

New insights in PHBHHx

Modified PHBHHx with interesting properties for food packaging applications

Polyhydroxyalkanoates (PHA) are a family of biobased polymers that have received a great deal of attention the last few decades for certain applications, such as packaging, medical devices, and controlled drug-delivery systems. PHAs are polyesters, that can be produced by a variety of bacteria from a wide range of renewable organic substrates. These polyesters are biodegradable as well as biocompatible [1].

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) can be considered as a candidate for replacement of specific fossil-based polymers, due to its ductile nature and wider processing window, compared to poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), which are the two most investigated PHAs. The mechanical properties of PHBHHx have been compared to low-density polyethylene, with a possible application for packaging. Unfortunately, the crystallization rate of PHBHHx is very slow, even at low 3-hydroxyhexanoate content. Therefore, many efforts are actually devoted to solve this problem (e.g., by addition of a nucleating agent or selected microfillers or nanofillers) [3].

The doctoral research of Jens Vandewijngaerden at the University of Hasselt (Belgium) aimed at the characterization and modification of PHA for application as food packaging material. Focus was placed on the polymer PHBHHx with a 3-hydroxyhexanoate content of 10 mol%. The research, which was performed from 2012 to 2016, involved the effective characterization and pinpointing the major positive and negative properties. Several types of modification techniques were investigated in order to enhance the applicability of these materials.

Gas permeability properties of PHBHHx

PHBHHx presented a moderate barrier for oxygen [O₂] (approx. 8 cm³·mm·m⁻²·day⁻¹·atm⁻¹) and carbon dioxide [CO₂] (approx. 40 cm³·mm·m⁻²·day⁻¹·atm⁻¹) and a fairly low water vapor permeability (approx. 1.4 g·mm·m⁻²·day⁻¹) [4]. Slow crystallization is an inherent property of PHBHHx which hinders the industrial processing of this material. Though the general properties of PHBHHx are promising, the crystallization must be enhanced further for effective application as food packaging material. Therefore, a selection of additives (nucleating agents) was tested, that could possibly also have a beneficial effect on other packaging-related properties.

Effect of ultra-fine talc

In the first phase, ultra-fine talc, with a particle size of less than 1 µm, was identified as a highly efficient nucleating agent for PHBHHx. An isothermal and non-isothermal crystallization study showed that ultra-fine talc drastically improved crystallization, in tested concentrations of 0.5, 1 and 2 wt%. A maximum reduction of the non-isothermal

crystallization half-time at 70 °C of 97 % was achieved by adding 2 wt% ultra-fine talc, as shown in Figure 2.

The gas permeability properties of the talc-filled composites remained within the same range of application as virgin PHBHHx. In terms of mechanical properties, the Young's modulus increased with a maximum of 13 % at a loading of 2 wt% of ultra-fine talc, whereas the tensile strength and elongation at break remained fairly constant. In conclusion, ultra-fine talc displays great potential to enhance industrial processing of PHBHHx as packaging material [5].

Effect of nanoclay on PHBHHx

In an effort to further enhance the barrier properties of PHBHHx, nanocomposites with organomodified montmorillonite clay (OMMT) were prepared, with an OMMT content between 1 and 10 wt%. In terms of gas permeability properties, the sample containing 10 wt% OMMT was most performant, with O₂, CO₂ and water vapor permeability coefficient reduced by 47%, 42% and 37%, respectively. This effect is attributed to the increased tortuous path, due to the platelet structure of OMMT. Unfortunately, using a concentration this high rendered the nanocomposite increasingly brittle, with the elongation at break reduced by 44 %. Taking into account all properties, it was concluded that an OMMT concentration of 3 wt% could be a promising compromise between enhanced barrier properties (about 20 % reduction) and a reduction of mechanical properties, though further research is necessary [6].

Effect of ZnO nanorods on PHBHHx

A final approach involved the preparation of zinc oxide nanocomposites. Zinc oxide with a nanorod structure was chosen, based on promising literature data for other polymeric matrices. Two types of zinc oxide nanorods were used, unmodified (ZnO) and surface modified (sZnO), in concentrations of 1, 3 and 5 wt%. A TEM (Transmission electron microscopy) study revealed that it was not possible to obtain fine dispersions of ZnO using concentrations higher than 1 wt%, whereas there were no dispersion issues for sZnO at all tested concentrations. The addition of up to 5 wt% sZnO did not appear to present any significant changes in gas permeability. The Young's modulus was increased by only 7 %, whereas the elongation at break was reduced by 19 %. An important downside of higher ZnO or sZnO concentrations is the higher opacity, which increased from 11.5 to 37.7 % upon addition of 5 wt% sZnO. It is however important to note that the addition of only 1 wt% provided a novel UV shielding property, of wavelengths below 370 nm, to PHBHHx, as shown in Figure 3. This could prove to be a valuable feature for food packaging materials as well.

Overall, this doctoral study revealed that PHBHHx certainly shows promise for use as food packaging material,



By:

Jens Vandewijngaerden^{1,2}, Robert Carleer²
Jan Yperman², Roos Peeters³, Mieke Buntinx³

Hasselt University Institute of Materials Research
Research groups Packaging Technology Center imo-imomec¹
& Applied and Analytical Chemistry imo-imomec/CMK²

Hasselt, Belgium

despite the fact that the selected modifications did not make it possible to obtain a high barrier material. However, a successful implementation of PHBHHx could be realized by enhancing the negative properties, namely increasing the crystallization rate using ultra-fine talc as nucleating agent. The intrinsic positive properties of PHBHHx should be correctly taken advantage of. PHBHHx has a fairly good water vapor barrier and could thus, for example, be used as protection layer for moisture-sensitive oxygen barrier layers. A successful UV blocking can be realized through the addition of low amounts of zinc oxide (1 wt%), as an added functionality of the material. The addition of zinc oxide in this concentration range can result in a fast crystallizing material, which can also protect a moisture-sensitive barrier layer (e.g. EVOH) in a multilayer film.

www.uhasselt.be/verpakkingscentrum

References:

- [1] Current progress on bio-based polymers and their future trends. Babu RP, O'Connor K & Seeram R. Prog Biomater 2 (8) (2013).
- [2] Effect of orotic acid as a nucleating agent on the crystallization of bacterial poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymers. Jacques N, Tajima K, Nakamura N, Miyagawa T, Pan P & Inoue Y. J. Appl. Polym. Sci., 114: 1287-1294 (2009).
- [3] Nucleation Effect of Layered Metal Phosphonate on Crystallization of Bacterial Poly(3-hydroxybutyrate)-co-(3-hydroxyhexanoate). Yu F, Pan P, Nakamura N & Inoue Y. Macromol. Mater. Eng., 296: 103-112 (2011).
- [4] Gas permeability properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). Vandewijngaerden J, Murariu M, Dubois P, Carleer R, Yperman J, Adriaenssens P, Schreurs S, Lepot N, Peeters R and Buntinx M. Journal of polymers and the environment, 22 (4), 501-507 (2014).
- [5] Effect of ultrafine talc on crystallization and end-use properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). Vandewijngaerden J, Murariu M, Dubois P, Carleer R, Yperman J, D'Haen J, Peeters R and Buntinx M. Journal of Applied Polymer Science, 133 (45) (2016a).
- [6] Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/organomodified montmorillonite nanocomposites for potential food packaging applications. Vandewijngaerden J, Wauters R, Murariu M, Dubois P, Carleer R, Yperman J, D'Haen J, Ruttens B, Schreurs S, Lepot N, Peeters R and Buntinx M. Journal of polymers and the environment, 24 (2), 104-118 (2016b).

Figure 1: PHBHHx film produced by sheet extrusion



Figure 2: Isothermal crystallization halftime t_{1/2} at 70 °C for PHBHHx/ultra-fine talc composites

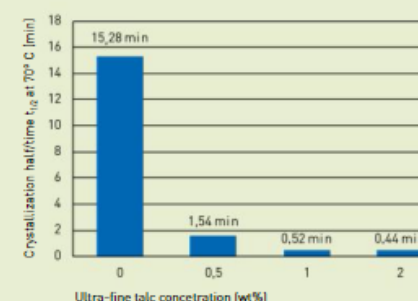


Figure 3: UV transmittance of PHBHHx/Zinc oxide nanocomposites

