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Characterisation of Molecular Structure of Polymers by Rheological Methods.

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ABSTRACT

Characterising the molecular structure of polymers, such as the molecular weight and molecular weight distribution (MWD), is an important part of polymer analysis.

Changes in the molecular structure has a great impact on the rheological and processing properties of a polymer.

Therefore these parameters are extremely significant in understanding a wide range of polymer processing operations.

INTRODUCTION

In commercial polymers there is generally a wide distribution of molecular weights and in order to determine the MWD, one has to fractionate the polymer.

Classical techniques, like gel permeation chromatography (GPC) are costly in terms of both equipment and operations. In these techniques a dilute solution of the polymer is separated, based on the hydrodynamic volume of the polymer coils.

GPC yields direct data about the molecular weights, but is often based on calibration methods with distinct weakness in the high molar mass region.

Rheological methods on the contrary, have very high sensitivity for determining the higher molecular weight fraction, which are usually of greater importance solving industrial processing problems.

During the last years several rheological methods for polymer characterisation have been established. This has been made possible by the considerable progress in developing theoretical relationships between molecular parameters and material functions that can be determined through rheology.

This paper will show how dynamic and creep/recovery measurements can be used to characterise the molecular structure of polymers. The methods described will be restricted to quantify differences in molecular weight and MWD among materials.

MOLECULAR WEIGHT

Almost all polymers consist of molecules with a distribution of chain lengths. In order to characterise the molecular weight, the concept of an average molecular weight is used.

The number-average molecular weight, M_n, is the first moment and analogous to the center of gravity. The weight-average molecular weight, M_w, the second moment, corresponds to the radius of gyration. Higher moments, as M_z and M_{z+1} may also be defined.

Zero shear viscosity

When viscosity is measured at sufficient low shear rates it approaches a constant value, the zero shear viscosity, η_o.

$$\eta \rightarrow \eta_o \text{ as } \omega \rightarrow 0 \qquad (1)$$

It has been shown in many studies that the η_o depends on the weight-average molecular weight (M_w) and is independent of MWD. Below some critical molecular weight, M_c, the viscosity is direct proportional to M_w. Above M_c the dependence becomes much steeper, with viscosity varying with the 3.4-power of M_w. This is schematically shown in Fig. 1.

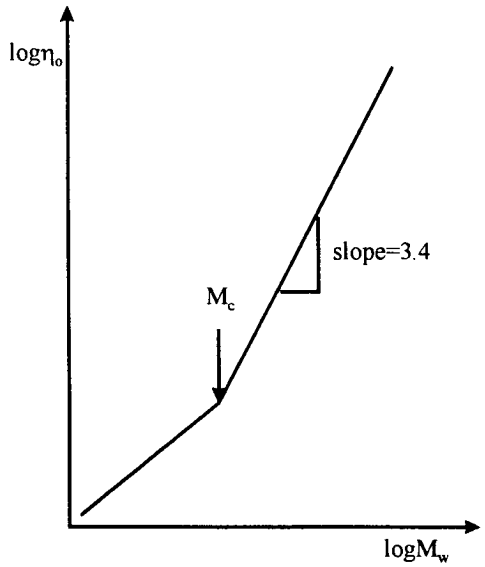

Figure 1. Molecular weight dependence of the zero shear viscosity.

This relationship can be written as:

$$\eta_o = K_1 M_w \quad \text{for } M_w < M_c \qquad (2)$$

$$\eta_o = K_2 M_w^{3.4} \quad \text{for } M_w > M_c \qquad (3)$$

This dependence has been observed experimentally for a wide range of polymers. The critical molecular weight varies widely for different polymers. M_c appears to depend primarily on chain stiffness.

It has recently been shown[1] that K_2 strongly depends on the stereoregularity of the polymer. For example, syndiotactic polypropylene exhibits a higher viscosity than an isotactic polypropylene, given at the same molecular weight.

For polymer solutions, the concentration has to be incorporated in the relationship.

$$\eta_o = K_3(cM_w)^{\alpha} \qquad (4)$$

where α is typically in the range of 0.5-1.

Crossover frequency

For polymers with high molecular weight it is not always possible to measure at sufficient low frequencies to reach the constant zero shear viscosity. On the contrary for these polymers, the cross-over frequency can often be determined. The cross-over frequency, ω_c, is defined as the frequency where $G' = G''$.

From Doi-Edwards molecular theory using the reptation concept the following relationship for the zero shear viscosity can be written:

$$\eta_o = \pi G_N^{\circ}/12\omega_c \qquad (5)$$

where G_N° is the plateau modulus.

This relationship implies that as cross-over frequency decreases, the zero shear viscosity increases and so also the molecular weight. This is shown graphically in Fig. 2.

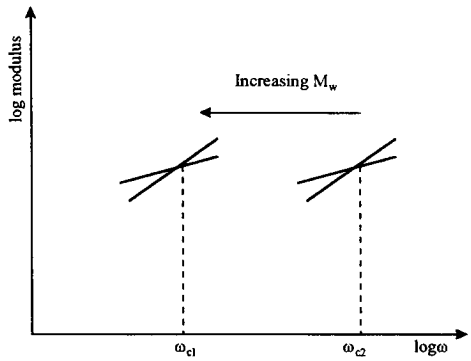

Figure 2. The cross-over frequency dependence of molecular weight.

MOLECULAR WEIGHT DISTRIBUTION

There are many different methods proposed for determining the width of the molecular weight distribution in literature. In this paper some of them will be described. The requirements for all methods are that they should be:

1. Independent of molecular weight.
2. Independent of temperature.
3. Sensitive and robust.

These requirements are best fulfilled if linear viscoelastic data are used.

Steady-state compliance

The steady-state compliance, J_e, is best determined in a creep/recovery measurement. As like the viscosity approaches a constant value at low shear rates, the steady-state compliance approaches a constant value at low stresses:

$$J_e \rightarrow J_e^\circ \text{ as } \sigma \rightarrow 0 \qquad (6)$$

From many studies and from literature it is well known that J_e° is independent of molecular weight but depends strongly on MWD. This is shown schematically in Fig. 3.

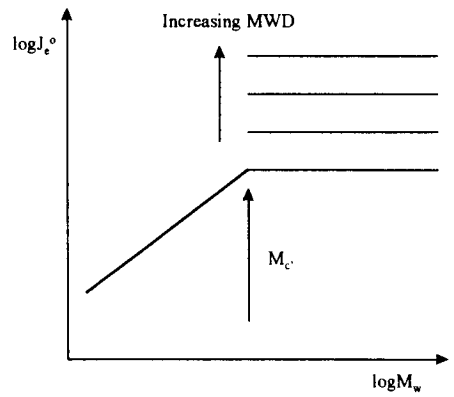

Figure 3. Molecular weight and MWD dependence of steady-state compliance.

Above $M_{c\cdot}$ the steady-state compliance is constant and independent of M_w and given by:

$$J_e^\circ = 0.4M_{c\cdot}/\delta RT \qquad (7)$$

where δ is the density, R the gas constant (8.314 kJ/mol) and T the absolute temperature in Kelvin.

Because of the very strong dependency of J_e° to MWD, exact relationships between J_e° and MWD are difficult to find. Below some relationships found in literature are given:

$$J_e^\circ = f(M_z M_{z+1}/M_w) \qquad (8)$$

$$J_e^\circ = f((M_z/M_w)^{3.7}) \qquad (9)$$

Cross-over modulus

Zeichner and Patel[2,3] have proposed a measure of polydispersity, $PI = M_w/M_n$, for polypropylenes as:

$$PI = 10^5/G_c \qquad (10)$$

where G_c is the cross-over modulus in Pa where $G' = G''$.

In Fig. 4 this relationship is graphically shown.

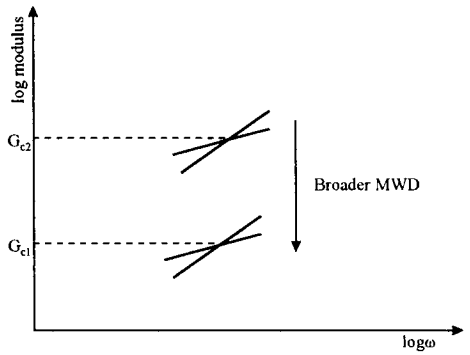

Figure 4. The cross-over modulus dependence of molecular weight distribution.

This relationship has the limitation to be valid only for polypropylenes made by Ziegler-Natta catalysis and degraded by random chain scission.

Other polydispersity measure

Shroff et al.[4] have examined and proposed several different rheological methods to measure polydispersity. Two of them will shortly be described here.

It can be shown that in the limit of low frequencies, where $\omega \rightarrow 0$ the following relationships are valid:

$$G' = J_e^{\circ}(G'')^2 \quad (11)$$

$$\tan\delta = G''/G' = G''/J_e^{\circ}(G'')^2 = 1/J_e^{\circ}G'' \quad (12)$$

The complex modulus is related to G'' through:

$$G^* = G''/\sin\delta \quad (13)$$

Combination of eqs. (12) and (13) gives:

$$\tan\delta = 1/J_e^{\circ}G^*\sin\delta \quad (14)$$

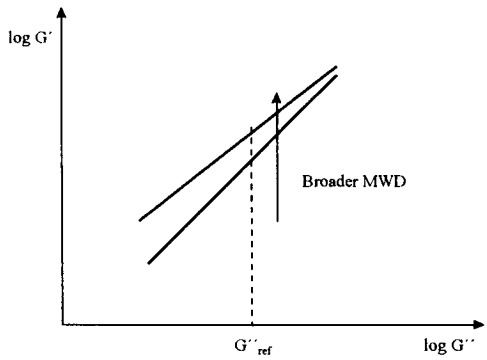

Figure 5. G' versus G'' plot.

By using eqs. (11) and (14) the following expressions for two polydispersity index can be written:

$$PI_1 = C_1G' \text{ at } G''_{ref} \quad (15)$$

$$PI_2 = C_2/G^* \text{ at } \tan\delta_{ref} \quad (16)$$

These relationships are schematically shown in Fig 5-6.

G''_{ref} is chosen as low as possible. One can use the fact that a log-log plot of G' versus G'' is very nearly linear at low frequencies and extrapolation is possible.

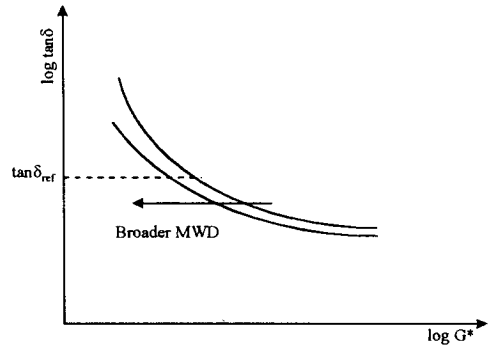

Figure 6. Tanδ versus G* plot.

The advantage of PI_2 (tanδ versus G*) is that one can use a high enough $\tan\delta_{ref}$ corresponding to low modulus values and thus characterise higher molecular weight fractions.

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