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Biodegradation of Blown Films Based on Poly(lactic acid) under Natural Conditions

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Summary: Commercially available polymer Bioflex® 219F, blend of polylactic acid and biodegradable co-polyester, was used for film preparation, performed on mono-extrusion blown moulding machine. Resulting thin film was investigated on biodegradability in composting conditions for 6 weeks. The influence of microbial attack on mechanical, physico-chemical properties, weight loss and surface morphology was tested weekly. The results obtained during 6 weeks of composting indicate relatively good accessibility to biological degradation. Moreover, the time course of studied properties was observed through the test period.

Keywords: biodegradable; composting; films; packaging; polylactic acid

Introduction

The environmental pollution by non-degradable plastic waste attracts attention to the development of biodegradable polymers made from renewable resources.[1] Polylactic acid (PLA) is one of the polymers which fulfil these conditions. In the environment it can be degraded within less than two years in contrast to conventional plastics such as polyethylene or polystyrene.[2,3] The extensive research on the PLA based materials results in the development of a number of products for various applications including medical items or compostable packaging. Some of them are commercially available, nowadays. It is related to the fact that PLA producers have to meet new requirements in the form of desired processing properties and maintenance of biodegradability simultaneously.[4]

There have been established several standards to assess whether material can be considered as biodegradable or not. These standards usually follow the methodology of decomposition products observation.[5] However, they mostly do not provide any information concerning the practical applicability point of view, such as mechanical properties (e.g. toughness, ductility) of the material or its visual aspects.

In this work, we deal with the determination of biodegradation course of blown film based on commercially available blend of PLA and biodegradable co-polyester in a composting environment. The main attention is paid to mechanical properties of investigated samples and their changes during the time of biodegradation. Beside that, mass loss, and observation of structural changes of PLA films due to the biodegradation process are the subsequent aims of this paper.

Experimental Part

The material investigated in this work is commercially available polymeric blend based on PLA, Bioflex® 219F, density 1380 $kg \cdot m^{-3}$, melting point 155 °C, softening temperature 72 °C (Vicat A). The film preparation was performed on a mono-extrusion blown moulding machine at the temperature range 170–175 °C. The screw

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parameter, L/D, was 26. The thickness of resulting film was about 45μm. The rectangular specimens were cut off the film (along the direction of extrusion) and introduced into the composting environment. Composting conditions were kept according to the standard ČSN EN ISO 14855. Total time of biodegradation was 6 weeks. The influence of microbial action on surface morphology, weight loss, mechanical and physico chemical properties were studied weekly.

The surface morphology of blown PLA based films was investigated by using optical microscopy in polarized light. The changes of surface that occurred due to microbial attack are shown in Figure 1. While the original blown film proves relatively smooth surface without imperfections, the noticeable defect appeared in case of the samples after 6 weeks of composting. These macroscopic surface changes relating to the polymer chain scission are in accordance with the results of other studied characteristics discussed further.

The observation of weight loss was chosen because it comes under general methods of determination of polymer biodegradability in solid state and furthermore, it does not demand any special instrumentation. The results shown in Figure 2 are in agreement with the optical microscopy observation (Figure 1). The percentage of weight loss gradually increases with the time of composting. However, this method has its limitations.

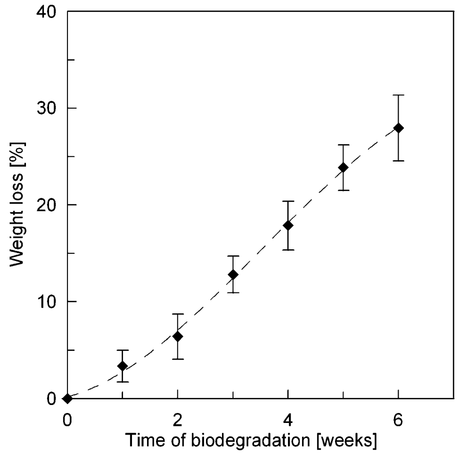

Figure 2.
Weight loss of the Bioflex® 219F blown film during the time of biodegradation test.

The usable experimental data cannot be observed due to high disintegration of the samples. In case of our samples, 6 weeks of incubation period represents the boundary time of testing to get relatively reliable results.

The results presented above have also strong connection to the changes of mechanical properties of the samples. As can be seen in Table 1, the values of E modulus, tensile strength and tensile strain decreases with the increasing time of composting. The most significant drop of tensile properties was found between second and third week in case of E modulus and tensile strength. On the other hand, maximal elongation drops already after the

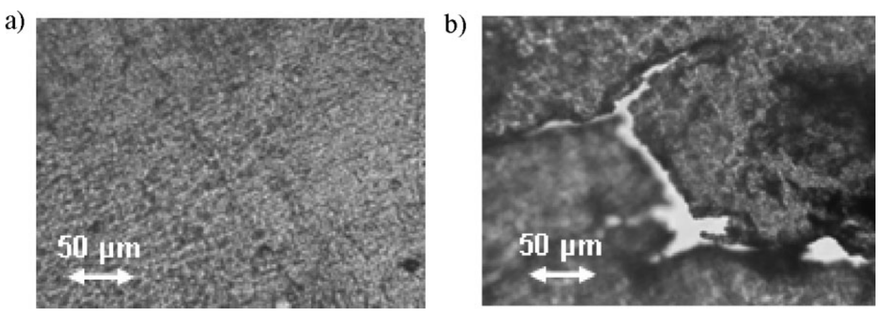

Figure 1.
Optical micrographs of Bioflex® 219F blown film before (a) and after 6 weeks of composting (b).

Table 1.
Mechanical properties of Bioflex® 219F blown films during biodegradation in composting environment.

Time of biodegradation [weeks]	E modulus [MPa]	Tensile strength [MPa]	Tensile strain [%]
0	854 ± 136	19.6 ± 1.78	<300
1	837 ± 158	16.9 ± 3.70	147 ± 24.4
2	704 ± 75	12.7 ± 2.01	19.5 ± 3.10
3	532 ± 80	8.26 ± 1.28	5.00 ± 0.30
4	408 ± 68	7.03 ± 0.39	2.18 ± 0.39
5	–	–	–
6	–	–	–

first week of testing. The maximal elongation of the original samples is more than 300% (limit of the tensile testing machine). The samples in last two weeks of testing proved very poor mechanical properties, and thus they could not be further examined.

The detailed investigations of the structural changes, which occurred due to microbial action, were carried out using the Fourier Transform Infrared Spectrometer equipped with Attenuated Total Reflectance accessory (FTIR-ATR) containing Zn-Se crystal. The spectra of the samples before and after biodegradation are shown in Figure 3. In case of original sample, the typical absorption peaks at 1710 cm^{-1} (C=O stretching); 1267, 1186 and 1103 cm^{-1} (C–O and C–O–C) stretching) 1125, 877 and 728 cm^{-1} (CH bending); 2920, 1457 cm^{-1} (CH stretching); 1047 cm^{-1} (C–CH_3 stretching) can be seen.[6–8] The biological decomposition of the samples can be distinguished by the intensity changes of the peaks at 1756, 1208 and 1014 cm^{-1} (C–O–C stretching). A new peak, which may indicate C–C stretching, appeared at 809 cm^{-1}.[8] These results indicate the enzymatic degradation of the samples, use to secrete by active microorganisms present in the composting bed.

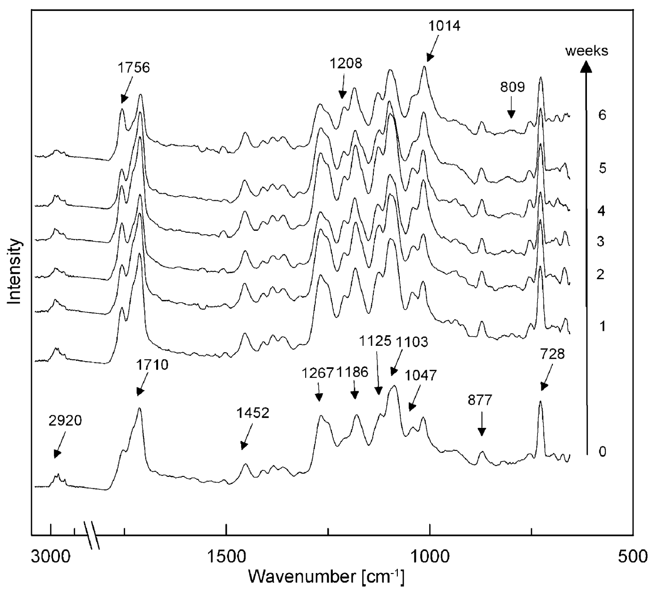

Figure 3.
FTIR ATR spectra of the Bioflex® 219F blown films after various time of microbial exposure.

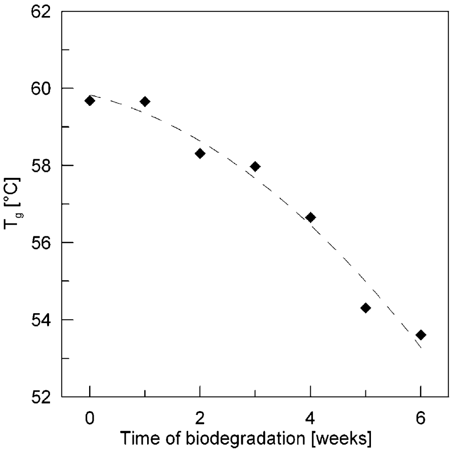

Figure 4.
Glass transition temperature (T_g) vs. time of biodegradation.

A differential scanning calorimeter (Perkin-Elmer Pyris 1 DSC) was used for determination of glass transition temperature (T_g) of the samples. This property can provide important information regarding the mobility of the polymeric chains. A small piece of specimen (approx. 4 mg) was placed in the steel pan and analyzed on DSC instrument, calibrated for temperature and heat flow using indium. The experiments were performed within temperature range from 0 to 200 °C at the scanning rate 20 °C $\cdot$ min^{-1}. (2 scanning cycles). The value of T_g was determined in the second heating cycle at the midpoint stepwise increase of the specific heat associated with glass transition. The results show the decreasing trend of T_g value with increasing time of composting (Figure 4). This fact reveals the increased mobility of polymeric chains. It can be the consequence of the microbial attack, which causes the cleavage of the chains and their shortening in amorphous phase of polymer and at the edges of crystalline phase. The formation of polymer bi-modal molecular weight distribution could be assumed.[9]

Conclusion

The biodegradation course of the blown film based on the commercially available polymeric blend based on Polylactic acid, Bioflex® 219F, was studied through microscopical observations, weight loss measurements, testing of mechanical properties and investigation of structure by using Fourier transform infrared spectroscopy and differential scanning calorimetry. The results show relatively good degradability of the samples in the composting environment. The weight loss was almost 30% after 6 weeks of composting. The significant drop of mechanical properties occurred already after 2 weeks of testing. Noticeable changes were also found in the structure of the polymer samples. It reveals degradation reactions connected with the cleavage of the polymeric chains, which was confirmed by the results from infrared spectroscopy.

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