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DETERMINATION OF THE ZERO SHEAR VISCOSITY OF POLYETHYLENE

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Abstract

The zero shear viscosity (ZSV) of 10 commercial polyethylene resins has been determined with a creep test and the traditional oscillatory frequency sweep test. Identical results were obtained from the two different test methods. The obtained ZSV by either method can be used to evaluate the long chain branching (LCB) content of polyethylene resins.

Introduction

One of the parameters commonly used to characterize the presence of long chain branching in polyethylene is the viscosity of the melt at very low shear rates ⁽¹⁾. This viscosity is usually determined using a small amplitude oscillatory test where a rheological model such as the Ellis model is used to fit the data from a frequency sweep test. One of the Ellis constants which correspond to the extrapolated viscosity value at vanishing shear rates, is known as the zero shear viscosity (ZSV), η_0^* . This approach is adopted because of the instrument constraint at running at very low shear rates. Alternate experimental approach includes utilization of step strain relaxation and steady state creep test ⁽²⁾.

As the ZSV is very sensitive towards the high molecular weight fraction, presence of molecular chain entanglement and long chain branching which influence the performance of blown film, it is important to verify the validity of the value determined by the oscillatory test with another method. The steady shear viscosity at a low shear stress was used to measure a wide range of polyethylenes with different densities and melt indices, and results were compared with the ZSV determined by the oscillatory method.

Theoretical

The ZSV or η_0^* , is defined for the oscillatory test as:

$$\text{ZSV} = \eta^*(\omega) \text{ for } \omega \rightarrow 0$$

A typical complex viscosity flow curve of a polyethylene melt is shown in Figure 1. As it is not possible to measure the complex viscosity at zero shear rate, the viscosity flow curve is normally fitted with a rheological model. The Ellis and Cross models expressed in different forms are essentially the same, and will give

the same ZSV. However, the range of shear rates used for the model fit will influence the ZSV. This is shown in Table 1 for a control resin of Ziegler-Natta (ZN) octene-LLDPE of density = 0.91 g/cm³ and MI = 1 dg/min. It is clear from Table 1 that there is no statistical significant difference for the ZSV when the curve is fitted in frequency range of 0.05 to 1.9 rad/s and 0.05 to 100 rad/s, but fitting in the high frequency range of 2.6 to 100 rad/s will yield a lower value of ZSV.

The viscosity at low shear rate can also be determined using the creep method, where a constant torque is applied, and shear viscosity is obtained when a constant creep rate is attained:

$$\text{ZSV} = (dJ/dt)^{-1} \text{ for } t \rightarrow \infty$$

where J is the compliance, and ZSV is then defined for the zone where $d\gamma/dt$ becomes constant or at $t = \infty$.

Experimental

A total of 10 polyethylene resins, covering a wide range of density and melt index were selected for this study, details are given in Table 2.

The frequency sweep test and creep test were carried out with the Anton Paar MCR501 rotational rheometer. The resin was compression molded into a 25 mm disc using the ASTM D1238 density plaque method. The frequency sweep test was conducted at 190°C with the parallel plate fixture using a strain amplitude of 10% (within the linear viscoelastic region), covering a frequency range from 0.05 to 100 rad/s. The creep test was next performed on the same sample, using a constant stress of 20 Pa for a minimum of 2 h under nitrogen atmosphere.

Results

The melt viscosities at 190°C determined from Dynamic Mechanical Analysis (DMA) frequency sweep and creep test are tabulated in Table 3. The overlay of the complex viscosity flow curve from the dynamic oscillatory test, and the overlay of the shear viscosity under creep flow conditions are shown in Figure 2 and Figure 3, respectively. It can be seen that, in general, the complex shear viscosity shifted vertically upward with decrease in melt index. However, the pair of samples C and D, and samples E and F, showed a cross-over of the

flow curve, possibly due to the difference in polydispersity. It is clear from Sample B, which has the largest polydispersity, the flow curve is significantly different from the other samples.

The ZSV from the dynamic oscillatory test shows a unique linear correlation with the creep ZSV, as shown in Figure 4.

$$\text{Creep ZSV} = 1.038 * (\eta_0^*)$$

It is noted that the shear rate at which Creep ZSV was determined ranged from 0.07 to 36 s⁻¹. Comparing the Creep ZSV with the complex viscosity at $\omega = 0.05$ rad/s resulted in a polynomial correlation, as shown in Figure 5.

$$\text{Creep ZSV} = 3\text{e-}5 * (\eta_{\omega=0.05\text{rad/s}})^2 + 0.753 * (\eta_{\omega=0.05\text{rad/s}})$$

Discussion

It has been a challenge in polyethylene research to come up with a universally acceptable method of measuring the long chain branching content other than the Nuclear Magnetic Resonance (NMR) method. Lai and Knight⁽³⁾ introduced the parameter “Dow Rheology Index” (DRI), based on measurements obtained from melt viscosity alone, and this parameter is claimed to be able to detect very low LCB content, though it is specific only to the Insite Technology. In 1999, Shroff and Mavridis⁽⁴⁾ came out with the concept of defining a Long Chain Branching Index (LCBI), defined by one melt rheological property (zero shear viscosity) and one dilute solution property from Gel Permeation Chromatography (GPC intrinsic viscosity), where in the absence of LCB, the LCBI = 0. Application of Shroff and Mavridis approach to a range of solution phase ZN and single-site catalyst (SS) octene-LLDPE known to have no long chain branching did not substantiate their claim. Further research into LCB perhaps is best summarized in the Patent Application US 2011/0015353 A1⁽⁵⁾. Here Michel et al. attempted to apply five different methods of quantifying LCB, including (1) DRI (2) LCBI (3) Janzen & Colby equation (4) Long Chain Branching Factor, g_{rheo} , and (5) from GPC, g' , defined as the ratio of the intrinsic viscosity of branch to the intrinsic viscosity of linear PE. Again, it should be noted that all the five methods may be applicable and yield inter-supporting evidence, when the

same series of polyethylenes prepared with the same process and catalyst system were considered. More recently, another parameter known as Creep Zero Shear Viscosity Ratio has been introduced by Hermael-Davidock and coworkers⁽⁶⁾. This is similar in approach to the Shroff & Mavridis approach, except that the intrinsic viscosity is replaced by GPC Mw, and the zero shear viscosity determined by the DMA method is replaced by the creep method.

Conclusions

The two methods of determining the zero shear viscosity using oscillatory frequency sweep test and creep at constant low stress gave essentially the same results. Either method can be used for quantifying the long chain branching content in combination with dilute solution intrinsic viscosity, $[\eta]$ measurement or standard GPC weight average molecular weight, Mw, measurement. The DMA frequency sweep test has the advantages of short testing time and reproducible results.

Acknowledgements

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Table 1. Zero Shear Viscosity from Ellis Model.

Fitting range	Zero Shear Viscosity (Pa.s)
Low frequency range: 0.05 – 1.9 rad/s	10109 \pm 2.1%
Full frequency range: 0.05 - 100 rad/s	9801 \pm 2.3%
High frequency range: 2.6 - 100 rad/s	8773 \pm 2.4%

Table 2. Properties of Resins.

Polyethylene Resins	Melt Index (dg/min)	Density (g/cm ³)	Mw (g/mol)	Mw/Mn
Sample A: solution phase ss o-LLDPE	0.65	0.916	121,500	2.96
Sample B: solution phase ZN b-LLDPE	0.72	0.936	144,600	9.93
Sample C: gas phase ZN h-LLDPE	0.80	0.934	117,800	2.96
Sample D: solution phase ZN o-LLDPE	0.75	0.921	117,900	3.40
Sample E: solution phase ss o-LLDPE	1.0	0.917	104,200	3.27
Sample F: solution phase ZN o-LLDPE	1.0	0.920	102,700	3.07
Sample G: solution phase ss o-LLDPE	2.0	0.925	85,870	3.08
Sample H: solution phase ss o-LLDPE	2.6	0.936	81,430	2.20
Sample I: solution phase ss o-LLDPE	4.4	0.917	69,020	2.29
Sample J: solution phase ss o-LLDPE	150	0.932	27,740	2.36

Table 3. Melt Viscosities at 190°C Determined from DMA and Creep Test.

Polyethylene Resins	Ellis ZSV (Pa.s)	η^* at $\omega = 0.05$ rad/s (Pa.s)	Creep ZSV (Pa.s)	Creep ZSVR (Pa.s)	DMA ZSVR (Pa.s)
Sample A	14160	13700	14411	1.74	1.71
Sample B	28668	21360	29924	1.91	1.83
Sample C	13134	12460	14199	1.92	1.77
Sample D	14230	13200	14746	1.99	1.92
Sample E	9032	8830	9055	1.91	1.91
Sample F	9675	9095	9744	2.17	2.16
Sample G	4673	4580	4632	1.98	2.00
Sample H	3176	3120	3133	1.63	1.65
Sample I	1874	1850	1854	1.76	1.78
Sample J	54.9	54.6	55.0	1.46	1.45

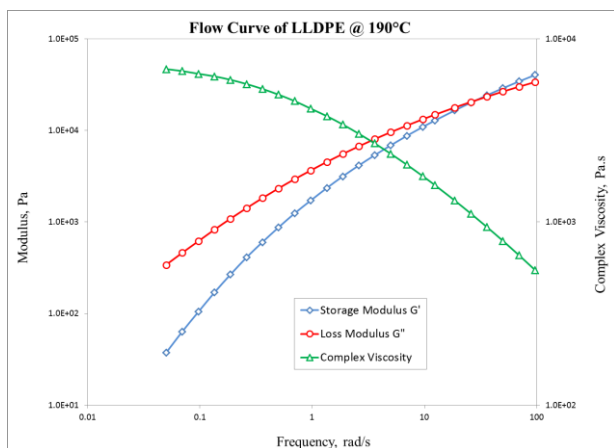


Figure 1. Complex viscosity flow curve of the control resin.

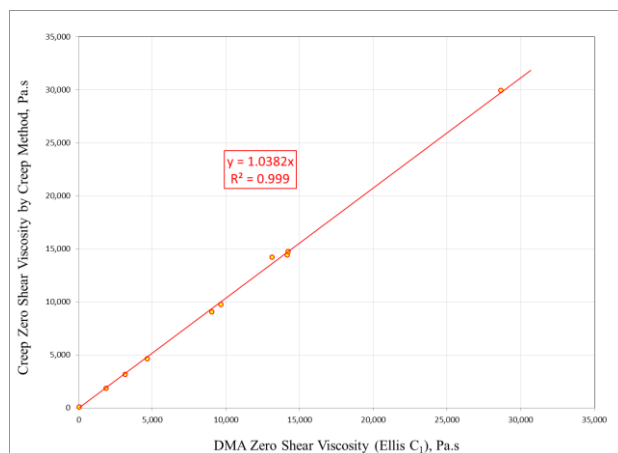


Figure 4. Correlation between the Creep ZSV and the DMA ZSV.

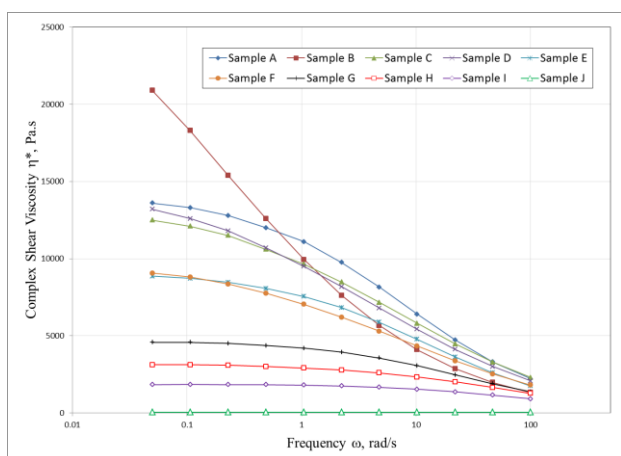


Figure 2. Overlay plot of the complex viscosity flow curve for the ten resins.

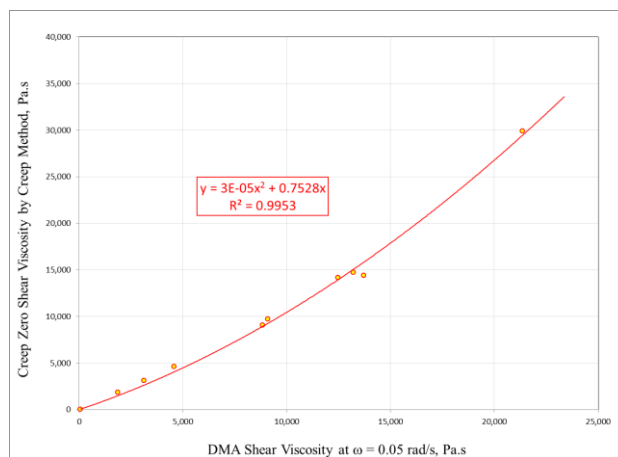


Figure 5. Correlation between the Creep ZSV and the DMA viscosity at $\omega = 0.05$ rad/s.

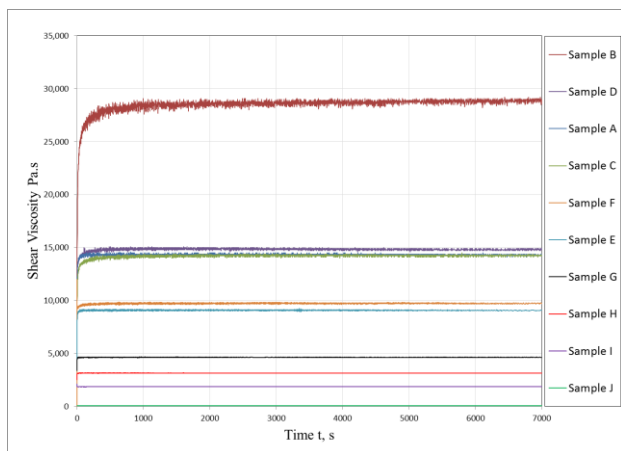


Figure 3. Overlay plot of the shear viscosity 'Creep' curve for the ten resins.