

## Biobased polymer composites for films and coatings

Dace Erkske<sup>a\*</sup>, Ilze Viskere<sup>a</sup>, Anda Dzene<sup>a</sup>, Velta Tupureina<sup>a</sup>, and Ludmila Savenkova<sup>b</sup>

<sup>a</sup> Institute of Polymer Materials, Riga Technical University, 14/24 Azenes Str., LV-1048 Riga, Latvia

<sup>b</sup> Institute of Microbiology and Biotechnology, Latvian University, 4 Kronvalda Boulv., LV-1010 Riga, Latvia

Received 24 October 2005, in revised form 15 December 2005

**Abstract.** Heterogeneous multicomponent biocomposites were elaborated on the basis of biodegradable polymer polyhydroxybutyrate through incorporation of additives of distinctive chemical nature (plasticizers, renewable fillers, compatibilizers). Plasticized polyhydroxybutyrate solutions were used as continuous matrices for the formation of films and paper coatings. Mechanical, thermal, hygroscopic, and barrier properties and biodegradation of the obtained materials were evaluated in terms of application as biodegradable packaging.

**Key words:** biocomposites, polyhydroxybutyrate (PHB), starch, biodegradation, water vapour permeability, hygroscopic properties.

### INTRODUCTION

Growing public concern about environmental pollution caused by accumulation of nondestructible solid waste has stimulated the development and design of biobased biodegradable polymers and composite materials [1, 2]. Biopolymers may be obtained from renewable resources, synthesized microbially, or synthesized from petroleum-based chemicals [3]. The most abundant biopolymers based on renewable resources are agro-polymers (starch and cellulose plastics), polylactides, and polyhydroxyalkanoates (PHA). One of the representative examples of PHAs – polyhydroxybutyrate (PHB) – has attracted great scientific and industrial attention due to its specific properties – biodegradability and biocompatibility, which are the reason for a wide range of untraditional applications of polymers [4, 5].

---

\* Corresponding author, [veltupur@ktf.rtu.lv](mailto:veltupur@ktf.rtu.lv)

Biodegradable polymers were intended to be developed as matrix polymers for composite materials because performance limitations and the high cost of biopolymers are the major barriers to their large-scale application and ability to replace traditional nonbiodegradable polymers [6–8].

It was recognized [8] that the high cost of biopolymers is not due to the costs of raw materials for polymer synthesis but is mainly attributable to low production volumes. One possible way to obtain cost-effective biobased polymer materials is through purposely designing multicomponent biocomposites based on biodegradable fillers such as starch. Use of starch as a filler in high-cost biodegradable plastics is attractive because it is totally biodegradable, inexpensive, and available in large quantities. Despite the listed advantages, starch-based bioplastics have been manufactured slowly due to the hygroscopic nature of starch. To overcome the apparent lack of affinity and increase the adhesion between starch and hydrophobic biopolymers, different strategies were suggested: based on melt processing, such as two-step co-extrusion, preparation of multilayered composites [9].

The aim of the present work was to develop a process for the formation of heterogeneous multicomponent biocomposite films and coatings on the basis of modified matrices of biopolymers (PHB) through incorporation of additives of distinctive chemical nature (disperse renewable fillers, plasticizers, compatibilizers) and to evaluate mechanical, thermal, and barrier properties and biodegradability of the obtained films and coatings.

## MATERIALS AND METHODS

### Chemicals

Three grades of microbiologically synthesized biodegradable polymers (PHB) were used as matrix polymers for biocomposite formation: PHB (synthesized at LU MBI, Latvia), v PHB (supplied by BIOMER, Germany), and Br PHB (purchased from PHB Industrial S/AS, Brazil).

PHB was recovered from the biomass of *Azotobacter chroococcum* strain 23 [10] with polymer content above 75% dry cell weight [11, 12]. Bisoflex DOP (BP Chemicals), a mixture of dioctyl phthalate and di-2-ethylhexylphthalate ( $M_w = 390$ ), was used as a harmless plasticizer. Native potato starch supplied by Aloja Starkelsen SIA (Latvia) and thermocell (product of the Latvian State Institute of Wood Chemistry) were used as fillers for PHB composites.

### Preparation of biocomposites, films, and coatings

Modified PHB biopolymer films were prepared by the conventional solution casting technique from 1–3% chloroform solution incorporating the corresponding plasticizers. Solutions of plasticized PHB were used as a continuous matrix for the development of potato starch and thermocell filled biocomposites. The

formation of such biocomposites was based on the so-called wet process of preparing the film forming suspension with the fillers (starch or thermocell) at first dispersed but PHB + Bisoflex dissolved into an appropriate liquid (solvent) phase with subsequent careful mixing of components. To improve fillers to polymer matrix adhesion, some kind of compatibilizer (stearic acid) was introduced at the dispersion preparation stage.

Paper coatings were obtained manually applying the polymer matrix solutions on a flat surface of paper by a special micrometer adjustable film applicator (Sheen Instruments Ltd) with subsequent moulding after the evaporation of the solvent in vacuum.

### **Testing methods**

The elongation at break ( $\epsilon$ ) and tensile strength ( $\sigma$ ) of biocomposite films were determined using a Universal Testing Machine UTS-100 as described in [13, 14]. Water vapour permeability was measured according to ASTM E 96-94 (dessicant method). Water vapour absorption of filled starch and thermocell PHB films was determined according to ASTM D 3201-94. Laboratory-accelerated soil degradation tests were carried out gravimetrically at  $25 \pm 2^\circ\text{C}$  in microbially active garden soil (humus content 2%, water content 45%, pH 6.8). The kinetics of the biodegradation of PHB biocomposites was observed by light microscopy (LEICA M 420).

## **RESULTS AND DISCUSSION**

The results of our previous studies [15] demonstrated that control and improvement of some physical, mechanical, and thermal properties of PHB limiting its processing can be achieved through modification, using different kinds of high and low molecular plasticizers.

Bisoflex, a harmless and safe plasticizer, was chosen for further studies considering the fact that its content of about 20 wt % and over assured sufficient mechanical strength and elasticity ( $\sigma_T \sim 15 \text{ MPa}$ ,  $\epsilon_T > 300\%$ ), reducing brittleness and essentially increasing the flexibility of polymer films by weakening attractive intermolecular forces along polymer chains and facilitating conformational changes in the polymer [14]. The presence of plasticizers in PHB films reduced the melting temperature and enlarged the processing window of such materials.

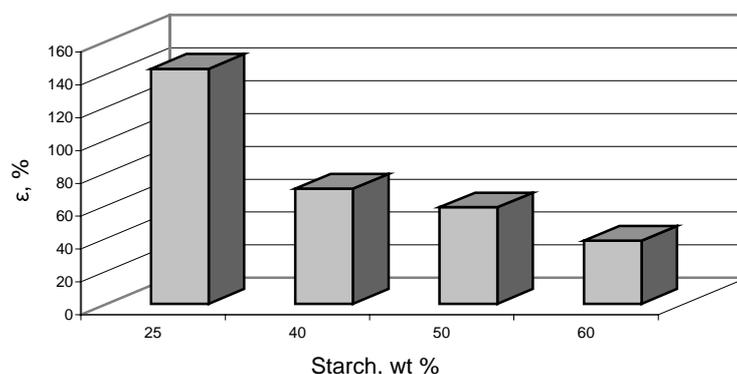
Such plasticized PHB solutions were employed as continuous matrices to elaborate heterogeneous multicomponent PHB biocomposites for incorporating some kind of fillers with distinctive chemical nature, for example native potato starch and microcrystalline cellulose – thermocell.

The formation of PHB-based biocomposites was performed by a two-stage suspension casting technique. First PHB + Bisoflex was dissolved in an appropriate solvent (chloroform) but starch was dispersed in a small amount of the same solvent containing compatibilizers (stearic acid). This was followed by careful

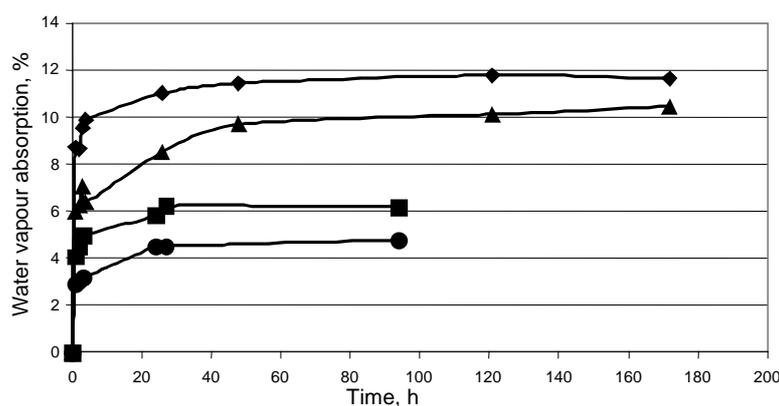
mixing of the components. Addition of compatibilizers facilitates improved adhesion between the filler and the polymer matrix and formation of a homogeneous structure of the obtained films.

The effect of starch content (25–60 wt %) on the mechanical and hygroscopic characteristics and biodegradation in soil was evaluated. It was found that tensile strength ( $\sigma_T$ ) and elongation at break ( $\epsilon$ ) of PHB–starch biocomposite films decreased with increasing content of starch (as a result of more pronounced heterogeneous structure at a high starch content), being in the range  $\sigma_T = 4\text{--}7$  Mpa and  $\epsilon = 40\text{--}120\%$  (Fig. 1). In our opinion starch content of 25–40 wt % in PHB–starch biocomposites could be considered as optimum for special applications.

The hygroscopic properties of filled PHB biocomposites were found to be dependent on the chemical nature and content of fillers (Fig. 2). Starch content of 25–40 wt % assured 9–11% water vapour absorption in comparison with 5–6% for the same content of thermocell. A significant advantage of PHB-based



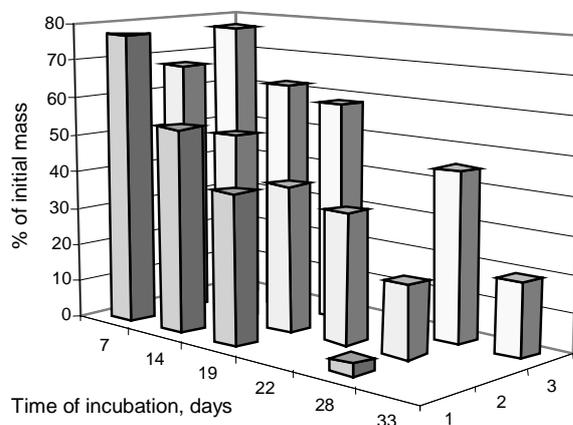
**Fig. 1.** Elongation at break ( $\epsilon$ ) of plasticized PHB–starch films.



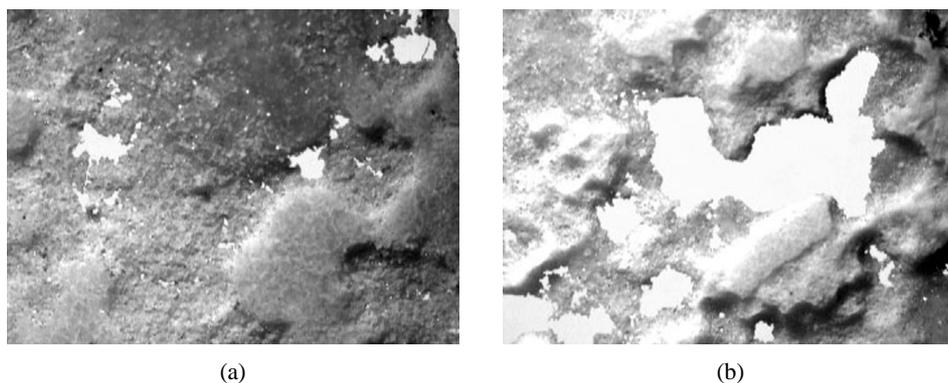
**Fig. 2.** Kinetics of water vapour absorption of PHB-based composites: ♦ – starch 40 wt %, ▲ – starch 25 wt %, ■ – thermocell 40 wt %, ● – thermocell 25 wt %.

biocomposites for special applications (short-life packaging, etc.) is microbial biodegradability. The tendency to biodegradation and the kinetics of the biodegradation process of PHB–starch biocomposites were evaluated in microbially active garden soil under controlled conditions (Fig. 3).

The results obtained testified that the biodegradation rate of PHB–starch biocomposites was dependent on the formulation variables (PHB : starch : Bisoflex ratio). A weight loss of 50–60% of the initial mass (which is considered as the criterion of the biodegradation process) was observed during two to three weeks for all systems tested. Figure 4 illustrates the dynamics of biodegradation in soil of some PHB–starch biocomposite films.



**Fig. 3.** Residue (% of initial mass) of plasticized PHB–starch films in soil after biodegradation. Starch content (wt %): 1 – 25; 2 – 60; 3 – 40.



**Fig. 4.** Biodegradation of starch filled (25 wt %) PHB films in soil after 14 days (a) and 28 days (b). Magnification  $\times 20$ .

It was ascertained in [16] that plasticized PHB-based films can be used for food biopackaging in terms of some barrier properties and possibility of using PHB-based biocomposites as paper coatings were evaluated. The coating formation process was performed by the solvent casting technique using a special device – a micrometer adjustable film applicator. Paper of 45 g/m<sup>2</sup> grammage was employed as substrate. PHB of different origin and distinctive molecular weight and their composite films proved to be suitable for coating formation (Table 1).

The water vapour permeability of the obtained laminated systems was evaluated. Experimental values of the results for paper–biocomposite systems are summarized in Table 2.

Comparison of the obtained results testified that the water vapour permeability of all the samples tested was of the same order of magnitude. The water vapour permeability of plane PHB films was found to be about 20 times lower than the corresponding value of untreated paper. Use of higher molecular weight PHB resulted in increased values of water vapour permeability. It could probably be related to some crack formation in high crystalline polymers in the moulding process of coated systems after the evaporation of the solvent. A pronounced increase of water vapour permeability was observed for starch containing coatings due to the hydrophilic character of starch and the formation of a heterogeneous structure.

**Table 1.** Characteristics of PHB of different origin

Producer	$M_w$ , kDa	$T_m$ , °C	Crystallinity, %
LU MBI (Latvia)	2600	181.0	61.8
Biomer (Germany)	686	177.8	58.2
PHB Industrial S/AS (Brazil)	205	177.9	50.8

**Table 2.** Water vapour permeability of PHB-based films and coatings

Content, wt %	Thickness, mm	Water vapour permeability, (g.m/Pa.s.m <sup>2</sup> )10 <sup>-11</sup>
Paper (grammage 45 g/m <sup>2</sup> )	0.051	4.713
PHB film	0.061	0.245
PHB + 23% Bisoflex (film)	0.071	0.307
Paper–PHB	0.063	3.674
Paper–v PHB	0.066	1.437
Paper–Br. PHB	0.073	0.737
Paper–v PHB + 23% Bisoflex	0.068	3.120
Paper–Br. PHB + 23% Bisoflex	0.065	2.914
Paper–v PHB + 23% Bisoflex + 25% starch	0.083	5.668

## CONCLUSIONS

Plasticized PHB solutions were employed as continuous polymer matrices for the elaboration of PHB–starch-based films and paper coatings. It was found that mechanical characteristics, hygroscopic properties, and the biodegradation rate in soil of PHB–starch-based biocomposites depend on the content of fillers and formulation variables. Weight loss of 50–60% of the initial mass was achieved during two to three weeks for all systems tested. It was demonstrated that the use of high molecular weight PHB- and PHB–starch-based coatings for paper significantly increases the water vapour permeability of the material. The results obtained so far testify that combination of inexpensive water sensitive starch with hydrophobic PHB offers a potential for creating ecologically sound biocomposites for special kinds of application.

## REFERENCES

1. Griffin, G. J. L. *Chemistry and Technology of Biodegradable Polymers*. Chapman & Hall, Glasgow, 1994.
2. Doi, Y. *Microbial Polyesters*. VCH Publishers Inc., New York, 1990.
3. Scott, G. & Gilead, D. *Degradable Polymers. Principles and Applications*. Chapman & Hall, London, 1995.
4. Guo-Qiang, C. Production and application of microbial polyhydroxyalkanoates. In *Proc. 7th World Conference on Biodegradable Polymers & Plastics, Terrenia (Pisa), Italy, 2002*, 155–167.
5. Sudesh, K. & Doi, Y. Polyhydroxyalkanoates. In *Handbook of Biodegradable Polymers* (Bastioli, C., ed.). Rapra Technology Ltd., Shawbury, UK, 2005, 219–241.
6. *Natural Fibers, Biopolymers and Biocomposites* (Mohanty, A. K., Misra, M. & Drzal, L. T., eds). CRS Press, London, 2005.
7. Lee, S. Y., Park, S. J., Park, J. P. et al. Economic aspects of biopolymer production. In *Biopolymers* (Steinbüchel, A., ed.). Wiley-VCH, Weinheim, 2003, **10**, 319–338.
8. Mohanty, A. K., Misra, M. & Drzal, L. T. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *J. Polymers Environ.*, 2002, **10**, 19–26.
9. Martin, O., Schwach, E., Avérous, L. & Couturier, Y. Properties of biodegradable multilayer films based on plasticized wheat starch. *Starch/Stärke*, 2001, **53**, 372–380.
10. Savenkova, L., Zagreba, E., Gercberga, Z. et al. *Azotobacter chroococcum* strain 23 – production of poly- $\beta$ -hydroxybutyric acid. Pat. LV 5297 (10.10.1993).
11. Lee, Y., Stegantseva, E., Savenkova, L. & Park, Y. Effects of nitrogen and oxygen supply on production of poly- $\beta$ -hydroxybutyrate *Azotobacter chroococcum*. *J. Microbial Biotechnol.*, 1995, **5**, 100–104.
12. Savenkova, L., Gercberga, Z. & Kizhlo, Z. Effect of phosphate supply and aeration on poly- $\beta$ -hydroxybutyrate production in *Azotobacter chroococcum*. *Process Biochem.*, 1999, **34**, 109–114.
13. Bibers, I. & Kalnins, M. Control of biopolymer poly- $\beta$ -hydroxybutyrate characteristics by  $\gamma$ -radiation. *Mech. Compos. Mater.*, 1999, **35**, 169–178.
14. Bibers, I., Tupureina, V., Dzene, A. & Kalnins, M. Improvement of the deformative characteristics of poly- $\beta$ -hydroxybutyrate by plasticization. *Mech. Compos. Mater.*, 1999, **35**, 357–364.

15. Savenkova, L., Gerberga, Z., Nikolaeva, V., Dzene, A., Bibers, I. & Kalnin, M. Mechanical properties and biodegradation characteristics of PHB-based films. *Process Biochem.*, 2000, **35**, 573–579.
16. Dzene, A., Tupureina, V., Kalnins, M., Savenkova, L. & Anishchenko, L. Biodegradable PHB based films for food packaging. *Sci. Proc. Riga Techn. Univ. Ser. I, Mater. Sci. Appl. Chem.*, 2002, **4**, 190–195.

## **Biopolümeersed komposiidid kiledeks ja kateteks**

Dace Erkske, Ilze Viskere, Anda Dzene, Velta Tupureina  
ja Ludmila Savenkova

Keemiliselt olemuselt eristuvate manuste (plastifikaatorid, täiteained, ühildajad) lisamisel biolagunevate polümeeride polühüdrosübutüraadile on välja töötatud heterogeenne multikomponentne biokomposiit. Plastifitseeritud polühüdrosübutüraadi lahuseid on kasutatud kui pidevat maatriksit kilena ja paberi katmisel. Saadud materjalidele on määratud nende mehaanilised, termilised, hügrooskoopsed, isoleerivad ja biolagunevad omadused, milliseid on hinnatud nende rakendatavuse järgi biolaguneva pakkematerjali valmistamisel.