



# Influence of the type of buffer solution on thermal and structural properties of polylactide-based composites



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## ABSTRACT

Hydrolytic degradation depends on internal and external factors. One of the external factors is pH of the degraded medium. In the case of buffer solutions changes in pH are strongly dependant on the capacity. For this reason the aim of this work was to determine the effect of the type of buffer solution on hydrolytic degradation of polylactide and its composites consisting of polylactide (L) as polymer matrix and Montmorillonite K10 (S). Hydrolysis was carried out within a period from 7 to 30 days at 60 °C in two buffers: phosphate buffer solution (pH 7.40) and phosphate–citric buffer solution (pH 7.40). In order to investigate the influence the type of buffer solution has got on hydrolysis, materials were analysed by means of differential scanning calorimetry, thermogravimetric analysis and <sup>1</sup>H NMR spectroscopy. Also changes in pH of buffers during degradation process were observed. The results indicated that the type of buffer solution, especially its capacity, strongly influences hydrolytic degradation of polylactide and PLA-based composites. In the buffer solution where pH of the degraded medium is similar to the pK<sub>a</sub> value, the degradation occurs at a lower rate.

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## 1. Introduction

Polylactide (PLA) is one of the most commonly recognized biodegradable polyesters, obtained from renewable materials such as corn starch, tapioca roots, starch, or sugarcane [1–3]. Furthermore PLA is a very promising material since it has got good mechanical properties and thermal plasticity, especially when compared to other biodegradable polymers. For this reason it is a material which has found applications in meat and soft drinks packaging, as well as in obtaining films used for packaging of agriculture products and hygiene products [4,5].

In the case of degradable materials their utility depends on their resistance to aging processes. One of the degradation processes is hydrolytic degradation which is caused by water. During this type of degradation water molecules diffuse into the polymer and start the hydrolysis of ester bonds [6,7]. Hydrolytic degradation depends on internal and external factors. Most important factors include: the degree of crystallinity of the materials, hydrophilicity, molecular mass, the presence of plasticizers, stabilizing agents, compatibilizers and nanofillers as well as particular properties of the sample such as surface roughness, thickness and porosity. Temperature and pH of medium are the most important external factors [8]. So far studies focused on particular nanofillers in one solution

and at one or, occasionally, at different temperatures [9–11]. Hydrolytic degradation of polylactide is a well known process. Numerous studies of hydrolytic degradation have been conducted at 37 °C to simulate this process in the human body and at temperatures ranging from 25 °C to 60 °C to illustrate hydrolysis in the soil and compost. It was suggested that the mechanism of hydrolytic degradation of the polylactide may be different above and below the glass transition temperature [12]. Furthermore the mechanism of hydrolytic degradation depends on the pH of hydrolytic medium [13,14]. In an alkaline medium the process of degradation starts with a nucleophilic attack of the terminal hydroxyl on another carbonyl group (Fig. 1). This mechanism yields oligomers of lactic acid and lactide which breaks down into lactic acid. However in an acidic medium, degradation of PLA is initiated by the protonation of the terminal hydroxyl group, and then by the formation of an intramolecular hydrogen bridge (Fig. 2). The products of this mechanism are lactic acid and oligomers of lactic acid.

Other factors which can influence hydrolytic degradation of polylactide are the different types of additives. The presence of a filler improves the hydrophilicity of the material and provides a large interfacial surface area. It is well known that the hydrolytic degradation of polylactide nanocomposites begins between two

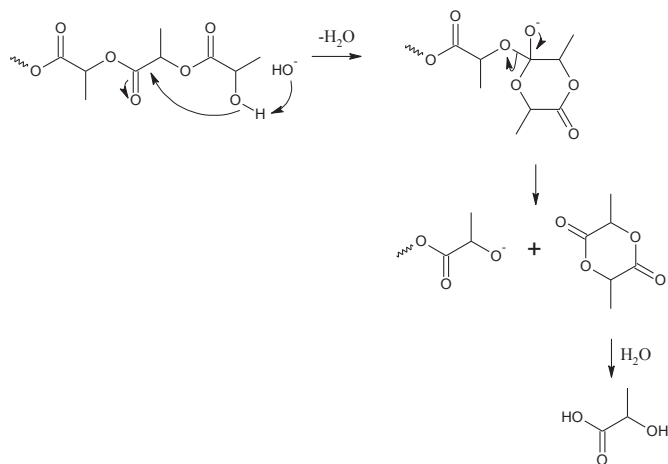


Fig. 1. Suggestions for mechanism of hydrolysis in alkaline environment [13].

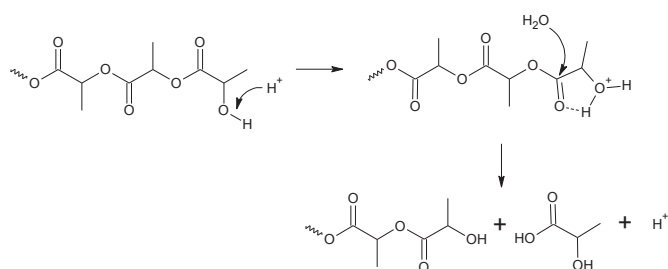


Fig. 2. Suggestions for mechanism of hydrolysis in acidic environment [13].

phases formed by PLA and a suitable filler [15].

Hydrolytic degradation of PLA-layered silicate in phosphate buffer (pH 7.40) at 37 °C was investigated by M.A. Paul [16]. K. Fukushima [12] studied hydrolysis of materials where polylactide was used as a polymer matrix and modified montmorillonite, modified fluorohexortyt and unmodified sepiolite as fillers. The degradation was carried out in phosphate buffer solution (pH = 7.0) at temperatures of 37 °C and 58 °C. Hydrolytic degradation of PLA-based composites in alkaline medium was analysed by H. Chen and all [17] in pH = 13 at 35.0 ± 0.2 °C and by Q. Zhou and all [18] in pH = 10.5 and at three different temperatures: 50 °C, 60 °C and 70 °C, while C. Stathokostopoulou and all [19] studied degradation under deionized water at a temperature of 37 °C. In spite of extensively documented study devoted to nanocomposite materials, there has been no focus on research into the influence the type of buffer solution has got on polylactide nanocomposites during hydrolytic degradation.

Therefore the main aim of this paper is to determine the impact the type of buffer solution as well as an additive, such as montmorillonite, have got on the polylactide hydrolysis. Thermal properties, during controlled hydrolysis, were studied by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These methods were applied in order to determine the melting points, heats of melting and decomposition temperatures of investigated PLA and polylactide-based composites. The molecular mass of the samples was calculated using <sup>1</sup>H NMR technique. The changes in pH of the mediums of degradation process were observed after 7, 14, 21 and 30 days of hydrolysis.

## 2. Experimental studies

### 2.1. Materials

Poly(lactide), type 2002D (NatureWorks®, USA), with melt flow rate of 5–7 g 10 min<sup>-1</sup> (2.16 kg; 190 °C), density of 1.24 g/cm<sup>3</sup> and number-average molecular weight  $M_n = 79,000$  was used as the polymer matrix. Montmorillonit K-10 (Acros Organics, Belgium) was used as the nanofiller. Investigated composites were obtained in the same way as described in our previous work [20]. Composition of investigated materials has been presented in Table 1.

### 2.2. Conditions of the degradation test

Hydrolytic degradation tests were performed in 100 ml of two buffered solutions (phosphate (pH 7.40) and phosphate-citric (pH 7.40)) at 60 °C. The compositions of the degradation media have been detailed in Table 2. The degradation medium was not renewed during the time of hydrolysis. After 7, 14, 21 and 30 days of degradation, samples were removed from the buffers, rinsed in distilled water and dried for further analyses.

To measure the pH of the solutions after respective degradation time the Elmetron CPC-505 pH-meter was used.

### 2.3. Methods of analysis

#### 2.3.1. <sup>1</sup>H NMR technique

Average molecular weight ( $\bar{M}_n$ ) distribution of PLA and PLA nanocomposite samples before and after different time of hydrolytic degradation was evaluated by means of the <sup>1</sup>H NMR technique. The spectra were recorded at 700 MHz using a Bruker 700 spectrometer. CDCl<sub>3</sub> was used as solvent. The CHCl<sub>3</sub> resonance at 7.26 ppm was used as chemical shift reference. All experiments were carried out at 27 °C.

#### 2.3.2. Thermogravimetric analysis (TG)

TA Instruments, SPT 2960 simultaneous DSC-TGA was used for studying thermal behavior of investigated materials. TGA traces were monitored starting at room temperature and up to 600 °C at 10 °C/min under air according to the procedure specified in PN-EN ISO 11358:2004.

#### 2.3.3. DSC method

The melting characteristics of composites were determined using DSC (Polymer Laboratories, Epson, GB under nitrogen screening). The heating rate was 10 °C/min and the temperatures ranged from 25 °C to 200 °C, according to PN-EN ISO 11357:2002. The degree of crystallinity ( $X_m$ ) was evaluated by applying the following Equation (1), also used by other authors [21,22]:

$$X_m = \frac{\Delta H_m}{\Delta H^0 \times X_{PLA}} \times 100\% \quad (1)$$

Where  $\Delta H_m$  is the measured heat of fusion of sample,  $\Delta H^0$  is the heat of fusion of a 100% crystalline polylactide and  $\Delta H^0 = 109$  mj/

Table 1  
Compositions of investigated materials (L – polylactide; S–Montmorillonite) [20].

Sample symbol	Sample composition (mass parts)	
	PLA	S
L	100	–
LS1	100	1
LS3	100	3
LS5	100	5

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