



# Acceleration of polylactide degradation under biotic and abiotic conditions through utilization of a new, experimental, highly compatible additive



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## ABSTRACT

This paper focuses on accelerating the biotic and abiotic degradation of polylactide by combining it with a newly developed experimental additive. Said additive is based on a highly carboxylic-functionalized poly(lactide) copolymer that possesses a comb-like architecture. Samples were prepared by melt blending, and analysis was carried out prior to degradation on changes in molecular weight and mechanical and rheological properties. Degradation studies were performed in compost and pH 7 water buffer environments. Such degradation was gauged by monitoring alteration in molecular weight, as well as in the content of carbon dissolved and CO<sub>2</sub> evolved during composting. Furthermore, experimental data were treated by applying appropriate kinetic models. Results showed that the newly developed hydrolysis additive efficiently promoted biodegradation - even at a low dosage of 5% w/w, primarily due to reduction in the lag phase at the commencement of the process.

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## 1. Introduction

Biodegradable poly(lactide) (PLA) based materials possess tremendous potential, as they could replace conventional polymers in specific applications, especially disposable products of the food or agricultural sectors, thus reducing the plastic litter entering the environment [1,2]. Processing such items after usage in composting facilities, along with other organic waste, is considered an appropriate means of recovering materials [3–5]. However, such materials have to demonstrate the capability to undergo biological decomposition in composting environments at a rate consistent with the other compostable matter, without any visually distinguishable residue remaining at the end of the process [6].

It is generally accepted [7–9] that PLA biodegrades most readily in the environment of compost, particularly during the thermophilic phase, characterized by relatively high temperature. In this phase, the glass transition temperature of PLA (56–58 °C) is exceeded, thereby markedly accelerating the abiotic hydrolysis of ester bonds. During this stage of primary degradation, which has been suggested to constitute the rate-controlling step of the biodegradation process, the low-molecular-weight fragments are

formed and that are subsequently assimilated and mineralized by microorganisms into end-products [10]. Unfortunately, this phase tends to last just a few days, depending on the given composting technology. A short period such as this might result in insufficient depolymerization of the PLA chains, thus delaying their eventual mineralization, and ultimately causing incompatibility with the composting process. Therefore, the capability to accelerate depolymerisation of the PLA chains during composting, i.e. shortening the time scale of biodegradation, is most desirable so that compatibility with other organic waste is ensured.

Basically, the rate of hydrolysis of PLA (thus its biodegradation) can be substantially altered by several approaches to treatment of the same, including copolymerization or grafting other monomers [11,12], blending with materials of superior biodegradability [13,14], or modifying characteristics such as crystallinity [15,16]; all these examples considerably influencing the rate of degradation processes. However, such modifications usually induce unwanted and significant alteration in desirable material properties inherent to original PLA, such as transparency or thermal resistance [17].

The hydrolysis of PLA may also be hastened by promoting cleavage of the ester bonds, whether the latter is catalysed by an acid or a base, by adding a suitable additive containing basic or acid groups. It is well-known that monomers or oligomers of polylactide acid or another organic acid are capable of acting as a catalyser of

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hydrolysis due to the carboxylic groups present [18,19]. However, such low-molecular-weight, water-soluble additives display a tendency to diffuse out of the polymer matrix, in addition to which they can exert a major plasticizing effect at higher concentrations. Other studies [8,20,21] have demonstrated enhancement of abiotic hydrolysis during biodegradation, arising through the presence of terminal hydroxyl groups of silicates or an excess of hydroxyl groups in certain organic modifiers of nanoclays. Crucially, appreciable acceleration was only reached therein as a result of such additives being highly compatible with the polymer matrix to avoid unfavourable separation of the additive. Therefore, it would be most desirable to identify an additive for accelerating biodegradation that had great compatibility and would not alter the properties of the given material.

Herein, the authors utilized a newly synthesized additive they had devised, based on a poly(acrylic acid)/poly(L-lactic acid) multicomponent co-polymer (PAA/PLA). It was incorporated as the hydrolysis accelerating agent in a PLA matrix at various concentrations, and research focused on the influence it exerted on the biodegradability of the final material under composting conditions. It was assumed that, due to its unique structure, the developed additive would exhibit great compatibility with the polymer matrix, accelerating hydrolysis without negatively changing the inherent properties of the material.

Testing and monitoring focused on the attributes of the material, including thermal, mechanical and rheological properties, and the extent to which the concentration of the given PAA/PLA affected such hastened degradation. To this end, different experimental techniques were employed in the process of abiotic hydrolysis and microbial decomposition. The experimental data from abiotic hydrolysis and aerobic composting were analysed by non-linear regression to fit first-order kinetic models and to calculate kinetic parameters.

## 2. Experimental section

### 2.1. Materials

A multicomponent co-polymer of poly(acrylic acid)/poly(lactic acid) (PAA/PLA), with properties as summarized in Fig. S1 and Table S1 (Supplementary Information), was prepared by the authors as described elsewhere [22]. Tetrahydrofuran (HPLC grade) was purchased from Chromservis, Czech Republic. Polylactide of resin type 40042D was obtained from Resinex s.r.o., Czech Republic.

#### 2.1.1. Preparation of PLA mixtures with a PAA/PLA hydrolysis additive

Prior to being compounded, PLA pellets were dried at 80 °C under reduced pressure for at least 8 h. A co-rotating twin-screw microcompounder (HAAKE MiniLab II, Thermo Scientific, United States) was utilized, equipped with two stainless steel screws and a bypass, thereby permitting continuous recirculation of the material at 190 °C; the screw speed was set to 100 RPM for the compounding operations. The given additive was blended with PLA at the concentrations 5, 10 and 15% w/w. Note, further in the text this is denoted as “%” only.

#### 2.1.2. Preparation of films

PLA films of 100 µm thickness were compression moulded. The material was brought up to the processing temperature of 190 °C for 1 min, then moulded for 2 min, and immediately cooled down under pressure after transferring the material to a second press kept at 20 °C.

### 2.2. Characterization

#### 2.2.1. Thermal properties - differential scanning calorimetry (DSC)

Thermal properties were investigated by DSC on a DSC1 STAR System (Mettler Toledo, Switzerland). Film samples at weight ca 8–11 mg were placed in aluminium pans. A nitrogen flow of 50 ml min<sup>-1</sup> was set, and the following heating program was applied: an initial heating cycle from 0 to 200 °C (10 °C.min<sup>-1</sup>), maintaining the same for 2 min and cooling to 0 °C (20 °C.min<sup>-1</sup>). Afterwards, the temperature of 0 °C was held for 2 min and a further heating scan was performed to 200 °C. Melting point temperature ( $T_m$ ) and exothermal response relating to cold crystallization ( $T_c$ ) were obtained from the first heating cycle. The region of glass-transition temperature ( $T_g$ ) was determined from the second heating scan. The degree of crystallinity  $\chi_c$  was calculated according to Equation (1) [23]:

$$\chi_c = \left( \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \right) \times \%PAA/PLA \times 100 \quad (1)$$

where,  $\Delta H_m$  is the heat of fusion,  $\Delta H_c$  represents cold crystallization enthalpy and  $\Delta H_m^0$  is the tabulated heat of fusion for theoretically 100% crystalline PLA homopolymer (93.1 J g<sup>-1</sup>) [23], while %PAA/PLA refers to the weight fraction of the additive in the corresponding mixture.

#### 2.2.2. Rotational rheology

Rheological properties were studied using a Physica MCR 501 rheometer (Anton Paar Ltd., Graz, Austria), aided by a plate/plate geometry of 25 mm in diameter with a gap of 500 µm. The thickness of sheet samples, prepared by compression moulding at the identical condition as a films, stood at 1 mm. Measurements were carried out at 190 °C under a nitrogen atmosphere to prevent any degradation of the samples. The following types of measurement were performed: firstly, a dynamic strain sweep test at the angular frequency of 100 rad s<sup>-1</sup>, in order to discern the linear viscoelastic region; and secondly, a dynamic frequency sweep test across the frequency range of 0.1–100 rad s<sup>-1</sup>, at a strain of 1%.

#### 2.2.3. Dynamic mechanical analysis (DMA)

DMA was performed on a DMA 2980 device (TA Instruments). Runs were conducted at 3 °C min<sup>-1</sup> at between 20 °C and 100 °C under an N<sub>2</sub> atmosphere. Analyses were conducted in the form of the tensile model with film samples at the approximate dimensions of 15 × 4 × 0.2 mm. The amplitude equalled 5 µm and auto strain was set to 115%. The resulting curves displayed storage modulus, loss modulus and tan δ versus temperature.  $T_g$  was determined as the temperature for the peak of the loss modulus (E'') curve.

#### 2.2.4. Tensile test

Investigations into tensility were carried out on a universal tensile testing device, the M350-5 CT Materials Testing Machine (Testometric Company, Lancashire, UK), at a crosshead speed of 5 mm min<sup>-1</sup> in accordance with ČSN EN ISO 527-1-4. The dimensions of dog-bone form specimens cut from the compression moulded films were 60 × 4.0 × 0.1 mm. Prior to testing, the samples were conditioned under conditions of 22 °C at 64% relative humidity for 24 h. A minimum of eight specimens from each group were tested.

Statistical analysis was applied to process the results of mechanical analysis. So as to eliminate extraneous results, the authors carried out a Dean-Dixon test for homogeneity (Q-test; confidence level  $\alpha = 0.95$ ). After eliminating peripheral figures, corresponding averages and standard deviations (SD) were calculated.

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