

## BIODEGRADATION STUDIES OF POLYLACTIC ACID COPOLYMERS

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### ABSTRACT

Medium molecular weight copolymers were synthesized by the condensation of L-lactic acid (LA), terephthalic acid (TPA) and 1,3-propanediol (PDO). The obtained copolymers were characterized for acid value, hydroxyl value and number average molecular weight. Also, the biodegradation behavior by different fungal species (*Aspergillus niger*, *Aspergillus versicolor*, *Alternaria alternata* and *Penicillium*) was performed. The degree of biodegradation was examined by weight loss. 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.

### INTRODUCTION

Polymer materials produced from petrochemicals are inert and resistant to microbial attack. Therefore, the degradable and biodegradable polymers are of considerable interest with respect to solid waste accumulation. In the last few years, polyesters have been considered the best candidates to replace traditional polymers because of their potential biodegradability due to their hydrolysable ester bonds. The biodegradability of aliphatic and aromatic polyesters is completely different: (i) aliphatic polyesters are easily susceptible to microbial attack (depolymerization or surface erosion followed by enzymatic hydrolysis resulting soluble intermediates that can be easily assimilated by microbial cells; aliphatic polyesters containing diacids of medium-sized monomers, are more easily degraded by fungi (*Aspergillus niger* and *Aspergillus flavus*) than those derived from longer or shorter monomers [1] and (ii) aromatic polyesters are not significantly influenced by the hydrolytic degradation [2, 3]. However, some growth of *Aspergillus niger* and *Aspergillus flavus* were observed on the surface of low molecular weight aromatic polyesters [4]. Recently, much progress has been carried out in polylactic acid (PLA), polyglycolic acid (PGA) and their copolymer (PLGA). PLA and PGA and their copolymer can be obtained by following processes: a) ring opening polymerization of cyclic dimers (lactide and glycolide) in the presence of metal/metal compounds catalysts to synthesize high molecular weight polymers and b) direct condensation reaction of lactic acid / glycolic acid to obtain low molecular weight polymers [5-8].

The aim of this work was to synthesize medium molecular weight copolymers of L-lactic acid, terephthalic acid and 1,3-propanediol. The obtained copolymers were characterized for acid value, hydroxyl value and number average molecular weight. Copolymers were biodegraded by four fungal species. Biodegradability studies were performed by weight loss.



## MATERIALS and METHODS

All chemicals were of analytical grade (Merck KGaA, Darmstadt, Germany) and used without further purification. The highest available purities were used. L-lactic acid was an 85-90 % (w/w) aqueous solution of monomer, 99% optically pure according to the manufacturer. Molecular sieves were activated at 250 °C for 24 h.

### Preparation of copolymers

Copolymers of L-lactic acid, terephthalic acid and 1,3 propanediol were prepared by direct polycondensation (different ratio of monomers, Table 1). The corresponding quantities of monomers were introduced in a 100 ml three-necked round bottom flask equipped with a Dean Stark trap containing molecular sieves 3 Å. In first stage temperature was kept at 100 °C for 8 h. The initial white suspension turns into a clear solution. In second stage the reaction was performed at 260 °C for 12 h and 0.2% SnCl<sub>2</sub> · 2H<sub>2</sub>O was added as a catalyst. After slow cooling of the reaction mixture room temperature, the copolymers were precipitated by addition of deionized water. Precipitated copolymers were collected by filtration and dried under reduced pressure and then white powders were obtained.

Table 1. Overview of the synthesis and characterization of the obtained copolymers

Copolymer	LA (mol)	TPA (mol)	PDO (mol)	Acid value*	Hydroxyl value**	M <sub>n</sub> ***
1	1.0	0.5	0.5	0.021	0.022	9524
2	0.1	2.0	2.0	0.020	0.025	10000

\* ASTM D 1639-90 (1996), Standard Test Method for Acid Value of Organic Coating Materials

\*\* ASTM D2840-69(1976) Method of Test for Average True Particle Density of Hollow Microspheres

\*\*\* M<sub>n</sub> = F×100/C (F - functionality of polymer, C - acid value).

### Characterization

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

*Biodegradation studies.* Synthesized copolymers were tested for their biodegradability by fungal species. For fungal species were selected for this study: *Aspergillus niger*, *Aspergillus versicolor*, *Alternaria alternata* and *Penicillium*. 15 ml of potato dextrose agar medium (PDA) was poured in each sterilized Petri dish. On each Petri dish a small quantity of the fungus culture was added. The Petri plates were incubated at 25 °C for 7 days in WTW OxiTop BOD measurement incubator. The growths of fungus were scrapped from Petri plates and introduced into 250 ml Erlenmeyer flasks containing 100 ml sterile distilled water. These samples were incubated at 25 °C for 10, 20, 30, 40, 50 and 60 days. The samples were taken out from the culture media, repeatedly rinsed by a stream of distilled water and dried under vacuum. All experiments were performed in duplicate and average values were reported. Non-inoculated flasks were used as controls and were treated in the same way as the samples. The effect of fungal treatment of copolymers was monitored by weight loss.

*Weight loss* (gravimetrically) was calculated by the following expression:

$$\text{Weight loss} = \frac{\text{Weight of sample before degradation} - \text{Weight of sample after degradation}}{\text{Weight of sample after degradation}} \times 100$$



## RESULTS

### Synthesis of copolymers

Copolymers containing different ratio of L-lactic acid, terephthalic acid and 1,3-propanediol were obtained by polycondensation reaction. The copolymers were obtained as white coloured solids having medium molecular weight. The acid value, hydroxyl value and number average molecular weight are presented in Table 1.

### Biodegradation by fungal species

The degree of biodegradation of copolymers 1 and 2 expressed as weight loss is presented in Figures 1 and 2.

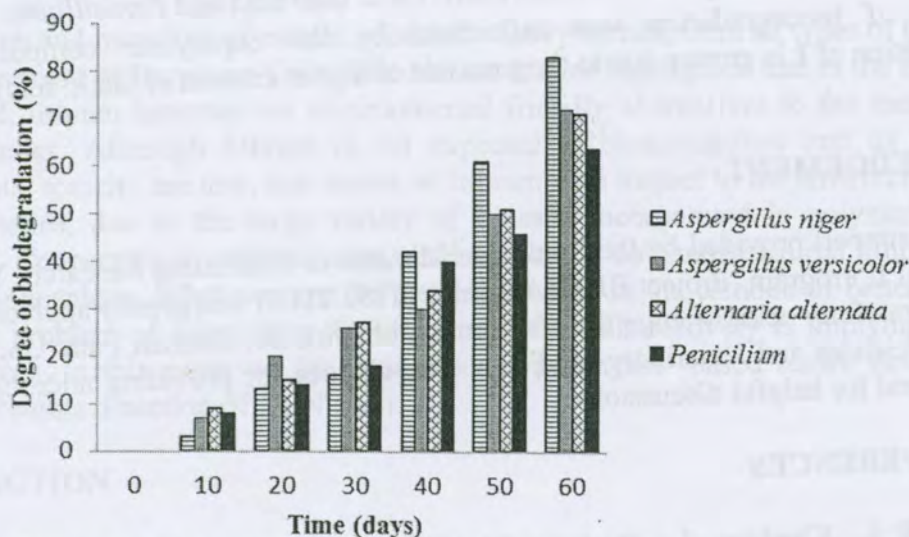


Figure 1. Biodegradation of copolymer 1 by different fungal species

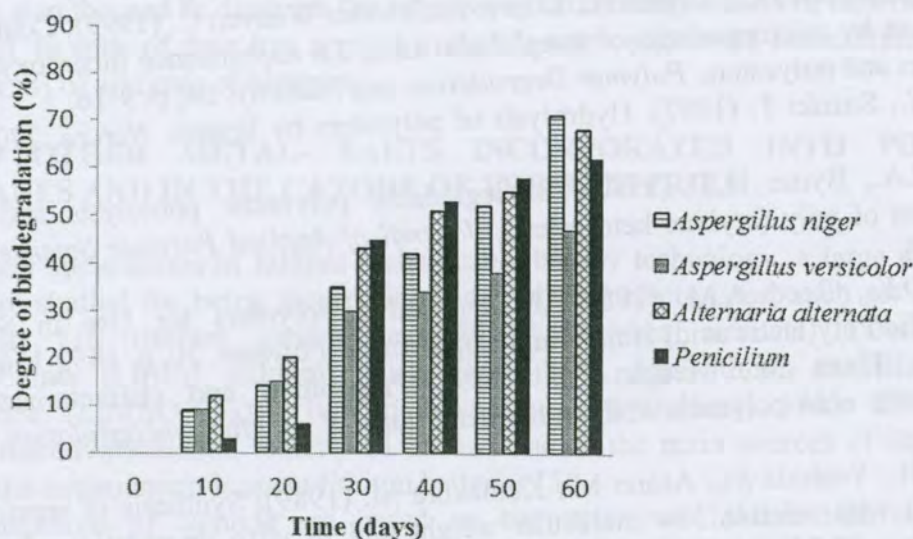


Figure 2. Biodegradation of copolymer 2 by different fungal species

The highest biodegradation occurs in the case of *Aspergillus niger* as compared to other fungal species (83% - 1 and 71% - 2). Also, good results were obtained for *Aspergillus alternata* (71% - 1 and 68% - 2). The biodegradation of copolymer 1 was higher than copolymer 2 for *Aspergillus versicolor* (72% - 1 and 47% - 2). In both cases, the least result was obtained by biodegradation by *Penicillium* (64% - 1 and 62% - 2). Similar results were



reported by Soni et al. [9]. The weight loss was directly proportional to the content of lactic acid. Accordingly, the degradation rate was faster and more effective in the case of copolymer 1 (LA : TPA : PDO = 2 : 1 : 1, molar ratio) having excess amount of lactic acid than in the case of copolymer 2 (LA : TPA : PDO = 1 : 20 : 20, molar ratio).

## CONCLUSIONS

- The title copolymers were synthesized by the polycondensation of L-lactic acid, terephthalic acid and 1,3-propanediol by using different monomer ratio.
- The obtained copolymers were successfully biodegraded by different fungal species (*Aspergillus niger*, *Aspergillus versicolor*, *Alternaria alternata* and *Penicillium*).
- The rate of biodegradation was influenced by the copolymer composition (the biodegradation of 1 is greater due to the presence of higher amount of lactic acid).

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