Application of a thermal degradation model for polylactides to polymers of different molar mass and end group structure

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1. Introduction:

In a companion paper [1, 2] the authors proposed a method of determining the effects of thermal degradation on the terminal relaxation time of a medical grade, relatively high molar mass poly(lactic acid) (PLA). Two straightforward ways in which polymers can be tailored to specific medical applications are changes in molar mass and in end group functionality. PLA is prone to thermal degradation under typical processing conditions, and this takes place as a combination of chain scission, de-polymerisation and recombination reactions. Here the term ‘thermal degradation’ encompasses the combined effects from all of these processes. The objective of this work is to apply the previously developed method for determining degradation effects to PLAs with different molar mass and end group and to determine the effects of thermal degradation on the linear rheological properties of PLA.

2. Materials and Methods:

Three medical grades of 70:30 poly(L-lactide-co-D,L-lactide) Resomer series: LR 704 S, LR 706 S and LR 708 were obtained from Evonik Industries A.G.. The designation “S” in the series identifies the polymer chain end groups as an alkyl, while the absence of the designation refers to free carboxylic acid end groups. The molar masses of the PLA grades were obtained using GPC and are 242 kDa, 464 kDa and 845 kDa respectively. The methodology employed in this work to quantify and to correct for thermal degradation during rheological measurements is detailed in the accompanying paper [1, 2]. In this work the conventional frequency sweeps were carried out at temperatures between 110 °C and 240 °C in decreasing temperature steps. Time-temperature superposition (TTS) was employed to construct mastercurves. The test procedure that corrects for degradation was applied to each material independently to determine its true TTS parameters.

3. Results and discussion:

Fig. 1a illustrates measurements of the fundamental relaxation time τ obtained during isothermal frequency sweeps from the inverse of the cross-over frequency, as a function of the residence degradation time t_{deg} in the rheometer at 170 °C, measured for the three PLA grades. The relaxation times are different due to different starting molar masses, and shorten over time due to thermal degradation. Similar isothermal measurements were made at several temperatures and all data were then shifted to a reference temperature T_{ref} to obtain a mastercurve. The mastercurve was constructed using vertical shift factors a_{T} and horizontal shift factors a_{D}, and these correspond to the temperature dependence of the relaxation time itself, and to the temperature dependence of the thermal degradation process respectively.

A previously proposed mathematical function is fitted to the data and expressed as the ratio of the relaxation time τ^* to the undegraded relaxation time τ_0^* as a function of time. The three degradation functions are shown in Fig. 1b. Considering the degradation profile of the two polymers with identical end groups, it can be seen that LR 704S degrades at a slower rate compared to LR706S. This can be explained by considering that the effect of a single degradation event on a high molar mass sample has a greater influence on the molar mass than the equivalent event on a low molar mass sample. Since the relaxation time is related to molar mass through a scaling law, it is expected that the degradation will appear faster on the high molar mass sample. The degradation profile of LR 708 is similar to that of LR 706S, despite its higher molar mass. This is even more unexpected since the free carboxylic acid end groups might be expected to accelerate the degradation process further.

An Arrhenius model is applied to the temperature dependence of a_D, and the activation energies E_a for LR 704S, LR706S and LR 708 were calculated as 99, 94 and 81 kJ mol^{-1} respectively. It is therefore likely that the activation energy for thermal degradation could be associated with the specific chemistry of the end group. The lowest E_a value is found in the polymer with the most reactive end group, while the two polymers with identical end groups have almost identical activation energies.

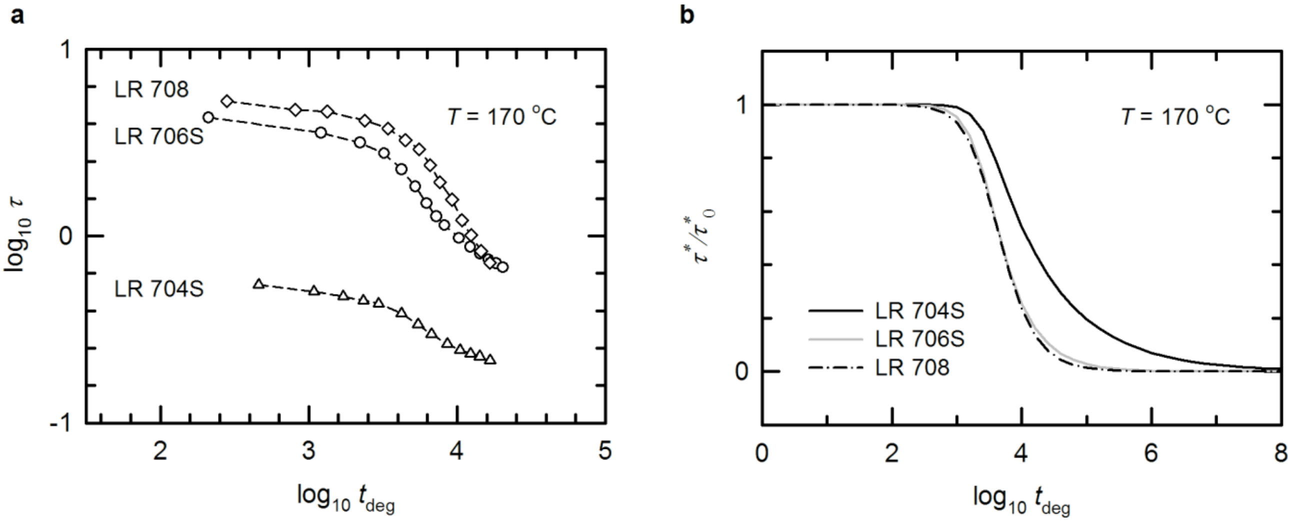

Fig.1 (a) Unshifted relaxation time τ as a function of degradation time for three polymer grades, measured at 170 °C. (b) Degradation profile of all grades at 170 °C, generated by optimised mathematical function parameters that describe the evolution of the ratio of τ^* over the relaxation time prior to rheometry τ^*_0

True TTS parameters are obtained after a series of iterations leading to converged model constants. The two polymers with alkyl end groups have almost identical shift factors. The shift factors for the carboxylic acid ended polymer is significantly different for T<150 °C. These corrected TTS parameters, together with the degradation model, allow reconstruction of the mastercurves in the undegraded state.

4. Conclusions

A procedure was developed to determine the effect of thermal degradation on the relaxation time, and was applied here to two further polymers. A variation in molar mass leads to a change in the timescale of thermal degradation only whereas a variation in polymer chain end group additionally affects the activation energy (and hence the temperature dependence of degradation) and the TTS shift factors. Our rheological study has shown that varying chain end chemistry of PLA can strongly affect the process of thermal degradation, in agreement with the literature [3].

References:

[1] G.Y.H. Choong and D.S.A. De Focatiis, *ICR2016*, abstract no. 5195.
[2] G.Y.H. Choong and D.S.A. De Focatiis, submitted to *Polym. Degrad. Stabil.* (2016).
[3] H. Nishida, *Thermal Degradation* in *Poly(lactic acid): synthesis, structures, properties, processing, and applications*, Wiley, New Jersey, 2010.