

On the Linear Viscoelastic Behavior of Polyolefins in the Molten State: Influence of Long Chain Branching

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This contribution presents a survey on the influence of long chain branching on the linear viscoelastic properties. The aim of this article is to provide evidence that rheological testing is a potent tool for characterising polymers in the melts. The materials chosen are linear and slightly long- chain branched metallocene- catalysed polyethylene of narrow molecular mass distribution, as well as linear and highly long- chain branched polyethylene of broad molecular mass distribution, and other sample of the big family of polyolefin's.

The linear viscoelastic flow properties are determined in shear creep and recovery experiments by means of a magnetic bearing torsional creep apparatus. The interest of this study consists in reviewing various experimental, theoretical and simulation results of the some viscoelastic properties. The samples with a slight degree of long- chain branching exhibit a surprisingly high zero shear-rate viscosity in comparison to linear one, whereas the highly branched polymers have a much lower viscosity compared to linear samples. Slightly branched polyethylene have got a higher steady- state compliance in comparison to linear products of similar polydispersity, whereas the highly branched polyethylene of broad molecular mass distribution exhibit a surprisingly low elasticity in comparison to linear broad molecular one. The same remarks are obtained for the other samples. The actual framework leads us to say that the number of branches is less important than the topology itself. Therefore, the position and architecture of the branches along the main polymer chain are the principal factors that control the material rheology.

Key words: *Polymers, Long chain branched, ramified, viscoelasticity, polydispersity, compliance*

1. INTRODUCTION

The applications increase of the plastics requires high technicality thorough knowledge of the manufacturing processes and a better adequacy of materials to the techniques of transformation. This step of optimization, even of selection, a material correlatively to a process invites to regard the facility of transformation as a property full of materials. In the case of polymers, implemented in a malleable state obtained by rise in the temperature thermoplastic polymers or starting from a liquid state before polymerization thermohardening polymers, this property is characterized by the rheological behavior in a molten state or liquid. If the treatment of problems can be carried out in many cases, considering molten polymer as a viscous fluid, the comprehension of a certain number of phenomena comes under the field of viscoelasticity. The term of viscoelasticity will be defined as characteristic of an intermediate particular mechanical behavior between the one of an ideal solid, say Hookean, and that of an ideal liquid known as Newtonien. That amounts considering that the mechanical properties observed are, in a general way, dependent on time (or of derived quantities) and on the temperature. The olefinic polymers are the most largely used today in the industry of the plastics. The polyolefin's constitute one of the thermoplastic classes which develop quickly, because of their good physical and chemical steady properties, of their low price and their weak molecular weights. They are

polymers formed by a periodic repetition of monomers of chemical structures identical to $(CH_2)_n$ in the form. In order to optimize their properties and their implementation, the mixture is often used. This is particularly significant for polyolefins. In general, the traditional catalytic systems generate broad molecular masses distributions of and SCB and then a not controlled presence of LCB. In these materials, it is very difficult to separately treat the effects of the various molecular characteristics. This work consists on comparative analysis of effects of long chain branching on the linear viscoelastic properties of polyolefins in the molten state under various conditions of polymerization.

1. THEORETICAL PART

Combination of dynamic and creep-recovery results

From the dynamic experiments, He and al [3] can obtain the storage and loss modulus from creep and recovery experiments, and derive from creep compliance $J(T)$. The dynamic data are more reliable at short times (high frequencies), while, those of creep and recovery are more reliable at long times. Moreover, to obtain a complete image of the viscoelastic behaviour of a material, these two sets of data must be combined. To this end, the conversion of all these data to a retardation spectrum is necessary, and the two modules are expressed in term of this spectrum on all the frequencies range. [3] Dynamic modulus $G'(\omega)$ and $G''(\omega)$ can be expressed in terms of the relaxation spectrum function $H(\tau)$ Ferry (1980) such as:

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d\ln\tau \quad (1)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega\tau}{1 + \omega^2 \tau^2} d\ln\tau \quad (2)$$

Because of lack of the experimental data on all the frequency range, the exact function $H(\tau)$ cannot be calculated from of these two equations. However, it is not possible to obtain such data. Because of the limited precision and, range of actual data, a single spectrum cannot be easily carried out, and special computational techniques used are required to determine a spectrum close to the real spectrum, i.e. the characterization of polymers. The nonlinear regularization technique of (NLGR) carried out by Honerkamp and Weese in 1993, gives the relaxation spectrum curve by taking into account noise produced by the sample during experiment. The resulting relaxation spectrum is reliable in the region on corresponding to the experimental time window. From this spectrum, the retardation spectrum can be obtained by using the following equation:

$$L(\tau) = \frac{H(\tau)}{\left[\int_{-\infty}^{+\infty} (t-1) \frac{H(\tau)}{\tau} d\ln\tau \right]^2 + \pi^2 H^2(\tau)} \quad (3)$$

The creep compliance can be then expressed in term of retardation spectrum $L(t)$, by the following relation:

$$J(t) = J_g + \int_{-\infty}^{+\infty} L(t)(1 - e^{-t/\tau}) d\ln\tau + \frac{t}{\eta_0} \quad (4)$$

Where instantaneous compliance J_g is supposed to be negligible.

By using the same technique of calculates (NLGR), the retardation spectrum can be deduced from the creep compliance. This spectrum $L(\tau)$ is used as an intermediate tool to combine the dynamic data with those creep-recovery.

Consequently, by taking the share of the contribution to $L(t)$ at times court from the complex modulus and that at long time from the creep compliance. Now, this spectrum is extended on all the range frequency (time), and with this information He and al [3] can calculate other viscoelastic functions such complex compliance and, complex modulus $G'(\omega)$ and $G''(\omega)$ can be expressed in term of retardation spectrum by the following relations:

$$J'(\omega) = \int_{-\infty}^{+\infty} L(\tau) \frac{1}{1 + \omega^2 \tau^2} d\ln\tau \quad (5)$$

$$J''(\tau) = \frac{1}{\omega\eta_0} + \int_{-\infty}^{+\infty} L(\tau) \frac{\omega\tau}{1 + \omega^2 \tau^2} d\ln\tau \quad (6)$$

$$G'(\omega) = \frac{J'(\omega)}{J'^2(\omega) + J''^2(\omega)} \quad (7)$$

$$G''(\omega) = \frac{J''}{J'^2(\omega) + J''^2(\omega)}$$

2. RESULTS AND DISCUSSIONS

In order to point out the effects of LCB on the linear viscoelastic properties of some polyolefin's. We have made of use of the most recent theoretical results and experimental data reported in the literature by Salazar et al., Kokko et al., Gabriel and al. and others authors. These results dealt with the viscosity under zero-shear, the storage and loss modulus, complex viscosity, and steady state compliance.

In highly branched polymers, long chain branching are often defined as the ratio of the radius of gyration of a branched molecule to that of a linear molecule of the same total weight molecular mass:

$$g = \frac{\langle R_g \rangle_B}{\langle R_g \rangle_L} \quad (8)$$

Where g is the contraction factor. This factor equal to 1 for a linear chains, and it is lower than 1 for a ramified chains.

The Newtonian viscosity is very influenced by the ramifications. For this purpose, in the figure 1, we have depicted the variations of the Newtonian viscosity as a function the hydrodynamic volume in the case of some polymeric systems under consideration. The continuous lines represent the theoretical results (obtained by the equation 9), whereas the symbols correspond the experimental results obtained for various others (see Fig 1).

$$\eta_0 = \bar{\Gamma}_1 K_1 (gM_w)^\alpha \quad (9)$$

Where: the constant $K_1 = 2012.894 \cdot 10^{17}$, and $\bar{\Gamma}_1$ indicates the increase in viscosity depends on architecture on the sample.

$\bar{\Gamma}_1 = 0.0014$ $\alpha=3.4$ in the case of linear polymers.

$\bar{\Gamma}_1 = 1.425$ $\alpha = 4.9$ in the case of the slightly ramified polymers

$\bar{\Gamma}_1 = 26.47$ $\alpha= 7$ in the case of strongly ramified polymers.

Figure 1, illustrating the dependence of Newtonian viscosity with the hydrodynamic volume, given by the product gM_w , highlights a compilation of

theoretical and experimental results. It clearly shows the influence of the long-chain branching (LCB) on viscosity η_0 obtained under null shearing. By analyzing these various results, one notices that viscosity decreases with the content of LCB, in other words, the most ramified polymers have respectively a very low viscosity compared to their linear counterparts and slightly ramified. This is explained by the compacticity of the ramified chains, which result the reduction of the molecular size of the sample [9]. Results reported by Mendelson and Al [7] are in contradiction with the theoretical results. This is caused by the not consideration of the factor g which expresses the comparison between a ramified chain and its linear counterpart. Concerning the experimental data, this variation as much distant from the linearity, this is an essential characteristic of linear polymers, that a polymer is more ramified.

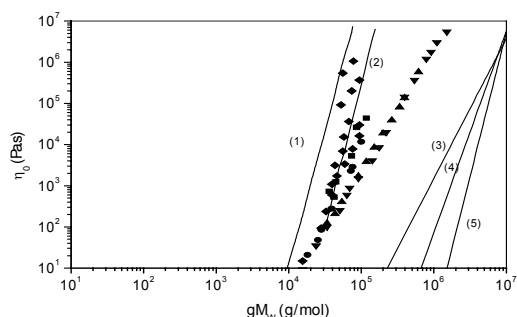


FIG. 1 Newtonian viscosity η_0 versus hydrodynamical volume, given by the product gM_w of polyolefins examined by various authors.[1, 7, 9]. LDPE(♦), LPE fractions(●), and the line (1) represents the BPE. EVAC (■), mPE (▲), [10], [11], and the LPE (▼)[12].[1] The solid line (2) represents the LDPE.[9]. The lines (3), (4), and (5) represent respectively the theoretical results obtained by the equation 9, for linear, slightly and highly branched polymers. [1]

In order to illustrate the dependence of the complex viscosity with the frequency, we have plotted in figure 2 the variations of this dynamical size as a function of frequencies.

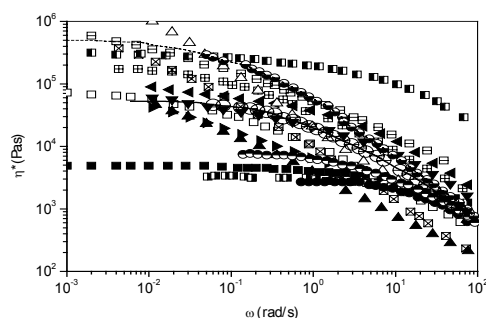


FIG. 2 Complex viscosity versus frequencies of some polyolefins examined by various authors. [1], [2],[3] ThemPE0(■),mPE1(●),mPE2(▲),mPE3(□),e

EAV1(⊞),PE221 (⊞), et (⊞) le PE222.[1] PE1 ($M_w=98000$, catalyst1) (▲), PE2 ($M_w=22000$,catalyst2) (▼), PE3 ($M_w=290000$, catalyst 3) (◀),PE4 ($M_w=142000$, catalyst 4) (▶), PE5 ($M_w=167000$, catalyst 5) (Δ).[2] The polypropylenes PP1(●),PP2(●), PP3(⊖),PP4 (⊖). [3] The contineous and discontieous curves represents respectively the results obtained from combined dynamics and creep measurements of polypropylenes PP3 and PP4.[3]

This figure illustrate a theoretical and experimental representation of the variation of complex viscosity as a function of frequency at temperatures $t=145^\circ\text{C}$, and $t=180^\circ\text{C}$ of some polyolefin's examined by highlight the effect of the LCB on complex viscosity.

The analysis of this figure shows that at high frequencies the behaviour of all samples is similar, which is not the case at the weak frequencies, where the differences between the samples becomes increasingly obvious. Indeed, in the group of the mPEs, it appears that the viscosity of the ramified mPE3 shows a drastic increase at weak frequencies. In this case, viscosity at weak frequency is similar to that of linear polymer mPE2, with the highest values of M_w . A similar behaviour is observed for polymer PE221 prepared by the chromium catalysts. Moreover, for these materials, the degree of fluxing in shearing grows [1] whereas its beginning occurs at the weakest frequencies. In addition, It is necessary to note that all the polymers, resulting from a catalysis containing chromium, are characterized by a similar behaviour. In the case of ethylene vinyl acetate copolymer of and (EVA1), one observes a reduction of viscosity compared to that of the linear PE of similar mass M_w .

The complex viscosity of the PE3 is very close to the theoretical value by suggesting the absence of branching. Results obtained by He and Al [3] are similar to those acquired by the other authors. Linear samples PP1 and PP2 slightly ramified reached a plate of the values of Newtonian viscosity respectively around $(10^{-1}$ and 10^0) rad/s; while for the PP3 and the PP4, the final zone is inaccessible by dynamic shearing. Then, to detect the relaxation behaviour at the weak frequencies, measurements of creep-recovery are necessary.

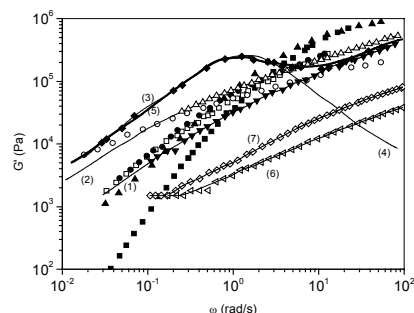


FIG.3 Storage modulus versus frequencies of some polyolefin's examined by divers authors. [1], [2], [3], [4] (mPE) (■) LmPE, (□) BmPE, EVAC (●). [1] (○) LDPE1-LCB, (▲) HDPE. [2] The polypropylenes (▼) PP3, (Δ) PP4. [3] (◆) LPB (◇) IPP, (◁) LDPE. [4] the theoretical results are represented as following (1) PP3, (2) PP4, [3], (3) PB adjustment of the molecular model, (4) PB adjustment of the empirical model, (5) PB adjustment of the distribution of the molecular mass (6) the LDPE, (7) le IPP. [4]

Figure 3 illustrates the influence of the polydispersity and the LCB on the elasticity of linear materials, slightly and strongly ramified. On this figure, one notices that majority the theoretical and experimental results confused show an increase in G' with the frequency; put aside the results obtained of linear PB with a tail of high molecular mass by using the empirical model (curve 4). The shape of this curve is a peak, whose maximum value of G' is around 10^5 Pa, from which one has a rough fall of the elasticity of this material. The linear polymers have a low elasticity compared to their slightly ramified counterparts, while that of the strongly ramified samples is very weak. This returns with the content of LCB. The results obtained by using the model based on the MMD and the molecular model are identical. Indeed, the no compatibility of curves 3 and 5 confirms that the elasticity of a polydisperse linear polymer cannot decrease at the high frequencies (the plate zone). These results permit possible to conclude that polydispersity of a linear polymer, and the low contents of LCB increase their elasticity. In addition, being a strongly ramified polymer (by not holding account effects of tangle), elasticity grows with the frequency, but it is very weak, when one compares it with that their linear counterparts and slightly ramified.

4. CONCLUSION

In the light of this review article, which has not the pretension of being exhaustive, it appears clearly that the rheological testing affords a powerful tool in characterizing of polymeric materials; indeed, since a long time, the viscoelastic response of polymers has been the subject of extensive researches based upon rheological measurements, because of these properties are

directly related to the molecular structure and the corresponding architecture.

Some particular efforts have been made for obtaining of experimental data, relative to models and conventional polyolefin's, and interpreting of those following the phenomena which appear on the molecular scale. Generally, in the case of linear polymers, one observes a good agreement between experimental data and some results derived from phenomenological equations and theory. However, it is worthwhile to note a pronounced effect of these structures on the viscoelastic response. The materials, containing a substantial quantity in LCB, exhibit marked effects of this factor on the general features, such as the viscosity function, the elastic character and the activation energy of materials in flow. The results, derived from literature, suggest that the effect of polydispersity on these variables would may be similar to that predicted by the presence of LCB; notwithstanding, for a given molecular weight, the effects of LCB appear to be stronger than those due to the polydispersity. The single models of molecular relaxation, developed for the polydisperse linear polymers, are failed, when one would want to explain the global viscoelastic response in the presence of LCB.

In all, the quantitative measure of density in LCB, from limit viscoelastic data and molecular characteristics, suggested by Salazar et al. and other authors, affords a powerful tool which is able to explain the rheological properties of various polymers, but, in the case of model polymers, the system fails when we compare the results with measurements of density in LCB.

Moreover, it is important to precise that the most accepted point of view of this question indicates that the contribution of a branching number to rheological behaviour is less than that due to the topology of branched polymer. Consequently, it is convenient to point out that the position and architecture of the branching, emanating from the main polymeric chain, are the pertinent factors which govern their rheology.

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