Relationship Rheological Behavior and Molecular Architecture of LDPE’s Designed for Extrusion Coating

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Abstract

In this paper the relationship between molecular structure and behavior of the LDPE melt is discussed from a scaling perspective on the bases of results from GPC-MALLS analysis. Long chain branches introduce a characteristic length scale that marks a transition in rheology behavior of the melt with decreasing length scale of deformation i.e. with increasing process rate or decreasing temperature. The characteristic length scale is associated with intra-molecular entanglements that cause a change in swell behavior of the polymer coil in solution or the melt. This change in swell behavior affects interaction with neighboring molecules in the melt. The characteristic length scale can be expressed in terms of a molecular weight, referred to as the “cross-over” molecular weight. Autoclave LDPE can be characterized by a single “cross-over” molecular weight while for tubular products a range of cross-over molecular weights appears to be required. In describing the flow behavior of the polymer melt, “cross-over” molecular weight gains importance with increasing length scale of deformation (slow processes, high temperature) while the effect of the overall molecular weight distribution expressed in one or more molecular weight moments, loses importance. With decreasing length scale of deformation (fast processes, low temperature), the situation is reversed. Experimental results are presented for the melt index measurement and for the behavior of the contraction of the polymer web (neck-in) in extrusion coating.

Introduction

Low density polyethylene (LDPE) is the oldest member of the polyethylene family. It was discovered in 1933 and produced on a commercial scale for the first time in 1939. The radical polymerization reaction is initiated by oxygen (from air) or by synthetic peroxides. The reaction takes place at high pressure, typically between 1000 and 3000 bar and at temperatures ranging from 80-350 °C in an autoclave or a tubular reactor (or a combination of the two).

LDPE is a branched polymer with branches of varying length which distinguish it from Ziegler Natta type catalyzed high density polyethylene (HDPE) which has a linear structure and linear low density polyethylene (LLDPE) which has only short chain branches (SCB), typically C4 to C8 depending on the comonomer used. Particularly the long chain branches (LCB) give LDPE some unique properties. For example, low power consumption in extrusion and low neck-in in coating and cast film applications. LCB could be defined as branches with molecular weight $M$ higher than the molecular weight for entanglement $M_e$. The autoclave and the tubular process, provide products with rather different branching frequency and molecular weight distribution. For this reason products from both processes usually serve different markets. In this paper the molecular structure of LDPE and its effect on behavior of the melt is discussed with emphasis on extrusion coating application.

Discussion

The final branching distribution of the LDPE molecule is the composite result of different chemical reactions. The main ones are 1) copolymerization with alpha olefin chain transfer agents (e.g. propylene) 2) intra-molecular hydrogen transfer or 'backbiting' and 3) inter-molecular hydrogen transfer or chain transfer to polymer. All three reactions lead to SCB. Only the transfer to polymer reaction is capable of producing LCB. In this reaction a free radical will abstract a hydrogen atom from a polymer chain. The free radical thus formed is capable of initiating a new polymer branch. Obviously branches with varying length (branch length distribution) are produced via this reaction. The overall molecular weight distribution as well as the branch molecular distribution depends on which one of the two basic types of reactor is used for polymerization. The autoclave reactor resembles a continuous stirred tank reactor (CSTR) whereas the tubular reactor behaves more like a plug flow reactor (PFR). The ideal PFR can be modeled as a cascade of infinite ideal CSTR's. The real autoclave reactor can be described with a single or a few
CSTR’s and the real tubular reactor with many. The two reactor types produce products with rather different molecular structure as a result of the fundamental difference between the CSTR and PFR model reactors and the different reactors conditions. Within a CSTR, conditions of temperature and concentration are considered everywhere the same and all molecules are produced at the same conditions. For a PFR, the conditions vary from the beginning towards the end of the reactor and polymer molecules are produced at different conditions. A second important difference between both model reactors is the residence time distribution. In a PFR all molecules spend the same amount of time in the reactor. In a CSTR some molecules pass right through from the inlet to the outlet whereas others will be there for a very long time. Since the hydrogen transfer reaction leading to branching may take place on “dead” polymer, molecules that spend a lot of time in the reactor will be branched over and over again and reach extremely high molecular weights.

An important research tool to study the molecular structure of polymers is gel permeation chromatography (GPC). For this analysis, a small quantity of polymer is dissolved in a good solvent and injected as a very dilute solution onto a suitable column. Separation in the column is based on the hydrodynamic volume of the swollen polymer molecules in the solvent. The hydrodynamic volume and degree of swelling of an individual polymer coil is determined by the overall molecular weight of the molecule, its branching characteristics and by the interaction parameter of polymer and solvent. The hydrodynamic volume can be expressed in terms of the radius of gyration \( R_g \). By using different detection techniques, refractive index and multiple angle laser light scattering (MALLS), both molecular weight and radius of gyration can be determined for each eluted volume fraction. The results of a GPC-MALLS analysis can be presented in two types of plots 1) the molecular weight distribution plot and 2) the conformation plot.

The molecular weight distribution plot shows the fraction of molecules as a function of molecular weight. Figure 1 shows an example of a tubular and an autoclave product. Autoclave products typically show a broader distribution than tubular products. This can be associated to the broad residence time distribution of an autoclave reactor, leading to very high branching frequencies and molecular weight. The molecular weight distribution can be characterized by a series of moments \( M_k \) calculated as \( M_k = \sum n_M \cdot M^k \) with \( k=0,1,.. \) etc. The first, second and third moment are usually referred to as the number average, the weight average and the z average molecular weight, represented by respectively \( M_n \), \( M_w \) and \( M_z \).

![Figure 1: Normalized molecular weight distribution plots for an autoclave and a tubular LDPE resin.](image)

The conformation plot shows the mean radius of gyration as a function of the molecular weight. Figure 2 shows an example for a HDPE, an autoclave LDPE and a tubular LDPE. The typical upward curl below \( 10^3 \) g.mol\(^{-1}\) is an artifact of the analysis and should be ignored. The difference between the radius of gyration of a linear molecule and
a branched molecule of the same molecular weight in the conformation plot provides information on the branching characteristics.

Figure 1: Conformation plots for an autoclave and a tubular LDPE resin and a linear HDPE resin.

Figure 2 shows that HDPE produces a linear relationship between radius of gyration and molecular weight on a log-log scale. It appears that the slope is the same for any linear polymer regardless of monomer type and molecular weight i.e. \( D=5/3 \) (Flory). Only the proportionality constant is different. In general

\[ R_g \propto M^{1/D} \tag{eq.1} \]

In the melt where a polymer molecule is “dissolved” in units from other chains, a power law relationship is observed as well, but with \( D=2 \), which is the value for an ideal chain. The power law relationship is an expression of the fractal geometry of the swollen polymer coil in solution or melt. The exponent \( D \) is also referred to as fractal dimension. Fractal objects have the same appearance regardless of the length scale the object is observed at. Unbounded mathematical fractals are said to be completely self-similar on all length scales without any characteristic length scale. Relationships between properties of a fractal object can be described with simple power laws. The reason for this is that power laws are the only mathematical equations with complete self similarity. A good example is the relationship between zero shear viscosity of the melt and molecular weight for high molecular weight linear polymers,

\[ \eta_0 \propto M^{3.4} \tag{eq.2} \]

Much effort went into explaining the value of the exponent. Most successful theory is based on the reptation model originally proposed by de Gennes. Equation 2 however is only valid down to some characteristic length scale, \( R_e \). At this point the exponent changes from 3.4 to unity. The characteristic length scale is associated with a characteristic molecular weight, \( M_e \) known as the molecular weight between entanglements. The molecular weight between entanglements is related to the flexibility of the polymer chain, hence to the chemical structure of the repeat unit. Monomer units like styrene with bulky side groups, result in relatively stiff polymer molecules with higher entanglement molecular weight. For linear polyethylene in the melt, \( M_e=4000 \text{ g.mol}^{-1} \) while for polystyrene \( M_e = 31000 \text{ g.mol}^{-1} \). This example demonstrates that introduction of a geometrical feature or characteristic length scale in an otherwise fractal system changes the behavior of the system at the characteristic length scale.
Figure 2 furthermore shows that both autoclave and tubular LDPE have lower hydrodynamic volume for the same molecular weight compared to the linear HDPE. The LDPE molecule requires less space due to branching. The conformation plot appears to indicate power law behavior, but with a transition in slope at some critical molecular weight. Branching apparently introduces another critical length scale. As such, again a change in rheology behavior of the melt may be expected at this critical length scale. To emphasize the scaling approach to the GPC-MALLS results, the conformation plot can be transformed into a molecular density plot. In such a plot, molecular density is defined as \( \rho_s = \left( \frac{M}{\pi R_g^2} \right) \pi \rho \) and is plotted as a function of the radius of gyration as in figure 3 (note that scatter and other artifacts have been removed for clarity). The subscript s is introduced to emphasize that this is the molecular density of a single coil in solution or melt and not the overall melt density. The radius of gyration axis can now be interpreted as a length scale axis. Figure 3 shows that the molecular density decreases with increasing length scale for both the HDPE and the LLDPE resin following the power law relationship \( \rho_s \propto R_g^{(3-D)} \). The decrease in molecular density is a characteristic behavior of fractal objects (bigger and bigger ‘holes’ appear with increasing length scale) as opposed to normal objects for which density is independent of length scale. The LLDPE resin has a higher molecular density over the entire range of length scales owing to the presence of SCB. Figure 3 shows that for both LDPE’s, power law behavior is observed as well, but only up to some critical point identified by a characteristic molecular density and characteristic length scale or characteristic molecular weight i.e. respectively \( \rho_1 \) and \( \xi_1 \) or \( \xi_2 \). This characteristic length scale is also referred to as the “cross-over” length. Likewise the molecular weight can be referred to as “cross-over” molecular weight. Below the critical point, behavior is like a flexible chain like LLDPE molecules containing only SCB. Above the critical point the molecular density of the autoclave product appears to level off to a plateau value initially while for the tubular resin the molecular density shows a sharp increase with increasing length scale. Since no transition is observed for SCB polymers like LLDPE, the critical point is associated with the transition from SCB to LCB. Since the transition from SCB to LCB is related to the molecular weight between entanglements, \( M_\xi \) must be related to molecular weight between entanglements. The polymer molecules in the sample used for the analysis however are isolated molecules and do not overlap with each other. Therefore these entanglements must be intra-molecular entanglements within a single molecule. This could happen when a branch on a molecule is long enough to entangle with other parts of the same molecule, effectively creating a 3 dimensional network like structure. Such long range intra-molecular interactions are expected to affect swell behavior in solution and entanglement density in the melt and support a transition in the behavior of molecular density or other properties as a function of length scale. These conclusions are supported by figure 4 showing a power law between critical molecular weight and critical molecular density for several LDPE resins relationship with exponent -1.1.

![Figure 3: Single coil molecular density as a function of the radius of gyration for two LDPE polymers, autoclave and tubular, a linear HDPE and a short chain branched LLDPE.](image-url)
In non-dilute solution, with overlapping polymer molecules, $M_e$ is a function of polymer concentration following $M_e \propto \phi^{-\varepsilon}$ where the exponent is within the range $1 < \varepsilon < 1.3$ (Graessley). The exponent in figure 4 is within this range thereby supporting the conclusion that $M_e$ marks a critical molecular weight for entanglement. Unfortunately for many autoclave products the transition appears to be just beyond the lower limit of detection of the GPC-MALLS analysis and for only few autoclave products an estimate of the transition point could be made. This explains at least in part the relatively poor quality of the correlation and the large standard error on the exponent (0.21).

![Graph](image)

Figure 4: critical molecular weight as a function of critical density for several LDPE resins.

Figure 3 also shows that there is a difference in conformation plot between the autoclave and the tubular LDPE. Examination of many autoclave LDPE products has shown that these products always transition towards a plateau value for molecular density with increasing length scale. The molecular density plot for autoclave products typically has the form illustrated in figure 5. At small length scales i.e. $R_g < \xi$, power law behavior is expected i.e. $\rho_s \propto R_g^{-(3-D)}$ with an exponent similar to values observed in other short chain branched polymers (typically $2 < D < 2.5$). At large length scales i.e. $R_g > \xi$, a plateau is observed with $D = d = 3$ ($d$ is the embedding dimension to which a real molecule is constrained) resulting in $\rho_s \propto \rho_s$ which is a constant. In this region molecular density is independent of length scale of the observation as for normal (non fractal) 3 dimensional objects. At very large length scales, when $R_g$ approaches the maximum length scale in the sample the molecular density decreases rapidly. This is simply a finite size effect and the rate of decrease depends on the “cross-over” length, $\xi$. The behavior of figure 5 for autoclave resins can be captured in a general equation for single variable scaling

$$\rho_s \propto R_g^{-(3-D)} \cdot F\left(\frac{R_g}{\xi^D}\right)$$

(eq.3)

In this kind of equation the function $F$ approaches a constant value when $R_g/\xi^D$ approaches either zero or infinity. The exponents can be obtained empirically or have to be derived from fundamental models like the reptation model or the pom-pom model or via Monte Carlo methods. As mentioned, direct experimental determination of the “cross-over” length usually is not possible for autoclave products with current analytical techniques. With the help of the empirical equation from figure 4, which is assumed to be generally valid for LDPE,
the correlation length or its associated molecular weight \( M_\xi \) can be estimated from the plateau value for the density e.g. \( \xi \propto \rho_\xi^{-(1+\epsilon)/3} \). For many tubular products, the molecular density increases with increasing length scale as in figure 3. This appears to be characteristic for hyper branching \((D>d)\) but in reality may be an expression of the existence of a range of critical points.

\[ \begin{align*}
\text{Figure 5: Schematic density plot of an autoclave LDPE.}
\end{align*} \]

The behavior of molecular density as a function of length scale for both reactor types can be understood in terms of the two model reactors. For an ideal autoclave LDPE product (single CSTR), a single correlation length is expected owing to the fact that all molecules have been produced at the same conditions of temperature, concentration etc. . Statistical probabilities of all sorts of chemical reactions remain the same regardless of the time spent in the reactor. A tubular reactor on the other hand can be represented by a cascade of CSTR's (the number of CSTR's is determined by the degree of axial dispersion (less dispersion means more CSTR's) with increasing temperature from the peroxide injection point to the peak. In a tubular reactor molecules are produced at different conditions and a range of “cross-over” lengths would be expected. In the example tubular product of figure 3, the relation between molecular density and length scale is a power law, which is however not exclusive.

In the polymer melt, the single coil molecular density is a measure for the overlap of a single molecule with surrounding polymer molecules (number of entanglements). As a result, polymer melt rheology is affected by single coil molecular density. Equation 2 for linear polymers could be rephrased as \( \eta_0 \propto \rho_\xi^{-6.8} \). For a set of linear homo polymers the molecular density plot is the same regardless of mean molecular weight or molecular weight distribution. From an empirical point of view melt rheology can be described in terms of a single variable, either molecular density, molecular weight or radius of gyration. In general, rheology behavior for linear polymers can be captured in terms of one or more moments \( M_\xi \) of the molecular weight distribution. In the terminal regime, equation 2 for polydisperse polymers for example usually is expressed in terms of the second moment i.e. \( M_\xi \) only.

For autoclave LDPE with a single “cross-over” molecular weight, the molecular density plot is divided into two separate regions. The rheological behavior as a function of length scale is expected to be different in each region. At high length scales, molecular density is constant right down to the “cross-over” length implying that the entanglement concentration is constant independent of radius of gyration or molecular weight. For slow processes operated at high temperature, only the largest molecules are involved in deformation (smaller molecules have the opportunity to relax) and for length scales of deformation \( L>\xi \), behavior is expected to depend only on the characteristic parameters. The shape of the molecular weight distribution in this region is irrelevant, only the total fraction of polymer beyond \( L>\xi \) is important in defining rheology. For tubular products characterized by a range of characteristic length scales only the highest characteristic length scale (at the local minimum density) is important.
with slow deformation processes. Support for these conclusions is provided by, figures 6 and 7. Figure 6 shows melt index (considered as a slow deformation process inside the die) as a function of $M_w$. While for linear polymers there is a strong correlation between melt index and weight average molecular weight, there is no such correlation for LDPE. Figure 7 shows melt index for the same sample set as a function of the cross-over molecular weight, $M_\zeta$. Clearly the correlation has improved drastically. Only some 6 low melt index tubular resins appear not to follow the correlation well. This could be caused by the fact that the requirement $L>\zeta$ is not met in which case single variable scaling is no longer applicable and behavior becomes more complex. For zero shear viscosity a similar result is obtained as for melt index as shown in figure 8. The zero shear viscosity here is obtained from dynamic measurements (by extrapolation from a 3 parameter Cross equation). The length scale of deformation therefore is higher than for melt index, but still not as high as required for determination of the real zero shear viscosity in the terminal regime. This is supported by the fact that the low melt index tubular resins do not follow the correlation really well.

![Figure 6](image-url)

**Figure 6:** Melt index as a function of weight average molecular weight for a series of autoclave and tubular LDPE resins and for a series of products from mixed reactor design.

For fast processes operated at low temperature, the scale of deformation extends well into the region $L<\zeta$, where density and rheology do depend on length scale. The result is that for polydisperse polymers, the molecular weight distribution starts to become important. The general picture therefore is that the “cross-over” molecular weight gains importance with slower processes operated at lower temperatures while the importance of the molecular weight distribution decreases and vice versa. An example of a very fast process is the extrusion coating process. Important for this process is a low contraction or neck-in of the polymer web in the air gap. The neck-in of several LDPE resins is measured at 4 different combinations of line-speed and temperature at 2 levels on the pilot coater on the Dow facilities in Horgen (CH). The neck-in is fitted with an empirical equation of the form,

$$\ln NI = I + \beta \cdot \ln M_\zeta + \alpha \cdot \ln M_{\text{ave}}$$

(eq.4)

with either $M_t$ or $M_w$ as average molecular weight $M_{\text{ave}}$ and with and without $M_\zeta$. Table 1 shows the regression results for all data at all combinations of conditions combined in the form of a standard deviation on predicted neck-in (square root of the mean sum of square errors). The results show that the contribution from the “cross-over” molecular weight to the prediction is relatively small, in line with expectations. The results also show that $M_\zeta$ better correlates than $M_w$, at least for the current data set and conditions employed. Figure 9 shows a plot of predicted versus observed neck-in for the optimal parameter combination i.e. $M_\zeta$ with $M_t$. Table 2 furthermore shows the intercept and the exponents for the 4 combinations of line-speed and temperature. Figure 10 shows the results in graphical format. The results indicate that the effect of $M_t$ and $M_\zeta$ on neck-in decreases with increasing line speed and decreasing temperature (decreasing length scale of deformation). The results also show that the ratio of the
exponents on both effects decreases with decreasing length scale of deformation in qualitative accordance with expectations (i.e. the importance of $M_z$ increases relative to the importance of $M_\xi$).

Figure 7: Melt index as a function of “cross-over” molecular weight for a series of autoclave and tubular LDPE resins and for a series of products from a mixed reactor design.

Figure 8: Zero shear viscosity (extrapolated from dynamic experiments at 170 °C) as a function of “cross-over” molecular weight for a series of autoclave and tubular LDPE resins and for a series of products from mixed reactor design.
Table 1: Regression results for the empirical model for neck-in on a series of LDPE resins processed on the pilot coater of Dow in Horgen (CH)

<table>
<thead>
<tr>
<th>MODEL Parameters</th>
<th>Standard deviation, s</th>
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<tr>
<td>$M_{ave}=M_z$</td>
<td>4.1</td>
</tr>
<tr>
<td>$M_{ave}=M_w$</td>
<td>7.8</td>
</tr>
<tr>
<td>$M_{ave}=M_z$ only, without $M_\xi$ ($\beta=0$)</td>
<td>6.9</td>
</tr>
<tr>
<td>$M_{ave}=M_w$ only, without $M_\xi$ ($\beta=0$)</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Figure 9: Plot of predicted versus observed neck-in for the power law model of equation 4 with $M_z$ and $M_\xi$ as parameters for all combinations of temperature/line-speed as mentioned in the legend.

Table 2: Model parameters for the monomial power law model for neck-in measured at four different combinations of line-speed and neck-in on a series of LDPE resins processed on the pilot coater of Dow in Horgen (CH)

<table>
<thead>
<tr>
<th>Line-speed m.min$^{-1}$</th>
<th>Temperature [$^\circ$C]</th>
<th>Intercept I</th>
<th>$\beta$ ($M_z$)</th>
<th>$\alpha$ ($M_\xi$)</th>
<th>$\beta/\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
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<tr>
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<td>11.71</td>
<td>-0.11</td>
<td>-1.06</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Figure 10: Exponents and their ratios from table 2 as a function of line-speed and temperature. The exponents represent the effect of $M_z (Mz)$ and $M_ξ (Mx)$ on neck-in. Their ratios represent the relative importance of one effect over the other.

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References