

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



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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.

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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 τ 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, τ 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].

Polyactides 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 polyactides [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 CO₂ extraction in manufacturing. The number and weight molar

mass averages, M_n and M_w , were measured as 300 ± 2 kDa and 464 ± 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⁻¹. The glass transition temperature, T_g , of the amorphous PLA is 59.8 ± 0.1 °C as measured by differential scanning calorimetry with a heating rate of 10 °C min⁻¹.

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 ± 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⁻¹ and 600 rad s⁻¹. 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⁻¹, 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

temperature directions but with separate fresh specimens for each temperature direction. Disc specimens were loaded at either 130 °C or 210 °C, depending on the initial temperature of the test.

3. Results

3.1. Evolution of relaxation time with degradation

Fig. 1 illustrates an example of selected frequency sweeps for an isothermal test at 170 °C over a residence time of $\sim 2 \times 10^4$ s. Since the material is undergoing thermal degradation during the experiment, the term degradation time t_{deg} is adopted to refer to the elapsed time at the test temperature. The shift of the cross-over frequency towards higher frequencies (i.e. reducing relaxation times) with increasing degradation time indicates that the molar mass of the polymer is decreasing during the experiment. The characteristic relaxation time τ is approximated by the inverse of the cross-over frequency, where the storage modulus, G' is equal to the loss modulus, G'' .

At sufficiently high temperatures, PLA undergoes changes in molar mass due to complex thermal degradation attributed to chain scission, de-polymerisation generating additional residual monomer, and recombination reactions, and these all lead to the observed changes in the linear viscoelastic response. These processes may be affected in different ways by temperature, but also by the specific type of end groups, residual monomer and moisture content [18,19]. In the following text we use the term 'thermal degradation' to encompass the combined effect from all of these processes, whilst the term 'undegraded state' refers to the pre-test state, prior to the application of heat and rheometric measurements.

Fig. 2 reports the measured relaxation times as a function of thermal degradation time during isothermal residence at $T = 160\text{--}220$ °C in 10 °C steps. All temperatures investigated exhibited the same general trend, of decreasing relaxation time with increasing residence time. The rate of degradation (indicated by the gradient of the line) is smaller at shorter times and lower temperatures. As temperature and time increase, so does the rate of degradation, until a similar degradation rate is seen in all tests at a sufficiently high temperature.

In Fig. 2, the relaxation time differs between temperatures even at short degradation times. This effect is attributed to the temperature dependence of the relaxation time, and linked with chain mobility rather than degradation. Classically, in polymer melts in the absence of degradation, the temperature dependence of the

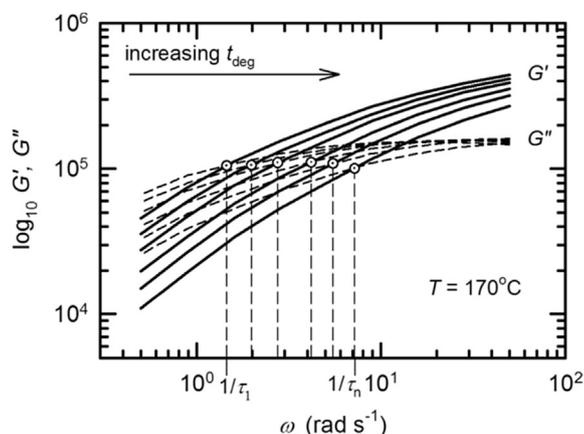


Fig. 1. Evolution of the cross-over frequency (indicated by dotted circles) with increasing degradation time at 170 °C. Only 6 sweeps are shown for clarity.

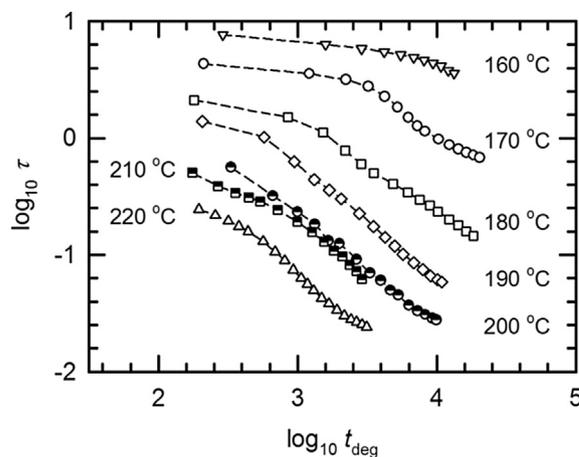


Fig. 2. Evolution of the characteristic relaxation time with degradation time for temperatures ranging between 160 °C and 220 °C. Dashed lines are a guide to the eye.

relaxation time is what allows time-dependent or frequency-dependent behaviour to be shifted to an arbitrary reference temperature using a shift factor, in order to construct viscoelastic mastercurves. This process is known as time-temperature superposition (TTS), and enables the study of time-dependent materials at timescales beyond the limitations of laboratory equipment. The temperature dependence of shift factors above the glass transition is commonly modelled using the William-Landel-Ferry (WLF) equation, given as

$$\log a_T = \frac{-C_1(T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})} \quad (1)$$

where C_1 and C_2 are empirical constants for a given reference temperature T_{ref} . Using data from the frequency sweeps, optimisation of the WLF parameters was carried out using REPTATE, a tool for analysis of rheological data [20]. Vertical shifting of the moduli was ignored due to the negligible effects of temperature on density for PLA resulting in vertical shift factors close to unity [21]. Using the data from the decreasing temperature frequency sweep, the parameters obtained for $T_{\text{ref}} = 170$ °C were $C_1 = 2.43$ and $C_2 = 120$ °C. It is acknowledged that at this stage there is error in this process since degradation also affects the isothermal frequency sweeps used to obtain the WLF parameters.

From these WLF parameters, a shift factor a_T is obtained for each degradation test temperature so that relaxation times $\tau^* = \tau/a_T$ can be computed at a single reference temperature T^* . Fig. 3 shows the evolution of relaxation times from Fig. 2 as a function of degradation time shifted to a reference temperature $T^* = 170$ °C.

It is apparent in Fig. 3 that degradation at different residence temperatures is affecting the polymer at different rates. It is possible to extract the rate effect of temperature on degradation by a horizontal shift along the degradation time axis. This was carried out manually, by applying a multiplicative factor $a_D(T)$ to the measured t_{deg} for each measurement temperature set until qualitatively satisfactory overlap of data from different temperatures was achieved. The reference temperature for degradation was maintained at $T_D = T^* = 170$ °C. This produces the degradation mastercurve illustrated in Fig. 4. The possibility of constructing such a mastercurve suggests that, across the time and temperature ranges explored, the different processes contributing to thermal degradation scale with time and temperature in the same way.

The degradation shift factors obtained from the data follow a

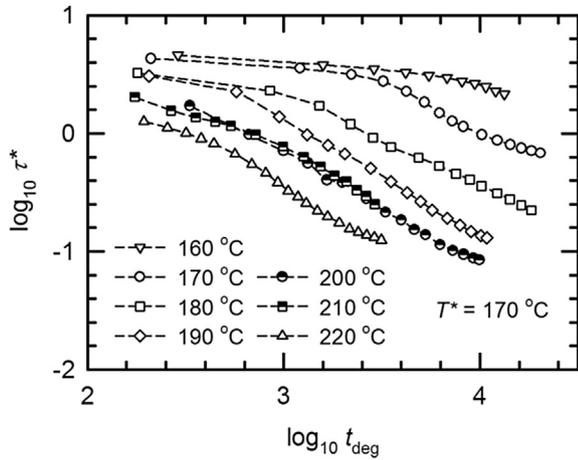


Fig. 3. Relaxation times τ^* measured for a range of temperatures at a reference temperature $T^* = 170^\circ\text{C}$. Relaxation times were vertically shifted by temperature-dependent shift factors obtained from separate frequency sweeps. Dashed lines are a guide to the eye.

distinctive pattern, which is well described by an Arrhenius equation of the form

$$\ln a_D(T) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_D} \right) \quad (2)$$

where E_a is an activation energy, R is the universal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), and T and T_D are the test and reference degradation temperatures respectively. The shift factors are plotted in linearised form in Fig. 5, and a regression line applied to the data yielded $E_a = 131 \text{ kJ mol}^{-1}$ with a coefficient of determination of $R^2 = 0.954$.

A function is proposed to describe the evolution of the characteristic relaxation time during thermal degradation at a selected arbitrary reference temperature. The mastercurve of the evolution of relaxation times, shown in Fig. 4, is constructed from all times and temperatures explored. The function expresses the reference relaxation time τ^* at a reference degradation temperature T_D as

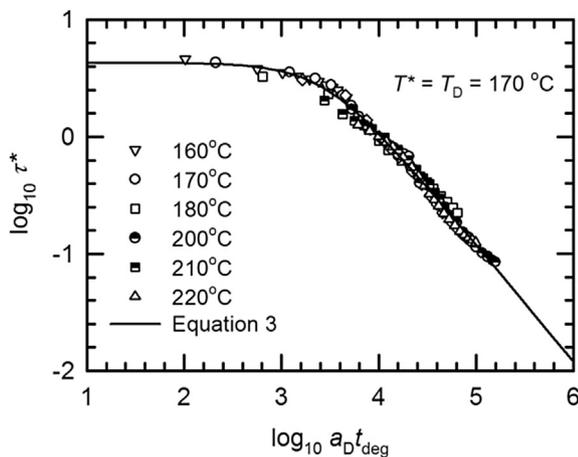


Fig. 4. Horizontally shifted plot of reference relaxation time at $T^* = 170^\circ\text{C}$ as a function of degradation time at a reference degradation temperature $T_D = 170^\circ\text{C}$. The temperature-dependent degradation shift factors, $a_D(T)$, were obtained by manual horizontal shifts of the data across the temperature range $160\text{--}220^\circ\text{C}$. Solid line represents the mathematical function given in Eq. (3) fitted to the data.

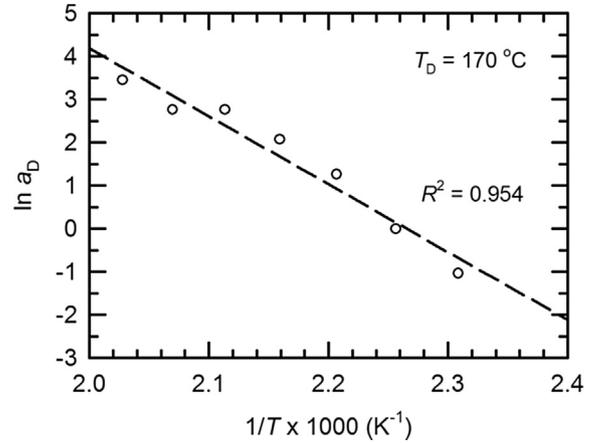


Fig. 5. The degradation temperature-dependent horizontal shift factors, a_D , as a function of the test temperature. The dashed line represents the linear regression through the data and the Arrhenius-type dependence.

$$\tau^*(T_D) = \tau_0^* \left(1 + \left(\frac{t_{deg}}{a_D(T)t_{trans}} \right)^d \right)^{\frac{c}{d}} \quad (3)$$

where τ_0^* is the plateau relaxation time at the reference temperature, t_{trans} is a timescale associated with the transition from plateau to power-law degradation, and c and d are constants determining the slope of the power-law and the speed of the transition respectively. The function was fitted to the data shown in Fig. 4 and regression was carried out to obtain the parameters as $\tau_0^* = 4.29 \text{ s}$, $t_{trans} = 2761 \text{ s}$, $c = -1.00$ and $d = 1.36$. As can be seen in Fig. 4, there is very good agreement between the function and the experimental data indicating that the 4-parameter function is sufficient to capture the evolution of τ^* with t_{deg} at a selected T_D .

3.2. Degradation of arbitrary temperature profiles

In principle, if a temperature profile is known, it is now possible to employ the function to back-calculate the undegraded relaxation time τ_0^* for any given history. To a first approximation, a set of viscoelastic moduli in the pre-degraded state can be obtained by shifting the frequency axis by the same amount as the cross-over frequency. When individual measurement points have different temperature histories (because they were obtained after different residence times in the rheometer), this procedure has to be carried out on each individual data point. For example, one can take a set of isothermal frequency sweeps, and monitor carefully the temperature history, as shown for the decreasing temperature measurements example in Fig. 6. Here the temperature ramps are linear approximations based on the neighbouring temperature set points.

A degradation shift factor, $D(t_{deg})$, defined as the ratio of the relaxation time τ^* of the degraded polymer to the relaxation time τ_0^* of the undegraded polymer, at time t_{deg} , is calculated as

$$D(t_{deg}) = \frac{\tau^*}{\tau_0^*} = \left[1 + \left(\frac{1}{t_{trans}} \int_0^{t_{deg}} \frac{dt}{a_D(T)} \right)^d \right]^{\frac{c}{d}} \quad (4)$$

where the integral is carried out over the temperature history through to time t_{deg} , and $a_D(T)$ is given by Eq. (2). For practicality, this process was carried out using discrete time intervals and the median temperatures across these intervals. The resulting

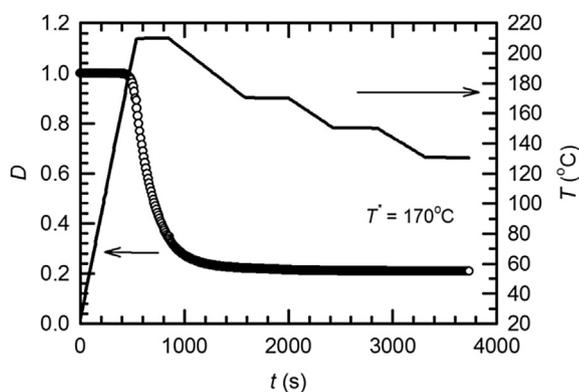


Fig. 6. Temperature history of isothermal frequency sweeps as a function of time and the corresponding degradation shift factor, D , computed using Eq. (4).

degradation shift factor is shown as a function of time overlaid on the temperature history in Fig. 6.

The time step interval for the numerical integration, Δt , was varied at 0.1 s, 1 s, 10 s and 30 s, and no significant difference in D was observed for $\Delta t \leq 10$ s. The profile shown in Fig. 6 illustrates that the most significant degradation occurs when the sample experiences the highest temperatures, not unexpectedly, and that this process slows down but does not arrest fully even at the lower temperatures. For example, D is already 0.346 by the time the first frequency sweep $T = 210$ °C is completed, but falls further only to 0.210 after the end of the final frequency sweep at $T = 130$ °C. Using the procedure outlined above, the change in relaxation time due to thermal degradation following an arbitrary temperature profile can be determined.

3.3. Obtaining degradation-corrected TTS and mastercurves

One problem with the procedure outlined above is that, due to degradation, there is an inherent error in the data used to obtain the WLF parameters. This is because degradation and temperature have a similar effect on the relaxation time – they both result in an effective shift of the moduli along the frequency axis. This in turn means that there is an error in the temperature-dependent shift factors, and hence in the degradation function. Fig. 7 illustrates the difference between applying a temperature-dependent frequency shift only and a combination of both the temperature-dependent frequency shift and the correction due to degradation in the temperature profile on an isothermal frequency sweep data set. We make the assumption here that the degradation parameter D applies the same horizontal shift to the experimental data away from the cross-over frequency as it does at the cross-over frequency. The data was measured at 210 °C and shifted to a reference temperature of 170 °C using the WLF parameters, and D values were calculated using Eq. (4). The data was measured from high frequency to low frequency, and hence measurement points at lower frequencies experience a longer residence time than those at higher frequencies, even within a single temperature frequency sweep. It can be observed that D is larger at high frequencies than that at lower frequencies ($D = 0.860$ at $\omega = 50$ rad s⁻¹ and $D = 0.346$ at $\omega = 1$ rad s⁻¹), resulting in a greater degradation correction, and hence horizontal shift, for data measured at lower frequencies.

Therefore, it is now important to go back and apply the degradation correction to the original frequency sweeps used to obtain the WLF parameters. In fact, in order to resolve this issue in full, an iterative approach has to be used in which the entire procedure is run through a number of times. Once a set of parameters are

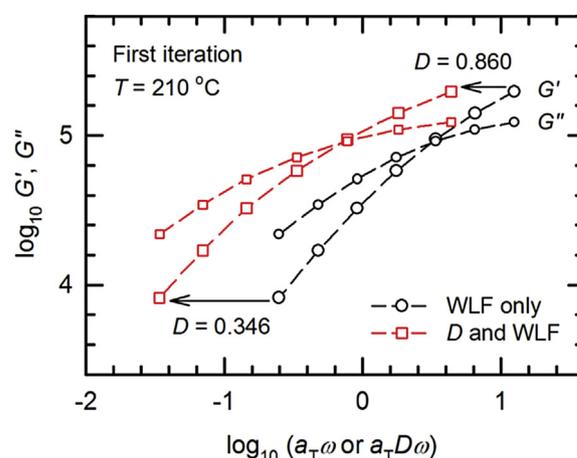


Fig. 7. Example of a reduced frequency sweep at $T = 210$ °C where only WLF shifting ($T_{\text{ref}} = 170$ °C) has been applied to the data (black circles). When degradation shifting using D is applied to the data in addition to WLF, the frequencies shift further to the left (red squares). The higher D value (i.e. less shift) at higher frequencies is due to the fact that the material is tested with decreasing frequency, and hence each measurement point experiences a different residence time. Dashed lines are a guide to the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

obtained enabling the degradation function to be evaluated, this can be used to correct the isothermal frequency sweeps for thermal degradation. With the corrected frequency sweeps, a new set of WLF parameters can be obtained, and the entire procedure can be repeated through to convergence. On each iteration, the WLF parameters, the activation energy, and the degradation function parameters are recalculated.

Convergence was defined as a steadying of the undegraded characteristic relaxation time as determined from the viscoelastic mastercurve. Fig. 8 shows the progression in the characteristic relaxation time at $T^* = 170$ °C as a function of the number of iterations through the procedure. It was found that the relaxation time settled after the 4th iteration, where the final degradation model parameters can be identified as $\tau_0^* = 3.86$ s, $t_{\text{trans}} = 2460$ s, $c = -0.97$ and $d = 2.36$. The WLF parameters after the same number of iterations are $C_1 = 7.07$ and $C_2 = 269$ °C at $T_{\text{ref}} = 170$ °C, and the activation energy is 94 kJ mol⁻¹.

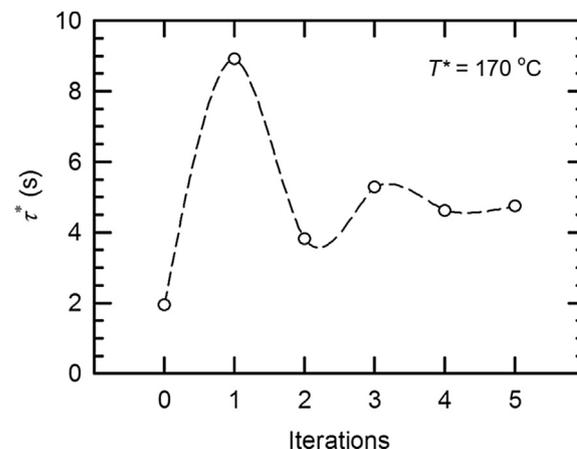


Fig. 8. Evolution of the undegraded relaxation time τ^* at $T^* = 170$ °C against the number of iterations to identify the parameters for Eq. (1). Dashed line is a guide to the eye.

3.4. Validation using isothermal frequency sweeps

In order to validate the procedure and to provide an independent check of the quality of the parameters obtained, a second set of isothermal frequency sweeps was obtained with a different thermal history, with *increasing* temperature steps (ITS) as opposed to *decreasing* temperature steps (DTS). Fig. 9a illustrates the viscoelastic mastercurves that are obtained from the isothermal frequency sweeps with the two different temperature histories using only WLF shifting. It is apparent that a different history produces a different level of degradation at the different temperatures, and hence a noticeable difference in the mastercurves. ITS produces a mastercurve that is shifted further to the left of the DTS mastercurve, mostly due to the excess degradation occurring at the elevated loading temperature, and the associated waiting period for the oven to reach the set point temperature after loading the specimen. The poorer superposition visible only at the highest frequencies in the ITS is attributed to imperfect contact between specimen and parallel plates at these reduced temperatures. In fact, it is worth noting that, in the absence of any degradation correction, the two experiments would lead to dramatically different WLF constants for $T_{\text{ref}} = 170$ °C: $C_1 = 16.2$ and $C_2 = 670$ °C for ITS and $C_1 = 2.43$ and $C_2 = 120$ °C for DTS.

The data for ITS and for DTS are now individually corrected for experiment degradation using the parameters obtained after the iterative procedure. Each data set follows a distinctive temperature history (for DTS this is shown in Fig. 6), but the same degradation function parameters, activation energy and WLF equation parameters are now used to correct and construct the undegraded mastercurves using Eq. (4). The corrected data is shown in Fig. 9b. There is remarkable agreement between the datasets, confirming that the mastercurves shifted to an undegraded state are in fact one and the same, with the same characteristic relaxation time. Relaxation times obtained from the ITS and from the DTS procedures are 4.74 s and 3.92 s respectively, well within experimental error for this type of experiment.

4. Discussion

The effect of temperature on thermal degradation is obtained by manually shifting reference relaxation time plots as a function of degradation time, as shown in the example in Fig. 4. The horizontal shift factors followed an Arrhenius temperature dependence, with

the activation energy of $E_a = 94$ kJ mol⁻¹ after five iterations of the procedure. Arrhenius behaviour was also employed in studies of the kinetics of degradation of other biodegradable polymers in the literature [8,12–14,22], and the value of E_a obtained here is in agreement with the range of 77–297 kJ mol⁻¹ reported in the literature for similar polylactides [5,6,9,22].

The main challenges in carrying out this rheometric technique arise in the data collection. An extended time is required for the frequency sweeps at isothermal conditions to monitor and record τ as a function of t_{deg} , particularly at low temperatures. There are reports in the literature of isothermal degradation of aliphatic polyesters being followed by a recombination process at long residence times [9,12]. This provides a possible explanation for the deviation of the data from the mathematical function at long times exhibited in Fig. 4. Waschen et al. found that, at 180 °C only, dried and purified PLA manifested an *increase* in molar mass after heating for 60 min in closed glass ampoules, although this behaviour was not manifested in tests extending to 230 °C. Partini et al. monitored the evolution of complex viscosity with residence time in polyesters, and found that a decrease in viscosity is eventually followed by an increase which is more pronounced as the temperature rises [12]. In order to effectively employ the method proposed in this work, caution is needed when acquiring data at low temperatures for long degradation times, since recombination reactions can become significant and change the degradation kinetics. At elevated temperatures, instead, the experimental challenge comes from the ability to rapidly record τ via a cross-over frequency measurement since degradation rates increase with temperature. It is then useful to identify the limitations of a rheometer with respect to frequency to ensure that data acquisition rates are sufficient to capture the material time-dependent behaviour.

It is also acknowledged that this work has been limited to a single PLA grade. Efforts to study the degradation of polymers with different starting molar mass are currently in progress. Further challenges arise when the relaxation time moves to much higher or lower frequencies as this can drive it outside of the range that can be sensibly measured using a rheometer. The same challenge may also apply with some different polymers, and it should be pointed out that this method is only practical in a certain temperature window for a given polymer. The good news is that polymer processing relies on flow, and that the majority of flow processes occur at a timescale comparable to the relaxation time at the process temperature in order to enable the flow to occur. This means that

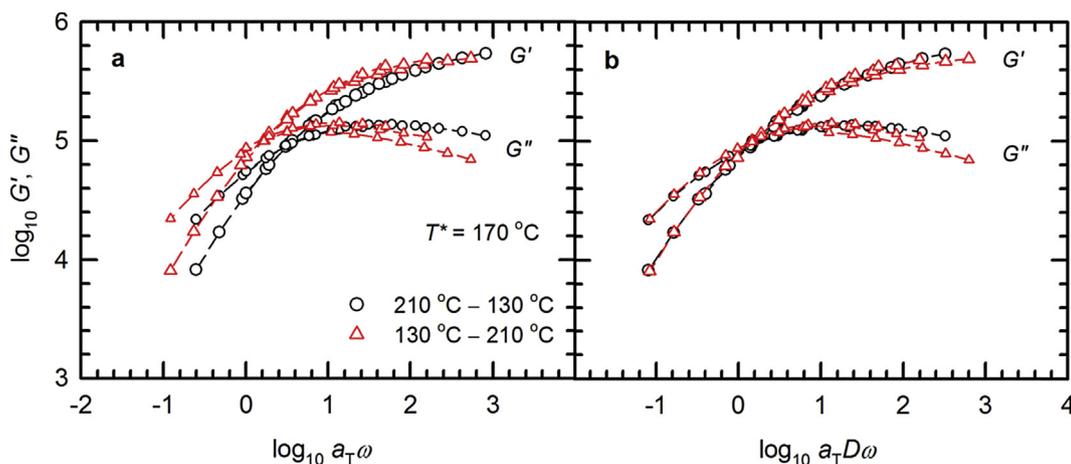


Fig. 9. (a) Application of TTS only to produce mastercurves for decreasing temperature steps (black circles) and increasing temperature steps (red triangles) at $T^* = 170$ °C. (b) The inclusion of a temperature dependent degradation shift based on the respective test thermal histories in addition to TTS to obtain the degradation-corrected mastercurves. Dashed lines are a guide to the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the relevant temperature window for thermal degradation is by definition close to the relevant temperature window for polymer processing, and hence the procedure proposed is likely to be of practical use.

In commercial processing of thermally sensitive polylactides, degradation due to shear is also an important consideration [10,18]. In this study, the polymers have experienced repeatable but limited shear during compression moulding, and only small strain oscillations during rheometry, and therefore we interpret these findings as approximations to 'zero-shear' thermal degradation, much like the concept of a 'zero-shear' viscosity is used to refer to sufficiently low shear rates. The subject of shear-induced degradation is currently being explored in our laboratory using both rotational and capillary rheometry. By using the understanding developed herein, it will be possible to separate the effects of shear from those of temperature, and hence to offer insight into the process variables affecting degradation and to help to optimise commercial melt processing of degradable polymers.

5. Conclusions

A rheometric procedure was employed to study the temperature dependence of the effect of thermal degradation on the characteristic relaxation time of a medical device grade of PLA. The experiments showed that repeated measurements of the relaxation time following a degradation period, estimated via the cross-over frequency, can be superposed by allowing for a time shift to a reference temperature using classical WLF theory, and an additional shift to a reference degradation temperature, thus accounting for the temperature dependence of thermal degradation. The change in the characteristic relaxation time with degradation time was shown to evolve with temperature with Arrhenius behaviour with an activation energy of $E_a = 94 \text{ kJ mol}^{-1}$, in line with values reported in the literature. The relaxation time also obeys classical time-temperature superposition described by the WLF equation with parameters $C_1 = 7.07$ and $C_2 = 269 \text{ }^\circ\text{C}$ at $T_{\text{ref}} = 170 \text{ }^\circ\text{C}$. A 4-parameter mathematical function was proposed that accurately describes the evolution of the characteristic relaxation time during thermal degradation for all times and temperatures explored. The function allows the effect of thermal degradation occurring during rheological experiments to be isolated, and viscoelastic data can therefore be shifted back to a pre-degraded reference state. The model parameters were determined only after a converged iterative process in order to isolate the degradation effects that are otherwise masked by the temperature dependence of relaxation times.

By integration of the effect of an arbitrary temperature profile, a cumulative change in relaxation time was obtained and applied to correct two rheological experiments consisting of a series of isothermal frequency sweeps differing only in the direction of the temperature steps. Without degradation correction these experiments lead to different viscoelastic mastercurves and WLF parameters, but through application of the procedure to obtain the pre-degraded response they were shown to originate from near-identical mastercurves. This provides convincing evidence that the methodology is able to correct rheological measurements for the effect of thermal degradation during the experiment, and thus facilitates the rheometric study of thermally sensitive polymers.

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