

Is the Cross-Over Modulus a Reliable Measure of Polymeric Polydispersity?

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SYNOPSIS

The answer to the question posed in the title of this paper is, "Sometimes yes and sometimes no; it depends on the specific case." The use of the reciprocal of the cross-over modulus (actually $100,000/\text{cross-over modulus}$, where the cross-over modulus has units of Pascal) as a measure of polymeric polydispersity [as determined by the M_w/M_n ratio, e.g., by gel permeation chromatography (GPC)] was first proposed by Zeichner and Patel (*Proceedings of the Second World Congress of Chemical Engineering*, Montreal, Quebec, Canada, 1981, p. 333) specifically for polypropylenes made by Ziegler–Natta catalysis and degraded by chain scission. However, their correlation is now being indiscriminately used without ensuring the applicability of the assumptions underlying the work of Zeichner and Patel to the specific case being considered. While Zeichner and Patel's correlation is indeed true in certain specific cases, it is not true in all cases. It would do well to dispel the apparently widespread misconception, especially among industrial rheologists, that the reciprocal of the cross-over modulus can always be used indiscriminately as a measure of polymeric polydispersity, and to emphasize the strict limitations under which this can indeed be done. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

The use of the reciprocal of the cross-over modulus (actually $100,000/\text{cross-over modulus}$, where the cross-over modulus has units of Pascal) as a measure of polymeric polydispersity [as determined by the M_w/M_n ratio, e.g., by gel permeation chromatography (GPC)] was first proposed by Zeichner and Patel¹ specifically for polypropylenes made by Ziegler–Natta catalysis and degraded by chain scission. However, their correlation is now being indiscriminately used without ensuring the applicability of the assumptions underlying in the work of Zeichner and Patel¹ to the specific case being considered. While Zeichner and

Patel's correlation is indeed true in certain specific cases, it is not true in all cases. A good analogy would be the fact that the melt-index² sometimes (but not always) correlates with the molecular weight. It is unlikely that a single rheological parameter (cross-over modulus) can always adequately determine the polydispersity (M_w/M_n ratio).

EXPERIMENTAL

Oscillatory measurements were made on a Bohlin CSM Rheometer. This rheometer is kept under statistical control^{3,4} to ensure the reliability of oscillatory measurements. The precision behavior of oscillatory measurements made on this rheometer is documented in literature.^{5,6} GPC was done using a Millipore Waters 150-C instrument which is kept under statistical control using a regular

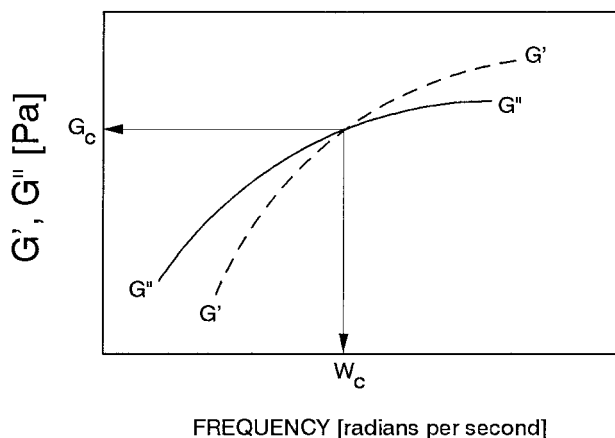


Figure 1 Pictorial depiction of cross-over modulus (G_c).

monitor program to ensure the reliability and accuracy of the measurements. The GPC is calibrated periodically with broad polypropylene standards.

RESULTS AND DISCUSSION

Storage (G') and loss (G'') moduli are measured by dynamic oscillation in the linear viscoelastic region for polymeric melts. The cross-over point of G' and G'' is called the cross-over modulus (G_c ; units = Pascal) and is depicted pictorially in Figure 1. The use of $100,000/\text{cross-over modulus}$ to determine the polydispersity (as measured by the M_w/M_n ratio, e.g., by GPC) as an absolute truth for all polymeric melts is a widespread misconception (especially among industrial rheologists). For example, Zahavich et al.⁷ use this cross-over modulus correlation to make conclusions about MWD changes with an increase in extrusion passes for HDPE. Eggen and Sommerfeldt⁸ make conclusions of the molecular weight distribution of various blow-molding HDPE resins based on this cross-over modulus correlation. Such conclusions are not necessarily always valid.

It is important to note that there are several cases where the correlation between $100,000/\text{cross-over modulus}$ and M_w/M_n ratio (determined, for example, by GPC) does not hold (even for PP). The use of $100,000/\text{cross-over modulus}$ was first proposed by Zeichner and Patel¹ for polypropylenes only and has been modified by Yoo.⁹ The situation for polyethylenes is probably a lot more complicated than polypropylenes since PE can crosslink as well as degrade and can also have

long- and/or short-chain branching. Indeed, Zeichner and Patel¹ specifically state that "The success of η_o and PI in characterizing melt flow properties is a result of similarities in molecular weight distribution of polypropylenes made by Ziegler-Natta catalysis and degraded by random chain scission." It would do well to dispel the apparently widespread misconception, especially among industrial rheologists, that $100,000/\text{cross-over modulus}$ can always be indiscriminately used as a measure of MWD, and to emphasize the strict limitations under which this can indeed be done.

For example, I tested two polypropylene resins (A and B). The GPC results were, respectively, 48,600 and 55,800 daltons for M_n , 234,000 and 275,000 daltons for M_w and, hence, 4.81 and 4.93 for the GPC polydispersity (defined as the ratio of M_w to M_n). Oscillatory measurements were also made on two different samples (for each of A and B) and three ascending and three descending sweeps were run on each sample (thus a total of 12 frequency sweeps were made on each resin). The averages of these 12 measurements of the cross-over modulus were 24,400 and 36,700 Pa for A and B, respectively. The corresponding Relative Standard Deviation, or RSD, were 1.15 and 1.83%, indicating the rheological measurements are very reproducible [RSD is defined as (standard deviation)*100/average].^{5,6} The rheological PI, calculated as $100,000/\text{cross-over modulus}$, are thus 4.10 and 2.72, respectively. Not only do the numerical values for the PI calculated from rheology and GPC disagree, but their relative ranking is also different.

This issue was also discussed by Chambon at the ANTEC-95 Conference, who provided his own data.¹⁰ Chambon pointed out that the rheological PI (calculated as $100,000/\text{cross-over modulus}$) relies only upon a single point of the relaxation process which, in addition, lies at a relatively short time scale. Chambon concluded that the "correlation found by Zeichner and Patel between the PI index and M_w/M_n (ratio) is not of general validity".¹⁰ Instead, Chambon proposes a method based on $\tan \delta$ to give a quantitative prediction of MWD via M_z/M_w .

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NOMENCLATURE

M_n = number-average molecular weight (daltons)

M_w = weight-average molecular weight (daltons)

M_z = z-average molecular weight (daltons)

PI = polydispersity index

Rheological PI = 100,000/cross-over modulus (units for cross-over modulus are Pa)

GPC PI = M_w/M_n ratio

η^* = complex viscosity [a complex number with phase angle (in radians) and magnitude (in Pa.s) components]

$|\eta^*|$ = magnitude of complex viscosity (Pa.s)

η_o = zero-shear viscosity (Pa.s)

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