



# A method for the determination and correction of the effect of thermal degradation on the viscoelastic properties of degradable polymers



Gabriel Y.H. Choong<sup>\*</sup>, Davide S.A. De Focatiis

Composites Research Group, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

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## ABSTRACT

Small amplitude oscillatory shear is carried out during isothermal degradation of poly(lactic acid) (PLA) in order to determine the evolution of the characteristic relaxation time with degradation time and temperature. After reducing the relaxation time data to a single mastercurve, a 4-parameter function is fitted to the data to allow prediction of the change in relaxation time following an arbitrary thermal history. The method enables separation of the effects of temperature and of degradation on the relaxation time, both of which lead to a horizontal shift of dynamic data along the frequency axis, and hence enable a correction for thermal degradation during rheometry to be carried out. To validate the method, two isothermal frequency sweeps were measured with different temperature histories, producing different mastercurves due to dissimilar in-test thermal degradation. After correcting for thermal degradation using the function and the thermal histories, the two frequency sweeps reduce to the same viscoelastic mastercurve in the undegraded pre-test state.

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## 1. Introduction

Biodegradable polymers have generated significant interest in both research and industrial communities, and degradable polyesters are the most widely studied of these. Their degradation is linked to their renewable origins, and helps to close the lifecycle with reduced waste build-up and environmental strain. In comparison with traditional commodity polymers, degradable polymers also degrade more readily during melt processing, and consideration of this effect is critical to both manufacture and end use. This is particularly important since processing conditions dictate final product properties in many product types. Therefore, if degradable polymers are to be successfully used in conventional melt processes employed to mass-produce plastic parts, it is fundamentally important to understand and predict polymer thermal degradation and its effect on the melt rheology.

Poly(lactic acid) (PLA) is a widely used degradable polyester produced commercially via ring opening polymerisation of lactides catalysed by stannous octoate. The stereochemical structure of PLA determines the crystallinity of the polymer, and hence influences processing, bulk properties and degradation behaviour. PLA has

become the forerunner among bio-based polymers, attributed mainly to the readily available supply and attractive cost. Currently, applications of polylactides range from disposable food serviceware and packaging through to resorbable medical devices such as orthopaedic screws, fracture fixation plates and sutures [1]. The competitive performance, sustainability and cost of PLA have also motivated efforts to develop degradable composites employing PLA as the base matrix [2–4].

Several characterisation methods have been used to study degradation of PLA, including thermogravimetric analysis (TGA), pyrolysis, thermal degradation process monitoring (TDPM) and different types of rheometric techniques. TGA measures the weight loss during degradation and the information is directly employed to determine kinetic parameters [5,6]. Pyrolysis involves decomposition at high temperatures (up to 600 °C) in the absence of oxygen, followed by chemical analysis to detect and identify released products [7]. These methods are useful for more significant degradation, but they are relatively insensitive to small levels of degradation in high molar mass polymers. TDPM consists of chromatographic measurements of molar mass after different thermal histories; kinetic parameters can be computed based on mathematical models that describe degradation statistically via specific reaction pathways [8–10]. The method is applicable also to smaller degrees of degradation, but requires a large number of sampling intervals to be viable.

<sup>\*</sup> Corresponding author.

E-mail address: [gabriel.choong@nottingham.ac.uk](mailto:gabriel.choong@nottingham.ac.uk) (G.Y.H. Choong).

Rheometric techniques rely on monitoring the effect of molar mass change on manifestations of polymer viscoelasticity, by exploiting the sensitivity of rheological measurements to changes in molar mass. The reptation time  $\tau$  is a measure of the timescale associated with motion of the whole polymer chains, and is strongly dependent on the length of the chains. For entangled melts,  $\tau$  follows a power-law relationship, scaling with molar mass with an exponent of between 3 and 3.7 [11]. Several authors have recorded changes in complex viscosity over time under isothermal conditions to study the thermal degradation of biodegradable aliphatic polyesters [12,13] and polyhydroxyalkanoates [14].

Poly lactides have poor thermal stability which can significantly reduce the molar mass of polymer chains at elevated temperatures, and in turn strongly affect melt-state and solid-state properties [5]. This presents major challenges to thermal characterisation techniques since the molar mass distribution can change during characterisation experiments. The issue can be addressed experimentally in two ways: the timescale of tests can be reduced, or the timescale of thermal degradation reduced through the introduction of stabilisers.

Using the first method, Dorgan et al. managed to reduce their measurement time to 5 min when characterising the terminal region of PLA using rheometry at 180 °C, but even with this reduction in time, a drop of 5.5% in melt viscosity was observed [15]. Reductions in measurement time are possible in some cases, but usually at the expense of experimental accuracy, in particular with respect to thermal equilibration time.

Several authors opted for the second method. Waschen et al. added tropolone (0.75 wt%) to L-lactide PLA (57 kDa) during compounding, which reduces degradation by deactivating the residual tin catalyst [9]. Dorgan and co-workers added tris(nonylphenyl) phosphite (TNPP) to a range of poly lactides [15–17], and postulated that the stabiliser functions to reconnect broken polymer chains caused by ongoing degradation. Nevertheless, identification of a suitable TNPP concentration had to be carried out for each system since the stabiliser seeks to balance the rate of degradation with the rate of chain extension, and an excess of stabiliser can cause an unwanted increase in molar mass during rheometry, and hence in viscoelastic moduli [17]. Stabilisers have also been used to enhance thermal stability of PLA nanocomposites filled with organo-modified clay, although the fillers' presence required an increase in stabiliser concentration [4]. While thermal stabilisers can help to alleviate the problem of thermal degradation, determination of the appropriate concentration can be a problem, and there are instances where some additives may be undesirable, such as in medical applications.

In this work, a rheometric method is employed to determine the temperature dependence of thermal degradation on PLA without the need for thermal stabilisers. The aim is to understand and account for the influence of degradation on the rheological response, and hence to be able to identify the state of the polymer prior to the thermal degradation following a particular thermal history. The approach is validated by demonstrating the ability of the method to correct two different viscoelastic mastercurves obtained by subjecting the same material to different thermal histories, and hence to variations in thermal degradation during the experiments.

## 2. Materials and methods

A medical grade poly(L-lactide-co-D,L-lactide) (PLDLA), Resomer LR 706 S, with isomer composition ratio of 70:30 designed for medical device applications was obtained from Evonik Industries A.G. The end-groups are ester terminated, and the grade is classified as having low residual monomer content due to supercritical CO<sub>2</sub> extraction in manufacturing. The number and weight molar

mass averages,  $M_n$  and  $M_w$ , were measured as  $300 \pm 2$  kDa and  $464 \pm 7$  kDa respectively using GPC equipped with a multi-angle light scattering detector at 30 °C in methylene chloride, using a value of  $dn/dc = 0.035$  mL g<sup>-1</sup>. The glass transition temperature,  $T_g$ , of the amorphous PLA is  $59.8 \pm 0.1$  °C as measured by differential scanning calorimetry with a heating rate of 10 °C min<sup>-1</sup>.

### 2.1. Sample preparation

Prior to moulding, granules of PLDLA were removed from freezer storage (–19 °C) and allowed to thaw in a desiccator for a minimum of 8 h. The granules were dried in a vacuum oven at 50 °C for a minimum of 12 h. Circular discs 25 mm in diameter and 0.5 mm in thickness were compression moulded using an in-house heated press. Compression moulding was carried out at 170 °C, including a 10 min warm-up period, a 3 min stage in which the pressure was applied and released repeatedly in order to dislodge trapped air, and a further 3 min of holding at the moulding temperature under light pressure to allow for relaxation of the polymer. After this time, the mould was cooled and removed from the press when the temperature was sufficiently below  $T_g$ . Disc specimens were stored in a desiccator cabinet at ambient temperature for no longer than 5 days prior to rheometry.

### 2.2. Degradation rheometry

Dynamic rheometry was performed using an Anton Paar MCR302 rheometer fitted with a CTD 450 environmental chamber. Oscillatory shear measurements were performed using a 25 mm parallel plate geometry with a 0.5 mm gap size under dry air atmosphere. All measurements were performed at a strain amplitude of 0.1% (within the linear viscoelastic limit) with gap correction. Temperature was controlled to within a tolerance of  $\pm 1$  °C during all isothermal tests, and logged using a thermocouple at the base of the lower parallel plate.

In order to study the evolution of the characteristic relaxation time with degradation time, isothermal frequency sweeps were carried out at constant time intervals across a residence time ranging between 1 h and 6 h depending on the temperature. Residence time is intended as the total time the specimen spends at the degradation temperature, prior to and during rheometry. The interval time between each sweep was varied between 30 s and 1200 s, depending on the test temperature, with shorter intervals used at higher temperatures. The residence times were decreased with increasing test temperature which ranged from 160 °C to 220 °C in 10 °C steps. A fresh specimen was used for each temperature studied. The frequency range for all temperatures was between 0.5 rad s<sup>-1</sup> and 600 rad s<sup>-1</sup>. Each isothermal condition required a different frequency range, typically covering two orders of magnitude, since the cross-over frequency is temperature dependent and shifts towards a higher frequency as degradation takes place. After loading the specimen between the plates, the time taken to close the gap, trim the specimen and return to the set point temperature was measured and accounted for in the residence time. The viscoelastic data was limited to 3 oscillation periods per frequency in order to reduce and to obtain a more precise time stamp of data acquisition for each data point.

### 2.3. Mastercurve rheometry

In order to construct viscoelastic mastercurves, standard isothermal frequency sweeps were carried out at logarithmically decreasing frequencies from 50 to 1 rad s<sup>-1</sup>, at a fixed strain amplitude of 1%. Frequency sweeps were performed at 130 °C, 150 °C, 170 °C and 210 °C in both decreasing and increasing

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