

Anaerobic Biodegradation of Polymer Composites Filled with Natural Fibers

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Abstract Polymer composites with natural fibers prepared by melt blending were investigated. Synthetic and natural macromolecules were used, including poly(lactic acid), polyhydroxybutyrate-co-polyhydroxyvalerate and low density polyethylene. These polymers were filled with flax fibers. Mechanical properties of the composites, biogas production and mass loss under anaerobic digestion have been presented. It has been shown that the mechanical properties sustain after 28 days of biodegradation. Such materials can be found in applications as packaging, as well as in medicine as polymeric scaffolds, and drug delivery systems etc.

Keywords Anaerobic biodegradation · Biodegradable composites · Natural fibers · Mechanical properties

Introduction

Traditional composites are usually made out of polymers reinforced with glass, carbon and aramide fibers. Generally, the mechanical properties of composites are higher than that of the polymeric matrix [1–4].

Critical discussion about the protection of natural resources has led to extensive research on biocomposites [5, 6]. Polymer materials manufactured from the natural

based matrix and reinforced with lignocellulosic fibers, such as jute, hemp, sisal, abaca etc., have focused recently an increasing interest due to their higher sustainability as compared to the petrochemically derived plastics. Biocomposites are useful mainly in the packaging industry where these materials compete with cheap synthetic plastics.

Packagings constitute the largest portion (39 %) in a total consumption of plastics. Since the life time of packaging is very short the plastics packaging waste dominates in a post-consumer waste stream. For that reason the plastic waste recovery and recycling technologies are steadily developing. Besides of incineration, the mechanical recycling is progressing however, the organic recycling gains steadily increasing importance. That method of waste management is valid for biodegradable plastics, whose physical and chemical properties undergo deterioration when exposed to microorganisms. Biodegradation can occur in the aerobic or in the anaerobic environment. With access of oxygen the products are carbon dioxide, water and biomass.

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Knowledge on the biodegradation efficiency in the aerobic or anaerobic conditions is important while considering a waste management of biodegradable polymers.

Among the most promising polymers of this group are polylactic acid (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB/PHV) which were used as major components in the biocomposites presented in this paper. The polymer matrix was modified with natural fibers (flax), therefore the composites were entirely biodegradable. Natural fibers show advantages over glass fibers, mainly because of lower density of natural fibers (1.5 g/cm^3) compared to glass fibers ($\approx 2.5 \text{ g/cm}^3$). The difference in density causes that light weight use of polymer composites

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filled with cellulose fibers is possible. Biocomposites display combined features of all components or novel properties resulting from mutual interactions between the components.

The aim of this study is to evaluate the influence of anaerobic conditions on the properties of biopolymers reinforced with flax fibers and yield of biogas generation as a function of incubation time.

So far the vast majority of biodegradation studies used to be carried out in soil and/or compost. In particular, enhanced biodegradation of these materials may occur in the presence of compost, a complex biological environment, in which a microbial diversity is relatively high and therefore an increased degradation potential for polymeric compounds exists [7–9].

Very little work has been reported until now on the behavior of biocomposites under anaerobic conditions [11–14].

Degradation of plastic materials is a very important problem. On one hand the degradation process reduces the life time of plastic products but on the other hand the degradation is crucial for the waste disposal. During degradation the mechanical properties of plastics deteriorate as a result of changes in the chemical and physical structure of the polymer [10]. The chemical changes include the chain scission or the incorporation of new chemical groups. Degradation of plastic depends on several factors such as: temperature changes, electromagnetic radiation [11], moisture [12] and biological activity [13]. Anaerobic digestion of organic compounds is an efficient way of their waste disposal combined with the energy recovery. It is a multistage process involving complex population of microorganisms. The main product of anaerobic digestion is biogas, e.g. a mix of methane, carbon dioxide and trace amounts of nitrogen, ammonium, water vapor and hydrogen sulphide. Since the methane may be used in the production of electricity or heat, biogas is considered as a renewable energy source [14].

Anaerobic digestion involves multiple steps, from which the decomposition of organic particles is usually a limiting step. Since the biodegradation of organic particles may occur only on the surface, this process is assumed to be surface limited. Addition of natural fibers to the polymers highly alters the material structure it may influence also the digestion kinetics.

In this work we have investigated the behavior of two biodegradable polymers and polyethylene as reference material and their composites with flax fibers in anaerobic digestion trials. The digestion tests were performed by means of wet fermentation at temperature of 37 °C and lasted for 72 days. Anaerobic sludge from a sewage plant was used as an inoculum. The biogas production kinetic as well as a change in mechanical properties were analyzed.

Materials and Methods

Materials

- Poly(lactic acid)—PLA 3051 (specific gravity 1.24 g/cm³, MFR = 10–30 g/10 min at 190 °C/2.16 kg), Natureworks, USA
- Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)—PHB/PHV P226 (density 1.25 g/cm³, MFR = 9–13 g/10 min at 190 °C/2.16 kg) Biomer, Germany
- Flax fibers (F1) 1 mm length, Ekotex, Poland
- LDPE Malen PFN 2003 (density 0.92 g/cm³, MFR = 1.6–2.5 g/10 min at 190 °C/2.16 kg), Basell Orlen, Poland

Composite Preparation

PLA, PHB/PHV and flax fibers were dried prior to processing in order to avoid a hydrolytic degradation of polymers. Proportion of the matrices to natural fibers was 70/30 by weight.

The composites were prepared in Rheomix HAAKE 600 by melt mixing for 10 min with a mixing speed of 60 rev/min at temp. range 150–180 °C—depending on matrices used. Tensile test samples (type 1 according to ISO 527-2:2012) were made using microinjection molding machine produced by Proma, Poland.

Test Methods

Anaerobic Digestion Batch Test

Anaerobic digestion tests were performed in 120 ml serum bottles closed with butyl rubber stoppers. After 60 ml of an anaerobic sludge (dry weight content of 55.3 g/l) was poured into the vessels, the air was removed by purging every bottle with nitrogen. Bottles with a sludge were preincubated at temperature 36 °C for 48 h. After this time plastic samples were introduced into the bottles and air was removed once again with nitrogen. Bottles with the test samples were put into the incubator at temperature of 36 °C. Fermentation vessels were mixed manually before gas measurement. Produced gas was measured with a water displacement device every 24 h. All samples were prepared in triplicate. The biogas volume was calculated for standard conditions (temperature 273.15 K, pressure 1,013.25 hPa). The control bottles did not contain plastic samples.

Tensile Properties

Tensile properties were evaluated using a testing machine LR10K LLOYD at a speed of 10 mm/min.

Results

Anaerobic Biodegradation

Biogas production curves obtained at the anaerobic digestion experiments have been presented in Fig. 1. Changes in the weight of the samples during the experiment have been illustrated in Fig. 2. Low density polyethylene, poly (lactic acid) and their composites with flax fibers were not digested at anaerobic conditions. Gas production from those polymers was at the same level as the control and no weight losses were observed.

Lack of polyethylene biodegradation under anaerobic conditions was expected, since polyolefins are not metabolized by microorganisms without activation [15]. The activation process involves the introduction of hydroxyl groups to the polymer molecules. An alcohol formed in this reaction can be further oxidized by microorganisms and included in metabolic pathways. The hydroxylation process is oxygen-dependent and does not occur in anaerobic conditions thus the anaerobic biodegradation of PE was not observed.

The resistance of polylactide to biodegradation in mesophilic conditions was reported also by other authors [16]. It is assumed that hydrolysis (the first step in biodegradation) of crystalline regions in PLA is negligible. In mesophilic conditions only the water soluble short polymer chains can be hydrolyzed [17]. The hydrolysis of long macromolecules of PLA is possible only at temperatures above the polymer glass transition in which the packing of polymer chains is less dense [16].

It is assumed that the addition of plant fibers to plastics which are hardly biodegradable should improve their decay rate [18]. Biological digestion of natural fibers should weaken a structure of the composite and enable its breakdown to smaller fragments which are more susceptible to decomposition.

In our experiment we did not observe any improvement in the digestion of polyethylene and polylactide composites in comparison to neat polymers. It is probable that in our case flax fibers were well protected against biological activity since they were isolated from the liquid by a polymer matrix.

All samples containing PHB/PHV polymer were completely degraded during the anaerobic digestion experiment. The biogas production from these polymers started after 5 days of incubation and stopped after 60 days of the experiment. Samples were completely digested during this time, showing high gas production efficiency at a level of 936,6 ml/g.

The time needed for complete degradation of samples was longer than that reported by other authors [19]. The difference might be due to the fact that they have used

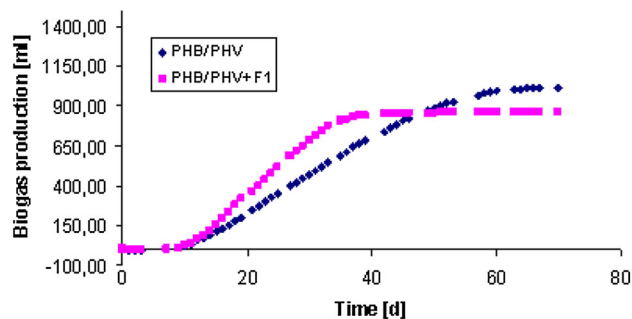


Fig. 1 Total biogas production from anaerobic digestion tests of PHB/PHV and PHB/PHV + F1 composite. There have been lack of changes in the value for other materials observed

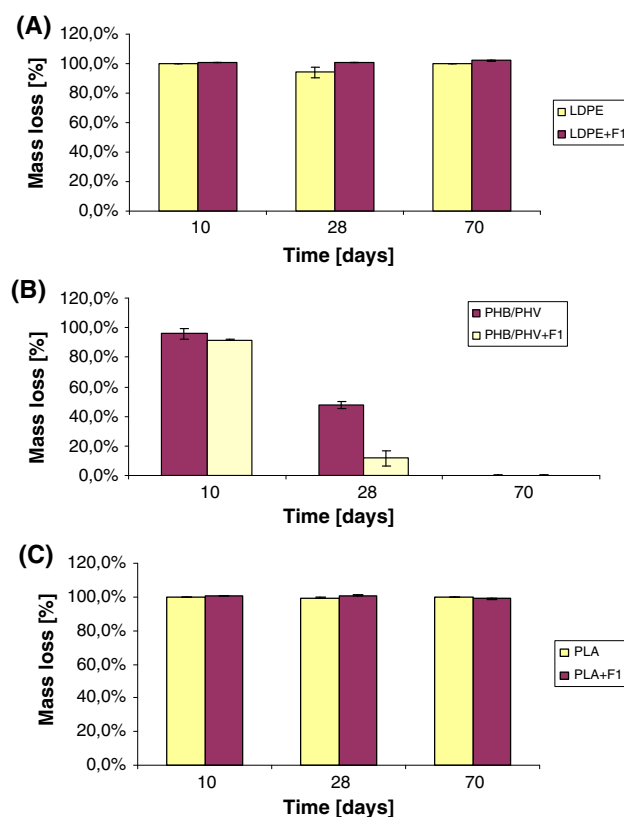
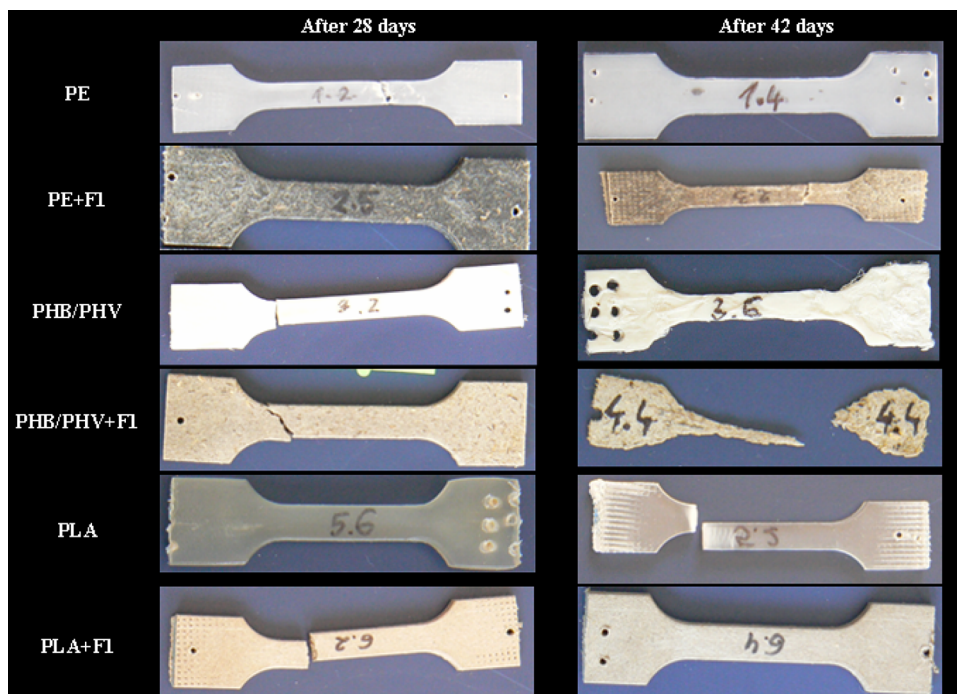


Fig. 2 Relative mass changes during anaerobic digestion tests. **a** LDPE and LDPE + F1 composite; **b** PHB/PHV and PHB/PHV + F1 composite; **c** PLA and PLA + F1 composite

powdered polymers. The powder has much higher specific surface which is accessible for microorganisms. Since the degradation of composites by microorganisms is a surface-limited process the form of substrate has a significant impact on the anaerobic digestion rate [20].

Anaerobic digestion of PHB/PHV with flax fibers was faster when compared to digestion of PHB/PHV but showed lower gas production efficiency. Biogas production

Fig. 3 Picture of PE, PE + F1, PHB/PHV, PHB/PHV + F1, PLA and PLA + F1 samples after immersion for 28 and 42 days (respectively)



from PHB/PHV composite stopped at 38th day of fermentation. One could also observe a higher mass loss of PHB/PHV composite in comparison to pristine PHB/PHV polymer. Total biogas production from PHB/PHV composite with flax fibers was at level of 865 ml which corresponds to the gas production efficiency of 762.7 ml/g.

Lower biogas yield from PHB/PHV composite resulted from high fiber content. Plant materials generally exhibit lower gas production efficiency in comparison to biodegradable polyesters. Usually a biogas production from plants is in a range of 220–550 ml/g of dry weight [21, 22], thus the addition of flax fiber should reduce the biogas yield from the composite.

Our investigations have shown that addition of natural fibers to the PHB/PHV polymer enhanced the biocomposite degradability in anaerobic conditions. Since the fibers are statistically distributed in the polymer matrix making a structure heterogeneous, the microorganisms may access a biodegradable component easier. This leads to an increase in the surface available to bacteria and to acceleration of the degradation process (Fig. 3).

The appearance of the samples is consistent with the results presented in Figs. 1, 2. Biodegradation goes from the surface into depth of a sample/After 28 days a surface of PHB/PHV + F1 composite was highly eroded than that of PHB/PHV polymer. After 42 days a biodegradation went across the composite because of easier access of microorganisms to biodegradable matrix. PHB/PHV structure was damaged by bacteria in contrary to PLA and

PLA + F1 composite which look resistant to the anaerobic sludge for the time reported.

Tensile Properties

Mechanical properties of neat PE and PE + F1 composite have been presented in Fig. 4. Polyethylene tensile properties did not change after 28 days of biodegradation. Only after 70 days a slight decrease in the tensile strength and Young's modulus can be observed. Addition of 30 wt% of flax fibers caused high increase in the elastic modulus that started decreasing after 42 days of biodegradation, although it did not result in any significant change of the tensile strength or elongation at break. These results suggest that microorganisms may cause a little change in the internal structure of polyethylene.

Mechanical properties of PHB/PHV and its flax fiber composite have been presented in Fig. 5. Tensile strength of neat PHB/PHV matrix did not change during first 42 days of biodegradation, however some stiffening was observed while analyzing Young's modulus and percentage strain graphs. That might be the result of a macroscopic disintegration of samples as a polymer digestion progressed.

Addition of flax fibers caused a significant increase in the composite Young's modulus values related to PHB/PHV matrix until 28 days of biodegradation (Fig. 5) however, subsequent degradation was so fast that the samples could not transfer a tensile stress at all.

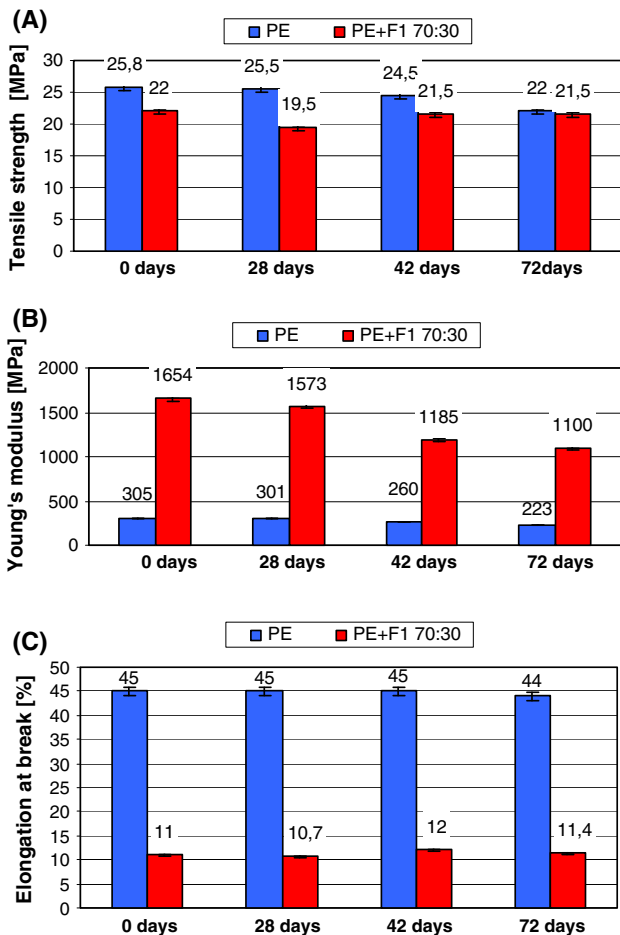


Fig. 4 PE and PE + F1 70:30 tensile properties: **a** tensile strength; **b** young's modulus; **c** elongation at break

Mechanical properties of PLA and PLA/F1 have been presented in Fig. 6. Tensile strength of PLA decreased gradually with a biodegradation time and quite significantly (80 % after 42 days). Percentage strain however stayed almost unchanged, whereas there was even slight increase in the elastic modulus (from 2,331 to 2,895 MPa after 70 days). A possible explanation is an increase in PLA crystallinity in course of the polymer degradation, since shorter chain gain more mobility to form crystals.

Tensile properties of PLA composites reinforced with flax fibers decreased in a course of immersing in an anaerobic sludge. Because there was no mass loss reported (Fig. 2) the possible reason is a change in the internal structure of PLA and loosening the matrix/fibers interactions.

Despite a steady reduction of tensile properties the material even after 70 days of biodegradation exhibit properties comparable to virgin polypropylene. That might be due to a scaffolding support of flax fibers that did not undergo a biodegradation.

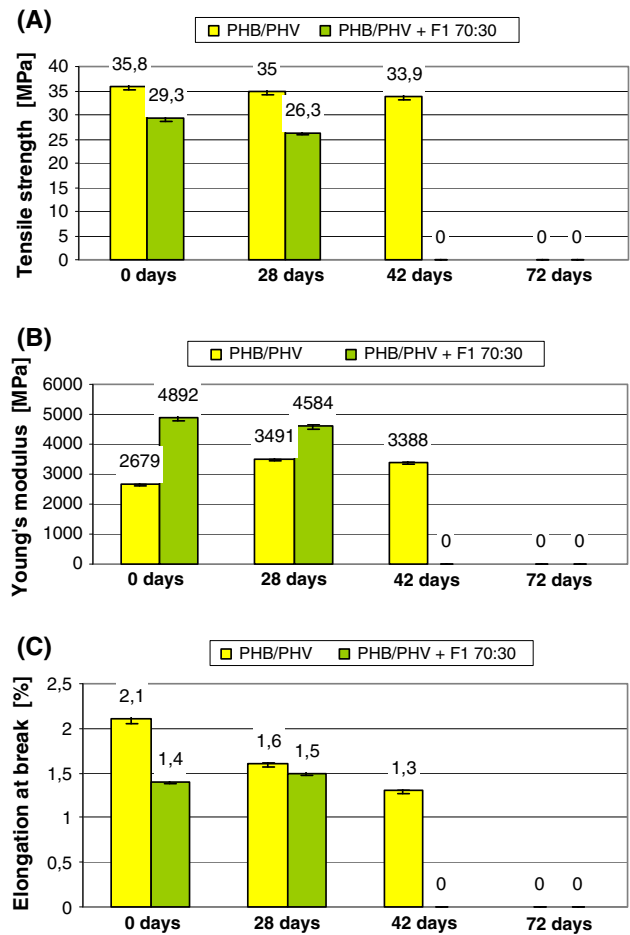


Fig. 5 PHB/PHV and PHB/PHV + F1 70:30 tensile properties: **a** tensile strength; **b** young's modulus; **c** elongation at break

Substantial decrease in the tensile strength suggests a progressive number of PLA chains that were broken in a serum. That may confirm an auto-catalytic mechanism which has been proposed for PLA [23] and PET [24].

Le Duigou et al. [12] have investigated aging of PLA and PLA/flax biocomposites in seawater at 20 °C. They have shown an increased number of PLLA chain breaks with the immersion time until the 1 month time. Further degradation was slower, that is an agreement with the results we have presented in Fig. 6.

Conclusions

1. Extensive anaerobic biodegradation of PHB/PHV and PHB/PHV composites with flax fibers was observed.
2. PLA exhibited a little change in properties after immersion in the anaerobic sludge.
3. Polymer composites undergo biodegradation faster than the matrix polymer however, the extent of

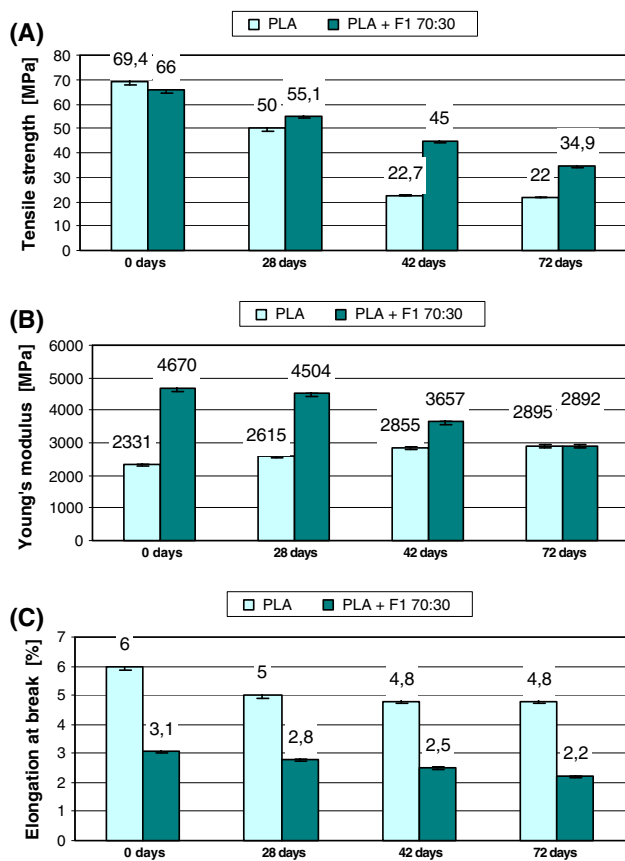


Fig. 6 PLA and PLA + F1 70:30 tensile properties: **a** tensile strength; **b** young's modulus; **c** elongation at break

degradation is lower if the fibers are more resistant to biodegradation than the polymer.

- Microorganisms brought about changes in the internal structure of polymers before the mass loss was reported.
- Tensile properties present an appropriate measure for a progress evaluation in the biodegradation of polymers.

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