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Rheological Techniques for Determining Degradation of Polylactic Acid in Bioresorbable Medical Polymer Systems

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Abstract. A method developed in the 1980s for the conversion of linear rheological data to molar mass distribution is revisited in the context of degradable polymers. The method is first applied using linear rheology for a linear polystyrene, for which all conversion parameters are known. A proof of principle is then carried out on four polycarbonate grades. Finally, preliminary results are shown on degradable polylactides. The application of this method to degrading polymer systems, and to systems containing nanofillers, is also discussed. This work forms part of a wider study of bioresorbable nanocomposites using polylactides, novel hydroxyapatite nanoparticles and tailored dispersants for medical applications.

Keywords: Polylactic acid, melt processing, oscillatory shear rheology, molar mass distribution
PACS: 83.85.Cg, 83.60.Bc, 81.20.Hy

INTRODUCTION

Determination of the molecular weight distribution (MWD) of polymers, and of its commonly used averages M_n and M_w, is fundamental in understanding their behaviour in both melt and solid states [1]. Nowadays this is traditionally measured using chromatographic (GPC) methods, but this technique relies on eluting a solution through porous columns. This makes GPC impractical for polymers that do not readily dissolve in solvents (eg. fluoropolymers) and polymer nanocomposites whose fillers interact with columns in an undesirable fashion. A connection between the rheological response and the MWD was first explored by Wu, who transformed the storage modulus, G', into a MWD [2]. Tuminello further refined this method to improve MWD predictions, validated the technique on several grades of polystyrene (PS) [3], and later employed the method on insoluble polytetrafluoroethylene (PTFE) [4].

As part of a wide-ranging study of degradation of polymer nanocomposites for medical applications, our laboratory is seeking to develop a simple method of detecting polymer matrix degradation in degrading polylactide nanocomposites during or after melt processing. Although there are solvent-based techniques such as Soxhlet extraction for separation of matrix and nanoparticles, rheological techniques that do not require large quantities of material of the use of solvents are desirable. This work outlines the methodology and presents preliminary attempts of the application of Tuminello's method on three polymers. The strategy for applying the method to nanocomposites is also discussed.

MATERIALS AND METHODS

The polymers used in this study consist of one linear atactic polystyrene (PS) DOW GP PS680E, four Makrolon polycarbonates of varying viscosities; two NatureWorks packaging grade polylactides (PLA), and one Evonik medical device grade PLA. Table 1 reports the average molar mass measurements obtained by GPC and the melt flow rate (MFR) as reported by the manufacturers. The eluent used as a solvent is tetrahydrofuran for PS and PC, and methylene chloride for PLA.

Linear rheology of PS is obtained from ref. [1], and of PC from ref. [5]. Linear rheology of PLA was measured using a Bohlin C-VOR Instruments rheometer fitted with an environmental chamber. Measurements were performed in stress-controlled oscillatory shear over a range of frequencies between 3.14 and 314 rad s^{-1}, at temperatures between 130 °C and 180 °C, using a 25 mm parallel plate geometry with a 0.5 mm gap size in air atmosphere. Disc specimens were compression moulded at 170 °C.

TABLE 1. Molar mass averages obtained from GPC and from Tuminello's method, and melt flow rates (MFR)

Materials	Code	MFR (g 10min^{-1})	GPC			Rheology (Tuminello's method)		
			M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
Polystyrene								
Dow	GP PS680E	n/a	74700	149200	1.99	73800	144200	1.95
Polycarbonate								
BASF Makrolon	2205	37[1]	13900	33600	2.73	16100	28100	1.75
	2405	20[1]	14200	38700	2.73	18700	35400	1.89
	2805	10[1]	18000	45700	2.54	25000	46400	1.86
	3105	6.5[1]	21400	50500	2.36	25300	55304	2.19
Polylactides								
NatureWorks	3251D	80[2]	45500	64200	1.41	54600	90500	1.66
	2003D	6.0[2]	87100	130600	1.50	93300	187600	2.01
Evonik	LR 706	n/a[3]	308600	445900	1.45	239300	522100	2.18

[1] At 300 °C, 1.2 kg; [2] At 210 °C, 2.16 kg; [3] Inherent viscosity (25 °C, 0.1%, chloroform) = 4.0 dl g^{-1}

RESULTS AND DISCUSSION

Application of Tuminello's method

Time-temperature superposition was applied to the rheological data used to obtain mastercurves for $G'(\omega)$ using the rheological tool Reptate [6] as shown in Figure 1 for all materials. The transformation of the rheological response into a MWD is based on the principle that the decrease of G' with frequency can be described by the progressive disentanglement of chains from low to high molar mass.
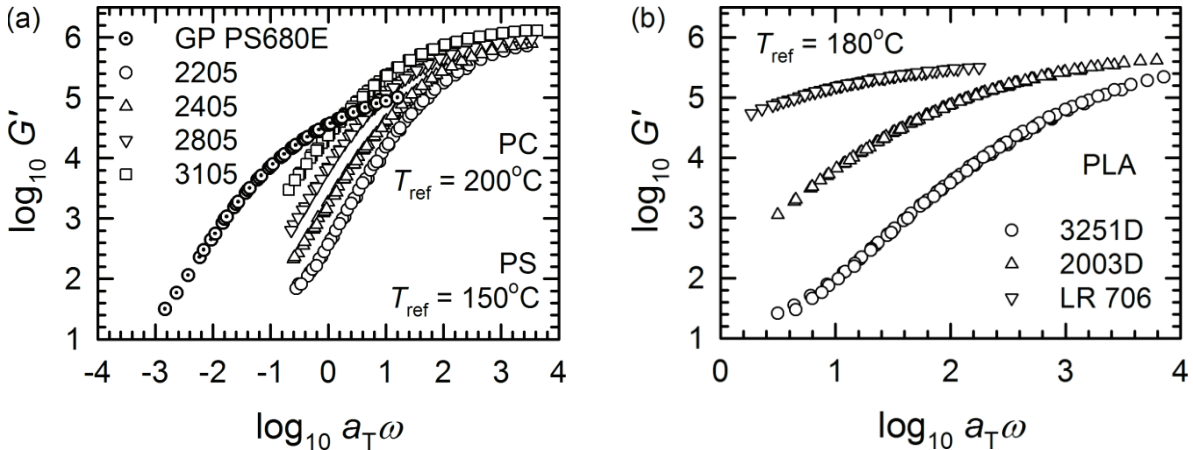

FIGURE 1. Reduced frequency mastercurves of (a) PS from [1] ($T_\text{ref} = 150$ °C) and PC from [5] ($T_\text{ref} = 200$ °C), and (b) PLA ($T_\text{ref} = 180$ °C)

Tuminello's approach is based on two important assumptions. The first is that unrelaxed chains at a given frequency ω are diluted by relaxed chains. Based on principles derived from the theory of concentrated polymer solutions, Tuminello proposed a proportionality between the volume fraction and the square root of the unrelaxed chains' contribution to the reduced modulus $G'(\omega)$. Ignoring density corrections, the weight fraction of the unrelaxed chains, W_u is expressed in terms of the plateau modulus G_N^0 [3]

$$W_\text{u} = \left(\frac{G'(\omega)}{G_N^0} \right)^{0.5}$$

(1)

The second assumption is that each component of the MWD has a single relaxation time. Above this time, a particular fraction does not contribute to G'. This is, of course, not entirely true since even monodisperse polymers

have a distribution of relaxation times, but based on these assumptions, G_N^0 is the modulus of all unrelaxed chains. W_u is fitted to a function of the form [3]

$$W_u = 0.5\left[\sum_i^N A_i\left(1+\tanh\left(B_i\left(\omega+C_i\right)\right)\right)\right]$$ (2)

where N denotes the order of the function, and A_i, B_i and C_i are fitting parameters (subject to $\Sigma A_i = 1$) that determine the curve's breadth and the position on the abscissa. The fit was carried out using a least squares using an in-house optimiser. Figure 2 illustrates this procedure for GP PS680E. A one-term fit was sufficient for all materials.
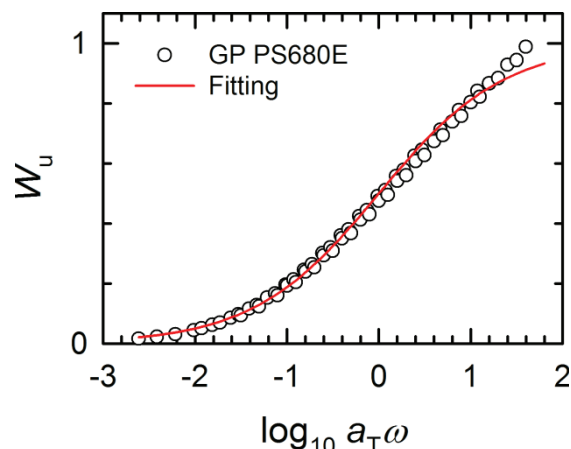

FIGURE 2. The weight fraction of the unrelaxed GP PS680E chains as a function of the reduced frequency. The circles are experimental data and the solid line represents the fitted curve according to Equation (2)

The frequency axis is then transformed to molar mass M using

$$\frac{1}{\omega} = K_1 M^{3.4}$$ (3)

Tuminello determined the scaling constant $K_1 = 1.04 \times 10^{-17}$ for PS at a reference temperature of $T_{ref} = 160\ ^\circ$C using a wide range of PS grades, by plotting the frequency at the maximum of $\dfrac{dW_u}{d\omega}$ as a function of the peak molar mass, M_p, as obtained from GPC measurements [3]. The MWD obtained using this method is compared to the MWD obtained from GPC for GP PS680E in Figure 3, illustrating excellent agreement between the methods. Weight and number averages are computed for these distributions and are shown in Table 1.
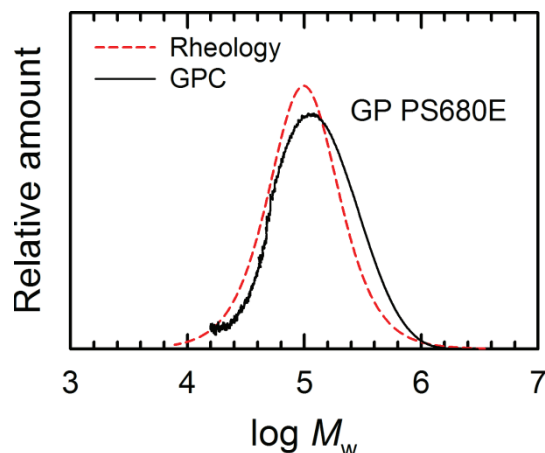

FIGURE 3. Molecular weight distribution of GP PS680E determined from GPC (solid black line) and rheometry using Tuminello's method (dashed red line)

Determination of the scaling constant

A value of K_1 can be determined for a new polymer using Equation (3) applied to a sufficiently broad range of molecular weights. This was carried out for the four PC grades, producing $K_1 = 1.47 \times 10^{-17}$ at $T_{ref} = 200$ °C. The resulting MWDs are shown in Figure 4(a), and the averages in Table 1. There is reasonable agreement between averages obtained by GPC and by Tuminello's method, with maximum deviations of +39% and -16% relative to M_n and M_w by GPC respectively. The distributions obtained (i.e. the PDIs) via rheology are narrower than those obtained via GPC. One factor that affects the breadth of the distribution is the exponent of 3.4 in Equation (3). There are some suggestions that this exponent can be polymer specific - for instance, values of 4.2 [7] and 5.7 [5] have been reported for PC. A higher exponent narrows the width of the distribution, and therefore it is unlikely that this is the explanation for the discrepancy observed here. The more probable cause is the fact that K_1 was determined on a relatively narrow range of molecular weights.
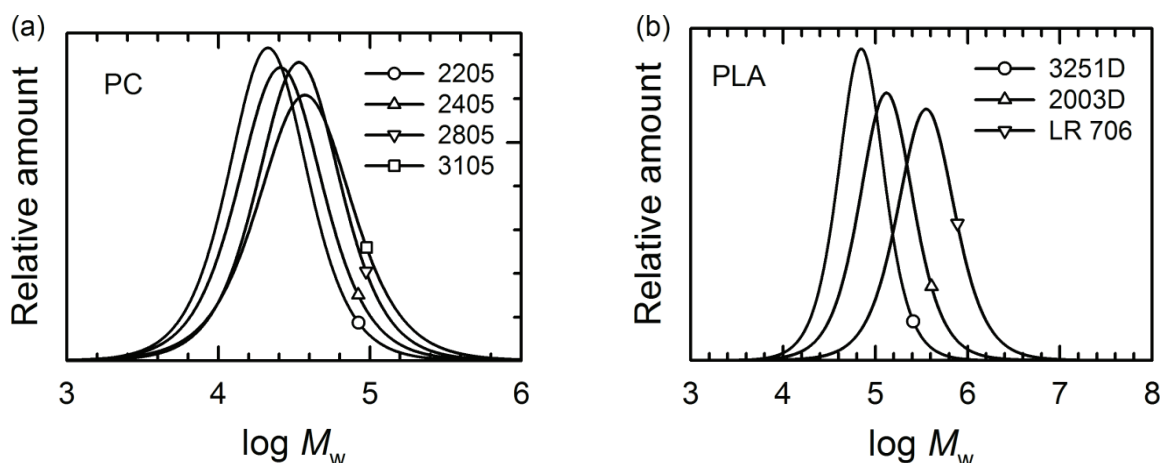
(a)

(b)

FIGURE 4. The MWDs of (a) PCs of increasing viscosities using $K_1 = 1.47 \times 10^{-17}$ at $T_{ref} = 200$ °C, and of (b) three grades of PLA using $K_1 = 1.88 \times 10^{-20}$ at $T_{ref} = 180$ °C

The determination of K_1 was carried out for the PLA grades, yielding a value of 1.88×10^{-20} at $T_{ref} = 180$ °C. Figure 4(b) shows the transformed MWDs. The molar mass distributions of the NatureWorks grades obtained by this method are consistent with the MFR data shown in Table 1. There is reasonable agreement between averages obtained by GPC and by Tuminello's method, with maximum deviations in M_n and M_w relative to GPC of -22% and +44% respectively. The PLA distributions obtained via rheology are broader (i.e. greater PDI) than those obtained by GPC. An explanation for the deviation could be attributed to the uncertainty in the K_1 value. Nevertheless, these preliminary results show promising potential for employing Tuminello's method on biodegradable polymers.

In order to obtain better estimates of K_1 for both PC and PLA, a larger study is required employing a broader range of molecular weights. A further small correction to M_w based on the zero shear viscosity can also be applied [3], but was not employed here.

Application to degradable polymers

There are further challenges in the application of Tuminello's technique to degradable polymers such as polylactides. A fundamental issue is that rheological measurements in the terminal region require high measurement temperatures, and the polymer is at risk of degradation *during* the experiment. Although some steps can be taken, such as careful drying and carrying out experiments in inert atmospheres, we can only suggest that a lower temperature measurement is repeated at the start and end of a rheological run in order to exclude substantial degradation. Figure 1(b) illustrates that, in the case of LR 706, this dataset can be very limited and far from the terminal region. An additional challenge is that some polylactides are crystallising, and this creates a lowerbound for measurement temperatures beyond which crystallization sets in. Finally, degradation may lead to bimodal or skewed distributions, which could be better captured through the use of higher order functions ($N>1$).

Application to nanocomposites

One strategy to determine MWDs of the matrix polymer in nanocomposites is to employ a model able to describe the effect of nanoparticles on the rheological response. From this, one can compute a matrix rheology which, in turn, can be transformed using the method described above to a MWD. One such two-phase model for the prediction of nanocomposite moduli was proposed by Song and Zheng, given as [8]

$$G'_{\text{nanocomposite}}(\omega) = A_{\text{f}} \sum_{j=0}^{3} G'_j \omega^j + G'_{\text{filler}} \omega^{\alpha}, \quad G''_{\text{nanocomposite}}(\omega) = A_{\text{f}} \sum_{j=0}^{3} G''_j \omega^j + G''_{\text{filler}} \tag{4}$$

Here, parameters A_{f}, α, G'_{filler} and G''_{filler} describe the contribution of the filler. In a previous study carried out in our laboratory on PC nanocomposites, these parameters were found to be relatively independent of matrix polymer MWD [5]. Research is on-going on the application of this technique to both PC-CNT nanocomposites and degrading PLA-hydroxyapatite nanocomposites. The sensitivity of the rheological response to molar mass, and the relative ease of the application of this technique compared with Soxhlet extraction followed by GPC suggest that this method may be the most appropriate for detection of degradation in degradable polymer nanocomposites.

CONCLUSIONS

This paper has revisited an existing method for the conversion of linear rheological data to molar mass distribution within the context of degradable polymers. The method was applied to linear rheology for a linear polystyrene, and weight average and number average molecular weights were within 1% and 3% of GPC values respectively. The technique was then applied to four polycarbonate grades, whose conversion parameters are not known, and K_1 was found to be 1.47 x 10^{-17}, producing averages within 39% and 16% of M_{n} and M_{w} GPC values respectively. When the method was applied to three PLA grades, K_1 was determined as 1.88 x 10^{-20}, producing maximum deviations of -22% and +44% in M_{n} and M_{w} respectively relative to GPC values. Further challenges concerning the application of the method to degradable polymer systems are discussed. A process for applying a two-phase model to enable matrix polymer distribution to be measured in polymer nanocomposites is suggested.

ACKNOWLEDGEMENTS

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