

Development of Fibres-Reinforced Biodegradable Composites

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In this work, blends of poly(3-hydroxybutyrate) (PHB), the most widespread member of the polyhydroxyalkanoates (PHAs), with wood fibres were investigated to assess the feasibility of producing biodegradable materials suitable for applications in packaging and agricultural environment. Due to its high crystallinity, PHB is stiff and brittle resulting in very poor mechanical properties with low extension at break, which limits its range of application. PHB was compounded successfully with wood fibres up to 30 % by weight in presence of polyethylene glycol (PEG) by extrusion. The composites were characterized by differential scanning calorimetry (DSC) and by scanning electron microscopy (SEM). Their mechanical properties were tested by dynamic mechanical thermal analysis (DMTA) and tensile tests. Preliminary tests in soil were carried out on the samples with wood fibres in order to investigate their biodegradation behavior, and further tests were performed in compost. Polyethylene glycol resulted effective as lubricating agent for the production of composites based on PHB and fibres. The good preliminary biodegradability results in soil showed that the blends PHB/wood fibres appear suitable for the production of natural fibre-reinforced thermoplastic items degradable in agricultural environment

1. Introduction

In the last years, the development of biobased and biodegradable polymers (BBDPs) derived from renewable resources has attracted significant and increasing scientific and industrial attention, particularly in terms of meeting the growing demand for sustainable development. Polyhydroxyalkanoates (PHAs) are an example of BBDPs (Bugnicourt 2014); PHAs are a family of biopolyesters produced by many bacteria as intracellular storage carbon and energy source against starvation. They are polyesters biodegradable, renewable, biocompatible and environmentally friendly (Amache et al., 2013), with thermo-processability, biodegradability, biocompatibility, and adjustable thermal and mechanical properties. They can be processed to make a variety of useful products, where their biodegradability and naturalness are beneficial in particular for application in single use packaging and agriculture. Polyhydroxybutyrate (or poly-(R)-3-hydroxybutyrate, abbreviated as PHB) was the first PHA member discovered and well studied. PHB can be produced from by-products biomass with no-food competition, such as waste waters from food industry (olive oil and dairy production) and slaughtering cattle, pig or poultry (Kettl et al., 2011).

Due to its high crystallinity PHB is stiff and brittle resulting in very poor mechanical properties with low extension at break, which limits its range of application. Very low resistance to thermal degradation seems to be the most serious problem related to the PHB processing. For this reason, PHB is commonly blended with plasticizers in order to improve its mechanical properties and to lower the processing temperature. In blends produced by solvent casting, polyethylene glycol (PEG) resulted well compatible with PHB (Zhang, 1997) and a good miscibility in PHB was reported using differential scanning calorimetry for low content of polyethylene glycol (2-5 %) (Rodrigues, 2005).

In addition, another limit in the application of PHB for the production of single use items concerns its relatively high cost (7-10 €/kg) compared to that of other biodegradable polymers. Consequently, the use of natural fillers with high availability and low cost could extend the use of PHB to the production of bio-composites for low-value applications such as single use packaging and agriculture.

Lignocellulose-based fibres or particles are widely used as biodegradable reinforcing elements in the production of composites. Such a success is derived by their environmentally friendly character, their low-cost and interesting mechanical and physical properties. Lignocellulosic fibres or particles are available mainly from wood, but several local annual plants and agricultural crops as well as industrial residues can also be considered as potential sources of raw materials. For these reasons, important industries, such as automotive, building and packaging (Khiari et al., 2011), have focused their attention to the development of new composite materials filled with natural fibres or particles. In the present study, bio-composites based on PHB with wood fibres were prepared by extrusion using PEG as lubricating agent. The effects of PEG and the natural fibres content on thermal and mechanical properties of blends were investigated. A preliminary investigation on the biodegradation of the produced composites during industrial composting and in soil was also carried out.

2. Experimental

2.1 Materials

PHB powder (PHB - LoT13), and pellets (P 226) were supplied from BIOMER® (Germany), with 60-70 % crystallinity, density of 1.24 g/cm³ and a glass transition temperature of 5 °C (Grassie 1984). PHB was used after vacuum drying at 105 °C for 48 h. Polyethyleneglycol (PEG), PEG 1500, from Fluka was used as plasticizers, as received. Wood fibres were supplied by Rettenmaier & Söhne (Germany) (type EFC100), with aspect ratio of 6:7.

2.2 Composite preparation and characterization

Blends of PHB, PEG without and with wood fibres were prepared using a Thermo Scientific HAAKE MiniLab II micro compounder with a sample volume of 7 cm³. PHB was compounded with PEG 1500 at 10, 15 and 20 % by weight.

The blends were extruded at 160-165 °C with a screw speed of 60 rpm for blends without fibres and 30 rpm for blends with fibres. Tensile specimens in accordance with the ASTM D638 V were produced using a Thermo Scientific HAAKE MiniJet II, with injection temperature of 165-170 °C, injection pressure of 450 bar for 30-40 s, post injection pressure of 400 bar for 10-15 s, and a mould temperature of 30-50 °C. Scale up production was performed by using PHB Biomer 226 in pellets on a COMAC co-rotating twin screw extruder EBC 25 HT.

Tensile tests were performed on injection moulded Haake Type 3 (557-2290) dog-bone tensile bars of PHB based composites with a width of 4.8 mm, and thickness of 1.35 mm. Stress-strain tests were carried out with an Instron 4302 tensile tester equipped with a 10 kN load cell and interfaced with a computer running the Testworks 4.0 software (MTS Systems Corporation, Eden Prairie MN, USA), at a crosshead speed of 10 mm/min. At least five replicates for each sample were carried out at room temperature.

Bars were cut from an Haake Type 3 dog-bone produced by injection moulding with a width of 4.8 mm and a thickness of 1.35 mm. DMTA analysis was carried out on a Gabo Eplexor® 100N (Gabo Qualimeter GmbH, Ahlden, Germany) at a static strain of 0.1% and a dynamic strain of 0.025 % at frequency of 1 Hz. Tests were run from - 100 °C to 200 °C with a heating rate of 2 °C/min.

The thermal transition temperatures of the dry samples, cut in small pieces and closed in aluminium pans, were determined by differential scanning calorimeter TA Q200 (TA Instruments, DE). Morphological analysis was carried out by a scanning electron microscope JEOL JSM-5600 (Tokyo, Japan).

Aerobic biodegradation test under controlled composting conditions was performed on pellets of PHB pure (Biomer 226) and pellets of composites PHB/wood fibres at 20wt% of wood fibres produced with the industrial twin screw extruder. The test was executed according to ISO 14855. The inoculum was derived from the organic fraction of municipal solid waste, which was stabilized further and matured in a composting bin at the laboratory under controlled aeration conditions during more than 20 weeks, and sieved on a screen of 5 mm, the fine fraction was the inoculum. 80 g of reference (cellulose) or test material (pellets) was mixed with 1,200 g of compost inoculums, and introduced into the reactors, which were closed airtight and put into the incubators; the tests were performed in duplicate. The temperature of the reactors was continuously controlled and kept at 58 °C. Pressurized dry air was sent over a gas flow controller, which regulates very precisely the flow rate and blown into the composting vessel at the bottom through a porous plate. Through biodegradation, solid carbon of the test compound is converted and CO₂ is produced. The gas leaving each individual reactor was continuously analysed on regular intervals for CO₂ and O₂ concentration. Likewise, the cumulative CO₂

production can be determined. The percentage of biodegradation is determined as the percentage of solid carbon of the test compound that is converted to gaseous, mineral C under the form of CO₂. The test was stopped after 78 days. For degradation in soil the inoculum consisted of a mixture, in equal quantities, of three natural soils collected from the surface layer of a sandy soil derived from a field in Lokeren, two forest soils from Moerbeke, and a garden soil from Zwijnaarde all in Belgium. Before use, the soils were sieved over a 2 mm screen to remove stones and other inert materials, recognizable roots and other plant debris, and thoroughly mixed. The fine fraction is the inoculum. The test was performed according to ISO 17556 that recommends that the soil inoculum has water content between 40 % and 60 % of the total water holding capacity and a pH between 6.0 and 8.0. At start-up, 1 g of test or reference item is mixed with 500 g inoculum and introduced into the reactors. The reactors are closed airtight and placed in the dark at 20°C±2°C. The carbon dioxide, released during the process was determined. At regular times, the soil was stirred and moistened if needed. The test was stopped after 28 weeks.

3. Results and Discussion

3.1 Effect of PEG

In Figure 1 the results of the tensile tests are reported for PHB and blends PHB/PEG at 10, 15 and 20 % w/w.

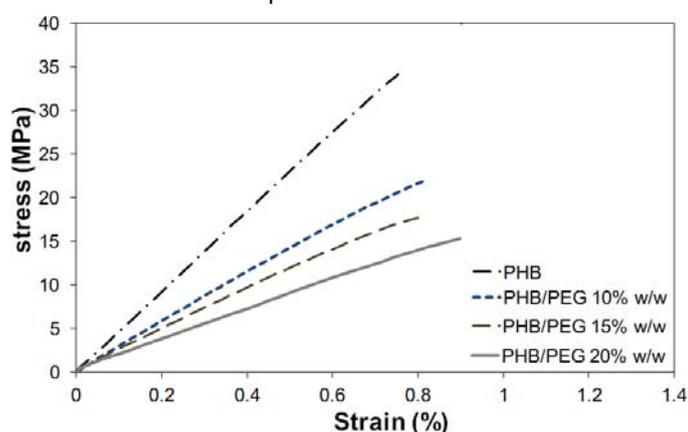


Figure 1: stress-strain curves of PHB and PHB/PEG blends at 10, 15, and 20 wt. % of PEG

As shown, the addition of PEG 1500 had a moderate effect on elongation at break, but a progressive reduction in Young's modulus and strength at break. PEG addition makes processing easier showing a lubricant effect on melted PHB, but reduced moderate effect on improving values of strain at break.

Figure 2 reports the DSC curve of PHB, PEG and PHB/PEG sample with 10 wt. % PEG. PEG 1500 has a melting peak at 48 °C as expected by the product data sheet; when blended with PHB this peak is no more evident; PHB shows a double melting peak at 135 and 151 °C.

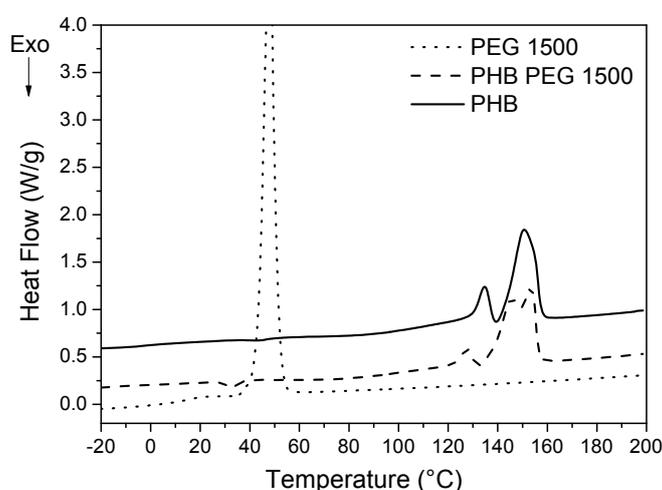


Figure 2: differential Scanning Calorimetry curves of PHB, PEG 1500 and PHB/PEG at 10 wt.% PEG

The PHB double melting peak is also reported in the literature (Erceg, 2005) and attributed to a bimodal distribution of crystallite size resulting from changes in molecular weight due to random scission of long PHB chains, i.e. to the decrease in the molecular weight. PHB is also known to present irregularly shaped exothermic peaks during crystallization as investigated by Di Lorenzo et al. (2006). When the number of growing spherulites is low, the evolution of latent heat is very sensitive to every act of nucleation as well as to the space limitations in the process of growth, resulting in non-monotonous development of latent heat, with sudden increases and decreases in crystallization rates. This results in non conventional DSC exotherms, under given crystallization conditions, characterized by spikes or shoulders associated to nucleation of new spherulites. Parra et al. (2006) investigated thermal properties of blends of PHB with PEG 400 in different proportion (2-40 wt%) prepared by casting of polymers solution in chloroform. In this work DSC thermograms also showed two melting peaks for PHB, lightly lowered by PEG addition. This behavior was attributed to a plasticizing effect of PEG that weakened the intermolecular forces between the adjacent polymer chains. Consequently, there was a change in free volume that reduced the melting temperatures of the system. Parra et al. (2006) classified PEG 400 as a plasticizer for PHB, due to reduction in melting temperature of PHB in PHB/PEG blends. DMTA curves of PHB and PHB/PEG1500 at 10 wt% PEG are reported in Figure 3. The $\tan(\delta)$ curves, representing the glass transition behavior of PHB component in blend, shift towards lower temperatures whereas the melting of PEG 1500 might be represented by the peak present at about 50 °C in the sample containing PEG1500, not present in pure PHB, in agreement with what observed in DSC curves (Figure 2). PHB has two glass transitions: the relaxation at ca. 20°C is the glass to rubber transition and the broad relaxation, centred at about 130°C, is due to motions in the crystalline phase (Scandola et al. ,1988) that depend on the thickness of the lamellae (Donth, 1992).

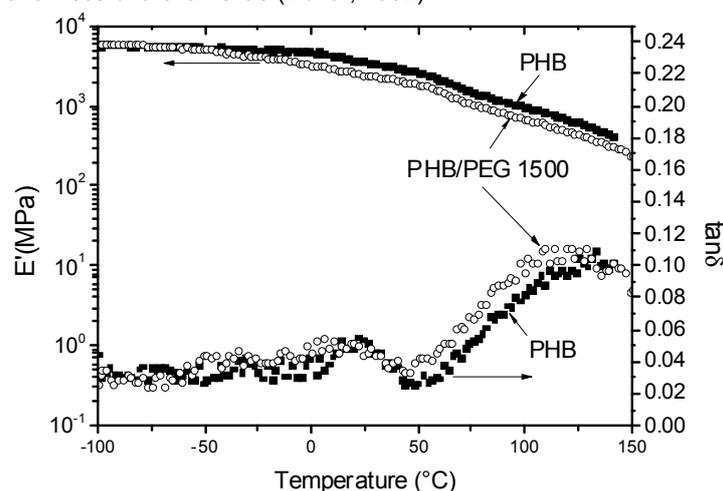


Figure 3: dynamic mechanical analysis curves of PHB and PHB with PEG1500 (10% by weight)

3.2 Effect of wood fibres

In Figure 4 SEM image of the wood fibres is reported. Blends were prepared incorporating wood fibres at 15 and 30 wt.% respect to the total weight of the blend PHB + PEG1500 at 15 wt.% PEG as shown in Table 1. The fibres induced a moderate reinforcing action in these composites for content of 15 % by weight, while 30 % by weight was more difficult to process, and reduction of properties for elongation and strength were observed.

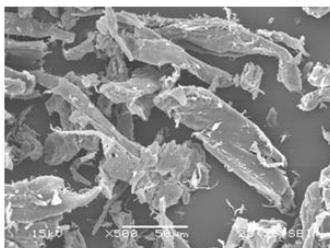


Figure 4: SEM image (X500) of wood fibres

Table 1: Mechanical properties of PHB based composites with wood fibres

Sample	Yield stress (MPa)	Young's modulus (GPa)	Strain at break (%)
PHB	21.7	2.2	1.4
PHB with 15 wt% wood fibres	21.6	3.2	1.0
PHB with 30 wt% wood fibres	18.8	4.3	0.5

3.3 Degradation tests in compost and in soil

The requirements for a compost inoculum to have a total dry solids (TS) content between 50 % and 55 %, a volatile solids content (VS) on TS of 30 % (± 5 %), and pH between 7.0 and 9.0, were fulfilled (Table 2). The test is considered valid if after 45 days the biodegradation percentage of the reference item is more than 70 % and if the standard deviation of the biodegradation percentage of the reference item is less than 20 % at the end of the test. Both requirements were easily fulfilled for all tests. The results of mineralization in compost are summarized in Table 3. The biodegradation of the reference item cellulose started almost immediately and within 9 days a biodegradation above 70 % was obtained.

Table 2: Characteristics of the compost inoculum

Characteristics	Compost Test	Characteristics	Compost Test
Total solids (TS, %)	51.3	Volatile Fatty Acids (VFA, g/L)	b.r.
Moisture content (%)	48.7	Total N (g/kg TS)	19.5
Volatile solids (VS, % on TS)	32.6	NH ₄ ⁺ -N (mg/L)	b.r.
Ash content (% on TS)	67.4	NO _x -N (mg/L)	637
pH	7.9	C/N ratio	8
Salt content (E.C.; μ S/cm)	3200		

b.r. = below reporting limit; reporting limit/ VFA = 0.3 g/L; NH₄⁺-N = 5.5 mg/L

The biodegradation of test items PHB pure (Biomer 226) and 80%PHB/20% wood fibres started after 5 days and proceeded at a moderate rate. After 17 days the biodegradation rate increased and the biodegradation proceeded further in a linear way. After 45 days an average biodegradation of 54.0% and 58.4% was measured, respectively. At the end of the test (after 78 days) an absolute biodegradation of 92.0 \pm 0.4% and 95.1 \pm 8.3% was obtained, respectively, or 96.0% and 99.3% relative to the reference substrate cellulose. From the results it can be concluded that the test samples were completely biodegraded within 78 days of composting. The soil inoculum showed a pH of 8.4, and a moisture content on dry matter of 30.0 or 46.4% of the total water holding capacity. The standard ISO 17556 prescribes a water content between 40 and 60% of the total water holding capacity (WHC_{tot}) and a pH between 6 and 8 (ISO 17556). The obtained values were acceptable from standard and experience. This was confirmed by the good degradation of the reference material, which easily passed the 60% biodegradation requirement for a valid test. Furthermore a C/N ratio of 9 was measured, ensuring a sufficient nitrogen presence (standards demands a C/N ratio below 40). In general it can be concluded that the soil inoculums was of good quality.

The results of the biodegradation of cellulose and test material 80 %PHB-20 % wood fibres in soil mixtures are summarized in Table 4 At end of test (after 195 days) a biodegradation of 93.9 % was measured for reference item cellulose, while 60.0 % was obtained for 80 %PHB-20 % wood fibres. At that time the biodegradation of 80 %PHB-20 % wood fibres was still proceeding at constant and moderate rate. It can therefore be assumed that the plastic compound PHB is degrading in soil, while also degradation for the natural fibres occurs.

Table 3. Total organic carbon (TOC) content, net CO₂ production and biodegradation percentage after 45 days (end of dynamic test) and after 78 days (end of test)

Test item	TOC (%)	Net CO ₂ Production (mg/g test item)	Biodegradation (%)		
			Average	STD	Relative
<u>After 45 days</u>					
Cellulose	41.8	1414	92.3	2.2	100.0
PHB	54.5	1078	54.0	2.0	58.5
80 %PHB/ 20 % wood fibres	52.8	1130	58.4	5.7	63.2
<u>After 78 days</u>					
Cellulose	41.8	1467	95.8	2.2	100.0
PHB	54.5	1838	92.0	0.4	96.0
80 %PHB / 20 % wood fibres	52.8	1841	95.1	8.3	99.3

Table 4: Total organic carbon (TOC) content, net CO₂ production and biodegradation of the fourth soil biodegradability test after 195 days

Test item	TOC (%)	Net CO ₂ production (mg/ g test item)	Biodegradation (%)		
			Average	STD	Relative
Cellulose	42.5	1463	93.9	0.7	100.0
80 % PHB/20 % Rettenmaier fibres	55.0	1210	60.0	5.7	63.9

4. Conclusions

Blending PHB with plasticizers improved processing and reduced brittleness as well as the use of natural fillers can reduce the cost of the final PHB-based composite while maintaining biodegradability of final products. PHB can be easily processed by double screw extrusion and injection moulding to produce composites up to 30 wt. % wood fibres, in presence of plasticizer. The produced composites appeared consistent and cohesive but present extremely limited values for strain at break. On the basis of tensile tests, PEG appears to be more effective as lubricant than as a plasticizer.

The presence of the wood fibres increased the Young's Modulus, while does not substantially modify the strain at break, and strength of the composites. Composites based on PHB and wood fibres resulted both compostable and biodegradable in soil, confirming high values of these formulations for the production of single use items that can be disposed in composting facilities or degrade in soil when proposed for agriculture applications.

Acknowledgements

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