

A STABILITY STUDY OF POLY(L-LACTIDE) IN THE MELT

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ABSTRACT

The melt stability of poly(L-lactide) (PLLA) was in this study evaluated by using a Haake melt rheometer. Calculations gave an increasing degradation rate constant for the melt degradation at increasing temperatures and amounts of tin-octoate added. The degradation rate constant decreased after addition of 0.05 mol-% tert.-butyl peroxybenzoate.

INTRODUCTION

Polyesters are in general extremely unstable at temperatures above their melting points. Poly(L-lactide) (PLLA), a biodegradable and biocompatible polyester, that during the last decades has been used for medical applications but also for bulk polymer applications, have recently been discussed.¹ PLLA has been found to undergo a drastic melt degradation during the processing.² The most relevant reason for the undesired melt degradation has been found to be the catalyst or catalyst residues activating the depolymerization of the polymer.³ This means that an expensive and complicated purification of the polymer has been necessary for depressing the melt degradation. Recently addition of small amounts of certain peroxides proved to retard the melt degradation of PLLA by a deactivation mechanism of the residual tin compound in the polymer.⁴

The aim of this study was to evaluate the melt stability of as-polymerized and peroxide modified poly(L-lactide) using a melt rheometer.

THEORY

The degradation of polymers has been defined as the number of chain scissions produced during a known time, and can be expressed by equation 1.⁵

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + k_D \cdot t \quad (1)$$

where \overline{DP}_0 and \overline{DP} are the initial and final numbers of average degree of polymerization, k_D is the degradation rate constant, and t is the time. This equation is valid for condensation polymers when the amount of broken bonds and the chain length of the largest volatile chains are low ($k_D \cdot t \ll 1$).⁵

The degree of the depolymerization can be monitored by the average molar mass data as a function of the degradation time. As the viscosity of a polymer can be related to the average molar mass, the degree of polymerization can be correlated to the viscosity changes (torque changes) and the following relationship can be stated (Eq. 2),

$$1/(\eta_{eff})^\alpha = 1/(\eta_0)^\alpha + k_D \cdot t \quad (2)$$

where the exponential factor α is, according to the relationship of molar mass and melt viscosity, a constant equal to 1/3.4 for molar masses above the critical molar mass.⁷ The factor η_{eff} in equation 2 is the effective melt viscosity, and here it is assumed that the polymer melt exhibits a Newtonian behavior. This simplification is incorrect since the melt viscosity of polymers is a function of the shear

rate. Eq. 2 is valid for the degradation in polymer melts by statistic random main chain-scission.⁷ Equation 2 in the introduction predicts a straight line for $1/\eta^{\alpha}$ versus time, when only one degradation rate is involved.⁶ The degradation constant k_D is equal to the angular constant of the straight line.⁷

MATERIALS AND METHODS

The melt stability of unmodified and peroxide modified PLLA was studied with a Haake melt rheometer. The experiments were conducted at temperatures between 180 and 210 °C. The torque (melt viscosity) was continuously monitored and the degradation rate constant (k_D) in equation 2 was calculated.

The poly(L-lactide) was a pilot scale sample prepared by Neste Oy, Finland. Commercial grade L-lactide (Purac) was polymerized in the melt using 0.11 wt % tin-octoate (Sigma-Aldrich) as initiator. The weight average molar mass (M_w) of the polymer was about 190 000 g/mol. An amount of 40 g PLLA was introduced to the mixer in every experiment. The PLLA was stored in a desiccator before use. The influence of the amount of initiator was studied by adding 0 - 1 wt % tin-octoate to the mixer. In order to melt modify and stabilize PLLA 0.05 mol-% tert.-butyl peroxybenzoate (Akzo) was used as received and introduced to the mixer together with the polymer.

RESULTS AND DISCUSSION

The monitored torque during melt mixing PLLA decreases even more rapidly than the molar mass because of the initial melting process of the polymer.⁸ However, based on the temperature curve of the melt, this melting process was found to be completed after about 60 seconds. The deviations from the programmed temperatures during a measurement were less than 3 °C and the deviation from the average temperature during the run was less than 3 %.

In order to study the degradation kinetics $1/\eta^{0.3}$ of the PLLA was plotted against time. The $1/\eta^{0.3}$ against time shows an increasing angularity, i.e. the calculated k_D value (Eq. 2) in the experiments increases when the amount of tin-octoate increases (Fig.1) and the temperature rises (Fig. 2).

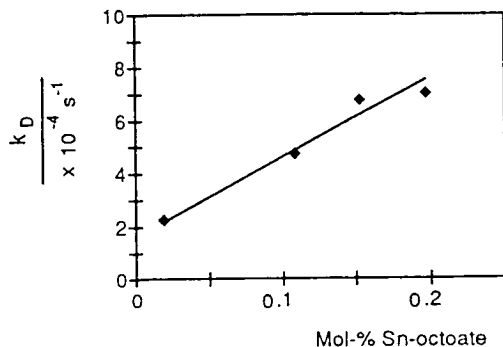


Figure 1. Degradation rate constants plotted against the amount of tin-octoate added.

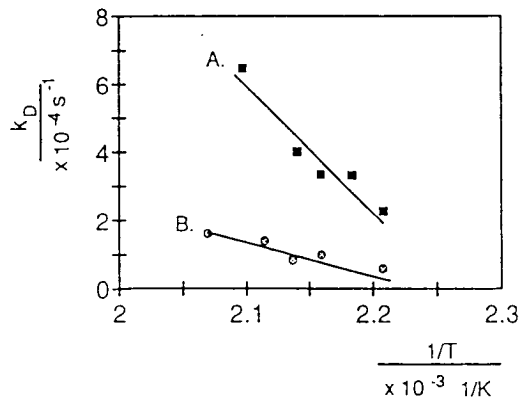


Figure 2. Degradation rate constants plotted against the inverted temperature at temperatures between 180 and 210 °C for A. Unmodified PLLA, B. Peroxide modified PLLA.

The calculated values based on the measurements had a correlation factor r^2 bigger than 0.92, which can be considered as acceptable. This means that the postulated random main-chain scission according to the suggested model is a relevant degradation mechanism. The calculated degradation rate constants were plotted as a function of the amount of tin-octoate (Fig. 1). This shows that the melt degradation rate is a linear function of the amount of tin-octoate present. The calculated degradation rate constants plotted as a function of the temperature for both the PLLA basepolymer and the peroxide modified PLLA (Fig. 2) proved that the melt degradation is strongly dependent on the temperature. The energy of activation for the degradation of PLLA at the temperatures between 180 and 210 °C was calculated from the Arrhenius equation and found to be 119.4 ± 0.7 kJ/mole. This value agrees well with the values of PLLA reported earlier.⁹ The addition of the tert.-butyl peroxybenzoate gave a significant reduction of the melt degradation rate constants at all the measured temperatures between 180 and 210 °C (Fig. 2). This confirms the deactivation of the catalytic active tin compound by the peroxide addition as no or little crosslinked regions could be detected.

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