Processing and optimizing polyhydroxyalkanoates: circular materials of the future for use as innovative food packaging material

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1. Polyhydroxyalkanoates are promising circular plastics

Bioplastics are promoted as eco-friendly plastics that could help to solve the problem of plastic pollution in the transition to a sustainable circular economy. Among the bioplastics, biobased and biodegradable polyhydroxyalkanoates definitely meet the criteria of sustainable circular plastics.

First, polyhydroxyalkanoates (PHAs) can be produced from various biomass substrates, including edible biomass, non-edible biomass from waste streams, algal biomass and electrical driven-fermentation processes. Second, these bacterially produced polyesters offer a spectrum of possible applications, such as packaging materials, daily-use objects, agricultural films, medical devices or implantable objects. Indeed, PHAs show great promise for use in food packaging applications with medium gas barrier properties. The copolymer poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) is useful for flexible (food) packaging applications, whereas the stiffer and more brittle copolymers poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are better suitable for rigid applications [1]. Finally, the PHA family can fully fit all end-of-life (EoL) scenarios in the bioplastics industry, as they can be either i) reused, ii) mechanically recycled, iii) chemically recycled to monomers, iv) composted, v) burned, or vi) biodegraded [2].

Using bioplastics such as PHAs, could address various Sustainable Development Goals (SDGs), although cost, processability and thermal/mechanical performance remain crucial factors to compete with fossil-based plastics. To improve their competitiveness, a promising and popular strategy is to incorporate 'nano' particles/fibres/platelets, creating advanced nanocomposite materials.

2. Nanocomposite materials for use as active packaging materials

Plenty of literature is available on how incorporating metal(oxide) nanoparticles (NPs) in a biopolymer network positively affects a multitude of properties. We have recently reviewed the use of ZnO nanocomposites for packaging applications with regard to gas barrier and mechanical properties [3], but they also display antimicrobial properties [4]. Ag NPs are also widely found in applications ranging from healthcare (covid masks), printing inks, coatings, sensors, cosmetics and (food) packaging. Due to their biocompatibility and easy functionalization, Ag NPs can be incorporated in different products and give them bactericidal capacity, such as in active packaging [5]. Active packaging concepts interact with the packaged product or the atmosphere inside the packaging to protect valuable nutritional components, prevent spoilage or loss of quality, and prolong shelf life [6].

Today, the world wastes or loses around a third of the food it produces while almost 690 million people go hungry. **SDG 12.3** aims to significantly reduce food waste and food loss [7], and antimicrobial active packaging materials made from biobased and biodegradable PHAs could help.

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3. Strategies to enhance PHA nanocomposite processing and properties

3.1 Gas permeability properties of PHBHHx compression molded films

Our PHBHHx films made using compression molding show an O_2 permeability (PO_2) that is 6–25 times lower as compared to common low barrier materials such as polypropylene (PP), and polyethylene (PE), which close to the PO_2 of poly(ethylene terephthalate) (PET) and poly(lactic acid) (PLA), but >900 times higher as compared to high barrier ethylene vinyl alcohol (EVOH). The water vapor permeability of PHBHHx is similar to materials such as PLA, EVOH, polyamide and PET, but slightly higher than more apolar polymers like PP and PE. The CO_2 permeability (PCO_2) of PHBHHx is lower as compared to PP and PE (2–20 times), but higher as compared to PET (>7 times) and EVOH and poly(vinyl alcohol) (>650 times). All effects are sensitive to relative humidity and temperature [8].

3.2 Incorporation of talc, organomodified montmorillonite clay and ZnO nanoparticles using melt blending and compression molding to enhance PHBHHx performance

Ultra-fine talc is identified as an efficient nucleating agent, although the gas permeability coefficients of the talc-filled composites remain within the same range as virgin PHBHHx. The Young's modulus increases with 13% at 2 wt% talc loading, whereas tensile strength and elongation at break remain fairly constant.

Adding 10 wt% OMMT reduces the O_2, CO_2 and water vapor permeability coefficients by 47%, 42% and 37% respectively. Unfortunately, the nanocomposites are more brittle upon increasing OMMT concentrations, with a 44% reduction of the elongation at break at 10 wt%.

Adding 1-5 wt% ZnO nanorods shows fine dispersions in PHBHHx, but does not significantly affect the gas barrier. The Young's modulus increases with 7%, whereas the elongation at break reduces by 19%. The opacity increases with 4% by adding 1 wt% ZnO, but this modification provides UV shielding, which can be a valuable feature for food packaging [9].

3.3 Ultrasonic spray coating (USSC) of ZnO NPs on PHBHHx films

Alternatively, USSC of ZnO NPs is shown to be an effective chemical deposition method for applying a functional UV barrier coating, though it is not sufficient to improve the gas barrier properties [10].

3.4 Optimization of mechanical properties during extrusion and injection molding of PHBHHx

We also show that the stretchability of PHBHHx can be significantly increased by setting appropriate melt processing parameters, such as extrusion and mold temperature, screw speed and cooling time using a design of experiments approach. Increased elongation at break of the moldings is attributed to relaxation and decreased orientation of the polymer chains and a homogeneous microstructure at higher mold temperature and slower cooling rates. This underscores that optimal processing conditions can make these biopolymers highly suitable for a wide range of flexible packaging applications [11].

3.5 Applying centrifugal fiber spinning to fabricate active ZnO/PHBHHx nanocomposite films

Adding ZnO into the polymer matrix to introduce UV barrier and antimicrobial activity requires optimal dispersion of the nanoparticles. Therefore, we have optimized a method to incorporate ZnO NPs into PHBHHx fibers via centrifugal fiber spinning (CFS). Subsequently, these fiber mats are deposited as 10-20 µm continuous layers on 160 µm-tick PHBHHx film substrates by post-process annealing in a hot press. The films demonstrate well-dispersed ZnO NPs, they effectively block UVC, UVB, and a major part of UVA wavelengths and show suitable hydrophobicity for packaging of food products (water contact angles >95°) [12].

We conclude that this novel incorporation method of ZnO NPs in PHBHHx is a promising approach for the development of packaging films with an active top layer.

4. Safe use of biodegradable nanocomposite materials

Apart from the advantages which inevitably will result in an increase of nanotechnology-based products over the coming years, many studies do not systematically address NP release mechanisms. Public concern about the potential risks related to migration of NPs from packaging into food is associated with insufficient knowledge about their safety and toxicity, especially if the host material is a biodegradable polymer. This drives authorities to use precautionary principles and handle the issue conservatively [13]. Therefore, the value-chain of PHA products from design through processing, value enhancement, and disposal should be strategic, considering safety as well as legislation. Taking into account the European Green Deal, regulation with regard to packaging and packaging waste [14], and (active) food contact materials [15] is currently very dynamic in the EU.

Our research group aims to develop new strategies for incorporating Ag and ZnO nanoparticles as well as methodologies to fully characterize the nanocomposites and to elucidate potential NP migration mechanisms from biodegradable PHAs both in consumer and specific end-of-life scenarios. This research will enable us to estimate the safety and application potential of active nanocomposite packaging materials.

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