

Morphology of Plastic Deformation and Fracture of a Biodegradable Biopolymer

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BIOGRAPHY

Élida Hermida has an MS and a PhD in physics from the University of Buenos Aires. After a research fellowship from the Alexander von Humboldt Foundation at the Max Planck Institute in Stuttgart, she is now a full professor at the University of San Martín in Buenos Aires. Her research interests include the mechanical properties of materials, the morphology and nature of polymers and composites, the recycling of plastics, and biodegradation.



ABSTRACT

PHBV is an important sustainable product as it is produced from renewable resources, is completely biodegradable, and can be moulded as a petrochemical thermoplastic. The mechanical behaviour and biodegradability of this semicrystalline material strongly depends on its morphology. In this article we show how the amorphous matrix and the spherulites of PHBV behave under tension until they fail. We prepared an acid etching agent to reveal details in the spherulitic structure of compressed moulded sheets. Microtensile tests on the stage of a polarized light microscope showed that crazing and shear bands are the strain mechanisms operating within the amorphous matrix of PHBV. In the closely packed spherulites, crack propagation occurred along the circumferential planes of the spherulites, trans-spherulitically along radial or circumferential planes, or through the boundaries between spherulites.

KEYWORDS

light microscopy, polarized light microscopy, image analysis, morphology, strain mechanism, fracture, crystallinity, biopolymer

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INTRODUCTION

Polyhydroxyalkanoates (PHAs) are polyesters derived from the fermentation of renewable hydrocarbon resources by bacteria under nutritional stress; they function as an intracellular reserve of carbon and energy for bacteria [1]. These biopolymers can be melted and moulded like petrochemical thermoplastics, with similar thermal properties. Since the most remarkable property of the PHAs is their biodegradation in different environments [2-4], they could become a useful replacement for petrochemical plastics and so contribute to the reduction of 'white pollution' – the millions of tons of plastics that litter the world. Furthermore, since some of these biopolymers are bioabsorbable, they are suitable for biomedical applications [1]. These intriguing biological polyesters have attracted the attention of microbiologists and have kept many polymer scientists occupied since the 1950s. An excellent summary of these studies is in the review by Sudesh et al. [5].

The first PHA, discovered in 1927 by Lemoigne, was later identified as poly(3-hydroxybutyrate) (PHB). Because of its stereoregularity it is highly crystalline and consequently fairly brittle. Other HA units were identified later: one of them was 3-hydroxy-

valerate (3HV) that together with HB units form the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), with a lower degree of crystallinity and better mechanical properties. PHB melts at about 175°C whereas PHBV melts 5-10°C lower depending on the 3HV fraction [5].

When PHB or PHBV are slowly cooled down from the melt, crystallization occurs. Each crystalline nucleus grows in a rather spherical arrangement of radiating lamellae alternated with amorphous regions made of disordered macromolecular segments. This spherical structure, called a spherulite, grows until it meets surrounding spherulites or until the temperature decreases so much that the thermally activated folding of the random chains ceases, leaving spherulites surrounded by an amorphous matrix. The mechanical behaviour and the biodegradation of the biopolymer strongly depend on the crystalline morphology of the samples [6].

Since a drawback of these semicrystalline polymers is their brittleness, many researchers have studied how their morphology could be modified in order to increase the toughness of the polymer. In particular, the correlation between the fracture behaviour and the spherulitic morphology has become a chal-

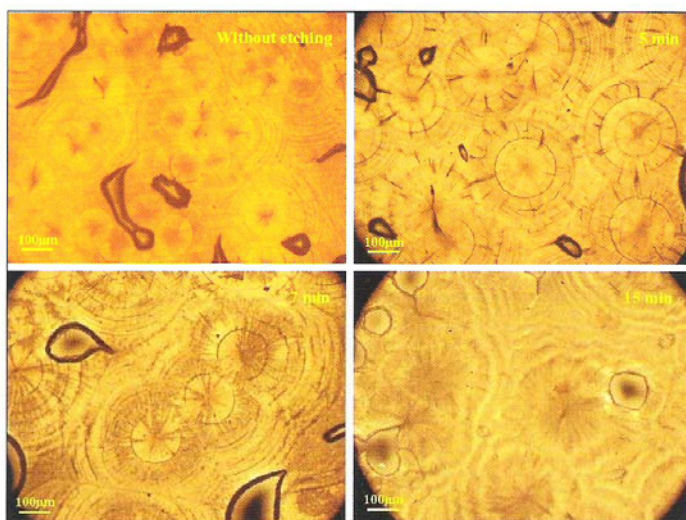


Figure 1: Morphology of compressed moulded samples of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) revealed after etching for the indicated times. The best results were observed after 7 minutes. After etching for 15 minutes the upper layer of spherulites had been removed and the new layer was being developed. Bundles of lamellae radiating from the spherulite centers are distinct whereas the spherulite boundaries are not well resolved.

enging issue for materials researchers. Indeed, changes in the spherulites of stretched samples have been investigated directly by polarized light microscopy (PLM) on films cast thin enough so that image resolution is not impaired by a multiplicity of spherulites across the film thickness [7]. Other researchers have observed spherulites in thin sections microtomed from samples deformed in bulk [8], however, it is not clear whether or not the microtome introduced artifacts (e.g. textures that are the effect of the preparation method and so could, incorrectly, be attributed to the specimen) [9]. Hobbs and Barham [10] observed the morphology of microtomed fracture surfaces deformed in bulk and of thin sheets of PHB with different ageing treatments. PHB undergoes crazing before failure regardless of the annealing history. Furthermore, there is an increased occurrence of fracture initiation in the spherulite cores after high temperature annealing which helps to extend the crazing zone. Later Barham and Keller examined thin sheets of PHB to study the relationship between morphology and fracture toughness; this work showed that the brittleness is due to either radial or circumferential cracks within the spherulites [11, 12].

However, changes in the semicrystalline morphology of PHBV during plastic deformation have not yet been shown. Thus, the aim of this study was to analyse the morphological changes produced in the amorphous matrix and the spherulites of PHBV under tensile stress. To achieve this goal, specimens with dispersed and impinged spherulites were produced by two different cooling treatments. Furthermore, a new etching agent that was used to reveal details in the spherulitic structure of compressed moulded sheets is presented. Microtensile tests allowed us to follow morphological changes during uniaxial loading by light microscopy while tensile testing to failure enabled us to determine the different crack propagation mechanisms.

MATERIALS AND METHODS

Sample Preparation

We used a copolymer of 3-hydroxybutyrate with 12 wt% 3-hydroxyvalerate (PHBV) purchased from PHBISA, Brazil [13]. The average molecular weight was 200 kJ mol^{-1} , the glass transition temperature T_g was $268 \pm 3 \text{ K}$ and the melting point T_m was $440 \pm 3 \text{ K}$.

Sheets of PHBV $0.35 \pm 0.05 \text{ mm}$ thick were prepared by compression moulding at $453 \pm 2 \text{ K}$ for 10 minutes under pressure cycles up to 5 MPa. Once melted, some sheets were set at 333 K for 10 minutes to promote nucleation and growth of spherulites, followed by slow cooling at room temperature. Others were left at room temperature for 15 minutes (slow cooling) and then quenched at 268 K in order to get dispersed spherulites in an amorphous matrix.

Dog bone samples, cut according to standard ASTM D638-03 [14], were stretched during microtensile tests under the microscope. The width of these samples, $3.18 \pm 0.02 \text{ mm}$, allowed a view of the whole crack propagation using low magnification objectives on the

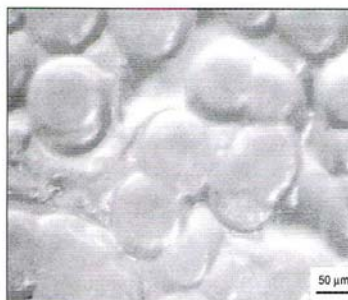


Figure 2 (left): Darkfield micrograph of a fine spherulitic specimen etched for 18 minutes, showing the surface relief.

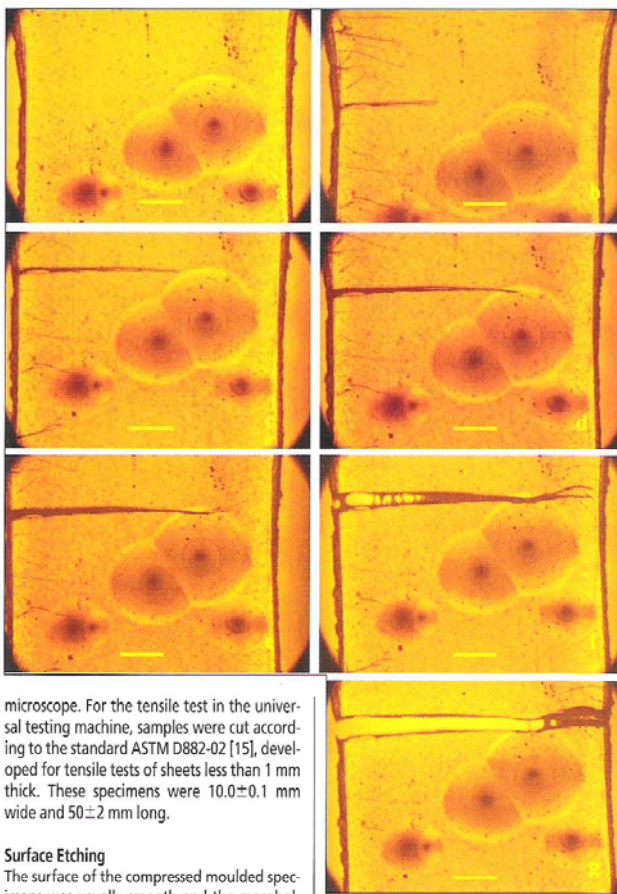


Figure 3 (below): Sequence of micrographs taken during a microtensile test; the tensile direction is vertical. Plastic deformation is due to the appearance of crazes that propagate until failure. The sample was slightly etched before the tensile test in order to improve the observation of the spherulitic and amorphous regions. Scale bars = $500 \mu\text{m}$.

microscope. For the tensile test in the universal testing machine, samples were cut according to the standard ASTM D882-02 [15], developed for tensile tests of sheets less than 1 mm thick. These specimens were $10.0 \pm 0.1 \text{ mm}$ wide and $50 \pm 2 \text{ mm}$ long.

Surface Etching

The surface of the compressed moulded specimens was usually smooth and the morphology undeveloped, as shown in Figure 1a, so a proper etchant was required. A review of etchants used to reveal spherulites and lamellae in polyethylene, polypropylene and other high polymers showed that permanganic acid (a weaker acid) selectively removes the amorphous regions of polyolefins [9]. Addition of orthophosphoric acid to the reagent decreases the presence of artifacts (textures that are an effect of the preparation method and cannot be attributed to the specimen) in drawn linear PE and in blends [14].

Based on this background, we prepared an etchant by dissolving a 1% w/v solution of

potassium permanganate in 10:4:7 mixture of sulphuric acid (98%), orthophosphoric acid (85%) and distilled water. This is a maroon solution that reaches $60 \pm 1^\circ\text{C}$ due to an exothermic reaction; this temperature was kept constant using a controlled heater. When samples were immersed into this solution the acid etching selectively removed the amorphous regions of the semicrystalline sample. After a certain etching time t_e the specimens were shaken in an ultrasonic bath with a 1:7 solution of sulphuric acid (98%) and distilled water cooled to its freezing point, for 10 min-

utes. Finally, the specimens were washed with distilled water, allowed to dry and set into a desiccator at 50% relative humidity.

Polarized Light Microscopy

The characterization of the morphology was performed using an Olympus BX60M light microscope. Samples were examined in bright field, darkfield, and brightfield with crossed polarizers using Olympus MPlan 5× 0.10 BD, 10× 0.25BD and 20× 0.40BD objectives. Images were taken with a Sony DSC-W200 12.1 megapixel camera.

Strain Testing

PHBV specimens with disperse spherulites in an extended amorphous matrix (etched slightly to enhance the observation of the morphology but without damaging the mechanical response) were uniaxially stretched at 293 K. A home-made microtesting machine set on the stage of the polarized light microscope was used to follow the evolution of the strain mechanisms. Tensile tests were performed 24 hours after moulding in order to avoid ageing effects.

RESULTS AND DISCUSSION

Surface Etching

The etching was suitable to reveal the semi-crystalline morphology, as illustrated in Figures 1b to 1d. Figure 1b shows that after etching for 5 minutes the nuclei of the crystalline regions and the radial and circumferential cracks began to appear. After 7 minutes the morphology of the spherulites (including their boundaries) was more clearly revealed as illustrated in Figure 1c. After etching for 15 minutes (Figure 1d) the morphology changed completely because the etching removed the outer layer of spherulites and began to reveal the next layer. In fact, the etching revealed the spherical shape of the spherulites, as shown in the darkfield micrograph shown in Figure 2. Hence, this etching might be useful to study the multilayered morphology of moulding products of PHBV, similar to those appearing in injection-moulded bars of isotactic polypropylene (iPP) [25,26].

Strain Mechanisms

Two modes of plastic deformation were found that depended on the conditions of stress: normal stress yielding (crazing) and shear yielding.

Crazing

The sequence of micrographs in Figure 3 illustrate the plastic deformation and failure of PHBV by crazing. If the edges of the specimen were amorphous, crazes initiated at any imperfection in them and ran perpendicular to the stress direction (vertical in the Figure). Note that the appearance of a craze was nearly identical to that of a crack in a tensile experiment, except that the craze was filled with load-bearing matter.

Shear Yielding

In specimens with smooth amorphous edges, the initiation of crazing was preceded by shear yielding. This was sometimes quite extensive, as shown by the kink bands running at about 60° to the tensile axis in Figures 4a and 4b. The

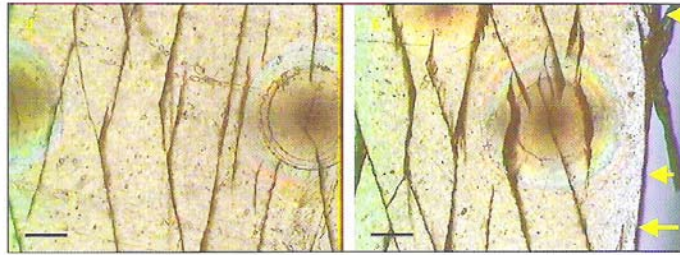


Figure 4:

Micrographs of the shear bands observed in two samples that were uniaxially stretched; the tensile direction is the horizontal axis. Specimens were etched after failure to enhance the shear bands. The fracture profile, indicated by the arrows, follows the limits of a shear band. Scale bar = 300 μm .

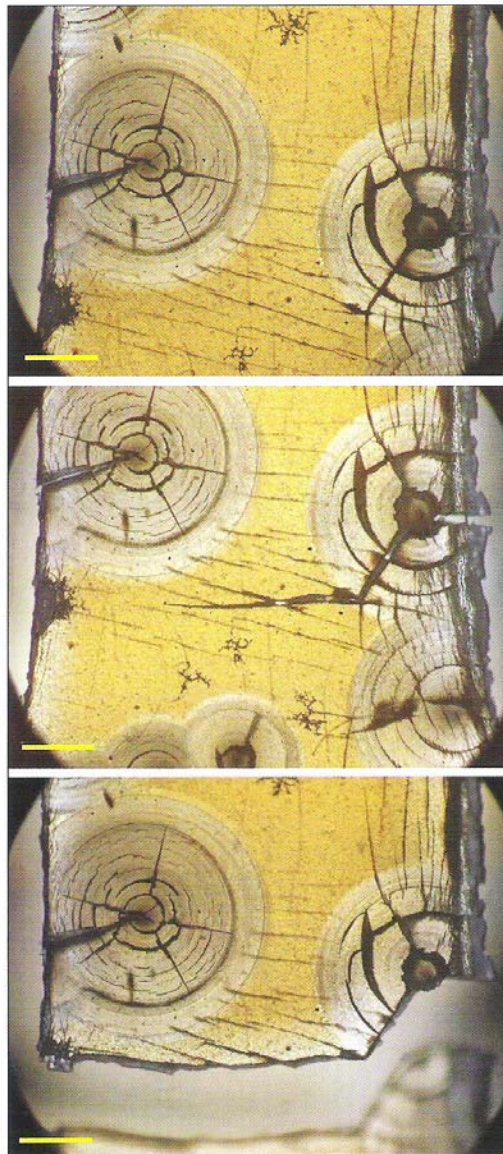


Figure 5:

Sequence of images showing the propagation of a crack. The tensile axis is vertical. Radial cracks propagate within the spherulites. At the same time shear bands appear in the amorphous matrix. Once the crack reaches the spherulite-amorphous interface, the fracture front follows along the shear bands. Scale bar = 500 μm .

limits of the shear bands distorted when they penetrated into the crystalline structure of the spherulites. Furthermore, as the shear bands were sites of highly localized deformation, the crack propagated along any of these lines, as shown in Figure 4b.

However, if the specimen had spherulites on the edges, they showed circumferential and radial cracks produced on cutting the sample from the moulded sheet. Then during the tensile test, there was a competitive evolution of shear bands that propagated along the amorphous matrix and cracks that opened and propagated along the spherulites, as shown in Figure 5. When one of the cracks reached the spherulite-amorphous interface, its propagation followed along the limits of the closest shear band.

Crack Propagation

In order to gain an insight into the crack propagation modes in the semicrystalline structure of PHBV with impinged spherulites, we used strips cut from the slowly cooled sheets. These samples were loaded uniaxially in an Instron 1122 universal testing machine at a rate of $1.65 \times 10^{-5} \text{ s}^{-1}$ up to failure; tensile tests were performed 24 hours after moulding in order to avoid ageing effects. After failure, the specimens were etched in order to enhance the morphological changes caused by the plastic deformation.

Figure 6 shows the three different modes of crack propagation observed. In effect, Figure 6a shows the fracture produced by crack propagation along the circumferential planes of the spherulites. On the other hand, Figure 6b illustrates trans-spherulitic crack propagation along radial planes or a combination of radial and circumferential planes. Finally, interspherulitic crack propagation is depicted in Figure 6c, where the fracture profile revealed the polyhedral shape of the impinged spherulites.

Crack propagation along radial cracks dominated the fracture of the impinged spherulitic morphology of PHBV. Modifications to the home-made testing machine to enable continuous recording of the applied stress will allow us to determine whether there is an important difference in the tensile resistance of each of the fracture modes, as occurs for iPP [26].

CONCLUSIONS

We have presented an acid etching agent that enhances the observation by polarized microscopy of the morphology of moulded PHBV specimens. It reveals properly circumferential bands, radial cracks, and boundaries between adjacent spherulites or between spherulites and the amorphous matrix, as well as providing an insight into the morphology of the inner spherulitic layers.

Microtensile tests of the compressed moulded PHBV samples show that crazing and shear bands are the strain mechanisms operating within the amorphous matrix. If, prior to the tensile test, the spherulites have micro cracks, they propagate along the spherulites and at the same time shear bands appear in the amorphous matrix.

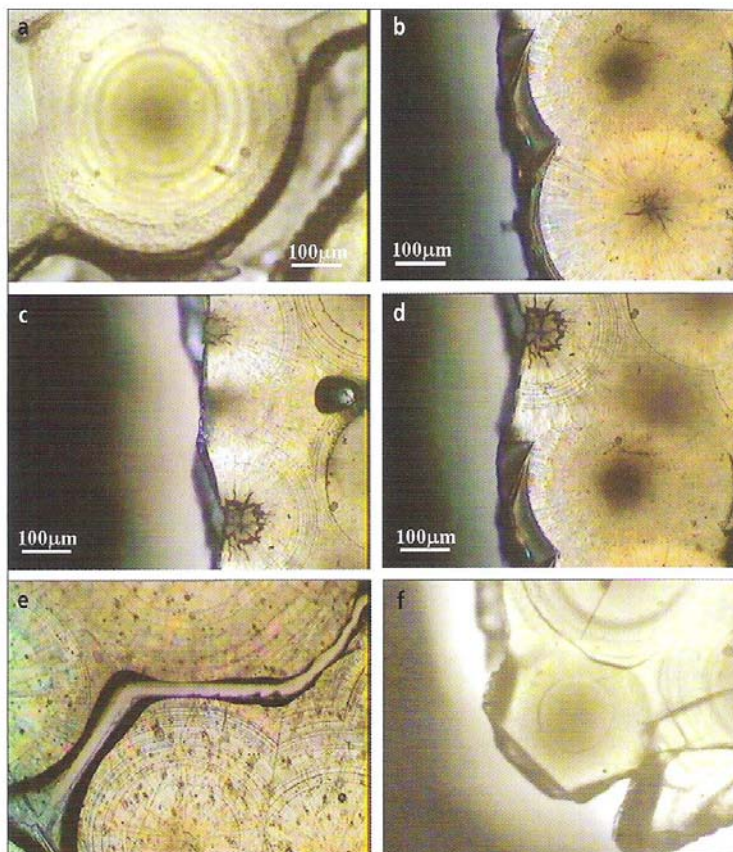


Figure 6: Crack propagation along (a, b) the circumferential planes of the spherulites, (c, d) the radial planes or a combination of radial and circumferential planes, and (e, f) the boundaries of adjacent spherulites, where the fracture front reveals the polyhedral shape of the impinged spherulites.

If the sample has impinged spherulites, its mechanical behavior is brittle with virtually no plastic deformation. In this case, three different modes of crack propagation were identified: (i) along the circumferential planes of the spherulites; (ii) trans-spherulitic along radial or circumferential planes; and (iii) through the sharp boundaries between adjacent spherulites. Furthermore, it was established that the crack propagation along radial cracks dominates the fracture of the impinged spherulitic morphology of PHBV.

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