

“ST26733”, International Conference "Agriculture for Life, Life for Agriculture"

PHB/Cellulose fibers based materials: physical, mechanical and barrier properties

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Abstract

In the latest years, researchers have been working to reduce the dependence on petroleum based fuels and products due to the increase in environmental consciousness. This leads to investigate the environmentally friendly sustainable materials in order to replace the existing ones. One of these polymeric materials is poly(3-hydroxybutyrate) (PHB) which is a semi-crystalline, linear polymer belonging to the class of polyhydroxyalkanoates. It is fully biodegradable and biocompatible, and produced from renewable resources. Although having promising properties, PHB is unstable during processing at elevated temperatures causing thermal degradation that reduces its mechanical performance. The purpose of the present study was to develop and characterize new composite materials based on PHB and different percentage of cellulose fibers (from 2% to 10%), in order to improve PHB's physical mechanical behavior. In this respect, a series of physical-mechanical analyses (melt processing, optical properties, differential scanning calorimetry, water vapor permeability, etc.) were performed. The results obtained during this study show the most appropriate composition of the tested mixtures and demonstrate that the polymeric material based on PHB and cellulose fibers have good physical - mechanical characteristics, being suitable for packaging industry.

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Peer-review under responsibility of the University of Agronomic Sciences and Veterinary Medicine Bucharest

Keywords: PHB; biodegradable; composite materials; renewable resources.

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1. Introduction

An important increasing quantity of plastic waste is registered every year and the precise time needed for its biodegradation is unknown. Environmental awareness has driven the development of new biodegradable materials, especially for single use plastic items (Puglia et al., 2014).

Polyhydroxyalkanoates (PHAs) are well known biopolymers that can be produced microbially by a variety of microorganisms as an energy storage mechanism (Ma et al., 2014). They exhibit similar end-use properties with petroleum-derived polymers and, thus, they can potentially replace conventional thermoplastics in various applications (Chatzidoukas et al., 2013).

Polyhydroxybutyrate (PHB) is an intracellular polyester belonging to the family of polyhydroxyalkanoates (PHAs), that can be used as an alternative for petroleum-based plastics as its structural properties are similar to polypropylene, with the advantage of its biodegradability, biocompatibility and can be produced from renewable carbon sources (Raveendran et al., 2013; Wellen et al., 2013). Polyhydroxybutyrate (PHB) is a biodegradable thermoplastic polyester accumulated as an energy/carbon storage or reducing power material by numerous microorganisms under unfavourable growth conditions in the presence of excess carbon source (Puglia et al., 2014; García et al., 2014). It is a partially crystalline polymer (Arrieta et al., 2014) with a high melting temperature and a high degree of crystallinity. If the properties of the PHB can be further improved by the addition of a small quantity of an renewable biodegradable material, this polymer could find applications in different areas of the industry. Preparation of polymer blends represent a good alternative for reducing the final cost and a good alternative way to develop a new material with desired and improved properties of native biodegradable polymers such as thermal, mechanical and barrier properties (Puglia et al., 2014; Mousavioun et al., 2013).

The use of natural fibres in polymer composites to replace synthetic fibres like glass, receives an increasing attention because of their advantages such as abundance, renewability, high stiffness, non-abrasiveness to the processing equipment, possibility to be incinerated, low density and low cost (Frone et al., 2013).

Different kind of fillers have been compounded with polymer matrices in order to increase the thermal and mechanical properties of the bio-composites. Cellulose is a basic component of plants, thus it is a nearly inexhaustible source of raw material. Cellulose is the most abundant renewable polymer on earth and is responsible for the structural integrity of wood, plants and algae, as well as some sea animals and microbial cellulose (Olsson et al., 2011). Wood fibre is widely being used with thermoplastic polymers to make bio-composites. The incorporation of wood fibre in bio-composites would reduce the cost of final products since it is cheap and readily available in nature. Besides, wood fibres have certain properties such as low density, high specific stiffness, renewability and biodegradability (Awal et al., 2014).

This study aims to develop and characterize new composite materials based on PHB and different percentage of cellulose fibres (from 2% to 10%), in order to improve PHB's physical mechanical behaviour.

2. Materials and methods

2.1. Materials

In order to obtain biodegradable blends based on PHB and cellulose fibres, the following materials were used:

- PHB type 319 E manufactured by BIOMER (Krailling, Germany).
- Bis[2-(2-butoxyethoxy)ethyl] adipate (DBEEA), Proviplast, was purchased from PROVIRON, presenting the following characteristics: density 1.015 g/cm³, water content max. 0.2 %, dynamic viscosity 17 MPa x s and molecular weight 434.56 g/mol.
- Cellulose fibres type EFC 1000 (Rettenmeier & Söhne AG, Germany) (CF). The CF had a 4.5 ± 0.1 % water content, 322 ± 14 mg KOH/g OH-group content, 28.7 % lignin, 87.3 % holocellulose content.

2.1.1. Composite preparation

It was carried out four formulations coded: PHB/CF0, PHB/CF2, PHB/CF5 and PHB/CF10, containing CF from 0 to 10 wt. %, as it is shown in Table 1. All composites contain plasticizer with a ratio between PHB and plasticizer of 9:1. Neat PHB was used as reference. Before processing, PHB pellets were dried for 3 h at 55 °C and CF were dried for 3 h at 80 °C.

Table 1. Composition of PHB/CF composites

Sample code	PHB, wt. %	Plasticizer, wt. %	CF, wt. %
PHB/CF0	90	10	-
PHB/CF2	88.2	9.8	2
PHB/CF5	85.5	9.5	5
PHB/CF10	81	9	10

The melting of PHB/CF blends was performed using a BRABENDER Plastograph, in the following conditions: cuvette of 30 cm³, temperature of 175 ± 5 °C, a mixing time of 10 minutes, and the rotors speed of 40 rpm. There were obtained films with a thickness of max. 0.1 mm (± 0.001 mm) and sheets with a thickness of 1 mm (± 0.001 mm) by pressing in the following conditions: temperature: 170 °C; preheated time: 5 min respectively 10 min; pressing time: 2 min respectively 5 min; cooling time: 40 min; and a pressure of 150 bar.

2.2. Methods

2.2.1. Processing behavior

Processing behavior was evaluated by analyzing the torque – time curves registered during melt blending in the Brabender mixer at 175 ± 5 °C, for 10 min and 40 rpm.

2.2.2. Fourier-transform infrared (FT-IR) spectroscopy

The FT-IR analyses were carried out with a FTLA 2000-104 Spectrophotometer (ABB Canada) equipped with ZnSe crystal, using the Attenuated Total Reflectance (ATR) method in the range of 3000 cm⁻¹ - 750 cm⁻¹. The recording was carried out at 4 cm⁻¹ resolution, in transmission mode.

2.2.3. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed using a DSC 823° from Mettler Toledo calibrated with standard indium. Samples were first heated from ambient temperature to 250 °C at a heating rate of 10 °C/min in order to erase any previous thermal history. Then, the samples were cooled until ambient temperature and heated again to 250 °C with an increasing temperature rate of 10 °C/min. Melting temperature (T_m) and enthalpy of fusion (ΔH_f) were determined from the obtained curves. The degree of crystallinity (χ_c) of PHB composites and PHB phase was calculated using the following equations:

$$X_{comp}, \% = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (1)$$

$$X_{PHB}, \% = \frac{\Delta H_f}{\Delta H_f^0} \times \frac{100}{\phi} \quad (2)$$

where: ΔH_f is the melting enthalpy of the specimens (J/g); ΔH_f^0 is the enthalpy value for a theoretically 100% crystalline PHB (146 J/g) and ϕ is the weight fraction of the PHB.

2.2.4. Optical properties

Each specimen was cut into a rectangular piece (of 50 x 30 mm) and placed directly in a UV/Vis HELIOS ALPHA spectrophotometer (Thermo Spectronic), the measurements being performed at wavelengths from 200 to 800 nm. The measurements were performed using air as the reference. The results have been expressed as a percentage of transmittance. Then, the transmittance at 600 nm and the absorbance at 500 nm were recorded. The transparency at 600 nm (T_{600}) was obtained using the following equation (Kanatt et al., 2012):

$$T_{600} = \frac{-\log \%T}{b} \quad (3)$$

where: % T is percentage transmittance and b is the film thickness (mm).

The opacity of the films was calculated conforming to equation:

$$\text{Opacity} = A_{500} \times b \quad (4)$$

where: A_{500} is the absorbance measured at 500 nm and b is the film thickness (mm).

2.2.5. Water vapour transmission rate (WVTR)

The WVTR of the PHB composites was determined with PBI-Dansensor L 80-5000. A dry room with a specified relative humidity is separated by a wet room where the atmosphere is saturated with water vapour at a known temperature through a sheet of material to be tested. Changing humidity in the dry chamber is achieved by water vapour passing through the tested material and is detected by a humidity sensor that is able to provide an electrical signal that is measuring relative humidity in the dry room. The WVTR of the samples was performed at 23 °C and 85% relative humidity.

3. Results and Discussions

3.1. Processing behavior

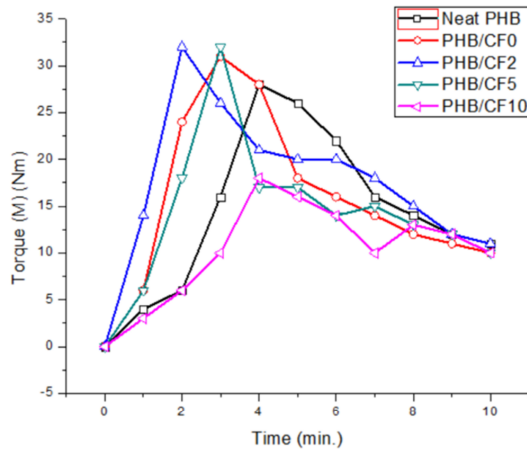


Figure 1. Torque-time profiles for PHB/CF composites and neat PHB

The torque values (Figure 1) for PHB and PHB/CF composites increased at the beginning because of the feeding and then decreased continuously after 4 minutes due to the addition of plasticizer, as it can be seen from Figure 1. Then, torque values increased slowly after the addition of CF suggesting a formation of crosslinking/branching structures, and decreased at the end of processing which means the decreasing of melt viscosity, making the composites easier to process.

3.2. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra of the PHB/CF composites and neat PHB are shown in Figure 2.

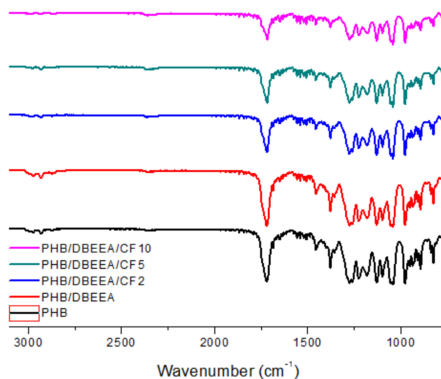


Figure 2. Transmittance of PHB composites

The main bands observed in the PHB spectrum (Figure 2) are assigned to the coupling of C–C backbone stretching with the CH₃ stretching vibration and the crystalline C–O–C vibration bands (978 cm⁻¹ and 895 cm⁻¹) (Bayar and Severcan, 2005), C–O–C stretching (1182 cm⁻¹) (Zembouai et al., 2013), C–O stretching (1227 cm⁻¹, 1277 cm⁻¹), wagging CH₃ (1379 cm⁻¹) (Xu et al., 2002), asymmetric CH₃ (1456 cm⁻¹), C=O crystalline (1720 cm⁻¹) (Xu et al., 2002), (Bayar and Severcan, 2005) and C–H stretching (2934 cm⁻¹ and 2995 cm⁻¹) (Hernane et al., 2011). In general, PHB composites show the same bands as PHB, with few band peaks shifted to lower frequencies means interaction between components. Characteristic band from 1720 cm⁻¹ was shifted to 1718 cm⁻¹ for PHB/CF 2 and PHB/CF 5 composites and respectively to 1717 cm⁻¹ for PHB/CF10 composite. In general, when the crystallinity of a polymer is altered, intensities and frequencies of some of the IR bands also vary (Bayar and Severcan, 2005).

3.3. Thermal properties of PHB composites

DSC spectra of PHB/CF composites and neat PHB are given in Figure 3, as first and second heating scans.

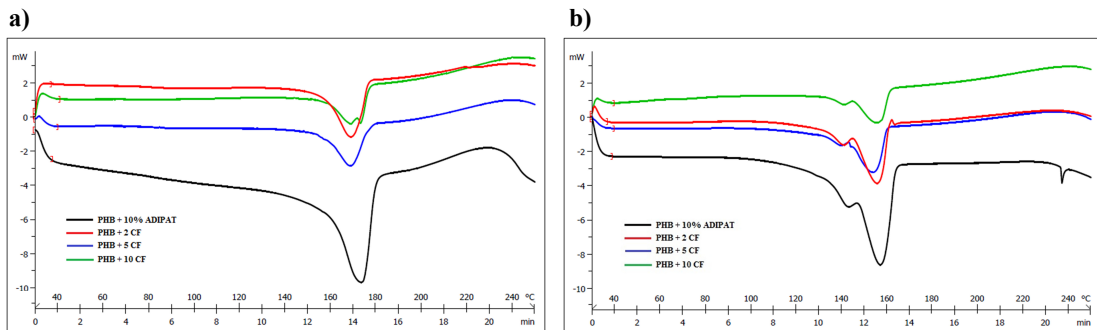


Figure 3. DSC spectra of PHB composites; a) - first heating run; b) - second heating run

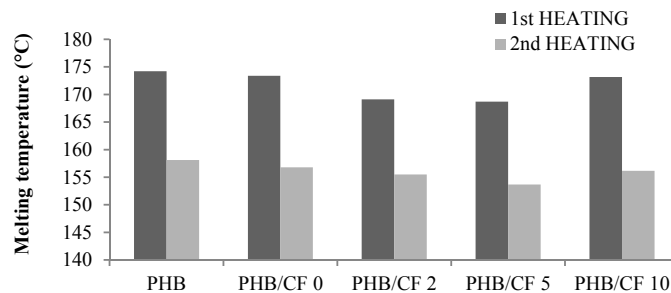


Figure 4. Melting temperature of PHB composites

For neat PHB the T_m is 174.21 °C, but at the second heating scan it shifted towards 158.1 °C (Figure 4). From the second scan, PHB/CF composites exhibit the appearance of a small shoulder before the maximum peak. This behavior was attributed to bimodal distribution of crystallite size resulted from changes in molecular weight due to random scission of long PHB chains, i.e. to the decrease in the molecular weight (Erceg et al., 2005). Similar process upon heating was reported by Dong et al. (Dong et al., 2013) who studied the melting temperature of PHB/PLA blend.

The crystallinity of PHB/CF composites decreased for all composites compared to neat PHB (Figure 5). In the first heating run, the degree of crystallinity of the composite based materials decreased from 53.57 % to 32.88 % as the CF content increased to 10 %. The decrease in the crystallinity of the tested composites it can be attributable to the hindered motion of the polymer segments due to the presence of fibres in the composite matrix (Wu, 2014).

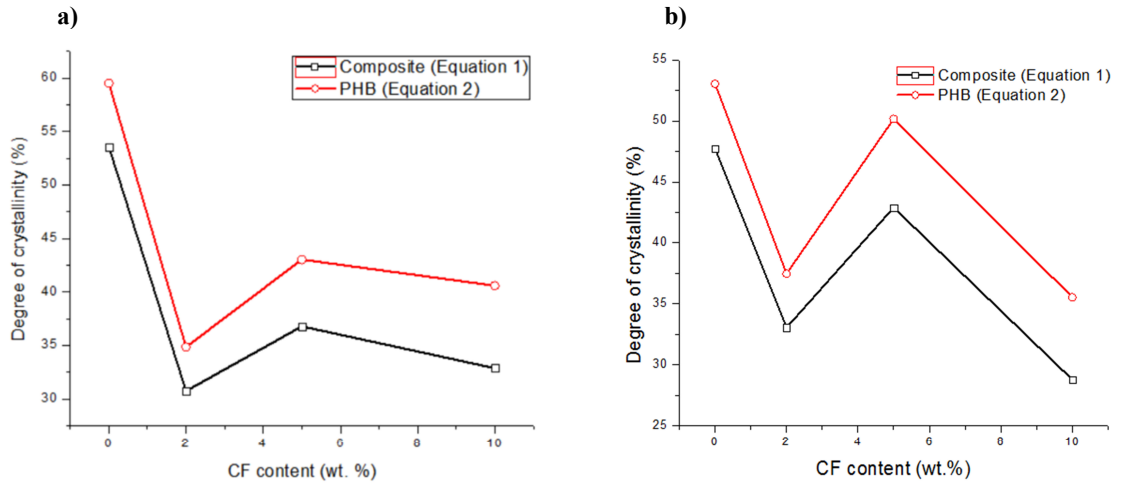


Figure 5. Degree of crystallinity of composites and PHB phase in composites
a) - first heating run; b) - second heating run

3.4. Optical properties

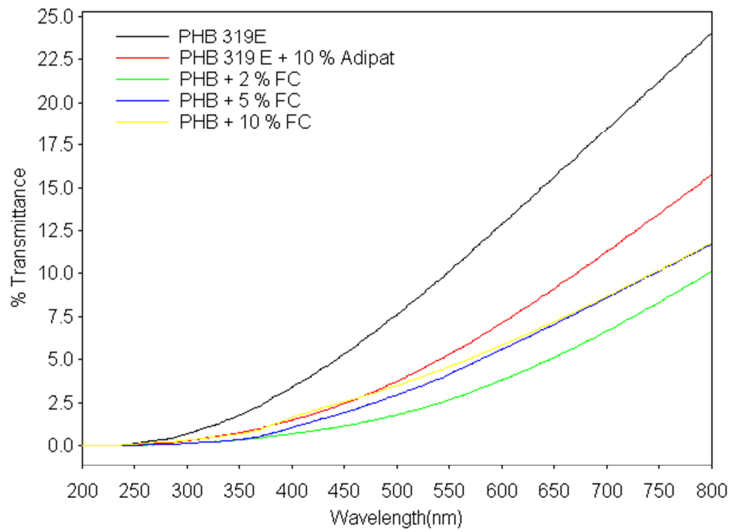


Figure 6. Light transmission properties of the composites films and neat PHB

The PHB/CF composites films showed a blocking effect in the UV light spectra region with the lowest UV light transmission (Figure 6). In the visible region, the transmittance decreased as the content of CF increased, as it can be seen in Figure 7.

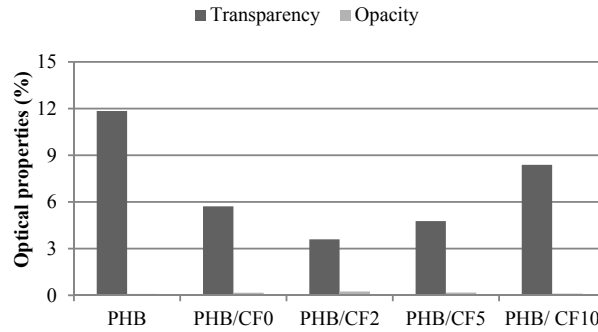


Figure 7. Transparency and opacity of PHB/CF composites

Neat PHB film proved to be the most transparent showing the highest transmission in the visible region of the spectra (400-700 nm). It can be observed from Figure 7, some significant changes in the visible region of the spectra due to the presence of cellulose fiber, thus composite materials with 2% CF content resulted in lower transparent films. The good transparency of PHB/CF5 and PHB/CF10 composites has been related to the good dispersion of the cellulose fibers in the PHB matrix. The lowest transmittance while maintaining the high transparency was also reported by Arrieta et al., 2014, that investigated the optical properties for PLA-PHB/cellulose films.

3.5. Water vapour transmission rate (WVTR)

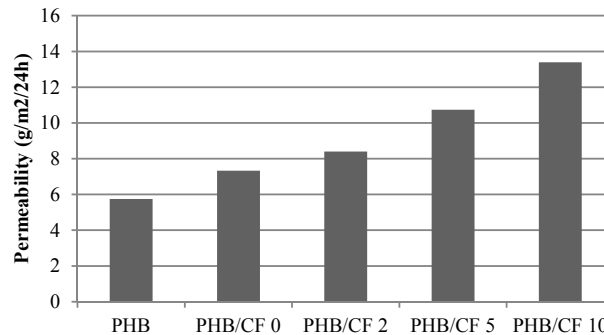


Figure 8. The effect of CF over the permeability of the tested PHB composites and neat PHB

From Figure 8, it can be observed that the water vapour transmission rate of the tested samples increased proportionally with the addition of CF in the PHB matrix. The value of WVTR of PHB composites increases with about 12, 25 and 75 % proportionally with the addition of 2, 5 and 10 wt% of CF, respectively. This means that the incorporation of CF is not effective in order to improve the barrier properties of PHB. Furthermore, the results obtained from the permeability tests are correlated with the crystallinity samples. It is a known fact that crystals in a polymer matrix reduces the water transmission due to their small cross-sectional restricting chain mobility, thus lowering water permeability (Zembouai et al., 2013).

4. Conclusions

From the processing behavior of the tested composites based on PHB and CF, we can conclude that after the addition of CF in the polymer matrix, a formation of crosslinking/branching structures and a decrease at the end of the processing procedure represents a decreasing of the melt viscosity, making the composites easy to process. After FT-IR analysis it can be observed that PHB composites show the same bands as PHB, with few band peaks shifted to lower frequencies, which means interaction between components. It was also observed that the melting

temperature decreased proportionally with the increasing content of CF for all composites except for PHB/CF10 sample. The lower melting temperature may have been caused by high CF content, that lowered the melting viscosity of PHB. The crystallinity of PHB/FC composites decreased for all samples compared to neat PHB. The decrease in the crystallinity of the tested samples can be attributed to the hindered motion of the polymer segments due to the presence of cellulose fibres in the polymer matrix. The PHB/CF composites showed a blocking effect in the UV light spectra region with the lowest UV light transmission. In the visible region, the transmittance decreased proportionally with the increasing CF content. Furthermore, all tested samples presented low transmittance while maintaining high transparency, which is a good property for a packaging material. The WVTR of the tested samples increased proportionally with the addition of CF in the PHB matrix, which take us to the conclusion that the incorporation of these amounts of CF is not effective in order to improve the barrier properties of PHB.

Acknowledgements

This paper was published under the frame of European Social Fund, Human Resources Development Operational Programme 2007-2013, project no. POSDRU/159/1.5/S/132765.

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