Light Transmission and Water Vapour Permeability of PHB Composite Materials
PHB kompozītmateriālu gaismas un ūdens tvaika caurlaidība

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Abstract. Poly-β-hydroxybutyrate (PHB) composite materials (plasticizers: dioctylsebacate, bisoflex, citroflex) synthesized at the University of Latvia Institute of Microbiology and Biotechnology in laboratory conditions and commercially produced in Brazil, moulded out at the Riga Technical University Institute of Polymer Materials, were used for light transmission and water vapour permeability (WVP) studies. The results were compared to the Lean Pouch and traditional flexible food packaging material PE film covered with light protective graphite layer usually used for dairy products. Light transmissions of the packaging material were determined in the wave lengths range of 200-800 nm, using a Cintra 40 spectrophotometer (GBC Scientific Equipment Pty Ltd, Victoria, Australia) equipped with a barium sulphate coated integrating sphere detector. Water vapour permeability was measured using the desiccant method partly according to ASTM E 96-80^{E2} standard. Results showed that the plasticizers only slightly influenced the light transmission. Bisoflex increased the light transmission contrary to dioctylsebacate and citroflex, which reduced it compared to pure PHB-based films. Light transmission of PHB based films is 1.5 times higher than Lean Pouch film. As expected, light transmission of polyethylene film is close to zero due to the incorporated graphite light barrier layer. The plasticizers affected the water vapour permeability of PHB composite films significantly. The pure PHB films were 6 times more permeable to water vapour compared to Lean Pouch films, and 3 times more permeable than polyethylene films covered with light protective graphite layers.
Key words: PHB composite materials, light transmission, water vapour permeability.

Introduction

Consumers demand higher quality and longer shelf life of foods while reducing disposable packaging materials and increasing recyclability (McHugh et al., 1993). Interest in biodegradable and edible films is the main factor to find environmentally friendly packaging to improve the quality of food products, and to find new markets for existing materials (Krochta, 1992; Kolesch, 1994; Chen, 1995). Edible and biodegradable films made from naturally derived polymers, such as polysaccharides, proteins and lipids, offer promise for food protection and preservation and help to solve environmental concerns. The history, technology, functionalities and potential usage of biodegradable/ edible films have been reviewed (Genadious et al., 1993; Kester, Fennema, 1986; Krochta & DeMulder – Johnston, 1997; Miller, Krochta, 1997). There has been considerable research on development of biologically based films for food packaging, but only few of them have been applied commercially due to limitations in their performance and physicochemical properties (Yang, Paulson, 2000).

Biodegradable/edible films should control mass transfer and provide mechanical protection to foods (Krochta, 1992; Chen, 1995). As a water vapour barrier, a film can extend the shelf life and meet the quality of foods by limiting moisture migration that could accelerate deteriorative reactions (Labuza, 1980; Rockland, Nishi, 1980; Mauer et al., 2000). Food components may undergo degradation when exposed to light, and food-packaging materials can reduce the degradation by preventing light being absorbed by the food components. Light transmission of packaging materials is important factor in estimating shelf life of foods (Gontard, Gulibert, 1994; Turhan, 2001).

It has been shown that environmentally friendly packaging material can be produced as transparent films with variable barrier properties (McHugh et al., 1994; Mate, Krochta 1996a, b; Miller, Krochta, 1997). However, such films are quite brittle. One approach to overcome the film brittleness is addition of food grade plasticizers to the film formulation. Plasticizers reduce intermolecular forces along the polymer chains, resulting in increase of the mobility of polymer chains and more flexible films. However, plasticizers not only improve the mechanical properties of films but also influence light transmission and increase the film permeability, which may be undesirable to provide food quality and should be taken into consideration when using plasticizers (Sothornvit, Krochta, 2000).

The aim of our investigations was to determine the light transmission and water vapour permeability of PHB composite material films, characterized by different plasticizers such as citroflex, bisoflex and dioctylsebacate, and compare them to Lean Pouch film and traditionally for dairy product packaging used polyethylene (PE) film covered with light protective graphite layer.

Materials and Methods

Materials. Poly-β-hydroxybutyrate (PHB) synthesized at the University of Latvia Institute of Microbiology and Biotechnology under laboratory conditions and commercially produced in Brazil were used for the experiments. Biodegradable poly-β-hydroxybutyrate (PHB) and its derived composite materials were synthesized and recovered from the biomass of *Azotobacter chroococcum 23* (Savenkova et al., Patent LV No. 12213, 1993) with the polymer content above 75% of dry cell weight (Savenkova et al., 1999). PHB was extracted from isopropanol-pretreated biomass by hot chloroform and precipitated with isopropanol. PHB composite material films were moulded out at the Riga Technical University Institute of Polymer Materials. Dioctylsebacate (DOS), citroflex (C) and bisoflex (B) were used as PHB plasticizers. Following packaging materials were used for light transmission and water vapour permeability studies:

- pure PHB (poly-β-hydroxybutirate) – commercially produced in Brazil (film thickness 60±5 μm);
- pure PHB (poly-β-hydroxybutirate) – synthesized in Latvia (film thickness 60±5 μm);
- PHB (77%) + dioctylsebacate (23%) - PHB+DOS (film thickness 60±5 μm);
- PHB (77%) + dioctylsebacate (23%) - PHB+DOS(2) (film thickness 35±3 μm);
- PHB (77%) + citroflex (23%) - PHB+C (film thickness 60±5 μm);
- PHB (77%) + citroflex (23%) - PHB+C (2) (film thickness 35±3 μm);
- PHB (77%) + bisoflex (23%) - PHB+B (film thickness 60±5 μm);
- PHB (77%) + bisoflex (23%) - PHB+B (2) (film thickness 35±3 μm).

All PHB composite materials with plasticizers were moulded in Latvia. The thickness of films was measured by digital micrometer (Electronic Digital outside Micrometer Q478) to the nearest 0.001 mm at 5 locations. Pure PHB and their composite material film properties were compared to polyethylene (PE) film covered with light protective graphite layer (film thickness 35±3 μm) and Ecolean packaging material – Lean Pouch (LP) (film thickness 78±5 μm). Ecolean material consists of abundant natural carbonates – such as chalk (40%) – and polyolefins. Ecolean material is created suitable for food packaging and friendly to the environment. It is recyclable and, with the addition of degrading agent, also biodegradable (Ecolean – Environment, 2003; Fuldman, 2002).

Methods. The light transmissions of the samples (thickness – 35±3 – 60±5 μm, width – 20 mm, length – 50 mm) were determined in the wavelength range of 200-800 nm on a Cintra 40 spectrophotometer (GBC Scientific Equipment Pty Ltd, Victoria, Australia) equipped with a barium sulphate coated integrating sphere detector. Data interval – 4.500 nm, scan speed – 400.00 nm min^{-1}, slit width – 2.00 nm. Water vapour permeability was measured according to ASTM E 96–80 standard, using the desiccant method. This method is based on the standard ASTM-E96 method for determination of the WVP of synthetic packaging materials, but the calculations are adapted in order to consider the more hydrophilic nature and the water vapour partial pressure in the fixed air layer between the film sample and the desiccant standard (Standart ASTM E 96–80^{E2}).

Statistical analyses. Statistics on completely randomized design were determined using the General Linear Model (GLM) procedure SPSS 10.0 (Arhipova, Bāliņa, 2003). Two-way analyses of variance ($p \leq 0.05$) were used to determine significance of differences between means of light transmission. Compare Means, One Way Anova ($p \leq 0.05$) were used to determine significance of differences between means of the water vapor permeability.

Results and Discussion

The results of estimated light transmission of pure PHB films synthesized in Latvia and commercially produced in Brazil are presented in Figure 1. Significant difference was not found in the light transmission among both pure PHB material samples ($p > 0.05$).

Selection of plasticizers for biopolymer films is of importance since they strongly affect the film physicochemical properties. The primary role of plasticizer is to enhance film flexibility and decrease brittleness. The addition of plasticizer leads to a decrease in intermolecular forces along polymer chains, which improves the flexibility and also makes it easier for film to be peeled off from the glass plate.

Film thickness influences light transmissions of

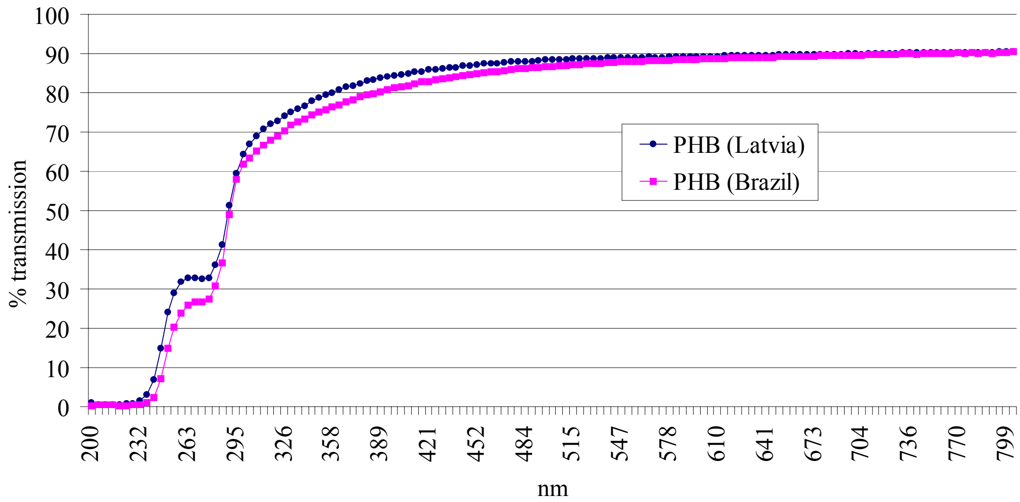

Fig. 1. Light transmission spectrum of pure PHB (Latvia) and PHB (Brazil) films.

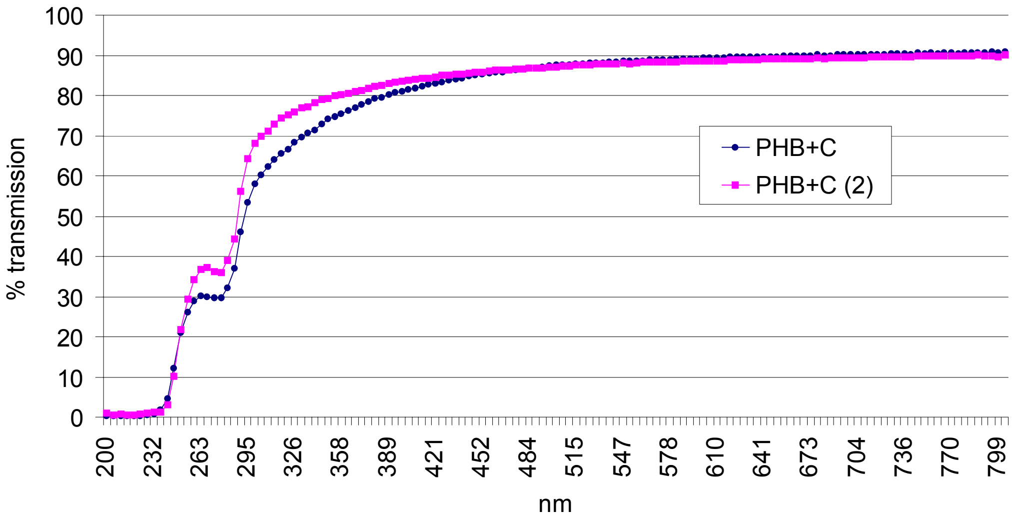

Fig. 2. Light transmission spectrum of PHB + citroflex with different thickness: f = (σ): PHB+C – σ = 60±5 μm; PHB+C (2) – σ = 35±3 μm.

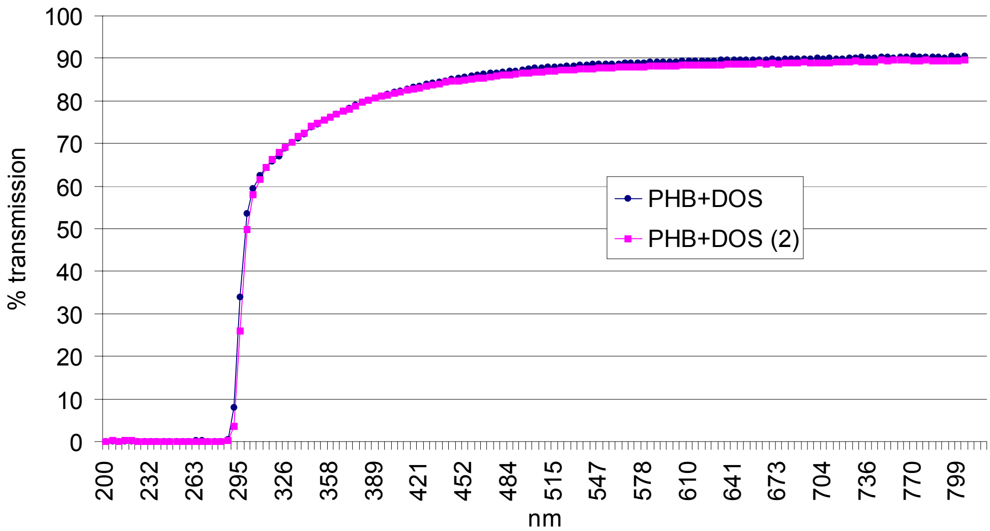

Fig. 3. Light transmission spectrum of PHB + dioctylsebacate with different thickness: f = (σ): PHB+DOS – σ = 60±5 μm; PHB+DOS (2) – σ = 35±3 μm.

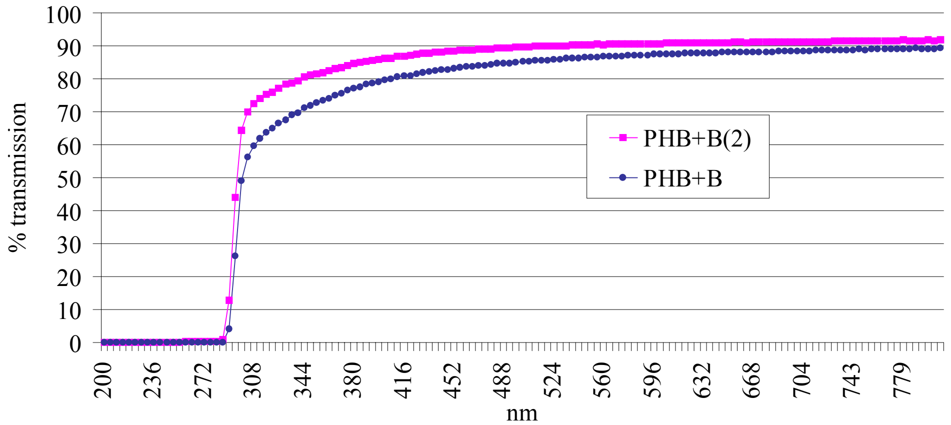

Fig. 4. Light transmission spectrum of PHB + bisoflex with different thickness:
f = (σ): PHB+B – σ = 60±5 µm; PHB+B (2) – σ = 35±3 µm.

PHB+C and PHB+DOS as well (Figs. 2 and 3). Figure 4 shows that PHB films with a thickness of 60±5 µm plasticized by bisoflex (PHB+B) have a lower light transmission than the same material with a thickness of 35±3 µm in the visible light wavelength range 400-750 nm, which is logical, since the thickness influence light transmission. Significant difference was found for listed before PHB+B composite materials with different thickness ($p<0.05$). The comparison of light transmissions results is demonstrated in Figure 5. Plasticizers citroflex and dioctylsebacate reduce the light transmission of PHB films in the visible light wavelength range, whereas bisoflex increases the light transmission compared to pure PHB films. Lean Pouch film has 1.5 times lower light transmission than all PHB-based films. PE film is impenetrable to light transition due to the graphite layer. Lean Pouch and polyethylene films covered with a light protective graphite layer with 95% probability substantially variously influence the light transmission compared to all other types (PHB and PHB composites) of investigated materials ($p<0.05$).

Water vapour permeability (WVP) values for films studied are shown in Figure 6. All plasticizers increase the WVP of pure PHB and its composite films. Bisoflex slightly increases the water vapour permeability – (76.4 ± 1.0) x 10^{-4} g mm kPa^{-1} h^{-1} m^{-2}, dioctylsebacate increases it by 2.5 times – (104.1 ± 2.1) x 10^{-4} g mm kPa^{-1} h^{-1} m^{-2}, whereas citroflex – 4 times (173.2 ± 1.3) x 10^{-4} g mm

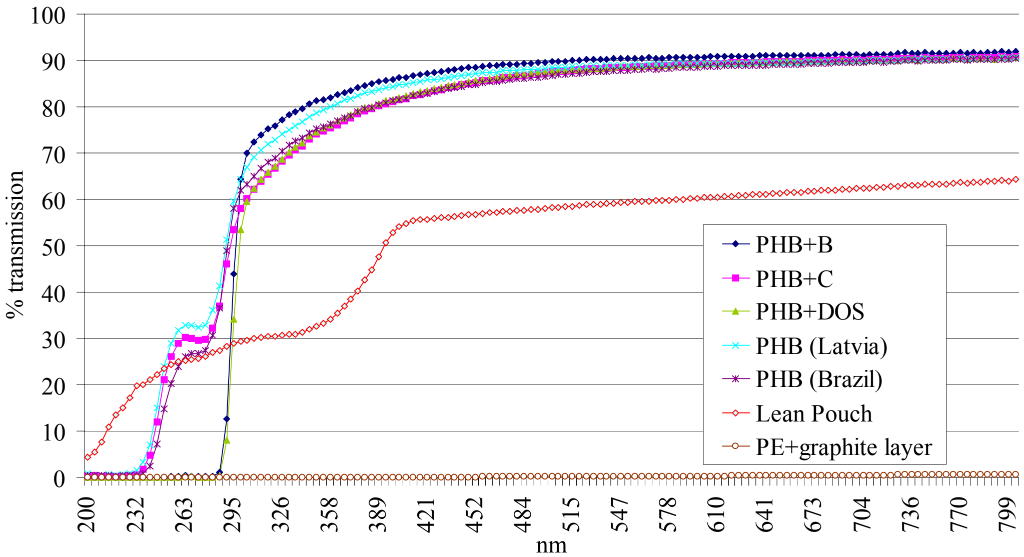

Fig. 5. Light transmission spectrum of all films studied.

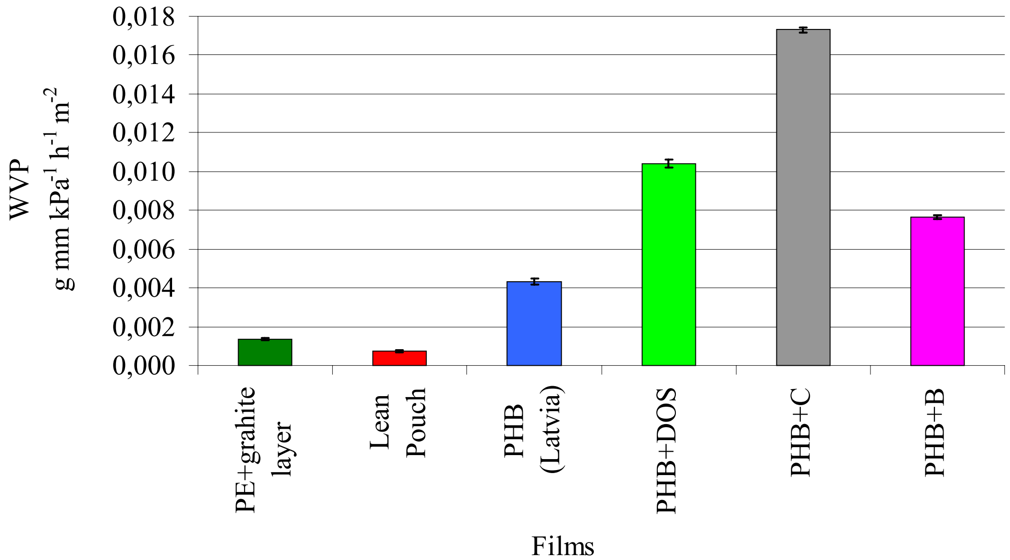

Fig. 6. Water vapour permeability of all films studied.

kPa^{-1} h^{-1} m^{-2}, compared to pure PHB film – (43.1 ± 1.6) x 10^{-4} g mm kPa^{-1} h^{-1} m^{-2}. The plasticizers increase WVP of PHB as expected due to an increase in mobility of the polymer chains. Such an increase may result in greater water transportation to or from the foods and thus altering the quality and shelf life hereof. The WVP value of polyethylene film covered with light protective graphite layer film is 3 times lower and that of Lean Pouch films – 6 times lower than that of pure PHB. All investigated materials mutually differ ($p<0.05$) in water vapour permeability.

Conclusions

1. Different plasticizers only slightly affect the light transmission of PHB and its composite films but significantly increase the water vapour permeability.
2. Lean Pouch film has 1.5 times lower light transmission than all PHB-based films. PE film is impenetrable to light transition due to the graphite layer.
3. The WVP value of polyethylene film covered with light protective graphite layer film is 3 times lower and that of Lean Pouch films – 6 times lower than that of pure PHB.

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Anotācija

Eksperimenti veikti ar Latvijas Universitātes Mikrobioloģijas un Biotehnoloģijas institūta laboratorijā sintezētu un Brazīlijā rūpnieciski ražotu poli-β-hidroksibutirātu (PHB). Rīgas Tehniskās universitātes Polimēru Materiālu institūtā paraugiem, pievienojot plastifikatorus (dioktilsebacinātu, bisofleksu un citrofleksu), veidoti kompozītmateriāli (plēves biezums no 35±3 µm līdz 60±5 µm), noteikta to gaismas (ar Cintra 40 spektrofotometru, viļņa garums – 200-800 nm) un ūdens tvaika caurlaidība (ar ASTM E 96-80^{E2} standartu, desikantu metodi). Rezultāti salīdzināti ar komercsistēmā piena produktu iepakošanai lietoto materiālu (ar gaismas necaurlaidīgu grafīta kārtu pārklātu PE, biezums 35±3 µm, un *Lean Pouch*, biezums 78±5 µm) plēvju paraugu īpašībām. Analizēta arī PHB kompozītmateriālu biezuma ietekme uz gaismas caurlaidību. Lietotie plastifikatori tikai nedaudz ietekmē kompozītmateriālu gaismas caurlaidību. Salīdzinot ar tīru PHB, pievienotais plastifikators bisoflekss paaugstina gaismas caurlaidību, bet pievienotie dioktilsebacināts un citroflekss to samazina. Visu pētīto PHB kompozītmateriālu gaismas caurlaidība, salīdzinot ar *Lean Pouch* materiālu, ir 1.5 reizes augstāka. Ar gaismas necaurlaidīgu grafīta kārtiņu pārklāta PE gaismas caurlaidība ir tuvu nullei. Pievienotie plastifikatori būtiski ietekmē kompozītmateriālu ūdens tvaika caurlaidību. Tīra PHB materiāla ūdens tvaika caurlaidība ir sešas reizes lielāka par *Lean Pouch* materiāla ūdens tvaika caurlaidību, bet trīs reizes lielāka par PE, kas pārklāts ar gaismas necaurlaidīgu grafīta kārtiņu.