Analytical Rheology

Analytic rheology is the subject of determining the microstructure of a material from measurements of its viscoelastic response. Analytic rheology is an extension of analytic chemistry in much the same sense as other analytic methods predicated on flow properties. Intrinsic viscosity is an example of an analytical technique that falls into this category. Analytic rheology can be applied to any material system where the rheological response depends strongly on the microstructure. There are many examples of such systems in rheology. For example, the droplet size distribution of a multiphase suspension can be determined from the measured linear viscoelastic response. Experimental methods of determining the linear viscoelastic material functions are highly evolved such that accurate and reliable measurements can be made in a routine highly automated manner. Analytic rheology exploits this experimental capability and develops advanced methods of interpreting and utilizing standard rheological measurements. With advanced data interpretation methods such as MWD determinations, the TAOrchestrator software allows the full power of rheological characterization methods to be realized. The specific application of analytic rheology that we are concerned with in this document is the calculation of the molecular weight distribution for linear flexible polymers from measured linear viscoelastic material functions.

Since there are currently many viable methods of determining the molecular weight distribution of flexible polymers, such as gel permeation chromatography, light scattering, intrinsic viscosity etc., it is important to appreciate what specific advantages, having a rheological MWD determination method provides. There are several unique advantages to rheologically-based methods of determining the molecular weight distribution. For example, virtually all conventional MWD methods are predicated on the ability to readily dissolve the polymer in a solvent at ambient temperatures. However, many polymers of commercial importance such as Teflon, polyethylene and polypropylene are only slightly soluble if at all in common solvents at ambient temperatures. This severely restricts access to conventional molecular weight determination methods for these commercially important polymer systems. Rheological methods do not require this time consuming solvating step. Indeed obtaining rheological data for polyethylene or polypropylene melts does not present any particular experimental difficulties. It should be noted that rheological methods are necessarily secondary analytic methods and hence require a primary analytic method in order to establish a calibration. Even when conventional MWD methods can be made to work for these polymers, the sensitivity and resolution of the analytic techniques is poor especially for the high molecular weight tail. As a practical matter, characterization of the high molecular weight tail is particularly important for characterizing the processability of a commercial polymer. Rheological methods of determining the MWD are intrinsically sensitive to the high end of the molecular weight distribution. This can be easily understood by considering the strong dependence of the linear viscoelastic material functions on molecular weight and molecular weight distribution. For example, the zero shear viscosity is well known to depend on the weight average molecular weight to the 3.4 power. Thus small changes in weight average molecular weight generate large changes in zero shear viscosity and hence sensitivity in the analytical method. Only a portion of the linear viscoelastic spectrum contains information on the molecular weight of the system. These ideas are obtained in the so called Bueche-Ferry /1/ theorem. Specifically, the Bueche-Ferry hypothesis states that on sufficiently short time scales the response of all flexible polymers is identical, regardless of molecular weight, chain architecture or polymer concentration. This implies that the MWD will not impact the viscoelastic response in the glassy regime. Physically, this result derives from the fact that the entanglement effect is only felt on relatively large length scales compared to typical monomeric dimensions. Therefore, provided a monomer does not reside near a chain end, its short time-scale dynamics.

Consequently all dependence of the mechanical response on molecular weight completely vanishes in the glassy time/frequency range. Figure 1 illustrates the various regimes of dynamic response for a monodisperse polymer melt. While restrictions on the time/frequency range over which data must be collected is welcome as a practical matter, the presence of the "glassy modes" in data sets demands that a viable means of culling these effects out of the experimental data prior to calculating the MWD be used. The principal complication is that lower Rouse modes for the high molecular weight components can mix with repetitive relaxation modes for the lower molecular weight species. The method we use to account for this effect is described below.
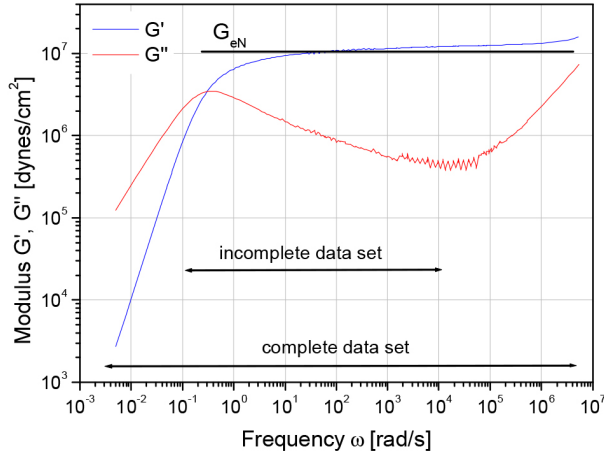
Figure 1: Dynamic responses of a monodisperse linear flexible polymer are identical to those of a monomer in a larger or shorter chain, or a polymer in dilute solution for that matter.

MIXING RULES FOR POLYMER MELTS

A quantitative relationship that relates the observed mechanical properties of a polydisperse melt and the underlying microstructure is called a mixing rule. We shall be exclusively concerned with mixing rules for the linear viscoelastic properties of entangled flexible polymers. Recently, a viable mixing rule for homogeneous systems of well entangled polymers has been independently derived by Tsenoglou and des Cloizeaux [2,3]. The mixing rule is called the "double reptation" model and is a relatively simple mathematical approximation to a more rigorous and complex molecular theory of polydispersity. The double reptation mixing rule has the following mathematical structure:

$$G(t) = G_N \left[\int_0^\infty F^{\frac{1}{2}}(M,t) w(M) dM \right]^2 \quad (1)$$

Here $G(t)$ is the relaxation modulus which can be determined from various combinations of linear viscoelasticity experiments discussed below. The function $F^{1/2}(M,t)$ is the monodisperse relaxation function which represents the time dependent fractional stress relaxation of a monodisperse polymer following a small step strain. $w(M)$ is the weight based molecular weight distribution. Physically, it is intuitive that all components of the molecular weight distribution will contribute to the modulus to some extent. This notion is reflected in the integral over the molecular weight distribution $w(M)$ which sums contributions from each component of the MWD to $G(t)$ weighted by the kernel function $F^{1/2}(M,t)$. The magnitude of each component's contribution to the stress will depend on the details of the interaction with the other molecules in the molecular weight distribution. This is a description of the "mixing" effect which describes how one component of a complex molecular weight distribution dynamically interacts with all of its neighbors. The TAOrchestrator software also contains options to work with the so called "weight average" mixing rule developed by

Marin et al. [4]

$$\left[\eta^*(\omega, w(M)) \right]^{\frac{1}{\alpha}} = \int_0^\infty \left[G_N \frac{\lambda(M)}{1 + \left[\omega\lambda(M) \right]^2} + iG_N \frac{\omega\lambda^2(M)}{1 + \left[\omega\lambda(M) \right]^2} \right]^{\frac{1}{\alpha}} w(M) dM$$

$$(2)$$

The weight average mixing rule (2) is entirely empirical in origin. The physical basis for this mixing rule is predicated on the empirical observation that the relaxation time scales as molecular weight to ~3,4 power coupled with dimensional analysis.

Material Dependent Input Parameters

To calculate a molecular weight distribution for a given material using (1) it will be necessary to supply material dependent data to the application. Specifically, the plateau modulus G_N and form of the monodisperse relaxation function $F^{1/2}(M,t)$ must be supplied. The plateau modulus is tabulated in several references. The monodisperse relaxation function can take several forms. Generally we shall use a single exponential form,

$$F^{\frac{1}{2}}(M,t) = \exp\left\{ \frac{-t}{2\lambda(M)} \right\}$$

with $\lambda(M) = K(T)M^x$ \quad (3)

Here $\lambda(M)$ is the characteristic relaxation time for the monodisperse system and $K(T)$ is a coefficient that depends on temperature. The exponent x is typically ~3.4 for flexible polymers. Other choices for the monodisperse relaxation function such as the Doi-Edwards are possible.

$$F^{\frac{1}{2}}(M,t) = \left(\frac{8}{\pi^2} \right) \sum_{k=1}^\infty \frac{1}{(2k+1)^2} \exp\left\{ -(2k+1)^2 \frac{t}{2\lambda(M)} \right\} \quad (4)$$

Generally, the accuracy of the experimental data is not sufficient that significant differences in the predicted MWD from (1) can be discerned using either (3) or (4). The temperature dependence of $K(T)$ is modeled with an Arhenius type activation energy although other choices such as WLF are possible. Data for the material dependent parameters can be obtained from standard references such as Ferry or the research literature. For more novel polymers, experiment and calibration will be required.

CALCULATION OF THE RELAXATION MODULUS FROM LINEAR VISCOELASTICITY DATA [5]

There are a number of methods of determining the relaxation modulus $G(t)$ from linear viscoelasticity data. In principle, all linear viscoelastic material functions contain equivalent information. However in practice, certain linear viscoelastic material functions are intrinsically more or less sensitive to the long or short time-scales than others. For example,

constrained elastic recovery experiments are very sensitive to long time-scale relaxation processes while dynamic moduli measurements are more sensitive to short time-scale relaxation processes. The TAOrchestrator software provides viable means of combining these data to allow the effective dynamic range of the relaxation modulus determination to be expanded. Generally, it is always advantageous to incorporate as much linear viscoelasticity data from as many different experiments as possible to have a self-consistent determination of the relaxation modulus over as large a dynamic range as possible.

As noted previously, only linear viscoelasticity data in the terminal and plateau regions contain information on the molecular weight and molecular weight distribution. Therefore, once a relaxation modulus is calculated, the short time-scale contributions due to the glassy modes must be eliminated. The TAOrchestrator software accomplishes this by first crudely estimating the MWD. From the estimated MWD, the Rouse-like glassy response is estimated by summing the all Rouse modes for all components of the MWD and subtracting this contribution from *G(t)*. In experimentally determining the relaxation modulus to calculate a molecular weight distribution there are two distinct experimental situations possible: 1) Complete dynamic moduli data, 2) Incomplete dynamic moduli data. A data set is "complete" if the data span a dynamic time/frequency range from fully terminal behavior through transition to the glassy modes (Figure1). Complete data sets are usually generated in research applications. In practical situations involving routine characterization of commercial polymers with broad molecular weight distribution, a far more common occurrence is to have an "incomplete" data set. In this case, either fully terminal behavior is not achieved because of the exceptionally long relaxation times of the high molecular weight tail or the high frequency regime could not be fully accessed because of inertial limitations of the instrument. Each of the above cases presents different computational issues which result in restrictions to the method that we explore below.

COMPLETE DYNAMIC MODULI DATA SETS

When dynamic moduli data are available from the terminal region through the plateau region, all rheological information required to invert the mixing rule is present. The problem at this point is reduced to a numerical one of inverting the double reptation model for the MWD in a stable and robust manner. The double reptation mixing rule is a Fredholm integral equation of the first kind for W(M). Methods of solving such ill-posed problems are well established. The molecular weight distribution is calculated using regularization methods applied to moments of the MWD calculated from the experimental data using Mellin transforms /5/. The result is a stable and robust numerical method.

INCOMPLETE DYNAMIC MODULI DATA SETS

When the experimental data does not span the entire frequency range from the terminal to the plateau region,

the data set is incomplete and the double reputation model cannot be rigorously inverted without the introduction of additional information. Prior information on the shape of the distribution from knowledge of the chemistry or other knowledge can be incorporated into the numerical algorithm. The method we adopt is to assume a prior knowledge about the shape of the molecular weight distribution. This is a valid assumption for virtually all commercial polymers where the chemistry of the polymer catalyst principally determines the shape of the MWD. Effectively the numerical method fits the predicted dynamic moduli curve from model molecular weight distributions to the measured experimental data in an optimal manner. The method proceeds to manipulate a candidate MWD to achieve an optimal fit to the rheological data. Additionally we allow for a variety of model molecular weight distributions to be tried as well as binary combinations thereof. The greater the number of fitting parameters that one uses, the greater the accuracy of the fit to the measured data. However, we have observed that for most commercial polymers model molecular weight distributions or combinations thereof perform very satisfactorily. The TAOrchestrator software provides for automated fitting or alternatively, a user defined manual fit to the data. This option allows the user to override the software and obtain precise fits to the particular region of the data desired.

Two types of model molecular weight distribution are built into the TAOrchestrator software. The first is a Wesslau or log normal molecular weight distribution that is typical of addition polymers or polymers produced with Zeigler-Natta catalyst systems. The second is a Schultz distribution which is a generalized most probable molecular weight distribution more typical of polymers produced via condensation reactions or with metallocene catalysts.

REPRESENTATIVE APPLICATIONS

Figures 2 & 3 show the dynamic moduli and calculated MWD for a bidisperse system of polybutadiene. The dynamic moduli data set is complete and the MWD calculated from the complete data set method is shown juxtaposed with the MWD measured from GPC. The agreement of the rheological MWD with the GPC data is excellent.
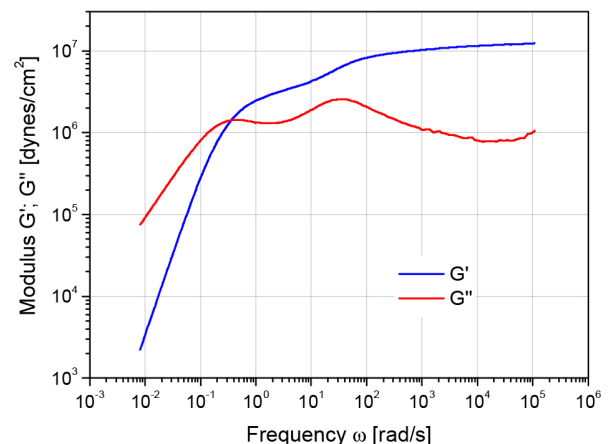

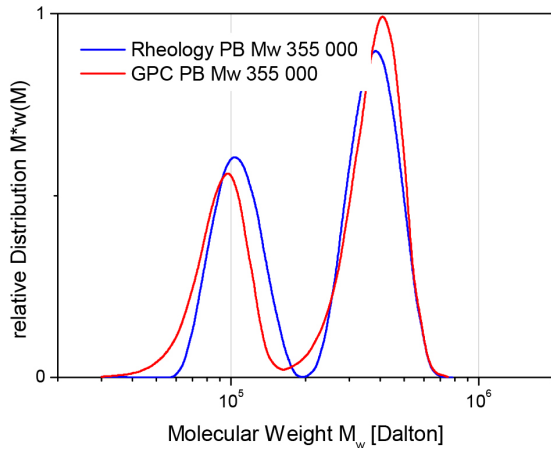Figure 2: Dynamic response of a bidisperse

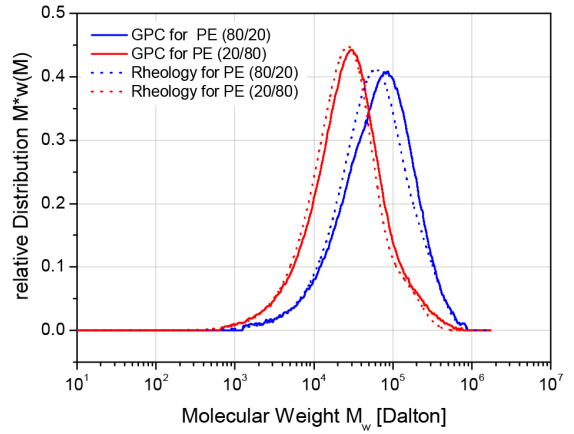*Figure 3: Calculated MWD of a bidisperse polybutadiene blend*

Figure 5: Calculated MWD of a binary polyethylene blend

Figure 4 shows two metallocene catalyzed binary polyethylene blends. The dynamic moduli data sets are definitely not complete either in the terminal region or the plateau region. Using the incomplete data set method with a combination of two Schultz model molecular weight distributions yielded the results shown in Figure 5. Clearly the agreement is very good illustrating the viability of MWD methods for practical commercial systems.
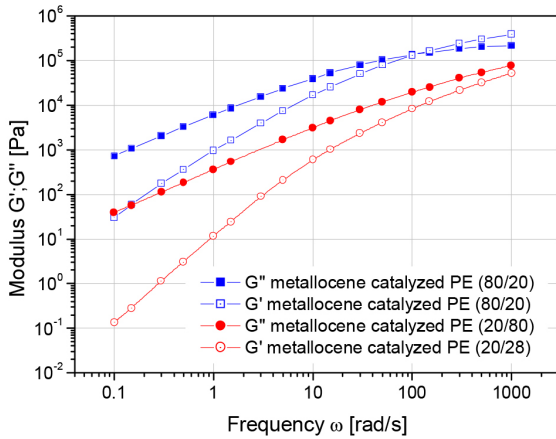

Figure 4: Dynamic response of a binary polyethylene blend

REFERENCES

/1/ Doi, M.: JNNFM 23, 151 (1987)

/2/ Tsenoglou, C.: ACS Polymer Preprints 28, 185 (1987)

/3/ des Cloizeau, J.: Macromolecules 23, 4678 (1990)

/4/ Montfort, J.P. ; Marin, G.; Monge, P.: Macromolecules 17, 1551 (1989)

/5/ Mead, D.: J.Rheol. 38, 1797 (1994)

Revised By A. Franck

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.