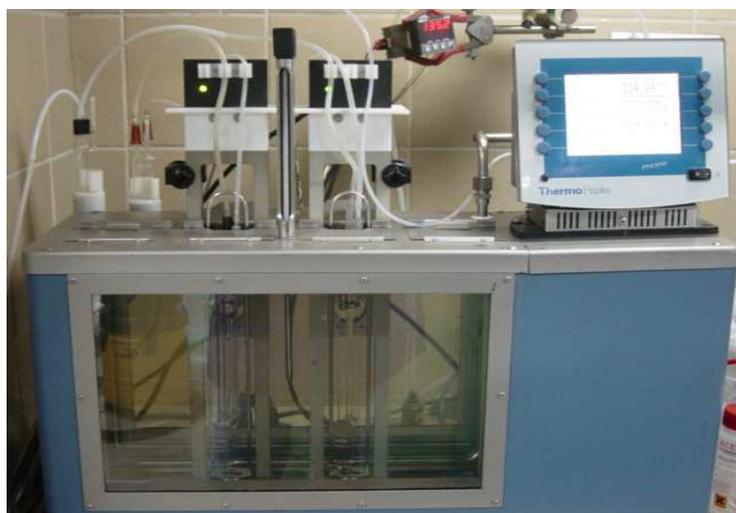




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**UHMWPE Molecular Weight Determination from
Viscosimetric Analyses**



Written By:

1. Giancarlo Roxo Polyolefins BU / I&T

Co-Worker(s):

1. Bernadete Bittencourt Polyolefins BU / I&T

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1 Introduction

There are some characterization methods which can be used as a measurement of molecular weight of polymers. Most of them, however, are too complicated to be used as a quality control basis at industrial operations. For practical purposes, laboratories use to measure some indirect parameter at a given polymer sample which can then be correlated with molecular weight. In the case of UHMWPE resins, the viscosity of dilute solutions is widely used for that purpose.

It's important to point out that the determination of dilute solution viscosity provides only one item of information towards the molecular characterization of polymers. When viscosity data are used in conjunction with other molecular parameters, the properties of polymers depending on their molecular structure may be predicted.

For linear non-filled polymer materials, empirical relationships can be developed between the dilute solution viscosity of a polymer and its average chain dimension. Such relationships depend upon all variables which influence the molecular size of the dissolved polymer. Some of those variables are solvent type, temperature, sample collection procedure, polymer concentration and the boundary conditions used in the development of the mathematical equations that correlate viscosity and molecular weight.

The present Technical Bulletin clarifies the most used concepts involving viscosity and molecular weight calculations. It also discusses the influence of some variables in the determination of molecular weight. Still, it correlates the most widely used Standards for viscosity measurements and shows the possible different results they might present.

2 Terminology

2.1 Relative Viscosity, η_{rel} : the ratio of the viscosity of the solution, η , to the viscosity of the solvent, η_s , that is, $\eta_{rel} = \eta / \eta_s$. During the solution viscosimetry analyses, η_{rel} is a direct correlation between the efflux time of the solution and that of the solvent, that is, $\eta_{rel} = t / t_s$.

2.2 Relative Viscosity Increment, η_i (also called **Specific Viscosity, η_{sp}): the ratio of the difference between the viscosities of the solution and solvent to the viscosity of the solvent, that is, $\eta_i = (\eta - \eta_s) / \eta_s$, or still, $\eta_i = (t / t_s) - 1$.**

2.3 Viscosity Number, VN (or **Reduced Viscosity, η_{red}): the ratio of the relative viscosity increment to the mass concentration of the polymer c , that is, $VN = \eta_i / c$.**

2.4 Intrinsic Viscosity (IV), $[\eta]$: the limiting value of the reduced viscosity or the inherent viscosity at infinite dilution of the polymer, that is, when solution concentration tends to zero.

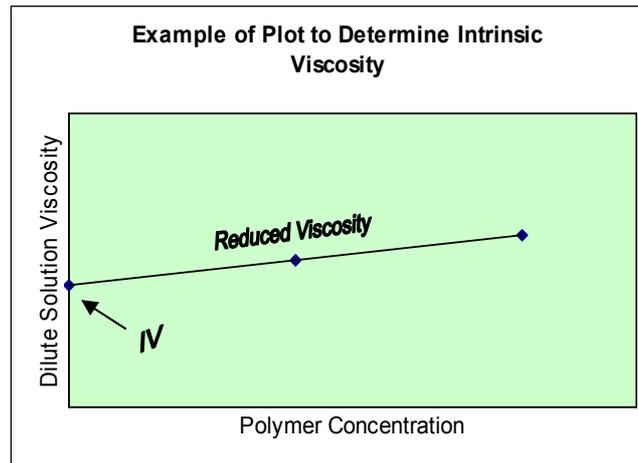


Figure 1: Correlation between solution concentration and viscosity of a given polymer sample

For some polymer systems, which is the case of UHMWPE, the slope of the correlation curve above is closely similar for all samples normally found. In such systems, the intrinsic viscosity can be approximated from data obtained at a single concentration by using one mathematical formula. The most widely used formulas for UHMWPE are those found on ASTM D-4020 and ISO 1628-3:

$$[\eta] = \eta_{sp} / [c (1 + k \cdot \eta_{sp})], k = 0.27 \text{ (ISO)}$$

$$[\eta] = (2 \cdot \eta_{sp} - 2 \cdot \ln \eta_{rel})^{1/2} / c \text{ (ASTM)}$$

$$\log \eta_{red} = \log [\eta] + k_1 \cdot [\eta] \cdot c, k_1 = 0.139 \text{ (Martin's Equation)}$$

2.5 Ubbelohde Viscometer : glass capillary viscometer used to measure the solution efflux time. For UHMWPE resins, ASTM D-4020 defines the Ubbelohde viscometer No. 1, with a capillary internal diameter of $0.63\text{mm} \pm 0.02\text{mm}$. A schematic drawing can be seen below.

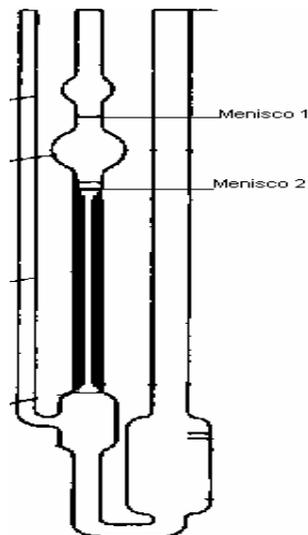


Figure 2: Example of an Ubbelohde Viscometer

2.6 Viscosimetric Molecular Weight, M_v : it's the molecular weight of a polymer measured through some viscosimetric technique. Technically, M_v and M_w (Average Molecular Weight) are different parameters (see figure below), although their absolute numbers are

similar. In the UHMWPE Industry, M_v is generally expressed and accepted as M_w , once it's much simpler to be determined.

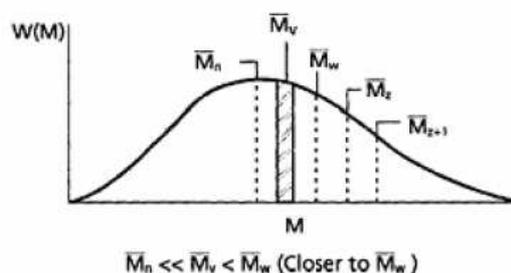


Figure 3: Molecular Weight Distribution (MWD) of a given polymer sample

As depicted on figure 3 above, the M_v value measured by IV analysis is only a single point on the MWD curve. Therefore, as UHMWPE resins from different producers have distinct MWDs, it's not always possible to make a direct comparison among those resins using only the M_v or IV values. For that purpose, additional techniques should be employed.

3 Standards for IV Measurement

The first Standard used to measure Intrinsic Viscosity was DIN 53479 (1975). This Standard was later substituted by ISO 1628 part 3 (2001). Both Standards present the same testing procedure and differ only in terms of solution concentration: it was changed from 0.0003% (DIN 53479) to 0.0002% (ISO 1628-3).

Besides ISO 1628-3, ASTM D-4020 (2005) also standardizes a test method for Intrinsic Viscosity. The main difference between ASTM and ISO Standards is the Ubbelohde-type Viscometer. ASTM specifies the No.1 viscometer, whose internal capillary diameter is 0.63mm. ISO refers to a viscometer with an internal capillary diameter of 0.46mm.

The equations indicated on both Standards to calculate the Intrinsic Viscosity from the measured efflux times are also different. However, they both lead to similar results when the constant k described in ISO 1628-3 is equal to 0.27.

As already mentioned, there's a third equation used by the industry called *Martin's Equation*, which also leads to similar results as the equations described on the aforementioned Standards, when the constant k is equal to 0.139.

There's a numerical example below which helps illustrate the differences among the Standards. In order to facilitate the understanding, it assumes both Standards use the same Viscometer type so that only the calculation differences show up.

Example. The flow times of a solvent and a solution of polymer at a specified concentration in that solvent are measured at 135 °C. The Reduced Viscosity and Intrinsic Viscosity are calculated from these measurements and from the known concentration of the solution.

Sample: UTEC 4040

Apparatus: Ubbelohde Viscometer No.1

Solvent: Decahydronaphthalene

Test temperature: 135°C

Solvent Density at 135°C (d135): 0.8020 g/mL;

Solvent Density at 20°C (d20): 0.8880 g/mL

Measurements:

<i>Polymer weight (m)</i>	<i>0.0075 g</i>
<i>Solvent Volume (V)</i>	<i>50 mL</i>
<i>Average efflux time of the solution (t)</i>	<i>98.00 seconds</i>
<i>Average efflux time of the pure solvent (t₀)</i>	<i>74.50 seconds</i>

The table below shows IV calculations by using the different Standards, as well as Braskem's method used to determine IV and Mv.

Table 1: IV calculations based on different Standards and Methods

	Standard ISO 1628-3	Standard ASTM D-4020	Standard ISO 1628-3 (IV calculation using Martin's Equation)	Braskem's Method
Reduced Viscosity (Viscosity Number) Equation	$\eta_{red} = (t - t_0) / (t_0 \cdot c)$	$\eta_{red} = [(t - (k/t)) / (t_0 - (k/t_0)) - 1] / c$ (k = viscometer kinetic energy correction constant)	Same as ISO	Same as ASTM
Calculated η_{red} (VN) Value (mL/g)	2328	2324	Same as ISO	Same as ASTM
Intrinsic Viscosity $[\eta]$ Equation	$[\eta] = \eta_{red} / (1 + k.c.\eta_{red})$ (k = 0.27)	$[\eta] = (2.\eta_{sp} - 2.\ln \eta_{rel})^{1/2} / c$	$\log \eta_{red} = \log [\eta] + k_1.[\eta].c$ (k ₁ = 0.139)	Same as ASTM
Calculated IV Values $[\eta]$ (dL/g)	21.46	21.17	21.20	Same as ASTM
Molecular Weight Equation	Not applicable	ASTM Equation: $5.37 \times 10^4 [\eta]^{1.37}$	Margolies Equation: $5.37 \times 10^4 [\eta]^{1.49}$	Margolies Equation: $5.37 \times 10^4 [\eta]^{1.49}$
Calculated Mv Values (g/mol)	---	Mv = 3.52×10^6	Mv = 5.07×10^6	Mv = 5.08×10^6

The numbers above show there's no significant difference in the IV values calculated by the different equations, although they appear to be quite different from each other at a first sight.

Braskem uses ASTM D-4020 to calculate the Intrinsic Viscosity of its resins. The Viscosimetric Molecular Weight is calculated using Margolies Equation rather than ASTM Equation, because that is the equation which best fits Braskem's Mv and IV measurements.

As can be noticed from the data above, the use of ASTM Equation will always result in a lower Mv value. This equation is seldom used by the industry in general.

The North American Market normally uses IV values to describe a given UHMWPE resin. On the other hand, the European Market is more used to Mv numbers.

4 Effect of Solution Concentration on IV Measurements

In UHMWPE systems, it's expected that if the solution concentration is small enough the measured IV values will be similar regardless of the concentration. In order to check that assumption some measurements were taken to evaluate the effect of the solution concentration (in the range of 0.01 to 0.02 g/dL) on the IV values.

Although 0.02 g/dL is the recommended concentration at ISO and ASTM Standards, there are some advantages to use a lower concentration value. The most remarkable one is that it takes less time to dissolve the sample, which reduces the risk of degradation and hence the analysis uncertainty.

The data below show the effect of solution concentration on IV measurements for both UTEC 3041 and UTEC 6540.

At UTEC 3041, the difference in the measured IV at concentrations of 0.015 and 0.023 g/dL is very small and within analysis uncertainty (see below). For UTEC 6540, there's no practical difference among the measured values in the range of 0.005 to 0.020 g/dL.

By analyzing this piece of data, it's possible to conclude that IV measurements at UTEC[®] resins are virtually independent on solution concentration in the range of 0.010 to 0.020 g/dL.

Sample	Concentration (g/dL)	Average Conc. (g/dL)	IV	Average IV	Mv (10 ⁶ g/mol)	Average Mv (10 ⁶ g/mol)
UTEC 3041 5A11V1	0.0148	0.0146	14.8	14.6	3.03	2.97
	0.0148		14.2		2.85	
	0.0142		14.8		3.03	
	0.0230	0.0229	14.3	14.9	2.88	3.05
	0.0227		15.0		3.08	
	0.0230		15.3		3.19	

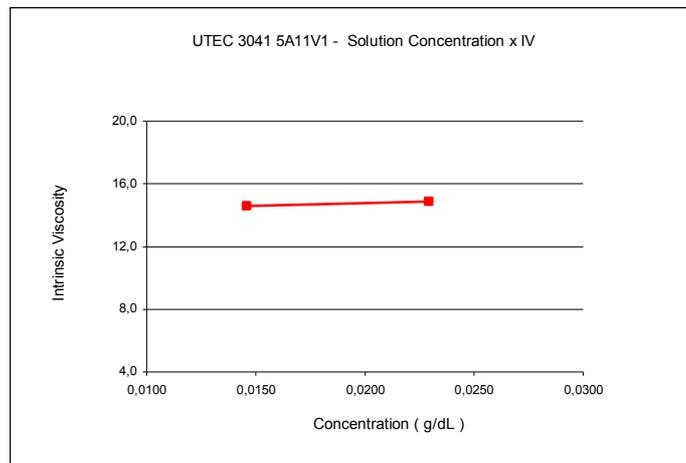


Figure 4: Measured IV values on different solution concentrations at UTEC 3041

Sample	Concentration (g/dL)	Average Conc. (g/dL)	IV	Average IV	Mv (10 ⁶ g/mol)	Average Mv (10 ⁶ g/mol)
UTEC 6540 5A15J1	0.0052	0.0052	28.7	29.3	8.15	8.39
	0.0052		29.4		8.45	
	0.0050		29.7		8.57	
	0.0100	0.0100	29.5	29.4	8.50	8.47
	0.0100		29.3		8.40	
	0.0100		29.5		8.50	
	0.0207	0.0206	29.4	29.1	8.35	8.25
	0.203		28.6		8.05	
	0.0207		29.4		8.35	

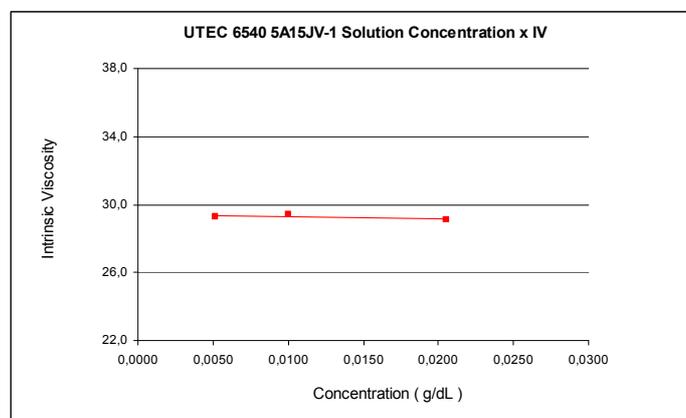


Figure 5: Measured IV values on different solution concentrations at UTEC 6540

5 Effect of Particle Size on IV Measurements

When the IV is measured, a continuous portion of the material should be taken, that is, there should be no separation of coarse and fine particles.

In some specific applications (such as filters) and/or new developments, however, it's interesting to know the influence of fine and coarse particles on IV values. This knowledge is also important to show what can happen to the analysis result if a sample is not properly collected.

On the table below one can see the Mv results obtained from fine and coarse particles of UTEC 3040 and UTEC 6540.

Table 2: IV measurements on samples separated by particle size

Sample	UTEC 3040 - 6B14D1			UTEC 6540 - 6C14F2		
	Coarser than 450 µm	Finer than 75 µm	Difference (%)	Coarser than 450 µm	Finer than 75 µm	Difference (%)
Molecular Weight (x10 ⁶ g/mol)	3.28	3.02	9%	7.12	6.20	15%

The higher the average IV, the greater the difference between fine and coarse particles values. In the case of UTEC 6540, the difference can be as great as 15%.

6 References

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