GENERAL

Fast determination of average Molecular Weight

- A simple way to characterize polymers using viscosity measurements -

Introduction

There are many different techniques that can be used to determine the molecular weight of polymers, such as size exclusion chromatography or time-of-flight mass spectrometry, these methods give precise results, however they are often costly, time consuming and require an operator with special training. FLUIDICAMRHEO offers a way to quickly and easily determine the molecular weight of many different types of polymers by viscosity measurements.

KEY **BENEFITS**

- FAST & SIMPLE
- USER-FRIENDLY
- EFFECTIVE

Reminder on the technique

FLUIDICAM Rheo uses a co-flow microfluidic principle to measure viscosity. The sample and a reference solution are simultaneously introduced into the microfluidic channel (typically 2.2mm X 150µm) with controlled flow rates. This results in a laminar flow where the interface position between sample and reference relates the viscosity ratio and flow rates.

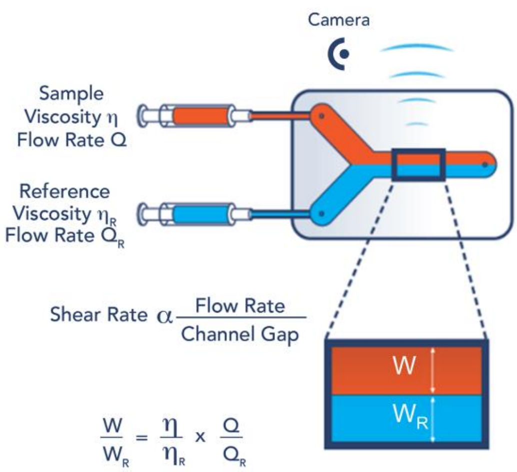
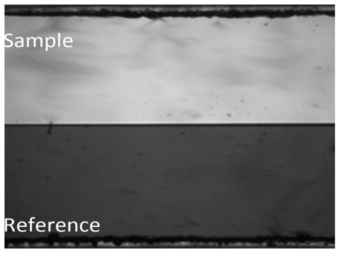


Fig. 1: Fluidicam measuring principle

Images acquired during the measurement allow the software to calculate the position of the interface and directly plot an interactive flow curve.



Experimental conditions

The polymer was dissolved in a solvent of choice at a concentration inferior to its C*, the polymer must be 100% soluble in this solvent. Several dilutions were made to vary the concentration, and therefore vary the viscosity. The viscosity of each solution was measured with FLUIDICAM^{RHEO} and the intrinsic viscosity was calculated using 2 different methods. This value of intrinsic viscosity was then used to calculate the average M_w.

Theory [1]

The intrinsic viscosity is defined by equation (1).

$$[\eta] = \lim_{c\to 0}\frac{\eta_{sp}}{c} = \lim_{c\to 0}\frac{\eta_r - 1}{c} \quad (1)$$

There are two methods that can be used to determine the intrinsic viscosity which are shown below.

Method 1: Huggins-Kraemer

The first method, that involves testing solutions at different concentrations, uses the relationships of Huggins (2) and Kraemer (3) to find the reduced and inherent viscosity respectively.

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c \quad (2)$$

$$\frac{\ln(\eta_r)}{c} = [\eta] + K_K\,[\eta]^2 c \quad (3)$$

Method 2: Solomon-Ciuta

The second method that can be used involves measuring a single concentration and it uses the relationship of Solomon-Ciuta (4)

$$[\eta] = \frac{[2(\eta_{sp} - ln\eta_r)]^{1/2}}{c} = \frac{[2(\eta_r - 1 - ln\eta_r)]^{1/2}}{c} \quad (4)$$

The Mark-Houwink equation (5) relates the intrinsic viscosity [η] with the molecular weight M_w.

The constants k and a, which can be found in literature, correspond to specific properties of the polymer.

$$[\eta] = \boldsymbol{K M_w^{\,a}} \quad (5).$$

Results

An example Huggins-Kraemer plot is shown in Figure 2, this data was obtained by using method 1 for Hydroxyethyl-cellulose LR 250 solutions. Each point corresponds to a different dilution of the polymer solution. The two trendlines were extrapolated to zero to find the intrinsic viscosity.

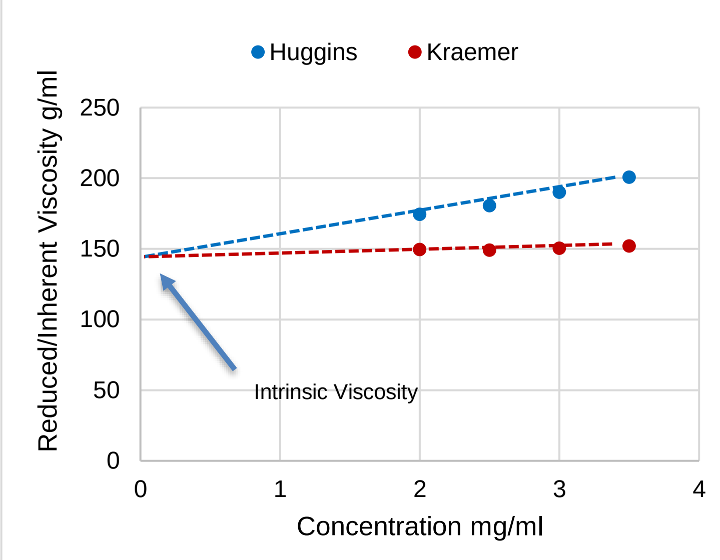


Figure 2: Huggins-Kraemer Plot HEC LR 250

Method 2 can also be used to determine the intrinsic viscosity. Once the intrinsic viscosity has been determined from either method 1 or 2, equation (1) can then be applied to calculate the M_w.

Results of the PVA and HEC polymers are summarized in table 1 along with the range of values that are found in the literature or given by the supplier.

Polymer	FLUIDICAM RHEO		Literature or Supplier
	M_w (g/mol) Method 1	M_w (g/mol) Method 2	M_w (g/mol) Range
HEC LR	**69000**	**70000**	**64000-90000[2-5]**
HEC GR	**257000**	**200000**	**19000 -300000[2-5]**
PVA	**89600**	**93000**	**89000-98000[6]**

Table. 1: Molecular Weight results

Table 1 clearly shows that both method 1 and 2 give results in the range of values found in the literature or given by the supplier. Method 2 is an attractive choice as it offers a way to quickly estimate M_w, for more precise results method 1 can be used.

Both methods can be applied to many different types of polymer, as long as the polymer is completely solubilized it can be analyzed with FLUDIICAM RHEO.

Advantages of FLUIDICAM

One of the main advantages of FLUIDICAM RHEO is that an average M_w can be determined quickly and easily in less than 10 minutes. It is an ideal method for rapid batch to batch comparison, fast routine measures and can be used as a formulation tool to assess the quality of different polymers. Also, FLUIDICAM RHEO uses small sample volumes so loss of product is minimized. Table 2 shows the amount of time and sample volume required to perform the measurements with FLUIDICAM RHEO.

Method	Analysis time (min)	Sample volume (mL)
1	**40**	**4***
2	**10**	**1**

Table 2: Fluidicam analysis time and sample volume

**For method 1, 1mL of 4 different concentrations to plot 4 points on the graph.*

References

[1] Harding.S, Prog. Biophys. Molec. Biol. Vol 68. 207-262. 1997
[2] Robb et al. **J. Chem. Soc., Faraday Trans.** Vol **91**. 3901-3906. 1995
[3] Sperry. J.Colloid Interface Sci. Vol 87. 375-384. 1982
[4] Anders et al. Int. J. Pharma. Vol 49. 231-240. 1989
[5] Ashland Product Data.
[6] Sigma Aldrich

CONCLUSION

FLUIDICAM RHEO can be used to determine the average molecular weight of polymers in solution. With its ease of use and convenience, FLUIDICAM RHEO is the ideal method for quick and accurate determination of intrinsic viscosity and thus average molecular weight and it can be applied to many different types of polymer. Fast quality control analysis and routine tests are made easy with FLUIDICAM RHEO, no expert operator is needed