

ABSTRACT

Branching in polymers contributes to many unique rheological properties in processing. For many years, researchers have used different rheological methods attempting to quantify the degree of branching in polymer chains. The large amplitude oscillatory shear testing (LAOS) provides a new and sensitive approach to characterizing the branching structure. The parameter, the polymer long chain branching index, can be quantitatively obtained through an empirical equation that uses LAOS higher harmonic signals (G_3' and G_5'). An instrument that can be used to determine this parameter is the Rubber Process Analyzer (RPA), which uses a bi-cone geometry with a closed die design. This design successfully prevents edge fracture and polymer oxidation during LAOS measurements. In this paper, we discuss using the RPA to analyze the degree of long chain branching (LCB) of a series of high-density polyethylene (HDPE) resins that possess a very small amount of long chain branching.

INTRODUCTION

Polymer branching, especially long chain branching (LCB), has a strong influence on melt processes, such as extrusion, injection molding, compression molding, and blow molding. Branching enhances chain entanglements, increases relaxation times, and increases the extensional flow viscosity as evidenced by the strain hardening phenomenon [1].

Linear	Short Chain Branched	Long Chain Branched
		

Quantitative characterization of polymer long-chain branching is complicated. Traditional chemical characterization techniques, such as FTIR and NMR are only capable of quantifying short chain branching. SEC and light scattering are not sensitive enough to differentiate polymers that contain small amounts of LCB. Rheological methods have also been used to differentiate polymers with different amounts of LCB. The most commonly used rheological techniques for differentiating linear and long chain branched polymers include traditional small amplitude oscillatory shear testing (SAOS), such as frequency sweeps at multiple temperatures for time-temperature superposition (TTS) analysis, and extensional viscosity testing.

Large amplitude oscillatory shear (LAOS) is a commonly used method to characterize nonlinear viscoelastic material response.

In LAOS testing, a sample is sheared in a sinusoidal deformation at various strains at a single frequency, but, unlike in linear viscoelastic testing, the stress signal is not a simple sinusoidal response (See Figure 1).

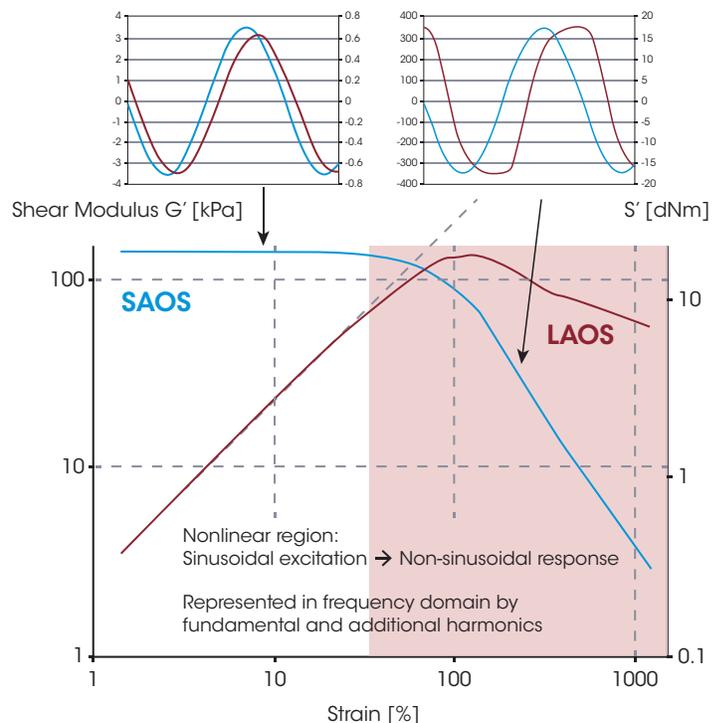


Figure 1. Amplitude sweep showing the area of SAOS and LAOS

The asymmetrical stress response can be decomposed into a superposition of sinusoidal waves starting with the fundamental testing frequency and including the odd multiples of the fundamental frequency called higher harmonics. Each one of these higher harmonic signals has their own phase angle. These higher harmonic signals are sensitive to a material's molecular architecture [2-4].

$$\sigma(t, \omega, \gamma_0) = \gamma_0 \sum_{n=odd} G_n^n(\omega, \gamma_0) \sin n\omega t + G_n^n(\omega, \gamma_0) \cos n\omega t$$

EXPERIMENTAL

Four (4) batches of high-density polyethylene (HDPE) resins were obtained from LyondellBasell. These polymers have similar molecular weight (MW) and molecular weight distribution (MWD) (shown in Table 1) but containing different amounts of long chain branching (LCB). Traditional SEC measurements cannot differentiate the difference (Figure 3).

Sample Name	Mw (kDa)	Mn (kDa)	Mz (kDa)	PD	% Below 1,000	% Above 1,000,000
1A	290.3	10.8	1444.8	26.80	1.30	8.23
1B	276.0	10.8	1408.6	25.53	1.33	7.50
1C	284.0	11.3	1452.7	25.09	1.22	7.96
1D	275.2	11.0	1334.7	24.94	1.22	7.42

Table 1. Molecular weight information of a series of HDPE

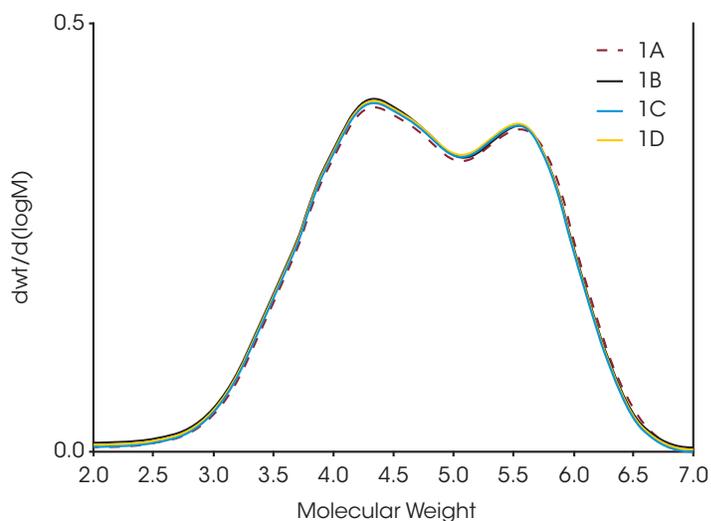
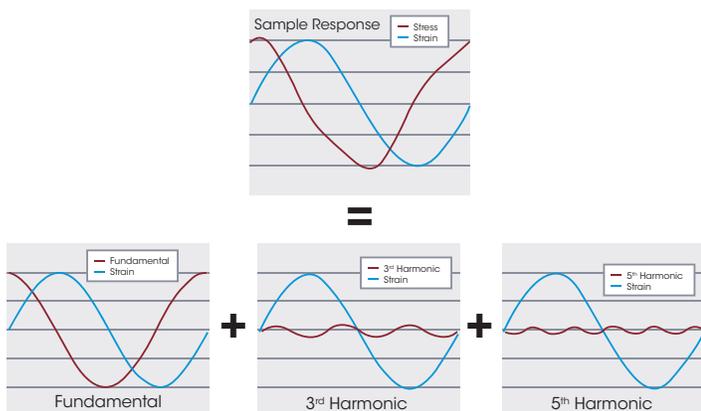
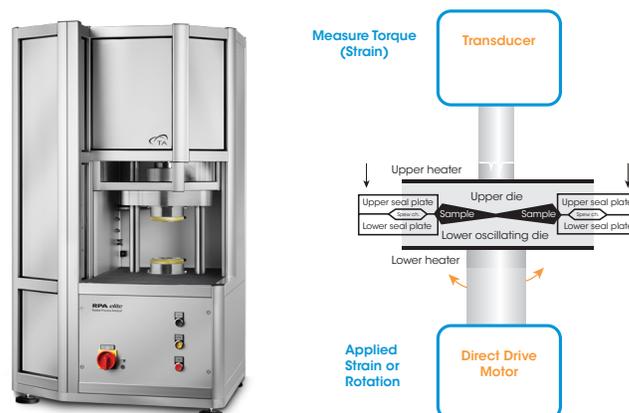


Figure 3. SEC results of 4 HDPE resins

The TA Instruments Rubber Process Analyzer (RPA) was used for LAOS measurements in this study. This instrument is equipped with a bi-cone closed die device, which prevents sample oxidation during a measurement and edge fracture that can occur in LAOS testing. The stiff frame ensures low instrument compliance at high torques and large amplitude measurements.



The LAOS responses can be visualized as parametric curves (Lissajous-Bowditch curves) of the oscillating stress vs. strain or strain rate. When performing LAOS tests on polymer melts, one can plot stress vs. strain rate for each strain. The Lissajous curves look like s-shaped loops, which indicates viscoelastic behavior. The width of the loop is proportional to the phase angle. In non-linear flows, when strong elastic nonlinearity occurs, the behavior meets these criteria:

$$-3 < G_1'/G_3' < 1 \quad \text{and} \quad -2 < G_1'/G_5' < 3$$

where G_1' is the storage modulus at the fundamental frequency, and G_3' and G_5' are the contributions from the higher harmonic signals. The Lissajous stress vs. strain rate curve for a linear polymer shows a double loop. These loops are not observed when a polymer contains long chain branching structure (Figure 2). This phenomenon has been reported in many LAOS analyses for rubber elastomers [6-7].

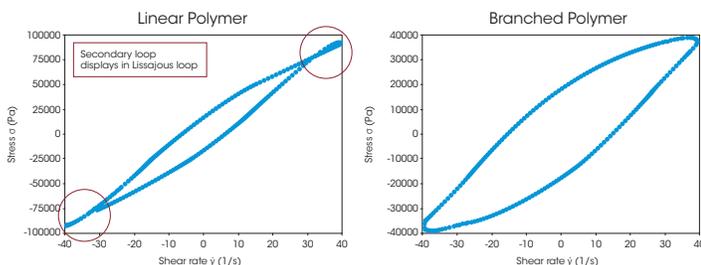


Figure 2. The Lissajous plots for a linear and a branched polymer

An empirical equation was developed to calculate the long chain branching index of rubber elastomers [8-9].

$$LCB = \frac{G_1'}{G_5'} - \left[\frac{5}{4} + \frac{1}{4} \left(\frac{G_3'}{G_5'} \right)^2 - \frac{1}{2} \left(\frac{G_3'}{G_5'} \right) \right] \quad (1)$$

For rubber analysis, a negative LCB index value means the polymer is mostly linear. The higher the LCB index, the more branching structure the polymer has. In this paper, we discuss using LAOS technique to differentiate the differences between a series of high-density polyethylene (HDPE) resins that contain a small amount of long chain branching.

Dynamic frequency sweep tests were performed at 190 °C at a strain of 5%, which is within the linear region of the polymers. Strain sweep tests (LAOS) were also performed at 190 °C. The LAOS tests were conducted at 1 Hz at strains ranging from 10% to 1200%. Both correlated and transient data were collected. Raw waveforms were extracted at large strains and Fourier Transformations were applied to calculate the higher harmonic moduli, G_3' and G_5' .

RESULTS AND DISCUSSIONS

The most commonly used rheological analysis technique on polymer melts is the dynamic frequency sweep conducted using small strains that are within the linear viscoelastic region. The low frequency modulus (G') and complex viscosity are sensitive to polymer chain architectures such as molecular weight, molecular weight distribution, and long chain branching. In order to study the differences of the 4 HDPE samples, the frequency sweep test results are analyzed using the van Gorp-Palmen plots, which compares sample phase angle change as a function of complex modulus (G^*) [5]. Figure 4 shows the van Gorp-Palmen plots of the 4 HDPE resins. Sample 1C and 1D show lower phase angle at low G^* , which indicates that these 2 resins may contain slightly more long chain branching structures. However, since the differences are not well pronounced, it is hard to use this method to quantify the differences in the amount of LCB in those polymers.

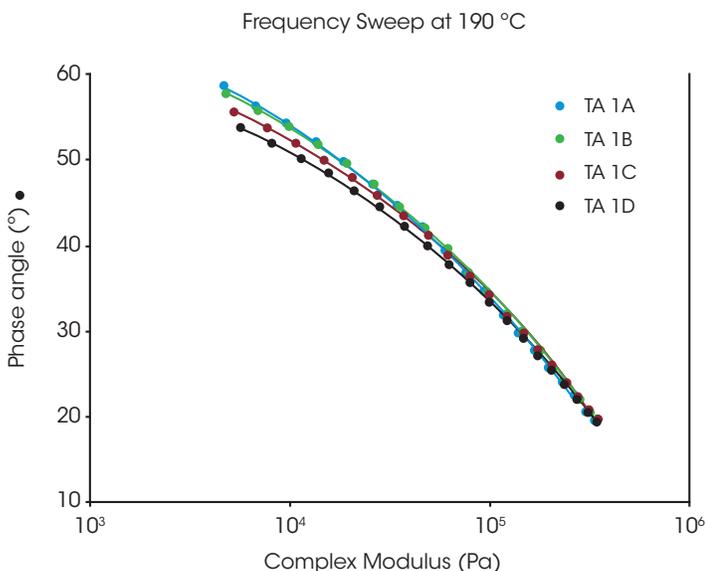


Figure 4. van Gorp-Palmen plots for the four HDPE resins. Dynamic frequency sweep tests were performed at 190 °C

Figure 5 shows the large amplitude oscillatory shear (LAOS) test results using the RPA instrument at 190 °C. The correlated data are presented as storage modulus (G') change as a function of strain amplitude. These 4 polymers show similar G' under small strain amplitudes that are within the linear region of the material. However, at large strains, G' begins to decrease with increasing strain. The decrease of G' on samples 1A and 1B seems more pronounced than the decrease observed with samples 1C and 1D. Using the RPA data analysis software to perform Fourier Transformation on the data, the higher harmonic moduli (i.e., G_3' and G_5') can be calculated. At a strain amplitude of 1000%, the higher harmonic moduli ratio meets the criteria of

$$-3 < G_1'/G_3' < 1 \quad \text{and} \quad -2 < G_1'/G_5' < 3$$

Using the empirical LCB index equation (Equation 1), the LCB index can be calculated. Figure 6 demonstrates how to use RPA data analysis software to extract higher harmonic signals and to calculate LCB index at a strain amplitude of 1000%. Table 2 summarizes the LCB index values of the 4 HDPE resins at strain amplitudes of 1000% and 1200%. Even though the LCB index values for the 4 polymers are all negative, which indicates that they are mostly linear, samples 1C and 1D clearly show a higher LCB index compare with samples 1A and 1B. This LAOS analysis technique provides a more sensitive and direct way to differentiate the differences of HDPE polymers, which containing small amounts of LCB.

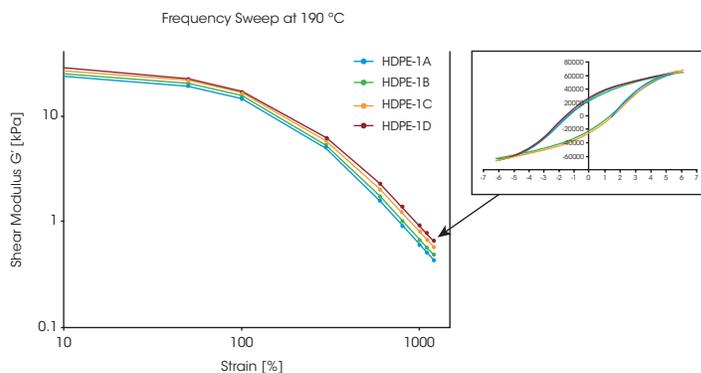


Figure 5. Dynamic strain sweeps at 190 °C. Raw waveforms can be extracted at each strain amplitude

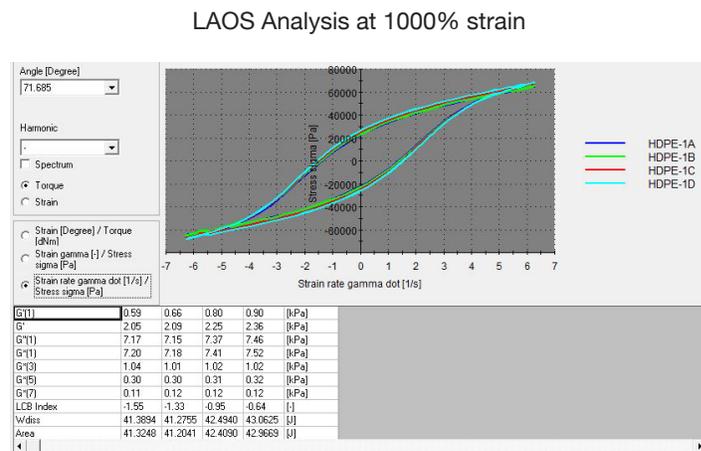


Figure 6. Demonstration of using RPA data analysis software to extract higher harmonic signals at 1000% strain.

Sample	LCB @ 1000% strain	LCS @ 1200% strain
1A	-1.55	-1.68
1B	-1.33	-1.56
1C	-0.95	-1.35
1D	-0.64	-1.14

Table 2 LCB index values for the 4 HDPE resins

CONCLUSION

Polymer long chain branching has a large influence on its processability. It provides shear thinning, strain hardening, and enhances melt strength. Rheological measurements are sensitive to polymer architecture, such as MW, MWD and long chain branching. Large Amplitude Oscillatory Shear (LAOS) can provide a quantitative measurement of polymer long chain branching. The closed die RPA is ideal for LAOS testing because it mitigates sample oxidation and prevents edge fracture. The TA Instruments RPA with SQS data analysis software can provide a sensitive approach for differentiating small amounts of long chain branching in polymers.

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