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BIODEGRADATION BEHAVIOR OF LACTIC ACID, ETHYLENE GLYCOL AND TEREPHTHALIC ACID COPOLYMERS UNDER CONTROLLED COMPOSTING CONDITIONS

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ABSTRACT. The copolymers were synthesized by the microwave-assisted polycondensation of L-lactic acid (LA), ethylene glycol (EG) and terephthalic acid (TPA) (different ratio of monomers). Biodegradation tests of the obtained copolymers and microcrystalline cellulose (MC) were performed under controlled composting conditions using a standard test method (ISO 14855-1, 2005). It was observed that the biodegradation of copolymer with higher quantity of lactic acid was faster and more effective than the biodegradation of copolymer with smaller quantity of lactic acid.

Keywords: *L-lactic acid, copolymer, microwave-assisted polycondensation, compost, biodegradation*

INTRODUCTION

Recently, an amplified contamination of the environment has been observed due to increasing volume of plastic wastes that persist for many years after disposal. The use of biodegradable polymers, namely in applications with a short life cycle of the products (packaging) would be an ecologically viable alternative for reducing the solid plastics waste [1]. The biodegradability of polymers is predetermined by their chemical and/or physical structure. In developing biodegradable polymers, it is very important to synthetize polymers having both satisfactory mechanical properties and biodegradability [2]. Aiming this target, in the last few years, polyesters have been considered the best candidates to replace traditional polymers because of their potential biodegradability given by their hydrolysable ester bonds. However, the biodegradability of aliphatic and aromatic polyesters is completely different, aliphatic polyesters are easily susceptible to microbial attack while aromatic polyesters such as poly(ethylene terephthalate, (PET) are not significantly influenced by the hydrolytic degradation [3-5].

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Recently, in order to decrease the average sequence length of PET and acquire good degradability, copolymerization with biodegradable aliphatic polyesters such as poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA) was carried out [6]. PET/PEG, poly(ethylene glycol) copolymers and poly(butylene terephthalate)/PEG copolymers were synthesized by polycondensation between ethylene diols, dimethyl (terephthalate) and PEG monomers or by the macromolecular transesterification method, starting from PET and PEG macromers [7, 8]. Due to their low cost and good biodegradability, these copolymers may have different biomedical and ecological applications [9].

The aim of this work was to synthetize medium molecular weight copolymers of L-lactic acid, terephthalic acid and ethyleneglycol using microwave radiation. The obtained copolymers were characterized for acid value, hydroxyl value and number average molecular weight. The obtained copolymers were biodegraded under controlled composting conditions according to ISO 14855-1 [10].

RESULTS AND DISCUSSION

Synthesis of copolymers

Copolymers of lactic acid, ethylene glycol and terephthalic acid were obtained by microwave-assisted polycondensation. Copolymers containing high amounts of L-lactic acid (**1** and **2**) were isolated as yellow solids while copolymers containing less amounts of L-lactic acid (**3** and **4**) were isolated as light brown solids. Details regarding the synthesis and characterization of the obtained copolymers were summarized in Table 1. The obtained copolymers average molecular weight ranged from 9500 to 11000. The main advantages of microwave-assisted polymerization are: short reaction time, low power consumption and no need for nitrogen protection or vacuum.

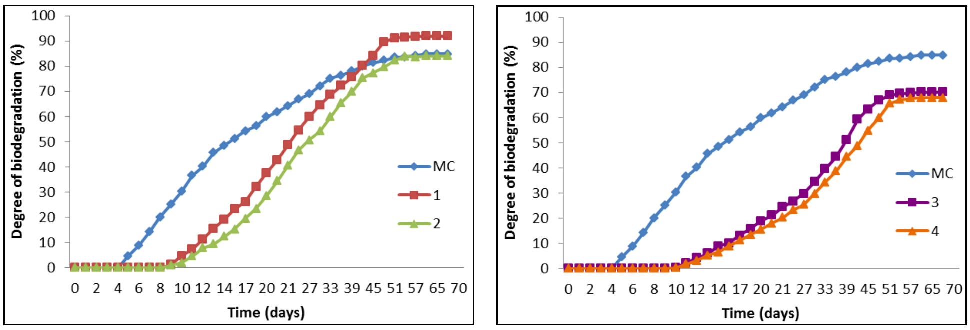
Table 1. Physical-chemical properties of the compost before (a) and after (b) biodegradability testing.

Parameters	**MC**		**1**		**2**		**3**		**4**	
	a	**b**	**a**	**b**	**a**	**b**	**a**	**b**	**a**	**b**
pH	7.91	8.24	7.91	7.10	7.91	7.23	7.91	7.98	7.91	8.04
Total dry solids (%)	50.9	48.9	50.9	48.2	50.9	48.5	50.9	49.3	50.9	49.3
Volatile solids (%)	28.1	25.0	28.1	18.4	28.1	20.3	28.1	24.1	28.1	25.0
Moisture (%)	50.8	51.9	50.8	52.3	50.8	52.0	50.8	51.4	50.8	51.8
C/N ratio	14.0	13.9	14.0	10.3	14.0	10.5	14.0	11.2	14.0	13.1

Biodegradation studies

The biodegradability of microcrystalline cellulose (MC) and lactic acid, ethylene glycol and terephthalic acid copolymers was determined under controlled aerobic composting conditions in the laboratory. In accordance with biodegradability testing, physical-chemical properties were determined both before (a) and after biodegradation testing (b) (Table 1). All physical-chemical parameters, of the inoculums gave suitable composting conditions according to ISO 14855-1: pH (7-9), volatile solid (less than 30%), moisture content (50-55%) and C/N ratio (10-40) [10].

Figure 1 (a and b) display the biodegradation curves of copolymers **1-4** and MC under controlled composting condition at 58°C according to ISO 14855-1. It can be seen that MC started to degrade after 5 days of induction, while copolymers **1-4** only after 10 days of induction. Copolymer **1** had the fastest speed of biodegradation. The biodegradation curves of all the samples tended to level off after 60 days. The ultimate degrees of biodegradation of **1**, **2**, **3** and **4** were 92.0%, 84.1%, 70.2% and 67.9%, respectively, after 60 days of biodegradation according to ISO 14855-1.



(a) **(b)**

Figure 1. Biodegradation curve of (a) copolymers PLA-EG-TPA (**1** and **2**) and (b) copolymers PLA-EG-TPA (**3** and **4**) under controlled composting conditions.

The aerobic biodegradation experiments were valid because the degree of biodegradation of reference material (MC) was over 70% after 45 days. The relative degree of biodegradation of a really biodegradable material, in less than 6 moths, under controlled composting conditions should not be less than 90% [11]. The relative degrees of biodegradation of **1**, **2**, **3** and **4** were 108%, 99.1%, 82.7% and 80%, respectively, relative to microcrystalline cellulose as a reference material. According to the above results, copolymers **1** and **2** were biodegradable materials. The order of biodegradation degree was

1 > **2** > **3** > **4**. As observed, the biodegradation of copolymer with high amount of L-lactic acid was faster than the biodegradation of copolymer with low quantity of L-lactic acid. Similar results were reported by Iovino *et al.* [12].

Consequently, it can be concluded that the biodegradation degree of tested copolymers (**1-4**) was closely related to their composition. This result is in good agreement with data reported by Soni *et al.* [13]. Copolymers **1** and **2** were completely biodegraded under controlled composting conditions, whereas the copolymers **3** and **4** containing lesser amount of L-lactic acid were not fully biodegraded within that time period.

CONCLUSIONS

PLA-EG-TPA copolymers were synthesized by the microwave-assisted polycondensation of L-lactic acid, terephthalic acid and ethylene glycol (different monomer ratio). The obtained copolymers were characterized using acid value, number average molecular weight and biodegradation behavior under controlled composting conditions (ISO 14855-1). The inoculum parameters (pH, volatile solid, moisture content, and C/N ratio) determined before and after biodegradation tests indicated good composting conditions during experiments. The biodegradability of plastics is a complex process and is influenced by the nature of each material. According to this work, the degree of biodegradation, **1** > **2** > **3** > **4**, was correlated with the copolymer composition (the biodegradation of copolymers containing high amount of lactic acid was faster than the biodegradation of copolymers containing reduced amount of lactic acid).

EXPERIMENTAL SECTION

Materials

Thin-layer chromatography grade cellulose powder with particle size <20 μm, all chemicals and materials were purchased from Merck. 85-90 % (w/w) aqueous solution of monomer L-lactic acid was 99% optically pure according to the manufacturer. All chemicals were used as received without further purification or processing. Deionized water was prepared using a Milli-Q system (Millipore, Watford, Hertfordshire, UK). The compost medium was made of organic fraction of approximately 3-months old mature compost obtained from organic agriculture waste (39% vegetable waste, 35% fruits pells, 12% wood chips and 14% old compost).

Apparatus

The apparatus used for polycondensation was a Panasonic domestic microwave oven (2450 MHz, 1300 W) without any modifications. All reactions were carried out in a hood with strong ventilation. The total organic carbon content was determined by a Multi N/C 2100S Analyzer (Analytic Jena, Germany).

Preparation of PLA-EG-TPA

The microwave-assisted polycondensation of L-lactic acid (LA), terephthalic acid (TPA) and ethylene glycol (EG) was carried out simply by heating different ratio of monomers in a domestic microwave oven according to values from Table 2. After the addition of $SnCl_2 2H_2O$ (0.2 wt.-%) as catalyst, at 10 min, the reaction was continued for 10 min (total, 20 min). After slow cooling of the reaction mixture at room temperature, the obtained mixture was dissolved in approximately 15 ml chloroform. A volume of 20 ml deionized water was added and the obtained precipitated polymer was collected, then dried at room temperature under reduced pressure (1300 Pa) obtaining a white powder. The obtained copolymers were further used for biodegradability testing.

Table 2. Summary of the synthesis and characterization of the PLA-EG-TPA copolymers (**1**-**4**).

Copolymer	LA (mol)	TPA (mol)	EG (mol)	Acid Value	Hydroxyl value	M_n
1	20	1	1	0.021	0.020	9524
2	2	1	1	0.020	0.022	10000
3	1	10	10	0.019	0.024	10526
4	1	20	20	0.018	0.027	11111

Characterization

The obtained copolymers were characterized for acid value, number average molecular weight and biodegradability.

Acid Value (C)

The acid value was determined according ASTM D 1639, by dissolving a known amount of polymeric material in ethanol and titrated against 0.1 N KOH using phenolphthalein as indicator. The acid number was calculated by the following expression:

$$C = \frac{56.1 \times V \times N}{m} \tag{1}$$

where V - volume of KOH solution, ml; N – normality of KOH, mol/l; m – weight of polymeric sample, g [14].

Hydroxyl value

Hydroxyl value was determined according ASTM D 2849 (method A) by dissolving approximately 0.50 g of sample in 50 ml phthoylating mixture and hydrolyzed by adding 100 ml of cooled distilled water in another flask. 20 ml benzene was added under vigorous stirring and the resulting solution was titrated against 0.5 N standardized KOH, using phenolphthalein as an indicator. A blank sample was also carried out. The hydroxyl value was calculated by following equation:

$$\text{Hydroxyl value} = \frac{56.1 \times (V_1 - V_2) \times N}{m} \tag{2}$$

where V_1 - volume of 0.5 KOH titrated for the blank, V_2 - volume of 0.5 KOH titrated for the sample; N, normality of KOH; m - weight of the polymer sample, g [15].

Number average molecular weight (Mn)

The number average molecular weight was calculated according to the following relationship:

$$M_n = \frac{n \times 100}{C} \tag{3}$$

where n - functionality of polymer; C - acid number.

Biodegradation tests

This study investigated the degradability potential of PLA-EG-TPA copolymers obtained by microwave-assisted polycondensation, under simulated aerobic degradation conditions. The synthetized samples were used as obtained, without further purification. The aerobic degradation testing conditions were performed in a laboratory scale installation in accordance to ISO 14855-1 [10]. This standard specify a general method to determine the ultimate aerobic biodegradability of polymeric materials, under controlled composting conditions by measurement of the amount of evolved carbon dioxide and the degree of biodegradation of the test materials at the end of the test. The test material is mixed with the inoculum and composted under monitored and controlled temperature, aeration and humidity during the 70 days of experiments. The used inoculums consist of 3-months old mature compost obtained from organic agriculture waste. The compost was sieved using a 4 mm sieve and its physical-chemical properties were determined: pH, total dry solids, volatile solids, moisture content and C/N ratio [16-21]. All the properties of the compost are in accordance with ISO 14855-1 requirements. This inoculum was stored at 5°C for 7 days. The experimental study was performed, in triplicates, in glass flasks of approximately 2 L internal volume containing: (*i*) test material (compost + copolymer), (*ii*) blank (compost) and (*iii*) reference material (compost + MC). In all cases the compost and test material were mixed in the ratio of 60-360 g (dry mass), transferred into a glass flasks and introduced in a water bath at 58°C and purged with 50 mL/min compressed air (carbon dioxide - free) flow rate. The carbon dioxide from the compressed air was removed by passing the air through a solution of 0.05 mol/l NaOH. During the experiment, the moisture content of the mixture was maintained at around 45-55% and the compost was regularly mixed to ensure maximal homogeneity. The activated compost used in this study produced 55 mg CO_2/gram of volatile solids over the first 10 days of the test [10].

The carbon dioxide produced during the biodegradation process was trapped in 0.05 mol/l NaOH connected with the composting glass flasks by polyethylene tubes. The carbon dioxide traps were changed from daily to three times a week depending on the degradation rate. The total organic carbon content from each trapping solution was determined by Multi N/C 2100S Analyzer, Analytic Jena, Germany [22].

According to ISO 14855-1, the theoretical amount of CO_2 which can be produced by the polymeric material ($ThCO_2$, g/flask) was calculated using the following equation:

$$\mathrm{ThCO}_2 = M_{TOT} \times C_{TOT} \times \frac{44}{12} \tag{4}$$

where M_{TOT} – total dry solids in the polymeric material added into the composting flask at the start of the experiment, g; C_{TOT} – proportion of total organic carbon in the total dry solids in the polymeric sample; 44 and 12 – the molecular mass of CO_2 and atomic mass of C, respectively.

The degree of biodegradation of test materials for each measurement interval determined from the released cumulative amounts of CO_2 was calculated according to the following equation:

$$(\%)\mathrm{Biodegradation} = \frac{(CO_2)_S - (CO_2)_B}{\mathrm{ThCO}_2} \times 100 \tag{5}$$

where $(CO_2)_S$ – the amount of CO_2 evolved in each composting flask containing polymer sample, g/flask; $(CO_2)_B$ – the amount of CO_2 evolved in blank flask, g/flask [23].

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