Polymer Testing 32 (2013) 209–214

Contents lists available at SciVerse ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material behaviour

A comparative analysis of mass losses of some aliphatic polyesters upon enzymatic degradation

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ARTICLE INFO

Article history:
Received 18 September 2012
Accepted 29 October 2012

Keywords:
Aliphatic polyesters
Enzymatic degradation
Mass loss
Crystallinity

ABSTRACT

Results of investigation of mass losses, geometrical surface structure changes and variations in crystallinity of poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL) and commercially available material (PHB) consisting of poly(3,4-hydroxybutyrate) and poly(lactic acid) are presented. These structural changes occurred due to degradation of these polymers in the presence of the following enzymes: proteinase K, protease, esterase or lipase. Independently of the enzyme type, the largest mass loss was found for PLA and the smallest for PHB. Thus, under the experimental conditions, the processes of enzymatic degradation proceeded most rapidly in PLA, more slowly in PCL, and the most slowly in PHB. It was also found that proteinase K caused the largest mass losses, protease caused smaller mass losses, and both esterase and lipase produced the least mass losses, while lipase did not bring about mass loss in PHB. Images of surfaces of individual samples, obtained by scanning electron microscopy (SEM), indirectly confirmed the results of the mass loss examination. Crystallinity of the studied polyesters increased with degradation in the presence of proteinase K and protease, while changes in the crystallinity due to esterase and lipase were not observed. The presented results illustrate well the relative susceptibilities of the individual polyesters toward degradation induced by various enzymes.

1. Introduction

A rapid growth in the mass of plastic waste being placed in dumping grounds or directly polluting the natural environment has been observed in most countries for more than 30 years. It is a source of many problems experienced by contemporary civilisation. Therefore, proper management of the plastic waste is a subject of special interest of scientists, economists and politicians, hence the issue is considered in various legal regulations, including the European Union directives [1].

Polymer degradation under different environmental conditions, together with biodegradation, is one of the important areas of that interest. Many attempts have been undertaken to perform enzymatic degradation of, not only typical biodegradable polymers, but also of regular polymers and mixtures of the latter with biodegradable polymers [2–8].

Biodegradable aliphatic polyesters are widely used in medicine and pharmacology as various implants and drug carriers because they are biocompatible and undergo natural biodegradation in a human body, while not releasing any compounds harmful to the organism. In particular, polylactide (PLA) [9–11], poly(ε-caprolactone) (PCL) [12,13] and poly(3-hydroxybutyrate) (P3HB) [14,15] are of growing interest because, according to current prognoses, they may largely replace regular, non-biodegradable polymers, mostly in the packaging branch of industry.

Processes of enzymatic degradation of PLA, PCL and P3HB as well as of their copolymers have been intensively studied and the investigation results have been reported in

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0142-9418/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymertesting.2012.10.011

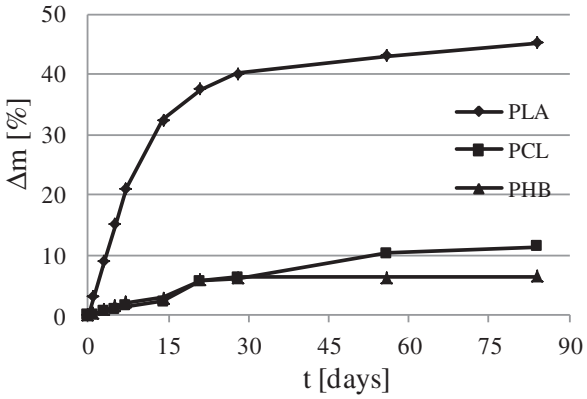

Fig. 1. Mass losses (Δm) of samples of a) PLA, b) PCL, and c) PHB vs. time (t) of degradation caused by proteinase K.

many publications [16–33]. Nevertheless, a direct comparison of the results of these studies is relatively difficult because of different experimental conditions (including carrying out degradation in different environments and with various enzymes), as well as due to different effects of activity of the enzymes being members of the same subgroup, but being produced by different microorganisms, or being present in different media [2,29,34]. A general conclusion resulting from the literature is that the course of the polymer degradation process is strongly affected by the following polymer properties: (a) chemical constitution, (b) average molecular weight, (c) wettability, (d) crystallinity and a crystal size, (e) content and type of additives, and (f) properties of the surface layer [35]. However, there is no agreement as to evaluation of the effect of the enzymatic degradation of some polyesters on their crystallinity. Some authors [23,26,36] claim that crystallinity of both PCL and PCL/PLA blends decreases upon degradation, whereas others [27] indicate that the PCL crystallinity increases. According to Canetti et al. [28], the increase in both the crystallinity and the crystal size of P3HB hinders the enzymatic degradation of this polymer.

The purpose of the present work, being a continuation of our previous studies [37], is to perform a comparative analysis of mass losses, geometrical surface structure changes and variations in crystallinity of three polyester materials. The alterations were to be caused by four commercially available enzymes that belong to a group of hydrolases [38]. The mass loss of an individual material due to the enzymatic degradation process may serve as a measure of the degradation degree [24,39]. The authors of the present paper have found no results of such studies. This allows them to believe that the presented data are original and may be used to

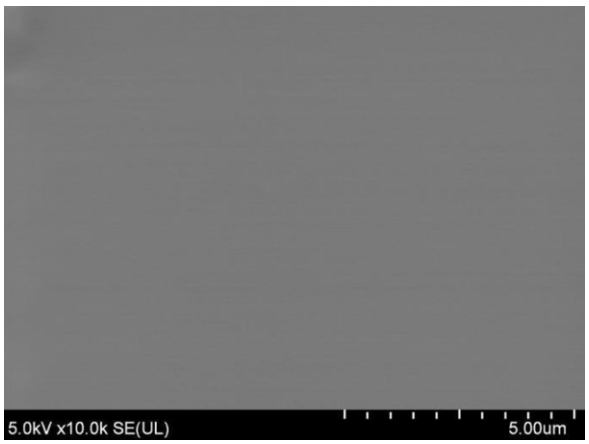

Fig. 2. SEM image of a surface of an original PLA sample.

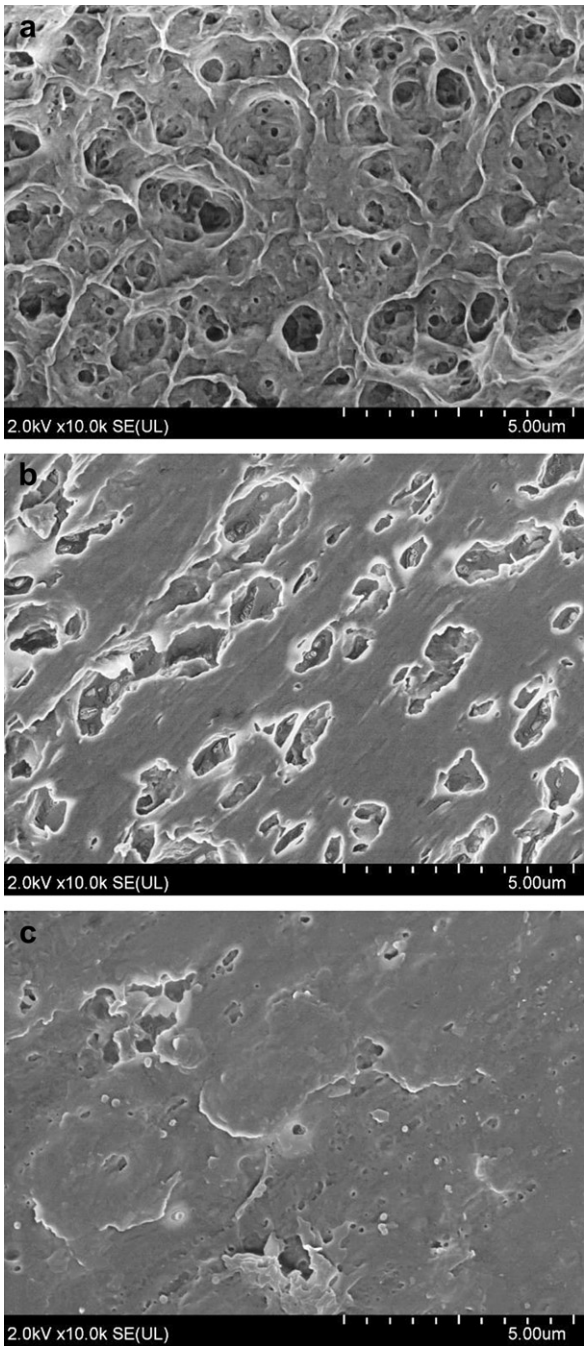

Fig. 3. SEM images of surfaces of samples of a) PLA, b) PCL, and c) PHB degraded for four weeks by proteinase K.