

Use of Rheology to Determine the Molecular Weight Distribution of Polymers

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ABSTRACT

The molecular weight distribution of polymers strongly influences their processability. It is usually determined using size exclusion chromatography, but this is sometimes difficult and time-consuming. Here we show that rheology can be used to provide the same information, and compare the algorithms developed by Mead and Friedrich et al.

INTRODUCTION

Viscometric and rheological measurements have long been used to provide information on the molecular weight of polymers¹. But although the various average molecular weights, such as the number average, M_n , and weight average, M_w , can normally be determined relatively easily, these are not usually enough to allow the physical properties of the polymer to be accurately predicted. These properties depend not just on M_n , or M_w , but in an intimate way on the whole distribution of molecular weights, $w(M)$ or MWD. For example, the shapes of $w(M)$ for two polymers may be very different, despite them having the same average molecular weights. The two polymers will then show different physical properties; they will have different softening points, solubilities and processabilities, for example.

It is therefore important, in many situations, that the full distribution of molecular weights of the polymer molecules should be known. Usually size-exclusion chromatography, SEC, is used for its determination. The polymer is dissolved and

passed under pressure through a chromatography column. The larger molecules pass through the column relatively quickly, the smaller ones are retained for longer. Some form of detector quantifies the amount of material coming off the column at any time, and $w(M)$ is thereby obtained. Useful though this technique is, it does have its disadvantages. For one thing, some important polymers such as polyalkanes and poly(tetrafluoroethylene) can only be dissolved in solvents that are expensive or difficult to handle. For another, SEC is rather insensitive to very high molecular weights species, which greatly affect polymer processability.

For the last few years, polymer rheologists have therefore been working to establish a method of obtaining $w(M)$ for polymer melts from rheological measurements. A thus inferred "rheological" MWD would have the additional advantage of being particularly sensitive to high molecular weight species, which have a great influence on polymer mechanical properties. Rheological instrumentation has developed to the point where low cost reliable rheometers are available to most polymer laboratories, and the required measurements can be made without difficulty. A standard technique is low amplitude oscillation, in which the sample is subjected to a small, sinusoidally oscillating mechanical stimulus, and the response is monitored. The complex modulus, $G^*(\omega)$, which has both magnitude and phase, and depends on the frequency of the applied oscillation, can then be calculated. $G^*(\omega)$,

the in- and out-of-phase components of which, $G'(\omega)$ and $G''(\omega)$ respectively, are usually reported, is the starting point for the derivation of the material functions such as $w(M)$.

Pioneering work in the field was conducted by Mead², and separately by Thimm et al.³. Mead's algorithm formed the basis of the molecular weight distribution module in Rheometric Scientific's Orchestrator software, whereas Thimm's was used by TA Instruments in their Rheology Advantage software. The merger of the two companies in 2003 allowed a full comparison of the two versions, and in this presentation we show the results for a series of polystyrene samples of varying molecular weight and molecular weight distribution.

THEORETICAL

The first step in the transformation from $G^*(\omega)$ to $w(M)$ is the computation of the linear relaxation spectrum, $H(\tau)$. This function can be appreciated from its relationship to the linear relaxation modulus, $G(t)$ ^{2,4}. If a small strain, that is a deformation, is applied instantaneously to a sample, then there will be a resulting stress; a stress being a force acting over an area. This stress will relax, that is decay over time, and the relaxation modulus is the stress divided by the strain, so it too decreases with time. Relaxation is due to various processes taking place within the sample, principally the motion of the whole or parts of the polymer molecules. Each relaxation process, or "mode" contributes a strength and timescale to the overall relaxation effect, and $H(\tau)$ represents the strength of relaxation at each timescale.

$H(\tau)$ can be calculated using Orchestrator or Rheology Advantage, Calculation of $H(\tau)$ from either $G^*(\omega)$ or $G(t)$ is not straightforward, but once this has been done, $H(\tau)$ can be used to generate $w(M)$. There are two main types of mode which contribute to $H(\tau)$ over standard

timescales. At short timescales, commensurate with high frequencies, Rouse modes dominate. These are due to the motions of segments of each polymer molecule. At longer timescales, or lower frequencies, motions of whole molecules give rise to reptation modes. The Rouse modes are only weakly dependent on $w(M)$, and they must be subtracted from the spectrum. The part of the spectrum due to reptation modes is then used to provide $w(M)$.

To effect the transformation of $H(\tau)$ into $w(M)$, an approximation formula based on the double reptation rule is used. The basic equation is the (generalized) mixing rule:

$$G_r(t) = G_N \left(\int_{M_e}^{\infty} F(M, t)^{1/\beta} w(M) \frac{dM}{M} \right)^\beta \quad (1)$$

Where G_r is the reptation modulus G_N is the plateau modulus, and $M_e \approx M_c/2$ is the entanglement molecular weight (M_c is the critical molecular weight). $F(M, t)$ denotes the relaxation kernel function, which describes the relaxation behaviour of a molecular weight fraction with a molecular weight of M , and β is a parameter which characterizes the mixing behaviour. Several forms of relaxation kernel have appeared in the scientific literature; an evaluation has been made by Maier et al.⁵. That used by Rheology Advantage essentially decays exponentially. The subscript "r" of the stress relaxation $G(t)$ indicates that only the contributions of the reptation dynamics of the whole polymer chain are considered, the dynamics of the chain segments (Rouse modes), which are only weakly dependent on $w(M)$, are not considered.

RESULTS

An additional feature of the Orchestrator version is the ability to assume a distribution function for the molecular weight, and to back calculate the corresponding rheological functions. This is advantageous if the

sample is formed from a mixture of polymers, each with a $w(M)$ that follows a standard distribution function such as Schultz or log normal.

Rheological data, supplied by Tuminello⁶ for a series of well characterised polystyrene samples with unimodal molecular weight distributions was used for this comparison. The molecular weight distribution of each was available from SEC measurements. These were then compared with the results given by Orchestrator and Rheology Advantage. Good agreement was achieved in both cases. Rheology data for samples blended to give bimodal molecular weight distributions of known form, were also taken, and analysed using SEC and the two rheological algorithms.

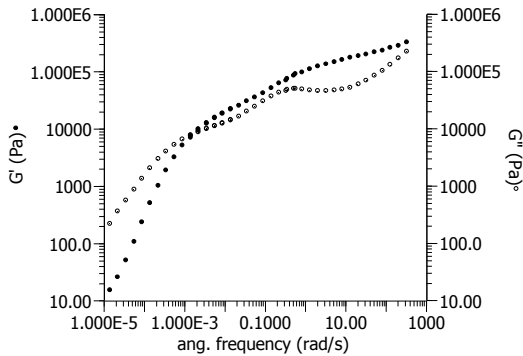


Figure 1: storage and loss moduli for a 1:1 by mass blend of polymers of M_w 115k and 1150k

Storage and loss moduli for polymers of M_w 115k and 1150k, blended in the mass ratio 1:1 are shown in Fig. 1. The relaxation spectrum, $H(\tau)$, calculated from these data using the algorithm of Honnerkamp⁴, is shown in Fig. 2.

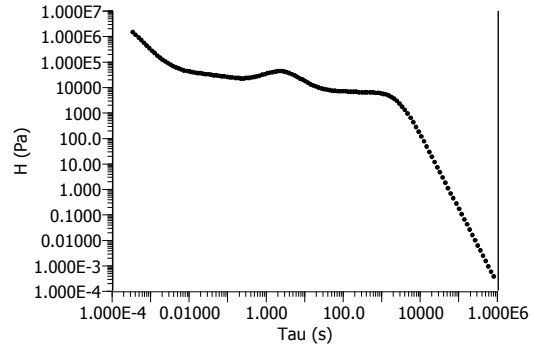


Figure 2: relaxation spectrum calculated from the data shown in Fig. 1

The Molecular weight distribution calculated from the data are shown compared with the SEC data for the same polymer blend in Fig. 3.

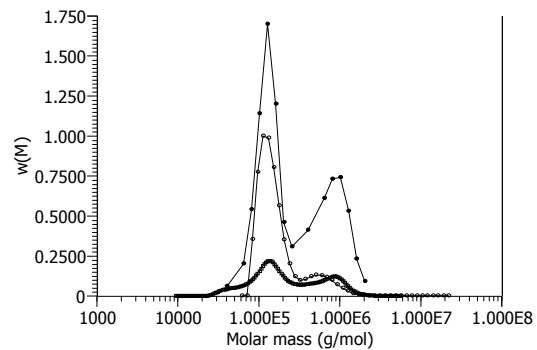


Figure 3: $w(M)$ calculated using the algorithm of Mead (closed circles) and Thimm et al. (closed squares) and obtained from SEC (open circles). The lines are to guide the eye only.

The data in Fig. 3 are shown un-normalised, to facilitate comparison. The lines are include to guide the eye only. Both algorithms show good agreement with the SEC data, although perhaps Mead captures the shape of the distribution more accurately, the distribution range is more closely described by Thimm et al.

CONCLUSIONS

Comparison has been made between two algorithms used to calculate the molecular weight distribution from the storage and loss moduli for a series of polystyrene samples, both unimodal and bimodal. It has been found that both algorithms give good agreement with SEC data, although the algorithm of Mead gives slightly closer correspondence with the shape of the SEC distribution function, that of Friedrich et al. gives slightly better correspondence with the range

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