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BIODEGRADABLE BLENDS BASED ON PHB AND WOOD FIBER

Mihai DIMONIE[1], Maria RÂPĂ[2]

S-au realizat cinci recepturi pe bază de polihidroxibutirat (PHB), fibră de lemn (WF) şi ulei de soia epoxidat (LSA), prin amestecare pe plastograful Brabender, la temperatura de

170 0C. S-a constatat că odată cu creşterea conținutului de fibră de lemn în matricea de PHB, rezistența la tracțiune şi temperatura de topire scad datorită slabei compatibilități între cele două faze încorporate. Microscopia optică efectuată sprijină constatarea referitoare la încercarea la tracțiune.

Prin expunerea la acțiunea solului, amestecurile indică o creştere a pierderii în greutate, odată cu mărirea conținutului de WF.

Five recipes based on poly-3(hydroxybutyrate) (PHB), wood fiber (WF) and epoxidated soy-bean oil (LSA) were prepared by Brabender Plastograf, at 170 0C. It was found that with increasing wood fibers content in the PHB matrix, the tensile strength and the melting temperature decrease, due to the poor compatibility between the two phases. The optical microscopy performed support the findings of tensile strength test. Under soil, the blends indicated that the weight loss is higher with the increase of the wood fibers content.

Keywords: biodegradation, poly(3-hydroxybutyric acid); wood fiber, plastic blend

1. Introduction

The increasing volume of plastic waste and decreasing landfill capacity for disposing of it has stimulated interest in biodegradable plastics. The major commercial plastics, such as polypropylene, polystyrene, and polyvinyl chloride, show very limited biodegradability [1, 2].

Biodegradable polymers are a growing field [4-6]. Plastics based on polyhydroxyalkanoates, natural microbial polyesters, are biodegradable but very expensive to produce [6].

The poly-(3hydroxybutyrate) (PHB) is a biopolymer which is present in all living organisms. Many bacteria produce PHB in large quantities as storage material (instead of fat, oil, or starch). PHB has thermoplastic properties. PHB

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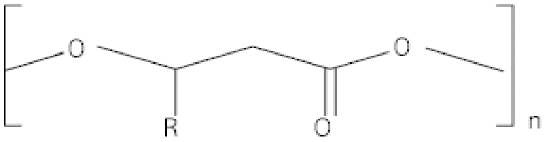
[1] Prof., Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania, e-mail: dimonie@rdslink.ro

[2] Eng., Depart. Research&Development from INCERPLAST, Bucharest, Romania, e-mail:rapa_m2002@yahoo.com

exhibits strength and stiffness comparable to that of polypropylene (PP) [4]. It is not toxic and it is totally biodegradable.

PHB is a isotactic, absolutely linear, thermoplastic homopolyester built on 3-hydroxy butyric acid. The formula of the subunit is presented in Fig. 1:



where R represents CH_3.

Fig.1. Structure of polyhydroxyalkanoates

Although PHB have a desirable mechanical properties and environmental friendly characteristics, the biopolymer is still not used extensively in commercial applications due to their high cost. Reducing the required quantities of polymeric material, by incorporating filler or fibers with biopolymers is an effective method of reducing the effective end-product costs.

During the last years, the use of vegetal-derived materials (wood flour, plant fibers) has shown continuous growth [7-10]. The drivers for this trend are the cost savings, weight reduction and recyclability. Wood fibers (WF) are from annual renewable resources, cheaply available and biodegradable [9]. They can be blend with PHB to form favorable biodegradable material, are particularly good candidates for obtaining desired physical properties with concomitant reduction in cost [10]. Wood fiber (WF) reinforced poly(3-hydroxybutyrate) (PHB) composites have the potential to replace petrochemical polymer based composites in many applications such as automotive panels and decking [11].

In this article, we have added WF up to 15 % in the PHB matrix. It was used the plasticizer based on vegetable oils of natural origin, 5 % content [12]. The five recipes have been characterized by differential scanning calorimetry (DSC), tensile strength at break, optical microscopy and weight loss of buried blends.

2. Experimental

2.1. Materials

Poly-3(hydroxybutyrate) (PHB), type P226 was used as supplied by Biomer Germania. The material has a density of 1.17 g/cm^3 and melting point of 173 ^{0}C. PHB is dried in the oven at 80 ^{0}C, time of 2 h, before blending.

Wood fiber (**WF**), resulted from mechanical processing, untreated, have medium particle size 150 – 200 µm, are obtained from secondary wood resources, renewable, ecological, refiners by dry industrial process (provided from Wood National Institute from Bucharest). The moisture content of the WF was (8 ± 2) %. The WF was dried in an oven at 70 ^{0}C, for 8 h prior to blending.

Epoxidated soy-bean oil (**LSA**) is used as plasticizer, with the acidity index value of 1.2 mg KOH/g and the density of 0.990 ± 0.01 g/cm^3.

2.2. Blends preparation

The blends were prepared using a BRABENDER Plastograph with two screws, with speed maintained at 40/70 rpm and blending temperature at 170^{0}C, and a reaction time of 10 min. Mass of WF was 2 %, 5 %, 10 % and 15 % weight.

The recipes were presented in the table 1. After blending, these recipes were pressed into thin plates using a BRABENDER Press.

Table 1

Compositional details of different samples

Code recipes	**PHB , % wt**	**LSA, % wt**	**WF, % wt**
C1	95	5	0
C2	93	5	2
C3	90	5	5
C4	85	5	10
C5	80	5	15

The pressing conditions were as the following: temperature, 160 ^{0}C; preheat time, 8 minutes; pressing time, 5 minutes; cooling time- 40 minutes; pressure, 250 barr.

The films obtained by BRABENDER Press, have shown a thickness of max. 50 μm.

2.3. Characterization of blends

2.3.1 Thermal analysis

For the the thermal analysis of the blends it was used the equipment METTLER-TOLEDO DSC-823 in the following conditions: the sample amounts were between 4 and 6 mg, the melting curves were recorded from 30 ^{0} to 250 ^{0}C, heated at a rate of 10 ^{0}C/min, air atmosphere, using a standard crucibles of Al.

2.3.2 Optical microscopy

The microscopy was performed on MOTIC DMW B-223 ASC optical microscope with 40X, 100X and 400X magnification.

2.3.2 Tensile strength at break

The tensile strength at break of the samples was determined on DINAMOMETER FP 10. Tests were conducted at room temperature using a strain rate of 500 mm/min, conform to ISO 527. Five samples were tested for each blend and an average value was subsequently calculated for the blend.

2.3.4. Biodegradation studies

Biodegradability of the samples was studied by evaluating weight loss of the blends over time in a soil with the pH (1:10 in water) of 7.5. Three samples of (30 mm x 30 mm x 1 mm) from each blend were weighed and then buried in boxes of soil. Soil was maintained at 20 % moisture in weight and samples were buried at a depth of 15 cm, conform to ISO 846. The buried samples were removed from the soil once a week, washed in distilled water, dried in an oven at 50 ^{0}C ± 8 ^{0}C for 24 h and equilibrated in a desiccator for at least a day, before being weighed and then returned to the soil. Dried films were weighed to calculate the weight loss.

The evaluation of the weight loss was performed by using the formula:

$$\text{Weight loss, \%} = \frac{(m_f - m_i)}{m_i} x100 \qquad (2)$$

where : m_f is the final weight of the tested samples;

m_i is the initial weight of the tested samples.

This ratio is, generally, negative due the weight loss.

3. Results and discussion

3.1. Differential scanning calorimetry analysis

Differential scanning calorimetry was used to study the thermal properties of blends. The melting temperatures (Tm) for the experimental blends obtained by DSC are given in Fig. 2. In Fig. 2 it can be seen that the melting temperature (Tm) decreases with increasing WF content for all blends and that the decrease was more noticeable for WF content of up to 5 %. The decrease in Tm is due to the lower melt viscosity of WF, compared to that of PHB, probably caused by the increased difficulty in arranging the polymer chain. This is due to WF prohibiting movement of the polymer segments. Another potential cause is the hydrophilic character of WF which would lead to poor adhesion with the hydrophobic PHB. The lower melt viscosity of blends based on PHB and WF make this blends easier to process.

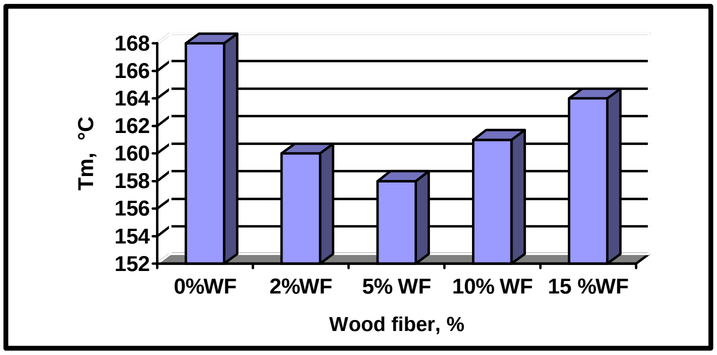


Fig.2. Melting temperature versus WF content for PHB/WF

3.2. Tensile strength at break

Fig. 3 shows the variation in tensile strength at break for the experimental recipes performed. It can be seen that the tensile strength at break decreases once the WF content increases. The recipe code C5 that contains 15 % WF shows a decrease of the tensile strength at break of 70% against the recipe code C1. This is due the poor dispersion of WF in the PHB matrix, showing the incompatibility between the two polymers [8].

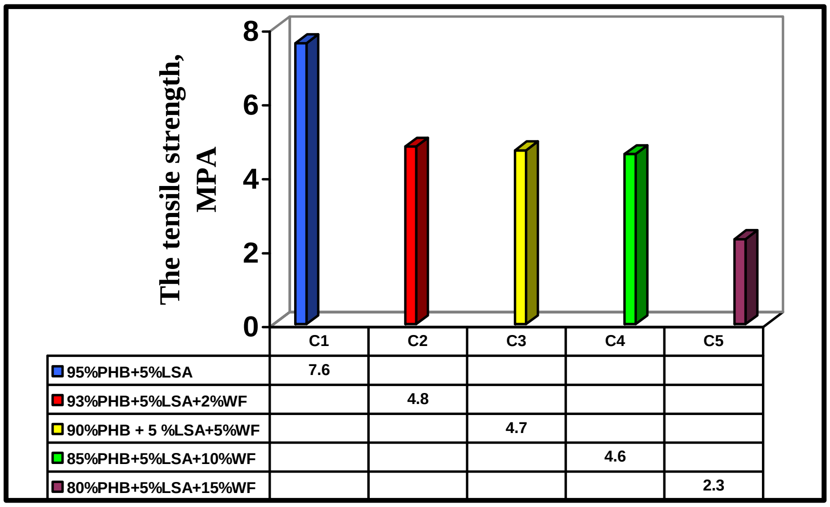


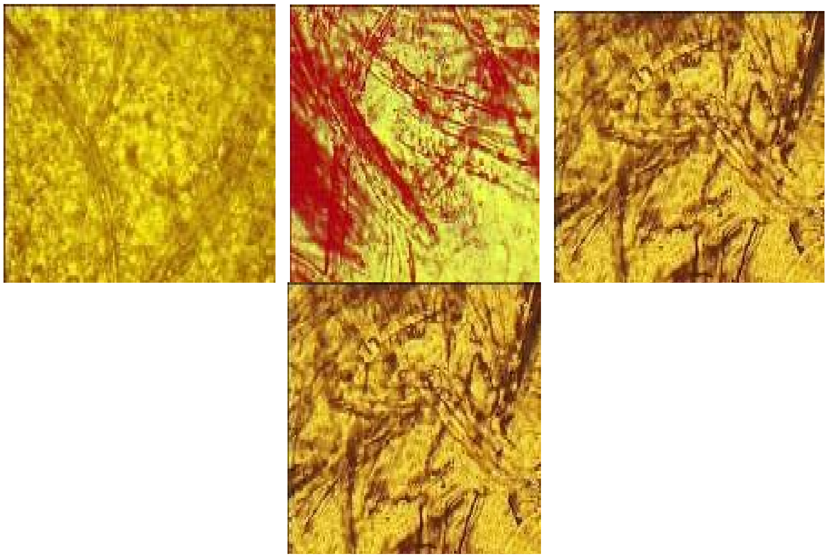
Fig.3. Tensile strength at break for PHB/WFs blends

When the polymer pairs exist in two phases, the mechanical properties of the blend material are governed by the distribution of the properties of the respective polymers within the blend. In other words, the properties are related mainly to the higher volume polymer phase, which usually forms the continuous matrix, while the secondary phase plays the role of reinforcing the matrix by adequate stress transfer between interphases [13].

This is due to the fact that wood fiber - wood fiber interaction becomes more pronounced than wood fiber - PHB matrix interaction with increasing filler content. The applied force cannot be transferred from the polymer matrix to rigid filler particles due to the reduction in the effective cross-sectional area of the composites caused by filler particles.

3.3. Optical microscopy

Fig. 4 shows the optical microscopy for the blends.



a) PHB/WF (2 wt %) Magnification 100X
b) PHB/WF (5 wt %) Magnification 40X
c) PHB/WF (10 wt %) Magnification 40X
d) PHB/WF (15 wt %) Magnification 40X

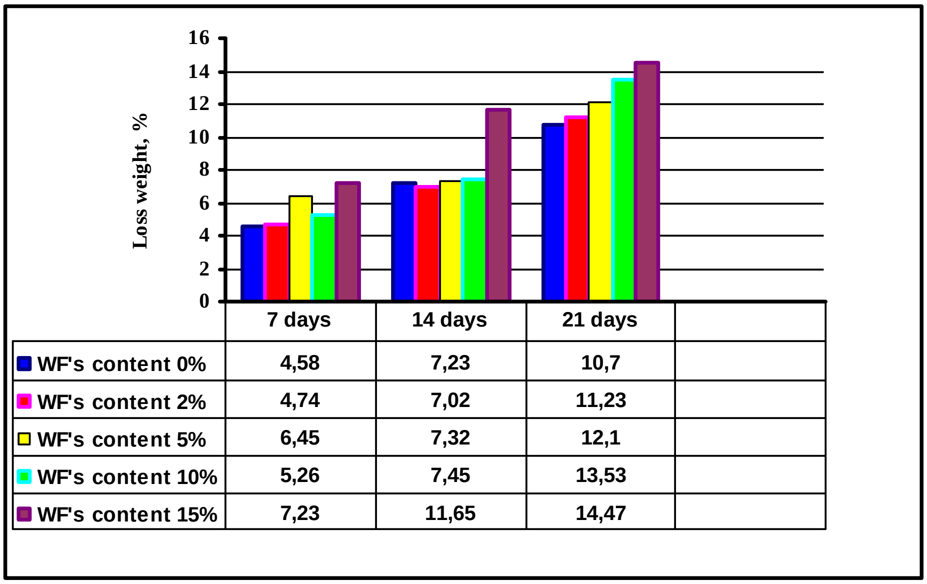
Fig.4. Optic microscopy images of PHB/WFs

The poor dispersion of WF in the PHB matrix is due to the formation of hydrogen bonds and the wide difference in nature between PHB and WF. The images from Fig. 8 show WF of 62 μm width and the aspect ratio of 1:18.

3.4. Biodegradation by exposure to soil

Fig. 5 shows the weight loss of the tested samples within three period of time: after 7 days, 14 days and 21 days. After removing blends from soil were observed discoloration, spots and breakings. In the soil, water diffused into the polymer sample, causing swelling and enhancing biodegradation.

The weight loss of the blends, indicated the extent of biodegradation of the blends, increases as the content of WF increases. After 21 days, the blend with WF content 15 % indicates a weight loss of 14 %.



	7 days	14 days	21 days	
🟦 WF's content 0%	4,58	7,23	10,7	
🟥 WF's content 2%	4,74	7,02	11,23	
🟨 WF's content 5%	6,45	7,32	12,1	
🟩 WF's content 10%	5,26	7,45	13,53	
🟪 WF's content 15%	7,23	11,65	14,47	

Fig.5. Loss weight of PHB/WF blends exposed to soil environment

4. Conclusions

Using WF for blending with the PHB matrix, the melting temperature (Tm) decreases against PHB, content due to the lower melt viscosity of WF.

Investigation of the properties of the blends based on PHB, WF and plasticizer indicates that the tensile strength at break depends on the dispersion of WF in the PHB matrix. The mechanical testing has confirmed a poor adhesion between WF and the PHB matrix.

The optical microscopy is in good agreement in the relation between tensile strength at break and morphology of blends.

The content of WF in blends plays an important role in the biodegradability of the blends, as indicated by exposure to soil test. The blends have showed a good biodegradation rate when they are exposed to soil.

The potential main application areas of the blends obtained are the building and automotive industries but they are also applied for packaging, agriculture, for the preparation of various household articles, for furniture, and for other items.

The further studies will be done in order to improve the dispersion of the wood fibers in the thermoplastic matrix of PHB, which leads to better homogeneity.

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