

# Anomalies in the Rheological Behavior of Polyethylene with Very Broad Molecular Weight Distribution

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## Synopsis

The rheological behavior of high density polyethylenes with very broad molecular weight distribution is studied in the molten state starting from freshly synthesized powders. The complex viscosity increases slowly up to a limiting value as a function of ageing of the polymer and faster when the molten polymer is stirred. The phenomena are explained by an heterogeneous distribution of very high molecular weight nodules in the polymer arising from the synthesis and is proved by the preparation and characterization of polymers presenting the opposite heterogeneity and behavior (very low molecular weight nodules).

## INTRODUCTION

Although a great number of theoretical studies is devoted to the rheological behavior of molten polymers as a function of their molecular weight distribution (MWD),<sup>1-5</sup> only few studies have dealt with the effect of very broad continuous distributions which appears only with polyolefins,<sup>6</sup> mainly with polyethylene. When the polydispersity ( $M_w/M_n$ ) exceeds 10, the rheological behavior shows some anomalies which are often assigned either to thermal or thermomechanical degradation<sup>7</sup> or to a change in the entanglement state of the polymers.<sup>8-10</sup> The polymers studied up to now are mostly commercial samples with unknown thermal and thermomechanical history. Even when degradation can be excluded the anomalies remain and the pure rheological behavior of the polymer is difficult to observe.

According to their molecular weight and their molecular weight distributions, the processability of high density polyethylene (HDPE) to be transformed and, as a consequence, their applicability, vary. For injection processing, PE must have low viscosity and reduced elasticity in the molten state in order to ensure dimensional stability. In this case polymers of low molecular weight and narrow molecular weight distribution (reduced entanglement) are used. Typical values are in the range 80.000 to 120.000 for  $M_w$  and 3 to 5 for  $M_w/M_n$ . For blow molding processing, the products used have higher molecular weight and broad molecular weight distribution (enhanced entanglement) in order to avoid melt fracture and to get better strength properties in the molten state ( $M_w > 150.000$  and  $M_w/M_n = 10$  to 13). The broadening of molecular weight distribution to very high values (polydispersity in the range 20 to 25) allows or improves the thermoplastic processability of very high to ultra high molecular weight PE ( $M_w > 200.000$ ). Examples of applications can be found among high modulus PE fibers, sporting equipment, and so on.

This work uses polymers synthesized in our laboratory, so all the steps of the synthesis and the following thermal history of the samples are known. We have tried to explain all the phenomena which hide the real properties of the polymer when the polydispersity index is as large as 25.

## EXPERIMENTAL

### Polymer Synthesis

The problem of the synthesis of PE with broad MWD by Ziegler-Natta catalyst has been reviewed by Zucchini and Cecchin.<sup>11</sup> Broad distributions are obtained by the appropriate choice of the catalyst and/or by particular processes.

In our study, the polymers have been prepared by Ziegler-Natta catalysis in a slurry process at 80°C with heptane diluent. Hydrogen is added to limit chain length. The catalyst used is  $\text{TiCl}_4$  supported on magnesium chloride, especially designed to produce very broad molecular weight distributions.<sup>12</sup> Three types of preparation have been used:

*One step process:* the polymer is produced in one batch.

With *process 2*, one half of the polymer is first obtained under conditions corresponding to low molecular weight polymer synthesis, then the second half of the polymer takes place inside the solid polymer particles under conditions of very high molecular weight synthesis. Process 2 is widely used for industrial production using two or more on-line reactors.

With *process 3*, the high molecular weight polymer is produced in the first step and the low molecular weight in the second step.

### First Characterization

Molecular weight determinations are realized by two methods: size exclusion chromatography (SEC) and melt flow index (MFI).

*Size exclusion chromatography.* SEC is the usual method for determination of different averages of molecular weight:  $M_n$ ,  $M_w$ ,  $M_z$ . But in the case of HDPE, the measurement must be carried out at elevated temperature which is very difficult mainly for those samples with broad distribution. Very high molecular weight PE are difficult to dissolve. SEC are realized with a 0.1% solution in trichlorobenzene at 135°.

*Melt flow index.* Determination of MFI is a convenient method widely used for industrial application and is normalized.<sup>13</sup> MFI at different loading 21.6 kilo ( $MI_{21}$ ) and 5 kilo ( $MI_5$ ) give fair indications of molecular weight ranges.

At high shear, MFI are sensitive to lower molecular weight. Melt index ratios, for instance  $MI_{21}/MI_5$ , fairly describe the width of the distributions and are commonly used to identify broad or narrow distributions,<sup>11</sup> but only apply to polymers of the same type (same short or long branching). For broad distributions, these ratios can reach values of 16 to 20, or more for a typical value of  $MI_5$  close to unity, which is convenient for extrusion. Typical values of the same ratio for narrow distribution are close to 7.

TABLE I  
Characterization of HDPE with Very Broad Molecular Weight Distribution

Sample No.	$M_w$	$M_n$	$\frac{M_w}{M_n}$	MI5	MI21	$\frac{MI21}{MI5}$
<b>Multisteps products</b>						
Process 2						
PE 9	164,000	9,300	17.4	1.4	33.8	17.4
PE 10	158,000	7,900	19.9	2.1	41.8	19.9
PE 13	215,000	8,800	24.1	0.4	11.1	27.1
<b>Opposite products</b>						
Process 3						
PE 21	247,000	10,400	23.7	5.4	73.7	13.6
PE 22	322,000	13,000	24.8	1.4	25	18.1
PE 23	229,000	10,400	22.1	2.5	41.5	16.8

### Rheological Characterization

The KEPES balance rheometer (CONTRAVES) is used in most cases for the rheological characterization of our products. Measurements were carried out at 170°C in a wide range of frequencies ( $10^{-2}$  to  $10^2$  Hz) under nitrogen atmosphere with the virgin polymers directly issued from the synthesis without any mechanical or thermal treatment.

In all cases, sample response linearity with respect to strain amplitude was verified. The Kepes rheometer gives access to the dynamic complex viscosity as a function of the pulsation and then to the elasticity ( $\eta'' = G'/\omega$ ) and viscosity ( $\eta' = G''/\omega$ ). The time required for a polymer characterization is about one hour.

## RESULTS

The characteristic data of "broad" HDPE are summarized in Table I.

### Properties in the Molten State

The rheological behavior is the same for the polymers obtained in process 1 (one step) and process 2 (two steps).

#### Viscosity

In a log/log scale, the curves show steep slopes especially for the very broad distribution products, as could be expected. A typical example is given in Figure 1. Accordingly, no Newtonian viscosity can be observed even at the lowest frequencies.

#### Elasticity

The elastic behavior is more surprising. Almost never do the curves show a maximum (Fig. 1). In most cases no circular Cole-Cole representation can be drawn: the elasticity remains high even at low frequencies.

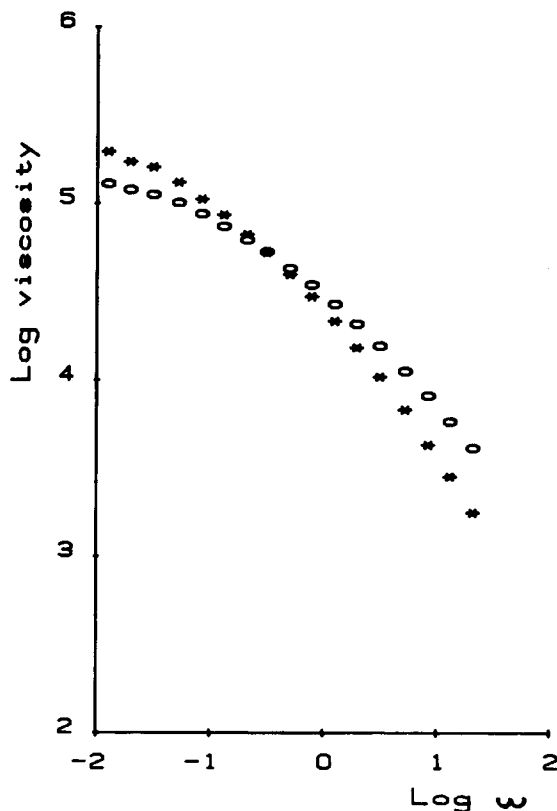


Fig. 1. Viscosity and elasticity (expressed in Poiseuille Pa.s) as a function of circular frequency (log/log scale) for PE sample no. 13: (\*) viscosity; (○) elasticity.

### Time and Shear Dependence

The rheological behavior of the polymers is quite unaffected by the way the measurements are made and are reproducible. But the absolute values vary with ageing of the product (ageing time scale in months at room temperature, in hours at 170°C). If a moderate mechanical treatment is applied together with a thermal treatment, the evolutions are faster, for instance, when the molten polymer is sheared out of the linear stress-strain domain. The shapes of the curves ( $\eta'(\omega)$  and  $\eta''(\omega)$ ) remain the same but the absolute values of viscosity and elasticity are both increased (Figs. 2 and 3). The molecular weight (or the entanglement state) of the polymer seems to be increased.

### DISCUSSION

We have first considered the possibility of a chemical or thermomechanical degradation of the material. It is easy to show that:

1. No carbonyl bands resulting from the oxidation can be observed on the infrared (IR) spectra using very sensitive Fourier transform IR spectrometer.

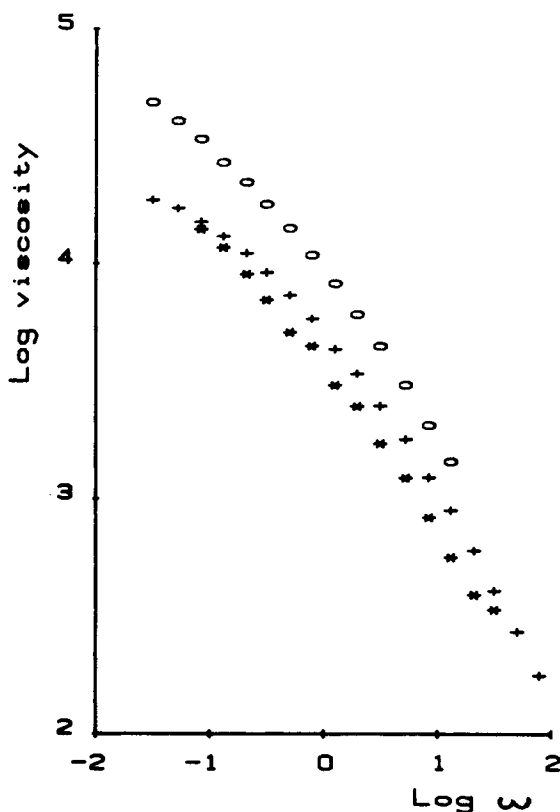


Fig. 2. Time and shear dependence for PE sample no. 10: Viscosity (Pa.s) as a function of circular frequency: (\*) fresh polymer; (+) after shearing; (o) 10 months aged polymer.

2. During the duration of an experiment (about one hour) no change is observed at 170°C. The variation of the viscoelastic appears at longer times (several hours). This behavior is not consistent with a radical process initiated by peroxydes.
3. The longer the polymer is aged at room temperature the less its viscosity varies in the molten state. This is also opposite to the effect which may be expected from oxydation.

Several authors have reported that no degradation takes place under similar or even more severe conditions<sup>14</sup> as controlled by SEC.<sup>10</sup>

These evolutions have a particular feature: a limiting value can be reached asymptotically and cannot be exceeded. Different treatments on other mechanical spectrometers (Reometrics, Instron) have been carried out, giving the same limiting value. The polymer reaches a stable state.

Because we can exclude a chemical effect, only a physical evolution of the raw product can explain the observations. Entanglement effects are often proposed to explain viscosity changes in the polymer during thermal or thermomechanical treatments:<sup>8-10</sup> for instance, solid polymer can be recovered from solution in non-equilibrium states and are then less entangled than at equilibrium. Thermal treatment may then increase the polymer

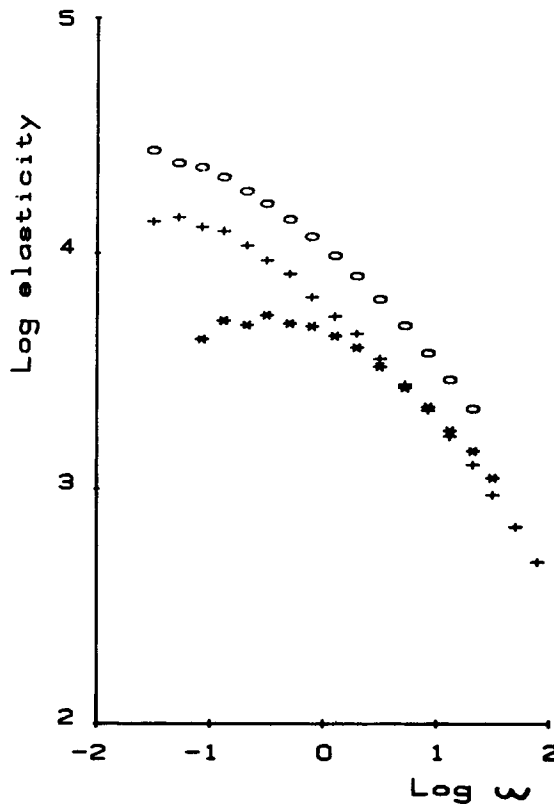


Fig. 3. Time and shear dependence for PE sample no. 10: Elasticity (Pa.s) as a function of circular frequency: (\*) fresh polymer; (+) after shearing; (o) 10 months aged polymer.

viscosity. But the polymer is supposed to remain homogeneous all along the process.

We propose and we will try to prove another explanation for the polymer behavior just after synthesis.

We think that the virgin polymers are heterogeneous products: such statement is easy to be understood when the product has been obtained by a multistep process. In the first step of process 2 a low molecular weight matrix is built up. From the tiny heterogeneous catalyst particles inside, the high molecular weight polymer grows in the form of small nodules in the second step. When the polymer is molten, these nodules are very viscous and an homogeneous mixture can be obtained only after long-term diffusion without stirring, or after a shorter time on stirring.

The slow evolution in the solid state can also be explained. The high molecular weight fraction produced in the second step crystallizes at the rather low temperature used for synthesis. Due to the very high viscosity the crystallinity remains low before any annealing treatment. At room temperature 120°K above the glass temperature, a very slow evolution of the amorphous phase is possible and requires months to be achieved.

Homogeneity is more easily and quickly obtained at high temperature and/or when the product is submitted to shear.

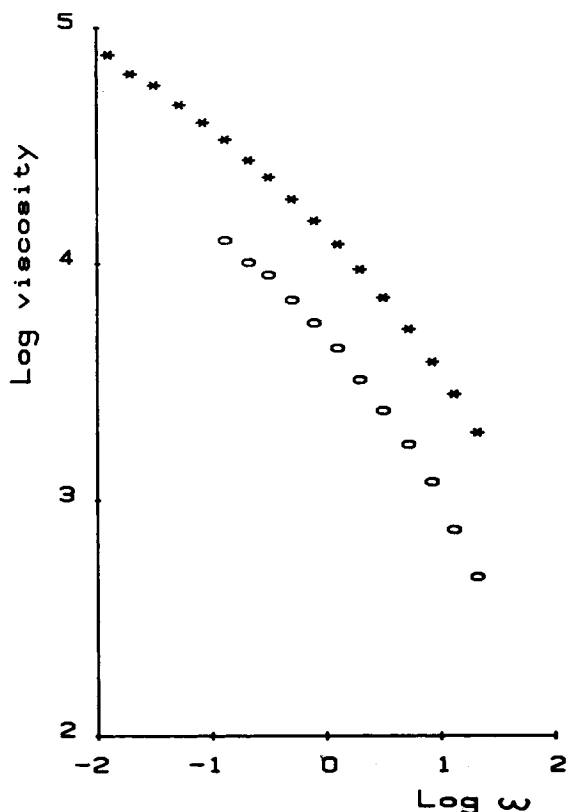


Fig. 4. Shear dependence for PE sample no. 22: Viscosity (Pa.s) as a function of circular frequency: (\*) fresh polymer; (O) after shearing.

The polyethylene with wide molecular weight distribution obtained by a one step process shows the same behavior and the same evolution. Therefore, they probably present the same kind of heterogeneity.

However, this interpretation is difficult to prove directly. Various other difficult to explain results have already been reported in the field. For instance, Quadrat and co-workers<sup>15</sup> reported an evolution of the molecular structure of ultra high molecular weight (UHMW) PE in solution. They observed a decrease of intrinsic viscosity and  $M_w$  over time. This decrease is attributed to a slow progressive disappearance of the aggregates of UHMW. Here, also, chemical effects are excluded.

In order to sustain our assertion we have prepared "opposite" products (process 3), namely, nodules of low molecular weight in a matrix of higher molecular weight polymer. In Figures 4 and 5 the typical variations of viscosity and elasticity are shown before and after a mixing treatment. In this case the low molecular weight material is very easily distributed over the higher molecular weight matrix. Viscosity and elasticity decrease during mixing.

Under the same conditions we observed an increase with the process 2 products. So all conditions being the same, these results clearly exclude both chemical or mechanical degradation of the polymer. The heterogeneity of the polymer introduces entanglement effects through the difficulty of mixing two

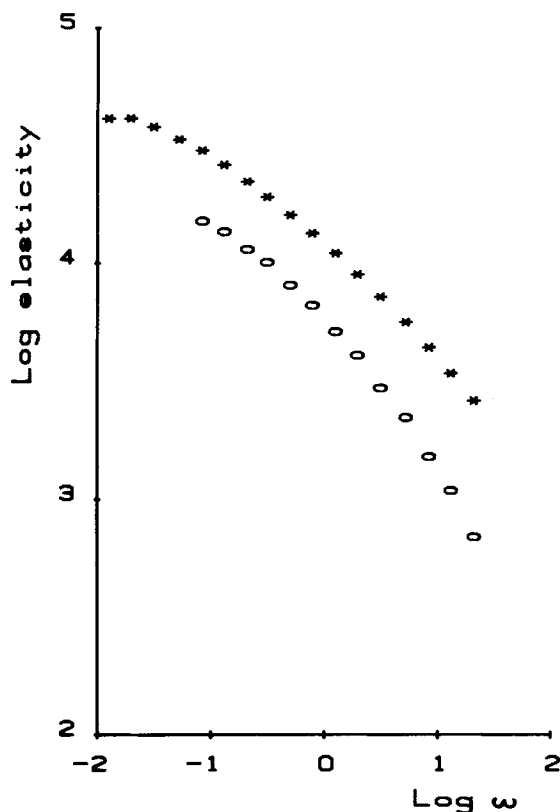


Fig. 5. Shear dependence for PE sample no. 22: Elasticity (Pa.s) as a function of circular frequency: (\*) fresh polymer; (o) after shearing.

phases of polymer liquids with very different molecular weights. The changes in the rheological properties are then due to a change in apparent mean molecular weight.

### CONCLUSION AND APPLICATION

A rheological study of HDPE of broad molecular weight distribution requires a well-defined product which must be as homogeneous as possible. Aside from the fact whether the products are homogeneous or not, the curves obtained are characteristic of products of broad molecular weight distribution. At low frequencies, the viscosity does not show a Newtonian plateau and we cannot generally determine a maximum for the elastic curve. The Newtonian behavior, if it could be observed, would appear only at very low frequencies. An exact measure of the high molecular weight distribution is necessary to establish correctly the theory of this behavior.

Molecular weight distributions of HDPE are defined industrially by the melt index ratios. The unusual behavior of these broad MWD-products has an influence also on the melt index values measured from the virgin powders. For melt indices at low shear, the viscosity increases during the time of measurement (some mixing occurs in the cylinder of the MFI apparatus). At high



shear the viscosity value is constant, due to the slope of the viscosity curve (at high shear the effect of the higher molecular weight fraction of the polymer becomes negligible). Then the melt index ratio varies as a function of the time and of the polymer level in the cylinder and cannot be used to describe the width of very broad polymers not in equilibrium.

The important decrease of viscosity with increasing shear allows easy thermoplastic processability ( $MI_5$  not too far from 1) of very high molecular weight HDPE ( $M_w > 300,000$ ) with very broad molecular weight distribution (Table I). Usually broad products ( $M_w/M_n < 16$ ) are not easy to process under common conditions when the molecular weight  $M_w$  exceeds 200,000.

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