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Potential use of rice straw as filler in eco-composite materials

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Abstract

Rice straw filled composites were prepared from poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) copolymer containing 13% (mol) hydroxyvalerate. The effects of rice straw content on thermal and mechanical properties of the composites were investigated. It was shown that the value of tensile modulus value almost doubled with the increase of rice straw content, while the tensile strength slightly decreased, compared to pure PHBV resin. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) results have demonstrated a minor effect of the rice straw on thermal behavior of PHBV resin. PHBV/RS composites are expected to be developed as materials for structural application, especially for panelized components with good thermal insulation, intended for improvement of the energy efficiency in eco-buildings.

Keywords: Rice; Poly (hydroxybutyrate-co-hydroxyvalerate) eco-composites; straw

Abbreviations:

PHBV-poly (hydroxybutyrate-co-hydroxyvalerate); PHB- poly(hydroxybutyrate); PLA- poly(lactic acid); PP- poly (propylene); RS- rice straw; PHBV/RS-poly(hydroxybutyrate-co-hydroxyvalerate) rice straw composites; DSC-Differential Scanning Calorimetry; TGA-Thermo Gravimetric Analysis; SEM- Scanning Electron Microscopy; T_c - Crystallization temperature; T_m- melting temperature; T_{onset} - onset temperature; x_c - degree of crystallinity; ΔH_f- experimental enthalpy of fusion; ΔH_f^o- enthalpy of fusion of an ideal crystal; ΔH_c - crystallization enthalpy

Introduction

In the last ten years, bio-composite materials based on biodegradable polymer matrices and natural fibers as reinforcements have received a significant scientific attention (Avella eta al., 2000; Reinsch & Kelly 1997; Mohanty et al., 2000; Luo & Netravali, 1999). Many research groups have directed their work towards defining numerous combinations of biodegradable matrix/natural fibers in order to promote new classes of biodegradable composites with improved mechanical properties, as well as to achieve products

with lower cost. Amongst many investigated natural fibers in this area, different fillers have the significant importance. For example, the development of wood-flour composites has been actively pursued (Maldas & Kokta, 1989; Lee et al., 2004a). With the increasing consumption of wood-based raw materials, their substitutions were inevitably needed. Recently, there is a growing interest in agricultural waste as a substitute for wood-based raw materials. Among the various agricultural straws, rice straw could be very interesting material as filler in biodegradable polymer composites, due to its good thermal stability compared to other agricultural waste (http://greenpressinitiative.org). The rice straw can be easily crushed into chips or particles, which are very similar to wood particles or fibers. The rice straw is mainly consisting of carbohydrate components such as hemicelluloses, cellulose, and lignin (Lee, 2004b). The carbohydrates content is variable, as well as other components, such as ash and silica. The hydrophilic character of the rice straw is one of the reasons for relatively high moisture content, approximately 60% on a wet base, or 10-12% on a dry base. The ash content of up to 22% and low protein content result in a material decomposing not as readily as other straws (Pan et al., 1999). The rice straw resistance to bacterial decomposition makes this material suitable as filler in building composite materials. On the other hand, high content of silica (up to 20%) represents an additional potential benefit regarding the flame-retardant when used in building industry. From this point of view, rice straw has been studied as potential filler in various thermoplastic matrices. Recently, Yang et al., (2004) have examined polypropylene filled rice straw composites. They reported improved mechanical properties, i.e. increased tensile modulus of the PP/rice straw composites with the increase of filler content.

In the present study, we used biodegradable matrix poly (hydroxybutyrate-co-hydroxy valerate) copolymer and rice straw to prepare the composites and to examine the possibility of using this agricultural waste as reinforcing filler in these eco-composite materials. Within the ECO-PCCM project framework supported by the EU FP6-INCO program, eco-composites based on PLA, PHBV and PP reinforced with different natural fibers have been designed and studied (EU FP6-INCO-WBC program). In order to address the INCO priorities, rice straw was chosen as natural reinforcement because of its availability in western Balkan region.

Materials and methods

Test Materials

PHBV copolymer with hydroxyvalerate content of 13 % mol was supplied by Biomer (Krailling-Germany), and used as received. The rice straw (RS) agricultural waste was taken from the richest rice-producing region, Kocani-Macedonia. Prior the preparation of composites, rice straw was dried for 24 hours in a vacuum oven at 80^{o}C, in order to obtain moisture content of 1% max.

Composites preparation

The composite materials with different content of rice straw were prepared by melt mixing in a Brabender like apparatus (Rheocord EC of Haake INC., New Jersey, USA) for 10 minutes at 170^{o}C, by progressively increasing the mixing speed up to 32 rpm. Finally, all the composites were compression molded at 170^{o}C for 7 minutes, in order to obtain 65 mm x 65 mm x 3.5 mm specimens.

Mechanical testing

The tensile strengths and tensile modulus were measured using Instron machine (model 5564) with cross-head speed of 5 mm/min, at room temperature, according to ASTM D 638-99 (ASTM International, 1999). Test specimens were 3.5 mm thick, 6.0 mm wide and 60 mm long. For each sample, 10 specimens were tested and the average tensile modulus and strengths were estimated.

Electron microscopy

After the tensile tests, fractured surface was analyzed using scanning electron microscopy. The measurements were performed with SEM microscope (JEOL model), after coating the samples with Au/Pd alloy.

Differential Scanning Calorimetry

The prepared composites were thermally characterized using Perkin Elmer Differential Scanning Calorimeter DSC 7. Samples of approximately 7 mg weight were first heated up to 170^{o}C (I run) and kept at end temperature for 1 minute, in order to erase their thermal history. The

Table 1. Mechanical analysis results: Tensile properties of PHBV and PHBV/RS composites

Sample	Tensile modulus (Mpa)	Tensile strength (Mpa)
PHBV	643	6.20
PHBV/RS, 80/20 $^{wt}/_{wt}$	1167	5.70
PHBV/RS 70/30 $^{wt}/_{wt}$	1172	5.24

samples were then cooled to 0^{o}C with a cooling rate of 10^{o}/min (II run). After the crystallization process, samples were reheated from 0 to 170^{o}C with a heating rate of 10^{o}C/min (III run). The crystallization temperatures (T_c) were measured as the minimum of the exothermic peaks of DSC traces during the cooling run. The melting temperatures (T_m) were measured as maximum of the endothermic peaks of DSC traces during the second heating scans.

Thermogravimetry

Thermogravimetric analysis of PHBV, rice straw and the two composites was carried out using Perkin Elmer Pyris Diamond Thermogravimetric/Differential Thermal Analyzer, with a heating rate of 10^{o}/min. The scanned temperature range was from 25 to 600^{o}C. The weight of the specimens was maintained at around 10 mg.

Results and Discussion

Mechanical properties

The average tensile modulus and corresponding strengths at break of the PHBV resin and the two prepared composites are presented in Table 1. It can be noted that modulus of the composites is about 82 % higher than that of neat PHBV.

As expected the tensile strengths of PHBV composites slightly decreased with the increase of filler content. According to Ke (2000) and Sun (2003), as the dispersed phase loading increase, the effective cross-sectional area of continuous phase is reduced, subsequently resulting in a decrease of tensile strength. These results can be also explained by the imperfect distribution of the filler through the polymer matrix, as well as very poor adhesion between the polymer resin and filler. This could be supported by literature data for irregularly shaped fillers, where the strength of the composites decreases due to instability of the filler to support stresses transferred from the polymer matrix (Ismail et al., 2002; Ismail & jaffry, 1999). Similar results are reported in our previous paper for rice straw/polypropylene composite materials (Grozdanov et al., 2006).

The above findings, related to very poor adhesion between the polymer matrix and the filler, are confirmed by SEM photomicrographs of the fractured samples given in Figures 1a and 1b.

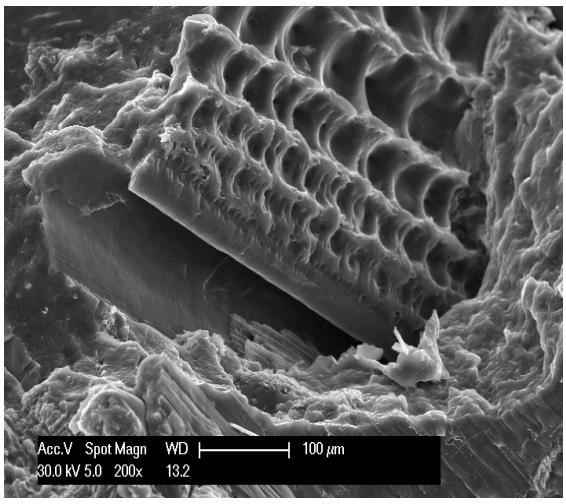

Fig 1a. SEM micrograph of PHBV/RS 70/30 $^{wt}/_{wt}$ composites

It can be seen that the rice straw husks are completely pulled out of the polymer resin, and empty voids are visible.

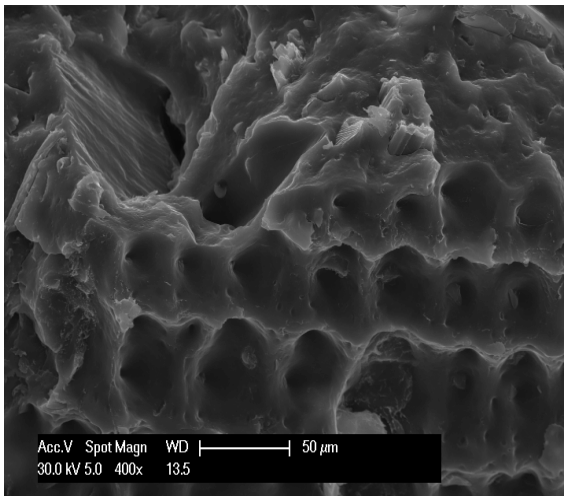

Fig 1b. Another SEM micrograph of PHBV/RS 70/30 $^{wt}/_{wt}$ composites

Thermal properties

The processing of thermoplastic composites usually proceeds under non-isothermal conditions, and from this point of view it was interesting to analyze the thermal properties under dynamic regime. The crystallization and melting behavior of PHBV/RS composites were analyzed by DSC. Typical non-isothermal crystallization thermograms of the investigated samples are presented in Figure 2.

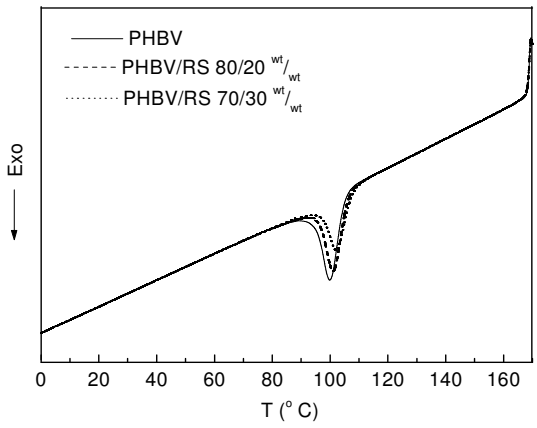

Fig 2. Crystallization exotherms of PHBV and its composites

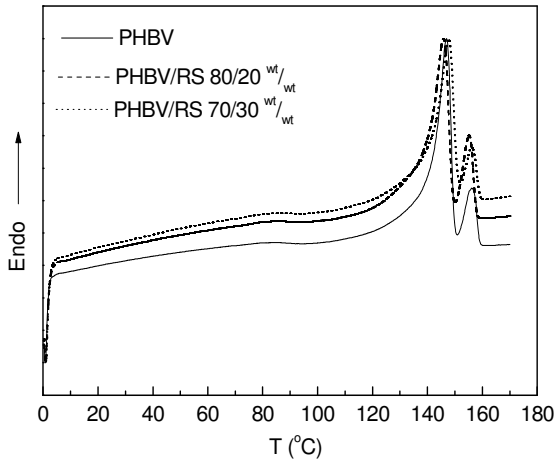

Fig 3. Seconds melting runs of PHBV and the two composites.

It can be noted that the crystallization peak temperatures slightly shift to higher values with the filler content. The calculated degrees of crystallinities (Table 2), according the relation $x_c = \Delta H_f / \Delta H_f^o$, where ΔH_f is the experimental enthalpy of fusion, and ΔH_f^o (taken as 109 J/g (Scandola, 1997) is the enthalpy of melting of an ideal crystal, have a decreasing tendency with the increase of the filler content.

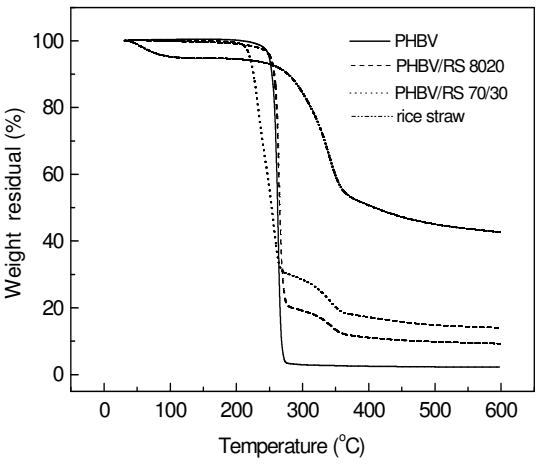

Fig 4. TGA thermograms of PHBV, rice straw and their composite

Table 2. Fundamental parameters obtained from DSC crystallization and melting curves for PHBV and PHBV/RS composites

Sample	T_c (°C)	ΔH_c (J/g)	x_c (%)	T_{m1} (°C)	T_{m2} (°C)	ΔH_f (J/g)
PHBV	99.8	-46.3	42.5	146.8	155.6	50.7
PHBV/RS 80/20	101.0	-44.7	41.0	145.5	154.5	51.9
PHBV/RS 70/30	102.2	-41.6	38.1	147.3	155.6	49.9

shows typical DSC curves corresponding to reheated samples (III run) of PHBV and PHBV/RS composites containing 20 and 30 wt % filler, respectively.

Double melting peaks are detected for all samples. This double melting effect was previously postulated to be a result of melting of the primary crystallites, and to the melting of recrystallized crystallites of different stability (Mandelken, 1964). From Table 2 and Figure 3, it is clear that the addition of rice straw causes only a minor effect on Tm_1, Tm_2 and the corresponding enthalpies of fusion, although some differences in crystal size (distribution) could be expected due to the visible different widths at half height of the lower melting peaks. The thermal stability of PHBV, rice straw and the two composites was studied using thermogravimetric analysis under nitrogen environment. Typical weight residuals vs. temperature plots are presented in Figure 4.

TGA curve for PHBV shows complete weight loss of the resin in a single step between 225 and 250°C, confirming earlier literature findings for PHB and its copolymers with hydroxyvalerate (Kunioka & Doi, 1990; Abate et al., 1994).

Thermal decomposition of rice straw starts at 238°C and continues with higher residue content (44.8% at T=500°C) after thermal degradation. From the thermograms and determined weight residues of 10% and 14.9 wt percentage (Table 3) for the two composites respectively at T=500°C, it is evident that the presence of rice straw does not affect the thermal decomposition of PHBV.

Conclusions

Poly (hydroxybutyrate-co-hydroxyvalerate)/rice straw composites with two weight ratios (80/20 and 70/30 $^{wt}/_{wt}$) were prepared by melt mixing and compression molding.

The characterized composites showed improved tensile modulus and very slight decrease of the tensile strengths, when compared to tensile properties of pure resin. The addition of rice straw to PHBV matrix did not affect the thermal properties of the resin, probably due to the poor adhesion between the hydrophilic rice straw and hydrophobic PHBV resin. Results suggest that the dispersion is not yet optimized, and further

Table 3. Thermogravimetric data of PHBV, rice straw (RS) and their composites: onset degradation temperature (T_{onset}) and residual weight at 500°C

Samples	T_{onset} (°C)	Weight residual at 500°C
PHBV	240	2.6
RS	238	44.8
PHB V/RS 80/20 $^{wt}/_{wt}$	230	10.0
PHB V/RS 70/30 $^{wt}/_{wt}$	210	14.9

improvement of the processing conditions or use of a compatibilizer is needed to find the best possible dispersion of rice straw. The obtained results of the PHBV/RS composites have shown that the rice straw waste could be used as alternative biodegradable eco-friendly reinforcement, but with further optimization of the conditions in order to obtain materials with improved mechanical properties.

References

Abate R, Ballistreri A, Montaudo G, Impallomeni G (1994) Thermal degradation of microbial poly(4-hydroxy butyrate). *Macromolecules.* 27:332-336

ASTM International "Standard Test Method for Tensile properties of Plastics", West Conshohocken PA, pp 46-58 (1999)

Avella M, La Rota G, Martuscelli E, Raimo M, Sadocco P, Elegir G, Riva R (2000) Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fiber composites: thermal, mechanical properties and biodegradation behavior. *J. Mater. Sci*. 35:829-836.

Grozdanov A, Buzarovska A, Bogoeva-Gaceva G, Avella M, Errico M, Gentille G (2006) Rice straw as alternative reinforcement in polypropylene composites. *Agron. Sustain. Dev*. 26: 251-255

Ismail H, Jaffry RM (1999) Physico-mechanical properties of oil palm wood flour filled natural rubber composites. *Polym.Test*. 18:381-388

Ismail H, Edyham MR, Wirjosentono B (2002) Bamboo fiber filled natural composites: The effect of filler loading and bonding agent. *Polym. Test*. 21:139-144

Ke TY, Sun XZ (2000) Physical properties of poly(lactic acid) and starch composites with various blending ratios. *Cereal Chem* 77:761-768

Ke TY, Sun XZ, Seib P (2003) Blending of PLA and starches containing various amilose content. *J Appl Polym Sci.* 89:3639-3646

Kunioka M, Doi Y (1990) Thermal degradation of microbial copolyesters: poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(3-hydroxybutyrate-co-4-hydroxy-butyrate). *Macromolecules.* 23:1933-1936

Lee SY, Yang HS, Kim HJ, Jeong CS, Lim BS, Lee JN (2004a) Creep behavior and manufacturing parameters of wood flour filled polypropylene composites *Compos. Struct*. 65:459-469 http://greenpressinitiative.org/AgriculturalResidues.htm

Lee E, Sun X, Karr GS (2004b) Adhesive properties of modified soybean flour in wheat straw particleboard. *Composites: Part A.* 35:297-302

Luo S, Netravali AN (1999) Mechanical and thermal properties of environment–friendly "green" composites made from pineapple leaf fibers and poly(hydroxybutyrate-co-valerate) resin. *Polym. Composite*. 20:367-378

Maldas D, Kokta BV (1989) Improving adhesion of wood fiber with polystyrene by chemical treatment of fiber with coupling agent and the influence on the mechanical properties of the composites. *J. Adhes. Sci. Technol*. 3:529-539

Mandelken L (1964) Crystallization of polymers. McGraw-Hill New York

Mohanty AK, Khan MA, Sahoo S, Hinrichsen G (2000) Effect of chemical modification on the performance of biodegradable jute yarn-Biopol composites. *J. Mater. Sci.* 35:2589-2595

Pan HJ, Sano Y, Ito T (1999) Atmospheric acetic acid pulping of rice straw II. Behavior of ash and silica in rice straw during atmospheric acetic acid pulping and bleaching. *Holzforschung*. 53:49-55

Reinsch V, Kelley S (1997) Crystallization of PHBV in wood fiber-reinforced composites. *J. Appl. Polym. Sci*. 64:1785-1796

Scandola M, Focarete ML, Adamus G, Sikorska W, Baranowska I, Swierczek Gnatowski M, Kowalczuk M, Jedlinski Z (1997) Polymer blends of natural poly(3-hydroxybutyrate- co-3-hydroxyvalerate) and a synthetic atactic poly(3-hydroxybutyrate). Characterization and biodegradation studies. *Macromolecules.* 30:2568-2574

Yang HS, Kim HJ, Son J, Park HJ, Lee BJ, Hwang TS (2004) Rice–husk flour filled polypropylene composites; mechanical and morphological study. *Compos. Struct.* 63:305-312