Characterization of Polycaprolactone Films Biodeterioration by Scanning Electron Microscopy

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ABSTRACT

Widespread studies on the biodegradation of plastics have been carried out in order to overcome the environmental problems associated with synthetic plastic waste. From this point of view aliphatic polyesters represent a class of biodegradable materials with potential for various applications. Polycaprolactone (PCL) as representative of aliphatic polyesters undergoes biodegradation by the action of enzymes and microorganisms and hence it is suitable candidate for biodeterioration and biodegradation study. Biodeterioration activity of *Bacillus* strain, naturally occurring in soil environment, on the surface of polycaprolactone films in mineral salt and mineral salt-yeast extract enriched media at 30 °C after 21 days was studied. Polyester square specimens (10 × 10 mm) were sectioned from film prepared by melt pressing. Control abiotic tests were carried out by immersion of studied samples into the media in the absence of microorganism. Changes in film surface were evaluated by means of scanning electron microscopy (SEM) using Magellan 400/L (FEI, Eindhoven) at primary energy of 2 keV. For characterization of the material surface, here presented samples were without any chemical treatment and air-dried; they were coated by 4 nm of Platinum.

EXPERIMENTAL CONFIGURACION

During 42 days of solid state cultivation of microorganism only unevenly distributed microcracks were observed on the polyester film surface. During submerged cultivation considerable acceleration of film surface deterioration was observed already after 21 days of test. The abiotic hydrolysis was base-catalyzed since pH values in the range of 8-10 were developed in media during microorganism cultivation as the consequence of metabolic pathway. Microorganism and namely enzymatic action proceeds on ester bonds close to chains end since decrease in number average molecular weight (Mn) of polyester was measured. The process initiated with chain scission of ester bonds on the film surface was followed by loss of material (up to 3 wt.%) as surface erosion. The evaluation of the PCL films was done by the SEM Magellan 400 (FEI) at the electron energy of 2 keV by recording the secondary electron micrographs at various magnifications. All samples were quickly washed by distilled water, air-dried and coated by 4 nm Platinum to enhance the image contrast.

EXPERIMENTAL RESULTS

For the characterization of the investigated material surface structure by SEM, the parameters were evaluated as in [2]. There are following deformations recognized and described in the study:

1. **Microcracks on the surface with sharp edges (long 0.1 – 5 µm, 0.5 µm in width, the depth of cracks up to a few µm) and their directional orientation;**
2. **Holes in the surface (often annular);**
3. **The lamellar structure in the surface (incidence of long fibers with a diameter of up to 0.1 µm and their clusters);**
4. **The surface roughness;**
5. **Places with smooth surfaces;**
6. **The occurrence of bacteria (biofilm).**

The flat surface of PCL films is presented at Figure 1a. Microcracks developed on the surface of biotically aged films in mineral salt and mineral salt with yeast extract media were randomly distributed (Figure 1b, 1d). Formation of the irregular holes on the surface may be associated with higher enzymatic activity in mineral salt medium enriched with yeast extract. Polycaprolactone sample due to semicrystalline and hydrophobic character displayed only low water uptake in abiotic control media and consequently no weight loss along with no surface erosion proceeded (Figure 1c, 1e).

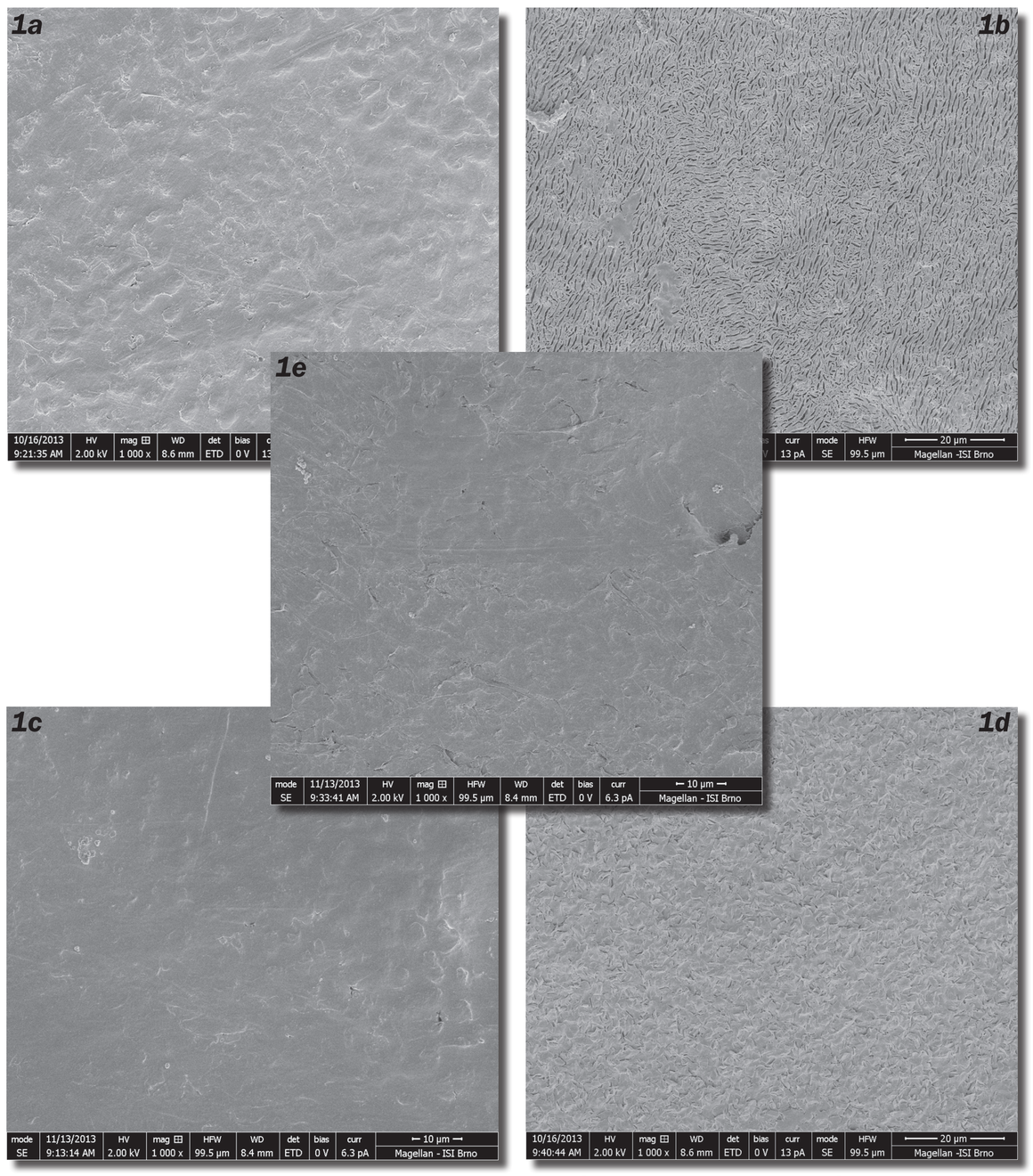

Figure 1: Scanning electron micrographs of polycaprolactone films. (1a) the original sample, (1b) PCL sample after 21 days in mineral salt medium inoculated with Bacillus strain, (1c) the control sample in mineral salt medium, (1d) PCL sample after 21 days in mineral salt medium supplemented with yeast extract and inoculated with Bacillus strain, (1e) the control sample in mineral salt medium supplemented with yeast extract.

CONCLUSION

The surface of PCL films was evaluated by SEM. Extensive tests with various preparation techniques [3] showed that the PCL films is not inert towards chemicals used within the standard protocols for chemical preparation. Acetone, commonly used for sample dehydration, dissolves PCL and, thus, cannot be used for dehydration. Also drying in solutions with low surface pressure, which require miscibility with acetone like hexamethyldisilazane was not possible to be applied. Critical point drying commonly used for drying of biological samples cannot be used due to instability of the PCL films under the high pressure and temperature that are the required for the technique. Therefore, all samples were quickly washed by distilled water, air-dried, coated by 4 nm Platinum and the surface investigation was done in the SEM Magellan 400 (FEI). The Scanning electron microscopy has proven to be a suitable method for the imaging and analysis of the investigated samples. We present the biodeterioration of PCL films and surface modifications induced by exposing to the *Bacillus* strain. Our results were compared with contorl samples incubated only in medium.

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