

X-ray Investigations of the Biodegradation Capacity of PBSA in LDPE/PBSA Blends

Abstract

The interdependence between the crystallinity of poly(butylene succinate-co-adipate) (PBSA) and its biodegradation capacity in blends with low-density polyethylene LDPE has been studied. The LDPE/PBSA blends were prepared by extrusion. As a compatibilizing agent, block copolymer polystyrene-block-poly-(ethylene-co-butylene)-block-polystyrene (FG) modified by maleic anhydride was used. The biodegradation test was performed in a soil and the crystallinity was analysed by the WAXS method. It was found that, six months after the test in question, the degradation of the crystalline part of PBSA took place. In the presence of FG, the PBSA degraded more rapidly due to the lower degree of crystallinity of the polyester.

Introduction

The most popular polymers – polyolefins – are generally not degradable under environmental conditions, leading to waste disposal problems. One of the ways to solve this problem is to blend such a polymer with a biodegradable component. Promising biodegradable materials are aliphatic polyesters, obtained by the polycondensation reaction of glycols such as ethylene glycol or butanediol-1, 4 and aliphatic dicarboxylic acids (e.g. succinic or adipic). Commercially available are poly(butylene succinate) (PBS, coded Bionolle #1000) and poly(butylene succinate-co-adipate) (PBSA, coded Bionolle #3000).

The Bionolles™ are semicrystalline polymers and their physical properties are similar to the synthetic polyolefins (e.g. the value of T_g is between polyethylene and polypropylene) [1]. However, due to the hydrophobic properties of polyolefins and the hydrophilic character of polyester, some compatibilizing agents should be applied in the production of blends [2, 3]. As the agents in question, the polypropylene (or polyethylene)-grafted-maleic anhydride (PP-g-MA, PE-g-MA) can be used [4].

However, the compatibilizing agents may change the crystallinity of the components as well as the physical and mechanical properties of the blends. On the other hand, the susceptibility of polyesters to enzymatic degradation depends on the super molecular structure [5, 6] because a hydrolytic attack is directed firstly to the ester bonds within the amorphous part of the polymer [7].

The aim of the present work was to analyse the interdependence between the crystallinity of PBSA and its biodegradation capacity in LDPE/PBSA blends containing the

polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene functionalized by maleic anhydride (commercial FG 1901X) as the compatibilizing agent. It analysed the crystallization behaviour of blends before and after biodegradation. The presented investigations are a preliminary step in our study on the mechanism of biodegradation of polyesters.

Experiment

Materials

LDPE, MFI 9.44 g/10 min (190 °C, 2.16 kg) (ZCh Blachownia Kędzierzyn Koźle, Poland); PBSA – Bionolle #3001 (PBSA) (Showa Highpolymer Co. Ltd., Japan); polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene – FG 1901X (Shell Kraton Polymers).

Blend preparation

Blends LDPE/PBSA with compositions of 0/100, 25/75, 50/50, 75/25 and 0/100

were prepared by the extrusion method using a one-screw extruder. The diameter of the screw was 25 mm and the rotor speed 30 rpm. The temperatures of particular zones from the feeder to the die were 20, 100, 130, 145, 160 and 160 °C. The extrudates were cooled by passing through a water bath and then palletized. For better miscibility of LDPE and PBSA, the compatibilizing agent FG in an amount of 10 wt.% was added. All the blends were prepared using a one-step melt mixing process. For the biodegradation test and structural analyses, the foils of ca. 0.3 mm thick were made by pressing at 160 °C.

Soil degradation test

The biodegradation test was performed in quasi-natural conditions in soil consisting of 1/3 compost, 1/3 pond soil and 1/3 garden soil [8]. The samples in the form of a standard-size dumbbell shape were placed in a series of 1.5 litre con-

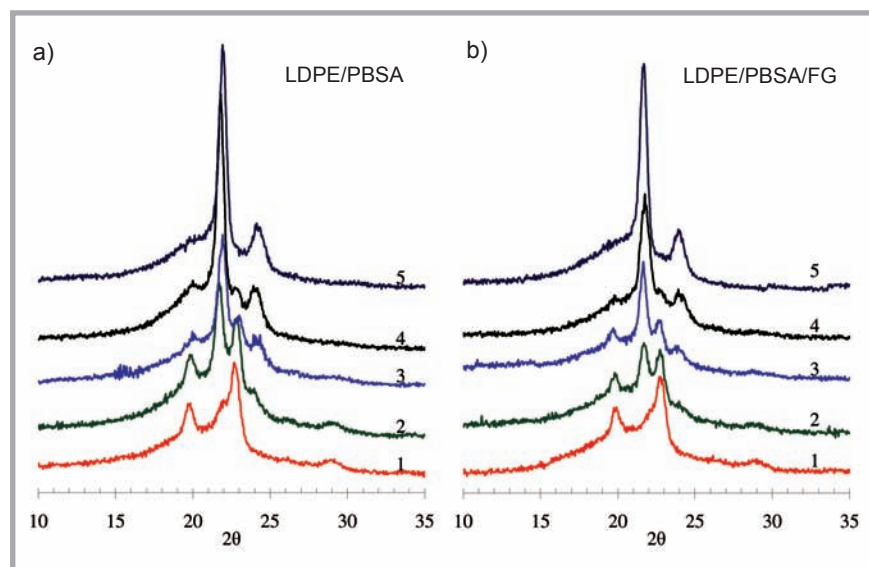


Figure 1. X-ray diffraction patterns of blends before the soil degradation test: a) LDPE/PBSA, b) LDPE/PBSA/FG; 1 – PBSA, 2 – 25LDPE/75PBSA, 3 – 50LDPE/50PBSA, 4 – 75LDPE/25PBSA, 5 – LDPE.

tainers with prepared soil. The moisture content of the soil was maintained at ca. 30% and the pH around 7-8, according to [9] and [10], respectively. The test was performed in the laboratory, where the air temperature fluctuated between 20 °C and 25 °C. The examined samples were removed from the soil after 1.5, 3.5, 6 and 9 months, washed thoroughly with water and dried in an oven at 50 °C in order to determine the percentage weight loss [4, 11].

X-ray analysis

Wide-angle X-ray scattering (WAXS) measurements were carried out using a horizontal diffractometer with CuK α Ni filtered radiation. The samples were scanned in the range from 10 to 40° 2 θ . The degree of crystallinity of PBSA in blends before and after biodegradation was quantitatively estimated from the diffraction pattern of the crystalline and amorphous phases separated by means of the computer program WAXSFIT [12, 13].

Optical microscopy

Optical microscopy was undertaken to examine the morphology of the degraded samples.

Results And Discussion

Figure 1 (see page 81) shows the X-ray diffraction patterns of the LDPE/PBSA blends before biodegradation. The LDPE/PBSA and compatibilized blends display peaks at the same 2 θ values as the pure LDPE and PBSA. PBSA shows peaks at 19.7° and 22.8° with a shoulder peak at 21.8° (2 θ) and a small peak at 29.2° [14, 15, 16].

The crystallinity of PBSA in LDPE/PBSA blends decreased when the content of LDPE increased. It was also noted that, in the presence of FG, the crystallinity of PBSA diminished; however, the addition of PBSA (25 wt.%) led to higher crystallinity of LDPE in LDPE/PBSA blends (*Figures 2 and 3*).

The degree of biodegradability of particular blends, determined by the percentage of weight loss, is shown in *Figure 4a to 4d*. The weight loss of pure PBSA as well as polyester in 25LDPE/75PBSA blends after 9 months was around 90% and in 50LDPE/50PBSA was about 15%. However, the blends with 75 wt.% of LDPE remained almost unchanged. (*Figure 4 a-d*).

In blends containing the compatibilizer FG, the poly(butylene succinate-co-adipate)

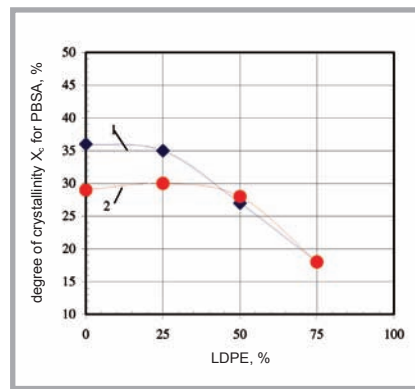


Figure 2. Degree of crystallinity of PBSA in blends before degradation; 1 – LDPE/PBSA, 2 – LDPE/PBSA/FG.

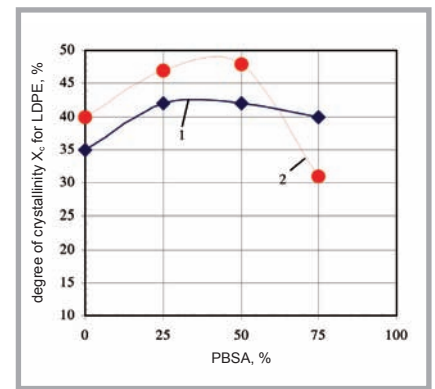


Figure 3. Degree of crystallinity of LDPE in blends before degradation; 1 – LDPE/PBSA, 2 – LDPE/PBSA/FG.

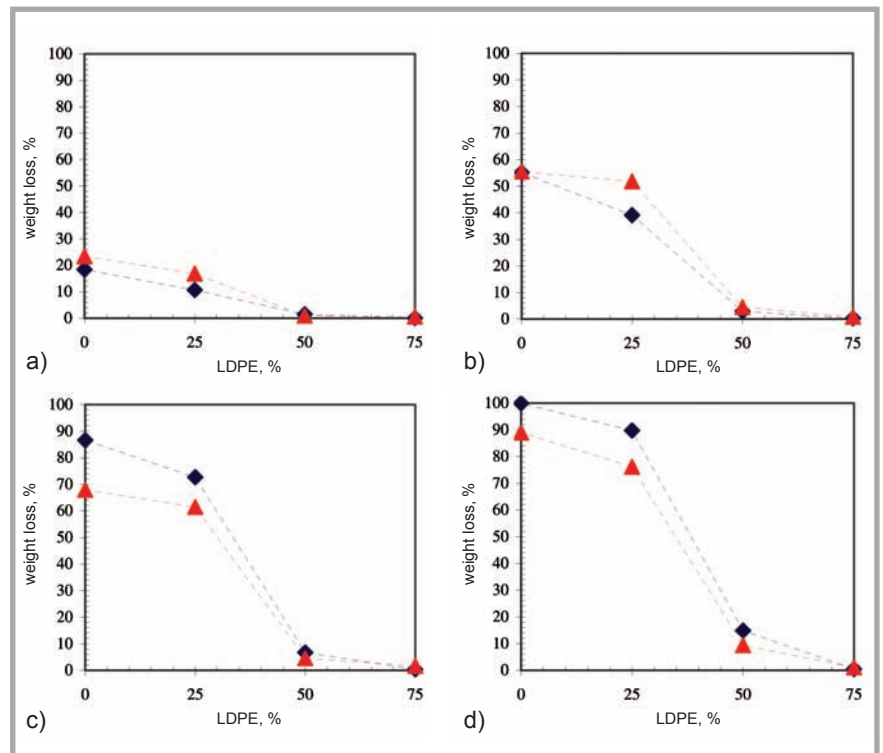


Figure 4. Percentage weight loss of PBSA in LDPE/PBSA blends: a) after 1.5 months of biodegradation, b) after 3.5 months of biodegradation, c) after 6 months of biodegradation, d) after 9 months of biodegradation; \blacklozenge – LDPE/PBSA, \blacktriangle – LDPE/PBSA/FG.

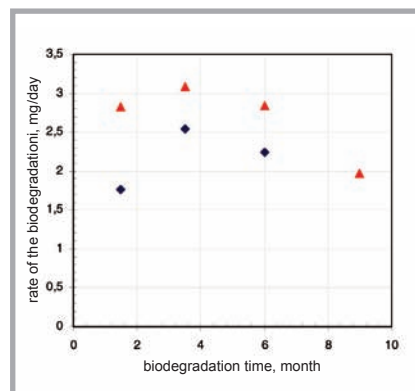


Figure 5. Relationship between the rate of degradation in soil of PBSA and the time of the biodegradation test; \blacklozenge – without FG, \blacktriangle – with FG.

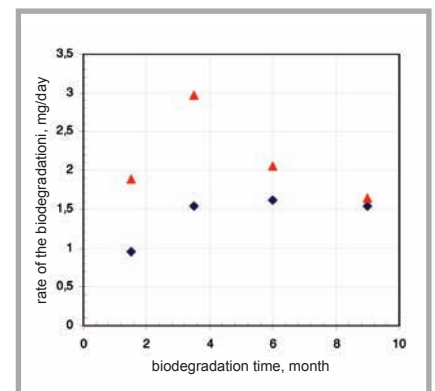


Figure 6. Relationship between the rate of degradation in soil of 25LDPE/75PBSA blends and the time of the biodegradation test; \blacklozenge – without FG, \blacktriangle – with FG.

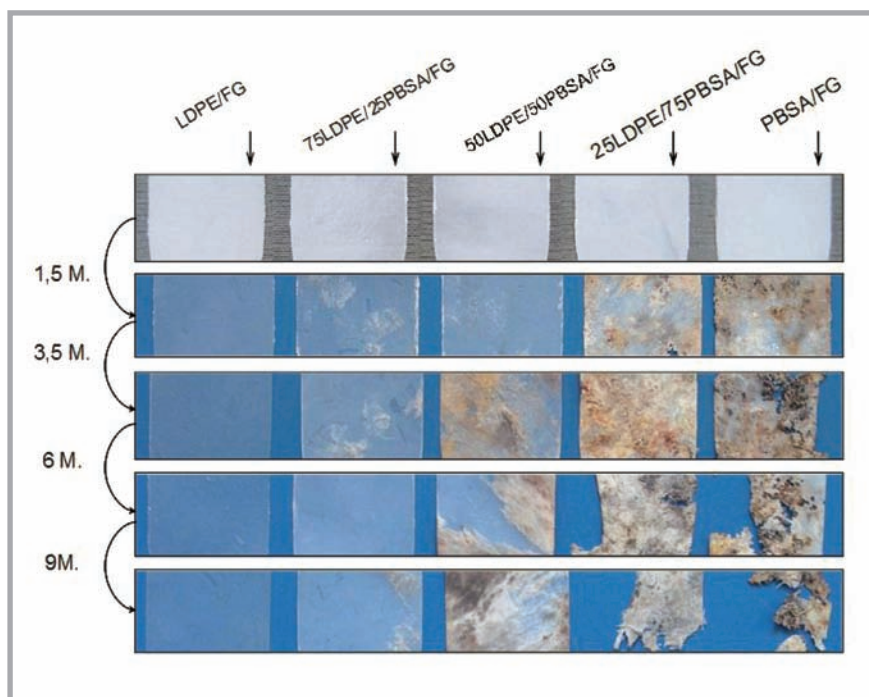


Figure 7. Photographs of fragments of LDPE/PBSA/FG samples before and after the soil degradation test.

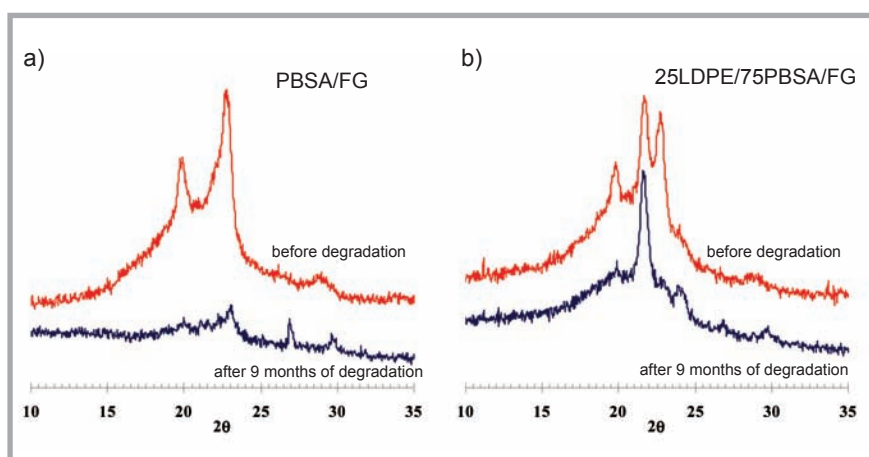


Figure 8. X-ray diffraction patterns of LDPE/PBSA/FG before and after 9 months of the soil test: a) PBSA/FG, b) 25LDPE/75PBSA/FG.

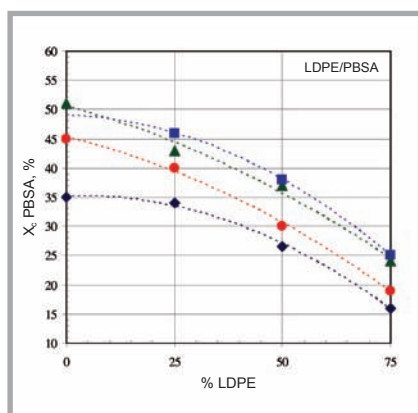


Figure 9. Degree of crystallinity of PBSA in LDPE/PBSA blends after the soil degradation test.

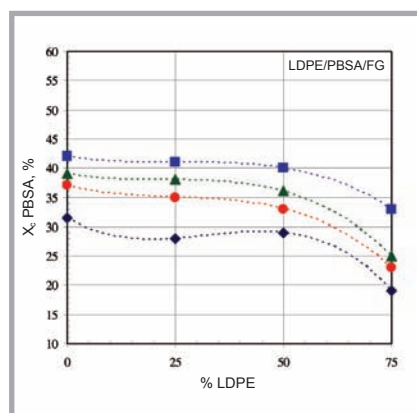


Figure 10. Degree of crystallinity of PBSA in LDPE/PBSA/FG blends after the soil degradation test.

was degraded more rapidly during the first stage of degradation (*Figure 4a-b*).

The PBSA component during the first 3.5 months degraded faster in the presence of FG than in samples without the compatibilizer. However, after 6 and 9 months, the blends without FG degraded more rapidly (*Figure 4 c-d*). After this time of biodegradation, the amorphous phase of PBSA with FG almost degraded completely; for that reason, the rate of degradation of LDPE/PBSA/FG slowed down.

Figures 5 and 6 show the relationship between the rate of degradation in soil and the time of the biodegradation test. The highest rate of degradation of polyester was reached after 3.5 months of degradation. Until this time, the amorphous regions of PBSA were probably degraded. After 6 months, the degradation rate decreased. In the presence of FG, polyester is more susceptible to biodegradation because of its lower crystallinity and more flexible polymer chains, which can fit into the active sites of enzymes [17].

To visualize the course of biodegradation during the soil degradation test, photographs of the samples (LDPE/PBSA/FG blends) were made (*Figure 7*). After 1.5 months, a significant change in the PBSA samples as well in the blends was clear to see. The 50LDPE/50PBSA blends started to biodegrade after 3.5 months, which could be seen clearly.

In the first stage of the biodegradation, the structure of PBSA in blends almost did not change. After 6 months of the test, the disappearance of the crystalline regions of PBSA was observed. *Figure 8* shows the X-ray diffraction patterns of LDPE/PBSA/FG before and after 9 months of the soil test. The 9 months of degradation led to almost a complete loss of the crystalline phase of PBSA (*Figure 8a*). The content of the crystalline phase of PBSA with FG was lower – the peaks characteristic of PBSA were less pronounced. Similar results have been obtained for 25LDPE/75PBSA blends (*Figure 8b*).

During the biodegradation process, the degree of crystallinity of PBSA increased. The highest increase was noticed after the first months of degradation (see *Figures 9 and 10*). It is most probably connected with the degradation of the amorphous part of the polymer. After 6 months of biodegradation, the crystallinity increase was less pronounced. This result was probably

obtained due to the slowing down of the degradation process.

Conclusions

The obtained results lead to the following conclusions:

1. The compatibilizer FG decreases the degree of crystallinity of PBSA and accelerates its biodegradation.
2. Increasing the amount of polyethylene in the LDPE/PBSA blends leads to lowering the biodegradation degree of poly(butylene succinate-co-adipate).
3. The highest rate of degradation of polyester (in blends with and without compatibilizer FG) takes place during the first 3-4 months of the process, which is connected mainly with the biodegradation of the amorphous part of PBSA.
4. After 6 months of the degradation test, the disappearance of the crystalline regions of PBSA was observed.



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(Endnotes)

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