ENZIMATIC DEGRADATION OF POLY(OCTAMETHYLENE SUBERATE) LAMELAR CRYSTALS

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Introduction

The development of biodegradable polymers has received great attention due to their potential applications as both commodity and speciality materials. Polyesters constitute the main family of applied biodegradable polymers in which, the ester groups are the hydrolyzable bonds susceptible to an enzymatic attack. Studies on biodegradation establish that degradation of semi crystalline polymers proceeds faster in the amorphous phases but also take place in the crystalline phases. This fact deserves a special interest when materials are submitted to an enzymatic degradation since the close packed crystalline regions must hinder the enzymatic attack.

We have recently undertaken a structural study on polyalkylen dicarboxylates that in general revealed a complex packing structure. The main goal of this work is to elucidate if crystal sectors can suffer a different enzymatic degradation. Polyoctamethylene suberate (PE 88), has been chosen since the influence of the crystallization conditions (solvent and temperature) on the morphology has been intensively studied. Due to lipases from Rhizopus sp. preferentially attack the lamellar surface of this polymers, they were selected.

Results

Poly(octamethylene suberate) crystallized from diluted 2,5-hexanediol solutions as lozenge truncated crystals which structure is defined by an orthorhombic unit cell (*a* = 0.503 nm, *b* = 1.478 nm and *c* (chain axis) = 2.170 nm) containing four molecular segments. The degree of truncation could be regularly varied with the crystallization temperature in such way that the growth along the [100] direction became enhanced with temperature.Thus, the relation between the lengths of {010} and {120} growth faces could be changed between 0.7 and 2.0 when crystallization temperature increased from 42 to 51ºC. Lamellar surfaces usually appeared irregular due to the formation of striations in the {120} sectors which developed parallel to the [100] direction and had a rather variable height. Lamellae had a bilayered organization when crystallization temperature was allowed to oscillate (±3 ºC), whereas monolayers developed when temperature was practically constant (± 0.5 ºC). In the former, the global thickness became close to 24 nm and the two layers could indeed be well differentiated when crystals edges appeared irregular. In the second case, crystals had regular faces and a thickness in the 10-12 nm range.

Enzymatic degradation by lipases from Rhizopus oryzae could took place on the lateral growth faces when crystals had a bilayered organization and irregular edges . However, the main attack was usually detected on the lamellar surfaces. The present work clearly stated that crystal sectors have a different susceptibility towards the enzymatic attack which was enhanced in the {120} sectors. In this way, degradation could be minimized when crystals had elongated morphologies and regular edges. Degradation was also observed to progress preferentially along one crystalline direction (i.e. [100]). Thus, molecular packing and the nature of molecular folds seem to be determinant factors for the enzymatic degradation process.

Acknowledgements

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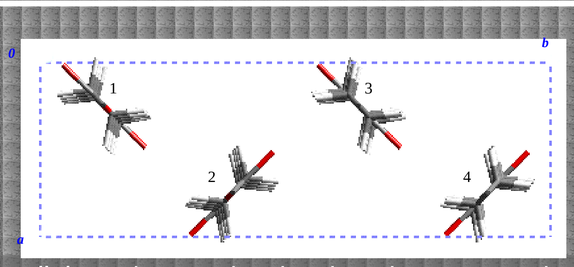

Figure 1: View parallel to the *c*-axis showing the proposed packing of PE 88. Molecules 1 and 3 or 2 and 4 are equivalent in the chain axis projection.

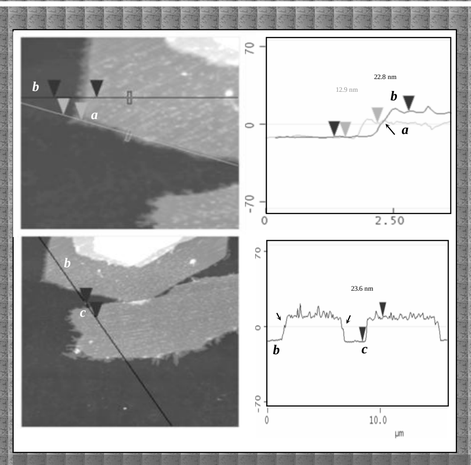

Figure 2: Atomic Force Microscope phase images (left) and height profiles (right) images of PE 88 single crystal prepared from 2,5-hexanediol at 45 ºC.

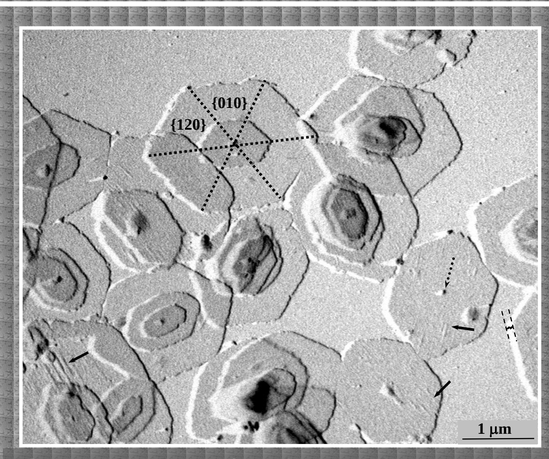

Figure 3: Crystals of PE 88 prepared at 45ºC and exposed to pH 7.2 buffered medium without enzyme. Nuclei can be usually observed in the centre of each lamellar crystal (doted arrows) as well as striations in the {120} sectors (solid arrows).

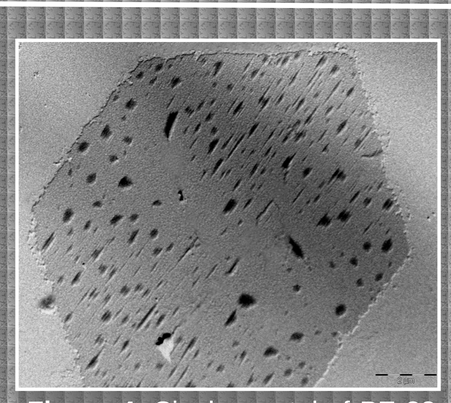

Figure 4: Single crystal of PE 88 at 45 ºC after being exposed to the enzyme medium for 30 min.

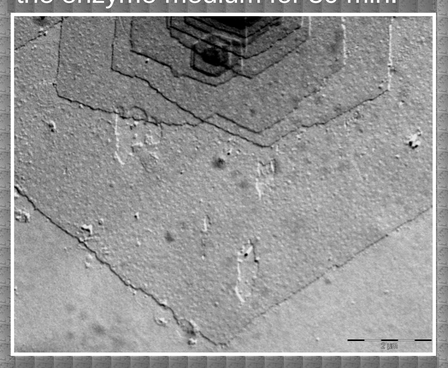

Figure 5: Crystals of PE 88 obtained at 45ºC (±0.5ºC) after 45 min of enzymatic degradation. Note the elongated holes that develop on the {120} sectors.

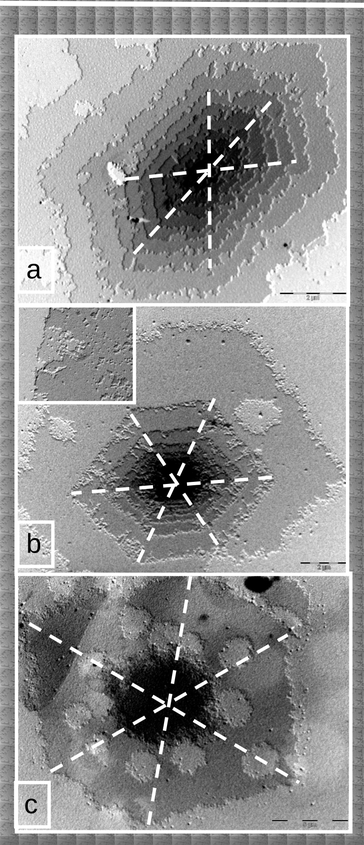

Figure 6: Crystals of PE 88 obtained at 51 (a), 44 (b) and 42 ºC (c), after 3 h of enzymatic hydrolysis. Crystallizations were performed in baths without temperature control. Insert of b) shows a double crystal layer.

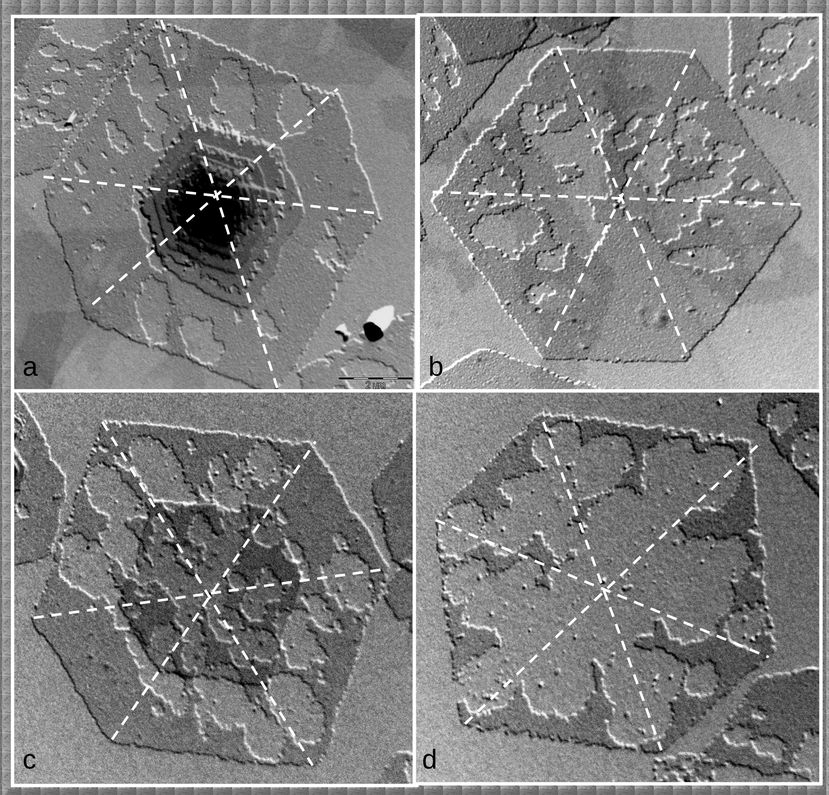

Figure 7: Lamellar crystals of PE 88 prepared at 42 ºC after being exposed to the enzymatic medium for 2 (a), 2.5 (b), 3 (c) and 3.5 h (d). Crystallizations were performed in baths with a strict temperature control (i.e. 0.5 ºC).