



## Influence of melt processing conditions on poly(lactic acid) degradation: Molar mass distribution and crystallization



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### ABSTRACT

The degradation of poly(lactic acid) (PLA) during thermal–mechanical processing was studied and the influence of processing conditions on degradation rate was determined by size exclusion chromatography coupled with multi-angle light scattering (SEC–MALS). A two-parameter model accounting for both chain scission and recombination processes was used to describe the experimentally observed molar mass distribution. The degradation and recombination rate constants were determined for undried and dried PLA. It was highlighted that the effect of processing temperature (in the 170–210 °C range), processing time (until 30 min) and shear rate (rotor speed varying from 0 to 150 rpm) on molar mass reduction can be relatively well simulated insofar as self-heating related to the mechanical energy conversion into heat was taken into account.

The influence of melt processing on the thermal behaviour of PLA was also investigated using temperature modulated differential scanning calorimetry (TMDSC). It was evidenced that the molar mass reduction affects the crystallizability of PLA. Cold crystallization temperature progressively decreases with decreasing molar mass and the metastable  $\alpha'$  phase is formed in place of the stable  $\alpha$  phase. The  $\alpha'$  phase can be partially converted into  $\alpha$  form during melting giving rise to a double-melting peak. The two peaks can be separated using reversing and non-reversing signals confirming that recrystallization of the  $\alpha'$  form occurs.

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### 1. Introduction

Nowadays, sustainability of raw materials is often considered as an added value and even, sometimes, as a requirement. As a result, bio-based and/or biodegradable polymer development receives much attention. Among all the so-called biopolymers, only a few of them (biopolyesters, e.g. poly(lactic acid) (PLA) or polyhydroxyalkanoates (PHA), polysaccharides and proteins) are already both bio-based and biodegradable. Unlike polysaccharides (starch, cellulose, chitin ...) and proteins (gluten, casein, keratin ...) which are directly extracted from biomass, PLA is a biopolyester produced by polymerization of lactic acid dimers obtained from starch fermentation [1]. Since it is somehow largely commercially available, PLA is often considered as a good alternative to petro-based polymers.

However, its thermal stability above the melting point remains very low and the ester linkages of PLA tend to degrade themselves during melt processing [2]. The final properties, e.g. mechanical properties, thermal behaviour and biodegradation rate, are then affected by the processing conditions [3–7].

Several mechanisms were postulated in order to describe the complex and various degradation reactions occurring in molten state: random chain scission [2,8], depolymerization [9], oxidative degradation [8], intermolecular [9,10] and intramolecular transesterification [3,11–15], hydrolysis [16], pyrolytic elimination [16] and radical reactions [3]. Acidic end groups, residual catalyst and monomers or other impurities also increase the degradation rate [11].

It has been usually reported that PLA degradation during thermal treatment is mainly due to intramolecular transesterification reactions leading to cyclic oligomers of lactic acid and lactide [9,14]. Simultaneously, recombination occurs by ring opening insertion of cyclic oligomers into linear polyesters [14,15]. Intermolecular transesterification with short molecules could also result in a

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decrease of average molar mass [9]. Hydrolytic degradation depends on water content [14,16]. Pyrolytic elimination leads to molecules with acrylic end-groups [14], the colour formation being attributed to the apparition of conjugated double bonds [16].

Degradation during melt processing, i.e. under shear conditions, was studied in single [7] and twin-screw extruders [4,16], injection moulding machines [6,7,17,18], and batch mixers [10]. In twin-screw extruders, Taubner and Shishoo [4] found that the molar mass reduction is dependent on residence time and temperature. They also found that moisture increases the degradation rate. However, in the harshest conditions, molar mass after extrusion was found to be the same in both case of dry and moist PLA, probably because degradation was so extensive that the presence of moisture in the polymer did not contribute to further degradation. Wang et al. [16] related the molar mass reduction to the colour formation using UV–visible spectroscopy and found that moisture does not influence the UV–visible spectra by forming conjugated double bonds while it reduces the molar mass. They concluded that pyrolytic elimination was the main degradation mechanism for dry PLA while an additional hydrolysis mechanism occurs in presence of moisture. Badia et al. [18] have shown that successive injection cycles induce a strong decrease of molar mass measured by viscometry. They highlighted that throughout reprocessing PLA cold crystallization appeared, indicating that chain scission emphasizes segmental dynamics.

Modelling degradation processes of polymers is generally achieved using a kinetic constant  $k$  which takes an Arrhenius form to account for the thermally activated feature of phenomena. The evolution of molecular weight distribution can then be estimated using models based on population-balance equations considering that degradation results from chain scission and recombination [19]. The modelling of PLA degradation during thermal processing was poorly covered in the literature. Wachsen et al. [15] developed a statistical model to describe the degradation of PLA in the melt. Yu et al. [2] used the same kind of mathematical model to account for the thermal degradation of PLA under nitrogen by random chain scission. None of the works found in the literature considered the role of mechanical energy in degradation processes neither by the elevation of temperature due to viscous dissipation (degradation reactions favoured by thermal effects) nor by the shear stress (chain scission to due mechanical effects).

In this paper it was attempted to study first the influence of PLA drying, of mixing temperature in the 170–210 °C range and time up to 30 min, on PLA degradation during processing considering a thermo-compression process. Then the influence of the rotor speed up to 150 rpm on PLA degradation during processing in a batch mixer was investigated to separate mechanisms related to shear conditions from those related to temperature. In all cases the degradation rate was assessed by measuring the molar mass reduction. A statistical model was implemented to describe the experimental results. It was therefore possible to examine the respective role of each processing parameter which provides a powerful tool for further investigations on PLA based materials such as PLA/natural fibre biocomposites. In the last part of this paper, the consequences of PLA degradation on its crystallization ability were studied.

## 2. Theoretical background: statistical model of polymer thermal degradation

The influence of time on the molar mass evolution was modelled using a two-parameter model based on reactions schemes describing both degradation and recombination processes (equations (1) and (2)) [2,15]:



where  $P_i$  is a PLA polymer chain with a degree  $i$  of polymerization. Using two statistic rate constants  $k_d$  and  $k_c$  respectively for degradation reactions and recombination reactions, the evolution of the concentration of each species  $P_i$  can be described by the following differential equation system (equation (3)):

$$\begin{aligned} \frac{d[P_i]}{dt} = & -k_d(i-1)[P_i] + 2k_d \sum_{j=i+1}^{\infty} [P_j] + \frac{1}{2}k_c \sum_{j=1}^{i-1} [P_j][P_{i-j}] \\ & - k_c[P_i] \sum_{j=1}^{\infty} [P_j] \end{aligned} \quad (3)$$

The first term of equation (3) describes the  $(i-1)$  possibilities of splitting of a molecule  $P_i$ . The second term describes every possible formation of this molecule by degradation of the molecules with a chain length  $j$  greater than  $i$ . The third term represents every possible formation of this molecule by recombination of two molecules with chain lengths  $j$  and  $(i-j)$  lower than  $i$ . The last term describes every possible disappearance of this molecule due to its recombination with other species.

The influence of temperature on both constants was modelled with an Arrhenius law (equations (4)–(5)).

$$k_d = A_d \exp\left[-\frac{E_{ad}}{RT}\right] \quad (4)$$

$$k_c = A_c \exp\left[-\frac{E_{ac}}{RT}\right] \quad (5)$$

where  $k_d$  and  $k_c$  are respectively the degradation and recombination rate constants,  $E_{ad}$  and  $E_{ac}$  are the respective activation energies for the degradation and recombination processes,  $A_d$  and  $A_c$  are the pre-exponential factors,  $R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is the polymer temperature (K).

A direct numerical integration of equation (3) for each individual molecular species is complicated and time consuming. Yu et al. [2] proposed to express the polymer chain length distribution using its moments  $\lambda_n$  up to third-order:

$$\lambda_n = \sum_{i=1}^{\infty} i^n [P_i] \quad (n = 0, 1, 2, 3) \quad (6)$$

where  $\lambda_n$  is the  $n$ th moment of distribution,  $\lambda_0$ ,  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  representing respectively the mean, variance, skewness and kurtosis of the distribution.

Using a z-transform to express the summations, the differential equation system becomes:

$$\frac{d\lambda_0}{dt} = k_d(\lambda_1 - \lambda_0) - \frac{k_c\lambda_0^2}{2} \quad (7)$$

$$\frac{d\lambda_1}{dt} = k_d(\lambda_1 - \lambda_0) \quad (8)$$

$$\frac{d\lambda_2}{dt} = \frac{k_d(\lambda_1 - \lambda_3)}{3} - k_c\lambda_1^2 \quad (9)$$

The following closure approximation (equation (10)) is made to solve the system:

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