Technical Note: On modelling thermo-chemical degradation of poly(lactic acid)

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Abstract: A well-established model for simulation of the chain-scission process of polylacticacid (PLA) during thermal processing has been simplified and revised. The key assumption in the new model is that the total number of monomer units is invariant as reactions progress. Surprisingly, this seemingly obvious assumption appears to have been previously overlooked. The revised model no longer requires solution of simultaneous differential equations and, for isothermal conditions, an analytical solution is readily available. The present model is in excellent agreement with the more complex model and experimental results for PLA degradation reported in the literature. This simplified model has potential to be applied to other thermoplastics.

Keywords: Modelling; Thermal Degradation; Polymeric Material; Chain-scission; PLA.

In 1997, a statistical model was proposed by Wachsen et al. [1] to simulate changes of molar mass of poly (L-lactic Acid) (PLLA) as a function of temperature and time. This model was later modified by Yu et al. [2] who proposed a more convenient form to estimate molecular properties of PLLA after thermal processing. Yu et al [2] described the molecular weight and polydispersity index in PLLA thermal degradation at various temperatures. Recently, Le Marec et al. [3] fitted the Yu et al model to experimental data for PLA. The statistical model for the polymer considered both degradation and recombination reactions which occur during the thermal processing. As a result, the average length of polymer chains decreases towards an equilibrium value [1-3]. Eqs. (1) and (2) describe the degradation and recombination processes respectively [2]:

$$P_n \rightarrow P_{n-r} + P_r \tag{1}$$

$$P_r + P_{n-r} \rightarrow P_n \tag{2}$$

where P_n is the polymer with a degree of polymerization, n, and a change in that parameter, r.

The effect of temperature on degradation and recombination is expressed using the Arrhenius equation (Eqs. (3) and (4)):

$$k_d = A_d \exp(\frac{-E_{ad}}{RT}) \tag{3}$$

$$k_c = A_c \exp(\frac{-E_{ac}}{RT}) \tag{4}$$

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where k_d is the degradation rate and k_c recombination rate, A_d and A_c are the pre-exponential factors, E_{ad} and E_{ac} are apparent activation energies, R is the universal gas constant and T is the temperature. It is assumed that the same values of k_d and k_c apply to polymers of any length. As expressed by Wachsen et al. [1], using these assumptions, the rate of change of concentration of a polymer of length n will be given by:

$$\frac{d[P_n]}{dt} = -(n-1)k_d[P_n] + 2k_d\sum_{i=n+1}^{\infty}[P_i] + \frac{1}{2}k_c\sum_{i=1}^{n-1}[P_i][P_{n-i}] - k_c[P_n]\sum_{i=1}^{\infty}[P_i] \qquad (5)$$

where $[P_n]$ is the concentration of P_n, *i.e* the number of moles of the polymer (of length n) per unit volume. Eq. (5) needs to be solved concurrently for a large number of polymer chains of different lengths, which is inconvenient for practical analysis. With the use of Eq. (5), we can estimate the degradation speed of all kinds of polymers in thermal processing. The major contribution of Yu et al. [2] was to re-express these equations in terms of moments (λ_i) of different orders defined by:

$$\lambda_i = \sum_{n=1}^{\infty} n^i[P_n] \quad i = 0, 1, 2, 3 \dots \qquad (6)$$

Considering only the first three moments, the differential equation system (Eq. (5)) was reduced to[2]:

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

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

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

To close Eqs. (7)-(9), the following approximation was made:

$$\lambda_3 = \frac{\lambda_2}{\lambda_1\lambda_0}[2\lambda_2\lambda_0 - \lambda_1^2] \qquad (10)$$

Equation (5) or Eqs. (7) to (10) have been used successfully to model the thermo-chemical degradation of PLLA, PLA and PP [2-7].

An important point, that appears to have been overlooked in studies that have made use of the Yu et al model (Eq. (7)-(10))[2] is that λ_1 can be considered to be a constant. This parameter can be interpreted as the total number of moles of monomer units per unit volume (see Eq. (6)). The key to the model developed in this Technical Note is an unwritten assumption in the model by Wachsen et al. [1] (Eq. (1)-(5)) that no degradation of the basic monomer unit occurs, and hence the total number of monomer units should not change as the reactions progress. This note rectifies this omission. A constant λ_1 decouples Eq. (7) from Eqs. (8) and (9) and makes it unnecessary to solve Eq. (8). Moreover, if the temperature is also constant then Eq. (7) can be solved analytically by separating the variables to give:

$$\lambda_0 = \frac{-k_d}{k_c} + \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{k_c} \tanh\left(\frac{(t+C)\sqrt{2k_c k_d \lambda_1 + k_d^2}}{2}\right) \tag{11}$$

where C is defined by the initial condition for λ_0 as:

$$C = \frac{2}{\sqrt{2k_c k_d \lambda_1 + k_d^2}} \tanh^{-1}\left(\left(\lambda_{0-initial} + \frac{k_d}{k_c}\right)\frac{k_c}{\sqrt{2k_c k_d \lambda_1 + k_d^2}}\right) \tag{12}$$

This analytical resultisin a convenient formfor prediction of degradation of polymeric materials such as PLA during melt processing [4-14] under isothermal conditions.

As Eq. (6) defines λ_0 as the total number of moles of molecules per unit volume, the initial condition may be specified as:

$$\lambda_{0-initial} = \rho / M_{n-start} \tag{13}$$

and λ_1 as:

$$\lambda_1 = \rho / m_0 = \text{constant} \tag{14}$$

where ρ is the density of the polymer, $M_{n-start}$ is the initial number-averaged molar mass for the polymer and m_0 is the molar mass of a monomer unit.

For all of the models, the number-averaged molar mass M_{n-avg} can be specified at any time as:

$$M_{n-avg} = m_0 \frac{\sum_{n=1}^{\infty} n[P_n]}{\sum_{n=1}^{\infty} [P_n]} = m_0 \frac{\lambda_1}{\lambda_0} \tag{15}$$

Since enforcing Eq. (14) rather than using Eq. (8) will in principle lead to different results for λ_1, it is important to consider the impact of the simplified model on predictions of thermo-chemical degradation of PLA. The present model (Eqs. (11) and (12)) was used to calculate results for comparison with the model of Yu et al.[2] (Eqs. (7) to (10)) using kinetic data for PLA degradation by Le Marec et al. [3] (Table 1). This comparison is shown in Fig. 1 which also includes the experimental data on molar mass degradation of PLA reported by Le Marec et al.[3]. The present model is in excellent agreement with the Yu et al model for the range of available datawith a maximum deviation of less than 0.1% for λ_0. For the data shown, the Yu et al model also predicts a maximum of only 0.1% change in the value of λ_1.

Table 1. Kinetic parameters and initial conditions for modelling polymer degradation of PLA

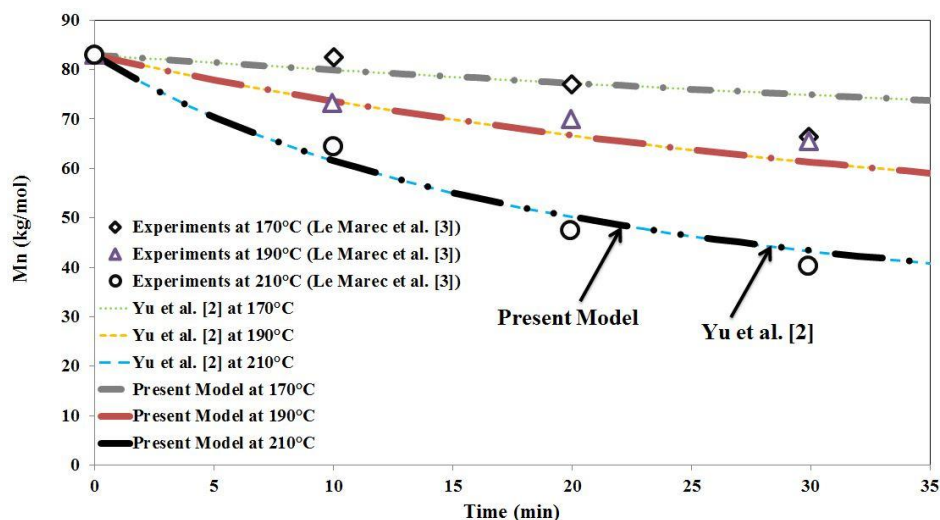| Ref.	A_c (L/mol/s)	E_{ac} (kJ/mol)	A_d (s^{-1})	E_{ad} (kJ/mol)	m_0 (g/mol)	$M_{n-start}$ (g/mol)	Start Polydispersity	Density (g/L)
Le Marec et al. [3]	121.6	37.7	1600	87.2	72.07	8.29× 10^4	1.425	1260

Fig. 1. Confirmation of the experimental dataextracted from Yu et al. [2] or Le Marec at al [3] model with the present model.

To sum up, the model for thermo-chemical degradation of PLLA proposed by Yu et al. [2] can be simplified significantly by assuming that the total number of monomer units is invariant as reactions progress. The present model accurately simulates the experimental data of Le Marec et al. [3] for PLA in Fig. 1, without the need to recalculate the original activation energies or pre-exponentials. Moreover, since there is recently a need to predict or estimate the degradation process in thermal processing, the current model can significantly simplify the process of calculation for other thermoplastics.

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