

Examining the rheological behavior of three nearly identical linear low-density polyethylene (LLDPE) samples

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Introduction

Plastic materials can be found in nearly every aspect of our daily lives from food packaging to furniture, building materials, automobiles, medical devices, and even clothing (to name a few).¹ Plastics are usually made of synthetic polymers consisting of small molecules linked together in a repetitive structure and are known for being lightweight, strong, flexible, durable, and often transparent, as well as chemical and corrosion-resistant.² Plastics can be readily produced and molded into countless shapes and forms making them the ideal solution for a wide range of applications. In order to make these everyday consumer goods, polymers are commonly processed at elevated temperatures in a molten state, referred to as polymer melts. Understanding how molten polymers flow and deform is the key to effectively processing and transforming them into specialized end products.³

Today, polymer flow behavior is commonly quantified via melt flow index (MFI), also referred to as melt index (MI) or melt flow rate (MFR). MFI is a measure of how easily a molten thermoplastic polymer will flow under pressure and is defined as the mass of polymer that passes through a capillary die over a ten-minute period (expressed in units of g/10 minutes, although it is commonly displayed as unitless).⁴ As a result, the melt index is inversely proportional to polymer viscosity, where a high melt index correlates to a low melt viscosity and vice versa.

Although melt indexing has become a centerpiece in most polymer quality control labs, it is still a rather limited technique. The problem is that melt index is a single-point viscosity measurement conducted at one temperature using a relatively low shear rate (typically between 1 to 100 s⁻¹, although this is highly material and instrument dependent), and MFI is often measured at conditions vastly different than the actual processing parameters.⁴ Making matters worse, polymer melt viscosity is also highly dependent on shear rate, which can vary by orders of magnitude during an extrusion process. In addition, the MFI test cannot directly quantify polymer branching or account for slight differences in molecular weight distribution.

Modern rotational rheometers, on the other hand, allow for a more comprehensive investigation of polymer flow behavior. Polymer melts are non-Newtonian fluids and their viscosities are highly shear rate, shear history, and/or thermal history dependent. Understanding the variation in melt viscosity over a range of industrial-relevant shear rates and temperatures is essential for designing polymer processing equipment, determining process energy consumption, and overall process optimization. For instance, polymer extrusion and injection or blow molding are high-shear rate processes, while overall end-product quality is often dictated by low-shear rate behavior.

In this study, we used small-amplitude oscillatory shear rheology measurements to examine three different linear low-density polyethylene (LLDPE) samples with identical melt flow indices and average molecular weights. The rheological measurements were used to observe the shear rate-dependent viscosities and viscoelastic behaviors of the LLDPE melts. The rheology data were then directly correlated to the polymer's molecular structure, such as molecular weight distribution and long-chain branching, as well as the overall flow behavior and processability of the LLDPE specimens.

Experimental

Materials

Three linear low-density polyethylene (LLDPE) samples (all in pellet form) were investigated for this study (Table 1). Each LLDPE sample, as stated by the supplier, had the same weight-average molecular weight (Mw) and nearly identical melt flow indices. Based on the information provided, the three materials differed only by their overall molecular weight distribution, which was broadly described by the supplier as either medium or narrow.

Table 1: Background information for the three examined LLDPE materials.

| Sample | MFI | Mw | MWD |
|----------|-------|-----------------|--------|
| LLDPE #1 | 0.920 | 10 ⁶ | Medium |
| LLDPE #2 | 0.916 | 10 ⁶ | Medium |
| LLDPE #3 | 0.918 | 10 ⁶ | Narrow |

Rheometry

The Thermo Scientific™ HAAKE™ MARS™ iQ Air Rheometer equipped with an electric plate and electric hood temperature control modules was used to measure the rheological behavior of the provided LLDPE samples. All measurements were conducted using 20 mm diameter parallel plates (unless stated otherwise) at a constant temperature of 190 °C to match the standardized MFI testing specifications for polyethylene.^{5,6} The LLDPE pellet samples were loaded directly onto the rheometer and melted into a disk-shaped specimen between the top and bottom plates with a thickness (or gap height) of ~0.75 mm. Most of the reported data were obtained using an oscillatory frequency sweep from 100 to 0.1 rad/s at a constant strain of 0.1%. Six data points were collected per decade of frequency and each data point was an average of five full oscillations.

Results

Viscosity profile

Polymer melts are categorized as non-Newtonian fluids and they commonly display shear thinning behavior, where their viscosity decreases with increasing shear rate. Typically, non-Newtonian viscosity profiles of dilute and semi-dilute polymer solutions are measured under steady-state rotational shear. However, due to their high elasticity and propensity for edge fracture under large deformations, small amplitude oscillatory shear is the preferred testing method for polymer melts.³ According to the Cox-Merz rule, the complex viscosity (η^*) plotted against angular frequency (ω) from an oscillatory frequency sweep measurement is equivalent to the resultant steady-state shear viscosity plotted versus shear rate from a rotational shear measurement.⁷ The Cox-Merz rule is an empirical rule that is valid for many polymeric materials. With that said, performing an oscillatory frequency sweep and then utilizing the Cox-Merz rule is the preferred method for obtaining apparent shear viscosity data for molten polymers.

The oscillatory frequency sweep response (η^* vs. ω) for the three examined LLDPE samples is shown in Figure 1. LLDPE #3 displayed classic polymer flow behavior where at low frequencies (<1 rad/s), it exhibited a Newtonian plateau, and

its viscosity was constant and independent of the applied frequency. Then at higher frequency values (>1 rad/s), LLDPE #3 began to shear thin. The LLDPE #1 and LLDPE #2 samples, on the other hand, displayed constant shear thinning behavior and never reached a Newtonian plateau across the investigated frequency range. At high frequencies, LLDPE #2 had the lowest viscosity while LLDPE #3 had the largest viscosity. However, at low frequency (0.1 rad/s), the opposite trend was observed and LLDPE #2 now had the highest viscosity while LLDPE #3 displayed the lowest viscosity. Also, at a frequency of ~1 rad/s, all three LLDPEs had nearly equivalent viscosities. The shear-dependent behavior of these three samples exemplifies how the viscosity of complex materials, like polymer melts, cannot be easily described by a simple single-point measurement. Their true flow behavior is best described as a full viscosity profile.

Shear rate-dependent viscosity data derived from oscillatory frequency sweep experiments can be used to evaluate both the molecular structure and processability of polymeric materials. The low frequency/shear rate data can be used to quantify the molecular weight (Mw) of a polymer melt, while the low-to-medium frequencies/shear rate data can indicate molecular weight distribution (MWD). Conversely, medium-to-high frequency/shear rate data can be used to quantify the flow resistance of a material during common polymer processing applications, such as compression molding (~0.01 to 10 rad/s), extrusion (~10 to 1000 rad/s), and blow or injection molding (>1000 rad/s). Although not applied here, the Time-Temperature Superposition (TTS) principle can be used to evaluate rheological behavior over a wider frequency range and it is especially helpful when trying to obtain viscosity data at high frequencies/shear rates (>100 rad/s) in a rotational shear rheometer.³

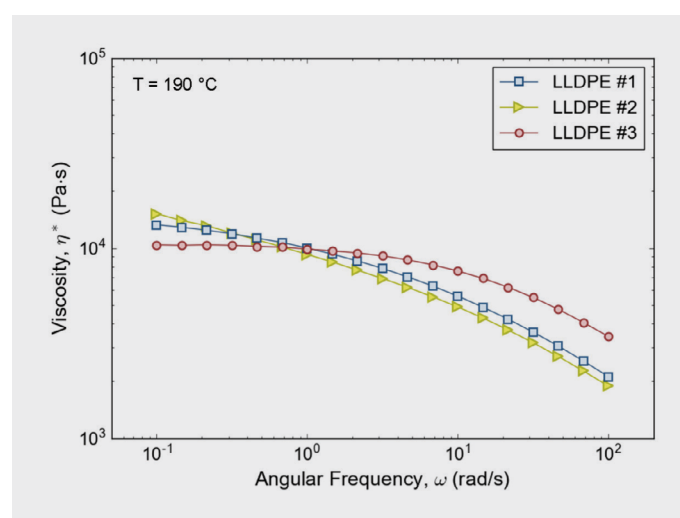


Figure 1: Complex viscosity as a function of angular frequency for LLDPE #1 (squares), #2 (triangles), and #3 (circles).

In Figure 1, LLDPE #3 sample has a significantly higher viscosity than the other two LLDPE materials at process-relevant shear rates (>10 rad/s). As a result, the LLDPE #3 material would be more difficult and energy-intensive to process, leading to additional wear on the processing equipment (increasing operating and capital costs and potentially leading to additional process downtime). Also, materials like LLDPE #3 commonly

require a “processing aid” in order to decrease the back pressure and melt viscosity, which helps reduce operating costs and makes the extrusion process more economical. Conversely, the lower viscosity of LLDPE #1 and LLDPE #2 would make them easier to process, and as a result, they would not require any additional additives or processing modifications.

Molecular weight

Molecular weight is a key material property for determining a polymer’s flow behavior at elevated temperatures, and relatively small changes in average molecular weight can result in significant differences in apparent viscosity.⁸ Polymer melt viscosity is typically constant at low frequencies/shear rates as displayed by LLDPE #3 in Figure 1. The constant viscosity in this low frequency/shear region is known as the zero-shear or Newtonian plateau viscosity. The zero-shear viscosity, η_0 , is directly related to the weight-average molecular weight (Mw) of a polymer melt; the higher the molecular weight, the higher the zero-shear viscosity (and vice versa).

For the LLDPE samples studied here, all three specimens were reported to have identical average molecular weights, and thus, one should expect them to all have similar zero-shear viscosity values. However, the LLDPE #1 and LLDPE #2 samples did not display a Newtonian plateau under the applied frequency range and they exhibited a continuously increasing viscosity with decreasing applied frequency/shear. Also, if the LLDPE #1 and LLDPE #2 materials were to show Newtonian behavior at frequencies beyond the measured range, the zero-shear viscosity would be significantly greater than the LLDPE #3 sample, suggesting that they have a much larger average molecular weight. However, an apparent viscosity that is more rate dependent at low frequency/shear can indicate a broadened molecular weight distribution and/or long-chain polymer branching.

Molecular weight distribution

At a constant molecular weight, the amount of energy required to process a polymer is directly related to its viscosity shear rate dependence (i.e., shear thinning behavior). The onset and degree of shear thinning varies among materials and qualitatively correlates with molecular weight distribution: Polymers with a broad distribution tend to thin more at lower shear rates than those with a narrow distribution with the same average Mw. Regarding material handling, shear thinning is considered the most important non-Newtonian polymer property because it increases material flow and reduces heat generation and energy consumption during processing. For example, molding and extrusion processes can be made easier by broadening a polymer’s molecular weight distribution. However, a molecular weight distribution that is too broad can negatively impact product quality, such as increased blown film haze or increased surface roughness during molding. Also, high molecular weight components can cause unwanted gelled regions during film production and an overly broad MWD can lead to non-uniform relaxation during cooling, which can cause post-extrusion die swell or warpage during injection molding.

For the LLDPE materials examined here, their apparent molecular weight distributions based on shear thinning behavior would rank as follows (from narrowest to broadest): LLDPE #3 < LLDPE #1 < LLDPE #2. The LLDPE #3 displayed a significantly narrower distribution, as its viscosity profile was flatter, and the onset of shear thinning was delayed. The LLDPE #1 and LLDPE #2 samples, on the other hand, exhibited similar shear thinning behavior and, thus, appear to have similar MWDs, which agrees with material data from the supplier (Table 1). In general, the LLDPE #1 and LLDPE #2 materials should be easier and less energy-intensive to process in comparison to LLDPE #3.

Long-chain branching

Polymer branches can vary in length, degree, and distribution along the main polymer backbone. Changing the number, size, and/or flexibility of the branches can significantly impact the overall rheological behavior of the melt.⁹ If the branches are long enough, branched polymers can entangle, and these entanglements will cause an increased melt viscosity at low frequency/shear values in comparison to their linear or less branched counterparts.¹⁰ In addition, long chain branching can increase the elasticity of a polymer which is manifested in the measured storage modulus (G' ; to be discussed in the next section) and the normal stress response.

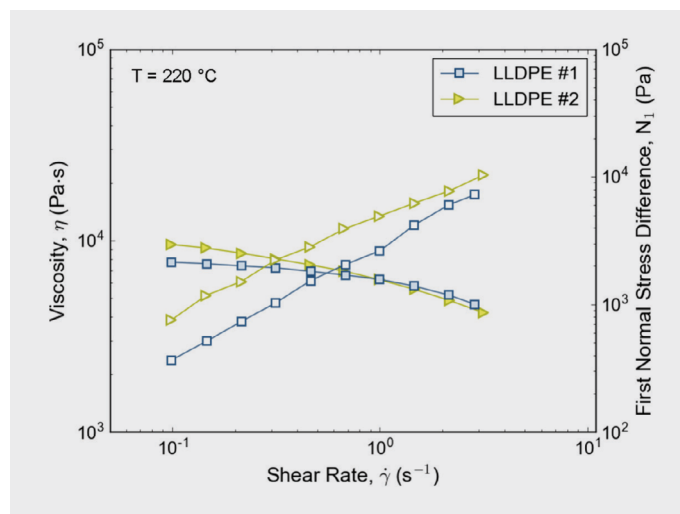


Figure 2: Viscosity (left y-axis; filled symbols) and first normal stress difference (right y-axis; open symbols) as a function of shear rate for LLDPE #1 (squares) and #2 (triangles).

The first normal stress difference, which can be measured using a cone-and-plate geometry under steady rotational shear, is a common metric used to assess polymer long-chain branching.¹¹ The apparent steady-shear viscosities as a function of shear rate for samples LLDPE #2 and LLDPE #1 (measured using a 35 mm diameter, 1° cone) are shown in Figure 2. Please note the data in Figure 2 were measured at 220 °C for ease of sample loading (all other data were collected at 190 °C), however, the displayed trends should hold true regardless of the measurement temperature. As observed using oscillatory shear, both samples displayed continual shear thinning behavior at low shear rate values (<1 s⁻¹) with the LLDPE #2 sample showing an overall larger viscosity. Correspondingly, the first normal stress difference,

N_1 (Figure 2; plotted on the right y-axis), was also significantly larger for LLDPE #2. The higher low-shear viscosity and increased normal stress response displayed by LLDPE #2 suggests increased long-chain branching (either in number or in length) in comparison to the LLDPE #1 material. Normal stress behavior can be correlated with the elastic response of linear and branched polymers and can be directly associated with processing behavior. Long chain branching can lead to increased die-swell during extrusion processing and thicker films during blow molding.

Viscoelasticity

In addition to complex viscosity, oscillatory shear measurements also provide a simultaneous measurement of a polymer's viscous and elastic properties, referred to as viscoelasticity. The elastic and viscous response are represented by the storage and the loss moduli (G' and G'' , respectively). The molecular structure, as well as the testing/processing conditions of a polymer, will determine which behavior is dominant: viscous or elastic. For instance, too much elasticity can lead to flow anomalies and unwanted effects during processing, such as die swell, sharkskin, or melt fracture (to name a few).^{3, 12} Understanding the viscoelastic properties of a given polymeric material is critical for adjusting product formulations and blends and for optimizing processing conditions.

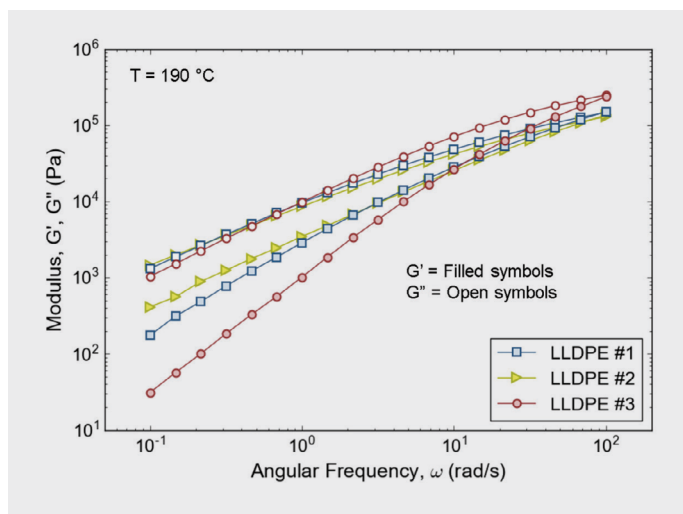


Figure 3: Storage modulus, G' (filled symbols) and loss modulus, G'' (open symbols) as a function of angular frequency for LLDPE #1 (squares), #2 (triangles), and #3 (circles).

When measured at different frequencies/time scales, oscillatory shear data can indicate the physical state and overall structure of a material and provide information on the molecular weight (Mw) and the molecular weight distribution (MWD). Figure 3 shows G' and G'' as a function of angular frequency for the three investigated LLDPE materials. The crossover point (where $G' = G''$) directly correlates with the Mw or the MWD of a polymer melt; shifts in the crossover frequency indicate changes in Mw, while shifts up or down in modulus suggest changes in MWD. The three materials investigated here display a crossover at similar frequency values, which suggests a similar weight-average Mw value. However, LLDPE #3 displays a crossover at a higher modulus value, again suggesting a

narrower MWD, whereas LLDPE #2 and LLDPE #1 display crossovers at similar moduli, indicating similar yet broader MWDs in comparison to LLDPE #3.

The difference in G' and G'' at low-frequency values (<1 rad/s) also relates to MWD. The closer G' and G'' are together, the broader the MWD and vice versa. Using this metric, LLDPE #3 again displays a narrower MWD, while the LLDPE #2 data suggest a slightly broader MWD than the LLDPE #1 material. The magnitude of the crossover modulus, as well as the modulus difference at low frequencies, both corroborate the MWD observations from the viscosity profiles in Figure 1.

As mentioned previously, polymer melt elasticity (G') is a key determining factor for viscoelastic melt behavior and can be the cause of many flow anomalies. Too much elasticity, measured by G' at low-frequency values, can lead to poor product quality during processing. LLDPE #3 displayed the lowest G' values, while LLDPE #2 had the highest elastic response. Although LLDPE #1 and LLDPE #2 might be easier to process due to their lower viscosities, their higher elasticity could make them more prone to surface defects, like die swell and melt fracture, during extrusion and/or warpage during molding.

Conclusions

Polymer melt flow behavior is complex and is highly shear rate and temperature dependent, and it cannot be fully captured using a simple single-point viscosity measurement like melt flow index. Rheology, on the other hand, is a powerful analytical tool that not only determines the flow behavior of thermoplastic melts, but it can also provide information on molecular structure as well as information on processing behavior and end-product quality. The three LLDPE samples studied here had identical melt flow indices and reported molecular weights. However, all three samples displayed unique rheological behavior, exhibiting different low shear rate viscosities, distinct shear thinning profiles, and varying degrees of elasticity. The viscosity profiles and viscoelastic response of the examined LLDPEs were used to identify distinct differences in molecular weight distribution, as well as detect the presence of long-chain branching. Understanding the variation in melt viscosity and viscoelastic behavior over a range of industrial-relevant shear rates is essential for the design of polymer processing equipment, determining process energy consumption, and for overall process optimization.



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