corresponding to very low shear rates, the points for all the materials are located in the same range, between 300 and 500 kJ/m^3 . This suggests that specific energy could control the onset of disentanglement, but this has to be verified for a larger number of cases.



(a)



(b)

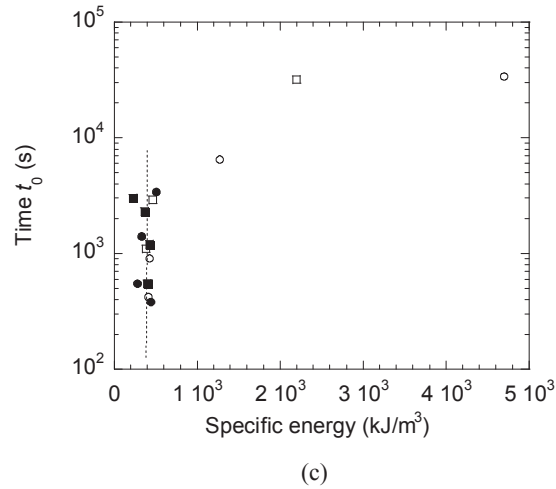
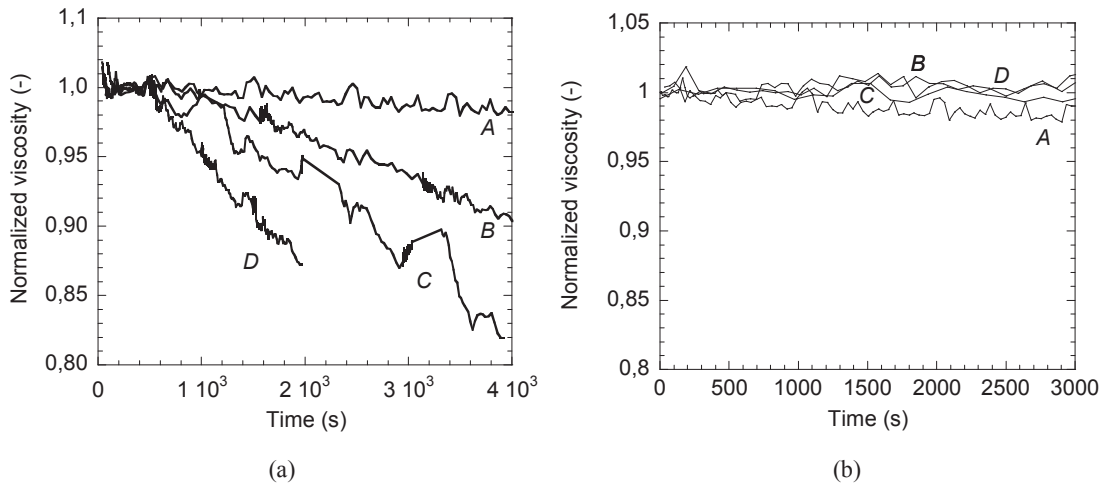


FIGURE 2. Onset time for the disentanglement of the four materials at 160 °C, as a function of: (a) shear rate; (b) shear stress; (c) specific energy (A : ●, B : ○, C : ■, D : □).

The disentanglement kinetics of the four materials can be compared by following the time evolution of the normalized viscosity at a given shear rate, e.g., 0.16 s^{-1} (Figure 3a). It can be observed that the polymers rank in the order A, B, C, D for the rapidity of disentanglement: D (the most viscous) presents the most rapid kinetics, and the most entangled polymers (A and B) are also the most difficult to disentangle.

For a given level of stress, the differences between the materials are much less pronounced (Figure 3b). It seems that once disentanglement has started, applied stress, rather than molecular architecture, determines its kinetics, in any case for short times. Indeed, for long times (Figure 3c), polymer C shows the most important viscosity drop ($\eta/\eta(0) = 0.90$ after 50 000 s), followed by polymer A ($\eta/\eta(0) = 0.91$), while D and B are very little modified ($\eta/\eta(0) = 0.98$ and 0.99 , respectively).

To summarize, the onset of disentanglement is not clearly linked to molecular structure. Conversely, the disentanglement kinetics and the levels of viscosity decrease seem to be correlated to it: a fluid and entangled polymer is more difficult to disentangle (case of material A). On the opposite, it is easier to disentangle a viscous and little entangled material (case of material D).



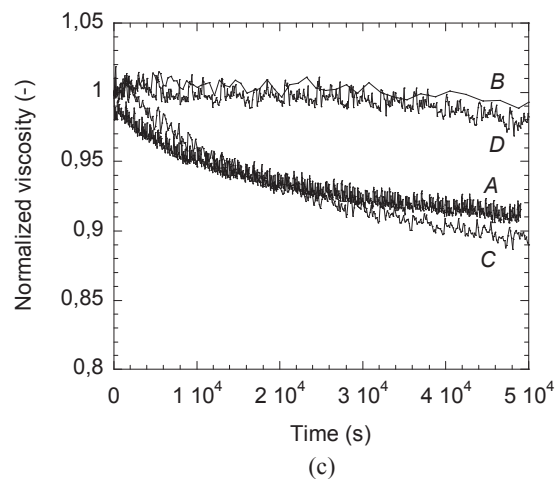


FIGURE 3. Time evolution of the normalized viscosity for the four materials at 160 °C: (a) $\dot{\gamma} = 0.16 \text{ s}^{-1}$; (b) $\sigma_0 \approx 1700 \text{ Pa}$, short times; (c) $\sigma_0 \approx 1700 \text{ Pa}$, long times.

CONCLUSIONS

Shear refinement is frequently mentioned, but its characterization is often crude. It is usually interpreted in terms of modification of entanglements, but the influence of molecular structure is rarely considered.

We have studied with a rotational rheometer the influence of a well-controlled pre-shear on the viscosity of four LDPE. These measurements have shown that the application of shear during a certain time induces a decrease of viscosity due to disentanglement, provided that this time is greater than a critical value t_0 .

An original point of this work is to have considered different parameters to analyze viscosity variations: shear rate, strain, stress, specific energy. According to the selected parameter (shear rate or shear stress) and the criterion used to characterize disentanglement (time at onset of disentanglement, short-term kinetics, limit value of viscosity for long times), the ranking of the four materials is not the same. This shows that disentanglement is a complex phenomenon, with perhaps several mechanisms involving different molecular characteristics (number of entanglements, length and distribution of branches, etc.). Nevertheless, the disentanglement kinetics and the levels of viscosity decrease are well correlated to molecular structure: it is more difficult to disentangle a fluid polymer with numerous entanglements than a viscous and little entangled one. Finally, an interesting result is that the onset of disentanglement, at different times, could correspond to the same level of specific energy.

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