Understanding silver nanoparticle leaching behavior from active biodegradable nanocomposites

Mieke Buntinx[1]*, Dries Hermans[1], Muhammet Gücyetmez[2], Wouter Marchal[2]
[1]Materials and Packaging Research & Services (MPR&S), Institute for Materials Research (imo-imomec), Hasselt University, Diepenbeek, Belgium
[2]Analytical & Circular Chemistry (ACC), Institute for Materials Research (imo-imomec), Hasselt University, Diepenbeek, Belgium

Abstract

Biobased and biodegradable polyhydroxyalkanoates (PHAs) can be seen as polymers of the future, which can replace fossil equivalents in a circular bioeconomy. Indeed, PHAs can be produced in bacteria from various biomass feedstocks. PHA biopolymers can be used in packaging, agricultural and medical applications, and they fit at least six end-of-life (EoL) scenarios. Incorporation of silver nanoparticles (NP) in bioplastic food contact materials (FCM) shows great potential as active packaging with antimicrobial performance, which can contribute to reduce food waste, as targeted by SDG 12.3. However, the lack of knowledge regarding NP release, associated risks on human health and accumulation in the environment leads to restricting legislation. Before investigating NP migration from biodegradable PHAs, the first objective is to update the dynamic European legislation regarding biobased and biodegradable packaging materials, FCM and active packaging.

In Nov 2022, the European Commission proposed the new Packaging and Packaging Waste Regulation to put the packaging sector on track for climate neutrality by 2050 in line with the European Green Deal's Circular Economy Action Plan. The new rules will clarify how bioplastics can be part of a sustainable future. In the meantime, the Commission also intends to modernize the rules on FCM (Regulation 1935/2004) to ensure food safety, while taking account of the latest science and technology, and supporting innovation and sustainability by promoting safe reusable and recyclable solutions. Two PHAs are on the Union List of permitted substances but authorisations for nanomaterials must be assessed on a case-by-case basis.

The PHA value-chain from design through manufacture, value enhancement and disposal should be strategic, considering safety and legislation. Therefore, our research will focus on elucidating mechanisms of silver NP migration from PHAs in consumer as well as specific EoL scenarios to estimate the safety and application potential of bio-nanocomposites as active packaging material.

Keywords: silver nanoparticles – biodegradable packaging materials – food contact materials – active packaging material – migration – polyhydroxyalkanoates

[1] **Correspondence to**: Mieke Buntinx, University Hasselt, MPR&S, Institute for Materials Research imo-imomec, mieke.buntinx@uhasselt.be

Introduction

Polyhydroxyalkanoates are promising circular plastics

In light of the current concerns about environmental problems caused by the excessive use of fossil resources, the transition to a sustainable and circular economy is increasingly coming to the fore. Bioplastics are promoted as eco-friendly plastics that could help to solve the problem of plastic pollution. Among the bioplastics, biobased and biodegradable **polyhydroxyalkanoates** (PHAs) definitely meet the criteria of **sustainable circular plastics**.

First, PHAs can be produced from various **biomass** substrates, including edible biomass, non-edible biomass from waste streams, algal biomass and electrical driven-fermentation processes, which are respectively classified as first, second, third and fourth-generation feedstocks [1].

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 [2]. 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 [3,4], 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 [5].

Finally, the PHA family is outstanding among current polymers that can fully fit all end-of-life scenarios in the bioplastics industry. PHA postconsumer products have **six basic end-of-life alternatives (EoL)**. PHA plastics can be either i) reused, ii) mechanically recycled, iii) chemically recycled to its monomers, iv) composted, v) burned, or vi) biodegraded. Of course, the end-of-life pathway varies greatly depending on the use of PHA products. [6]

Mechanical recycling has a relatively low environmental impact due to the low energy usage and raw materials reliance. However, recycled PHA suffers from polymer breakdown during usage or heat deterioration during extrusion and pelletization. Although recycling appears to be more energy-efficient than composting, sorting and cleaning are critical to preventing contamination. **Chemical recycling** is possible via: i) depolymerization of polymer chains into monomers and ii) pyrolysis to recover high-value chemicals/monomers such as organic vapors, char and gases using thermal methods, which are processed into oil through condensation. A greener alternative is **biodegradation**, where microorganisms break down the biopolymer chains into CO_2 or CH_4, water and biomass. PHAs biodegrade both aerobically and anaerobically. PHAs are the only fully biosynthesized materials that are biodegradable and compostable in soil, freshwater and saltwater when compared to other biopolymers [7]. In addition, **anaerobic digestion** has emerged as a critical EoL alternative for PHA waste. Finally, **incineration** of PHA waste with energy recovery is another EoL strategy, because of the relatively high calorific value of bioplastics. However, due to the increase of greenhouse gases in the atmosphere, energy recuperation is the least preferred end-of-life option for PHAs compared to recycling, composting and anaerobic digestion.

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**.

- **Nanocomposite materials for use as active packaging materials**

Plenty of literature is available on how **incorporating metal(oxide) nanoparticles (NPs)**, such as Ag, Cu, ZnO, TiO_2, SiO_2, Al_2O_3 NPs in a biopolymer network positively affects a multitude of physical, mechanical, barrier and antimicrobial properties [8].

Ag NPs have been hosted in durable polymers, such as polyvinyl chloride (PVC), polyethylene (PE), and polypropylene (PP) among others, as well as in biodegradable polymer matrices such as polylactic acid (PLA), PHBHHx, PHBV, starch, etc. Due to the Ag NP incorporation, these nanocomposites show enhanced **antimicrobial, mechanical and barrier properties** [9-12].

The antimicrobial action of Ag NPs against a wide range of micro-organisms is explained by the potential appearance of both Ag_0 and Ag^+ species. Ag NPs can cause cell death by accumulating in the bacterial cell membrane via reactive oxygen species (ROS) generation or binding to enzymes and DNA. Another contribution to the bactericidal effect is the release of potentially very reactive Ag^+ ions, which may react with the negatively charged cell membrane [13].

Ag NPs are already widely found in **many applications** ranging from healthcare (covid masks), water treatment, printing inks, coatings, sensors, cosmetics, pharmacy and (food) packaging [14]. As a consequence of their biocompatibility and easy functionalization, AgNPs can be applied in different products and give them bactericidal capacity [13]. Incorporation of Ag NPs in packaging materials results in active packaging.

Active packaging concepts interact with the packaged product or the atmosphere inside the packaging to protect the valuable nutritional components, prevent spoilage or loss of quality, and prolong shelf life [15]. They are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food; e.g. modified atmosphere, scavengers, absorbers, emitters or adaptors, which can be coated on or integrated in the packaging material, sachets, pads, etc. [16].

Antimicrobial active packaging materials can contribute to tackle **SDG 12.3**. Goal 12 is about ensuring sustainable consumption and production patterns, which is key to sustain the livelihoods of current and future generations. 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 [17].

- **Safe use of nanocomposite materials**

Apart from the widely-reported 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** from these advanced NCs. **Public concern about the potential risks related to the release 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. To be used as an active FCM in the EU, compliance with Regulations (EC) 1935/2004, (EC) 10/2011 and (EC) 450/2009 is required, resulting in a Union List of permitted substances. Biobased polymers such as PHBV and PHBHHx are currently on the Union List ((EC) 2019/37). However, authorisations for **nanomaterials must be assessed on a case-by-case basis,** leading to complex situations: Ag NPs intended for surface biocide use are only authorised up to 0.025% w/w in polar polymers, such as polyolefins that do not swell in contact with aqueous foods [18].

Goal of the research

The final goal of this starting PhD project is to develop more generalist insights into the possible leaching mechanisms of Ag NPs from biodegradable polymers, which can contribute to more widely-applicable decision-making in nanocomposite risk assessment. The first objective is to update the dynamic European legislation regarding biobased and biodegradable packaging materials, food contact materials and active packaging.

Results

▶ Bioplastic packaging materials in a circular EU

In November 2022, the European Commission proposed the **new Packaging and Packaging Waste Regulation** to stop the trend of the constantly growing source of packaging waste [19].

The new EU-wide rules must put the packaging sector on track for **climate neutrality by 2050**, as aimed by the European Green Deal's Circular Economy Action Plan [20]. In brief, unnecessary packaging will be banned, overpackaging will be limited, more reusable packaging options will be offered and clear labels will be provided to support correct recycling. While these actions will be visible to consumers, the rules must also create new business opportunities for the industry and decrease the need for virgin materials. The latter will boost Europe's recycling capacity as well as make Europe less dependent on primary resources and external suppliers.

Alternatives to conventional plastics, such as biobased, biodegradable and compostable plastics are emerging everywhere, not only in packaging, but also in consumer goods, textiles, automotive, transport, agriculture, horticulture, electrics, electronics and other sectors. In 2022, packaging occupied the largest field of application of the total bioplastics market (1 million tons, 48%). The global bioplastics production capacity is set to increase significantly from around 2.23 million tons in 2022 to 6.3 million tons in 2027 [21].

However, these **bioplastics** must meet a number of conditions to have positive environmental impacts, rather than exacerbating plastic pollution, climate change and biodiversity loss. The Commission's new framework has clarified **how these bioplastics can be part of a sustainable future** by setting out for which applications such plastics are truly environmentally beneficial and how they should be designed, disposed of and recycled.

An initially proposed partial ban on **compostable plastic packaging** was eventually lifted, because compostable packaging solutions can have environmental benefits, when they do not negatively affect the quality of the compost. They are especially useful when there is a proper biowaste collection and treatment system in place. Moreover, they can reduce the contamination of (organic) waste streams [22]. According to the new rules, bags for the separate collection of biowaste, very lightweight plastic carrier bags, tea bags, filter coffee pods and pads, fruit and vegetable stickers, must be compostable in industrial composting facilities [20]. The use of compostable plastics for other packaging is still possible if it allows material recycling [22]. Compostable products must always specify that they are certified for industrial composting, in line with EU standards, and explain the way to dispose of them.

In addition, **biodegradable plastics** also have their place in a sustainable future, but they need to be directed to specific applications where their environmental benefits and value for the circular economy are proven (e.g. agricultural mulch film). They must be labelled to show the timeframe for biodegradation under specified circumstances and environments (excluding a license to litter).

It is also emphasized that biomass used to produce **biobased plastics** must be sourced sustainably, without harm to the environment, and that producers must prioritize the use of organic waste and by-products as raw materials [20].

And finally, the share of biobased plastic content should be disclosed, whereas greenwashing and confusing claims on biodegradation of litter-prone products should be banned at all times [20].

▸ Revision of the rules on food contact materials

In the meantime, the Commission intends to modernize the rules on food contact materials (currently under framework Regulation (EC) 1935/2004) to ensure food safety, while taking account of the latest science and technology, and **supporting innovation and sustainability** by promoting safe reusable and recyclable solutions and help reduce the sector's environmental impact [23]. The framework Regulation was already amended in 2009 to enable active and intelligent packaging and in 2022 to allow safe recycled plastics in food packaging.

Legislation on food contact materials (FCM) is relevant for the success of key Commission policies under the EU Green Deal. The 'farm to fork' strategy commits to revise the FCM legislation in order **to improve food safety and public health**, in particular by reducing the use of hazardous chemicals, support packaging solutions using environmentally-friendly, re-usable and recyclable materials, and **contribute to food waste reduction**. A new initiative is therefore also critical to support the Circular Economy Action Plan including a follow-up to the 2018 Plastics Strategy. It is also necessary to contribute to the ambitions of the Chemicals Strategy for Sustainability towards a toxic-free environment and action related to the most hazardous chemicals as well as considering their cumulative and combinative effects [24].

After a roadmap open for feedback in 2021 and a public consultation in the fourth quarter of 2022, the Commission is expected to announce its proposal in the second quarter of 2023 [23].

▸ Active packaging on the EU market

The development of active food packaging to prolong product freshness and slow down spoilage can be promising to tackle SDG target 12.3, which specifically aims to reduce global food waste at the retail and consumer levels. The current trends of reduced food processing and using fewer food additives stimulate research on active packaging. If such **packaging innovations are allowed to advance**, their impact could be of benefit, not only in reducing food waste but also in improving food safety.

In the EU, active and intelligent packaging intended for food contact is regulated pursuant to Regulation (EC) No 450/2009. This regulation establishes a **premarket approval system** in which active and intelligent materials may not be marketed unless the individual substances responsible for the active or intelligent function are evaluated and included on the **European Community list** of eligible substances, with some limited exceptions. The safety of such substances must be evaluated by the European Food Safety Authority (EFSA) before their use in food packaging in the EU can be authorized.

EFSA's Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF) initially published guidelines on **submitting a dossier for safety evaluation** in 2009. A revision was endorsed in 2020, and the revised version of the guidelines was implemented in March 2021.

The guidelines explain that safety assessments focus on the risks related to the dietary exposure to chemicals due to: i) migration of the active or intelligent substance, ii) migration of their degradation and/or reaction products and iii) their toxicological properties [25].

Active substances **behind a functional barrier** do not need a safety evaluation, provided that they are not mutagenic, carcinogenic, toxic to reproduction, or deliberately engineered to the nanoparticle size. The use of **nanoparticles** in food contact materials is assessed and eventually authorized on a case-by-case basis by EFSA. In 2021, EFSA has updated its Guidance on risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain, human and animal health, which also cover the application area of food contact materials [26]. Both guidance documents on nano risk assessment and technical requirements elaborate on physicochemical characterization, key parameters that should be measured, methods and techniques that can be used for characterization of nanomaterials and their determination in complex matrices.

As new active packaging technologies find their way **into global markets**, legislative and regulatory issues must be considered. While Regulation (EC) No 450/2009 officially came into force in 2009, the provisions relating to composition will not take effect until the **Community list of eligible substances** is published. Until then, the relevant national provisions will continue to apply [27].

Conclusion and recommendation

Research into PHAs is growing exponentially. Thanks to their broad physicochemical features, including biodegradability and biocompatibility, PHAs can be seen as circular polymers of the future, replacing traditional petrochemical equivalents. Given the duality of long-term features and degradation needs, the value-chain of PHA products from design through manufacture, value enhancement, and disposal should be strategic, considering safety and current legislation.

In this PhD research, methodologies are being optimized to elucidate the potential mechanisms of Ag nanoparticle migration from biodegradable PHAs both in consumer and specific end-of-life scenarios in order to estimate the safety and application potential of bio-nanocomposites as active packaging materials. In this way, we aim to contribute to the implementation of sustainable, active, and above all safe bioplastic packaging materials.

References

[1] Gutschmann B et al. Native feedstock options for the polyhydroxyalkanoate industry in Europe: A review. *Microbiological Research*. **2022**; 264: 127177, ISSN0944-5013. https://doi.org/10.1016/j.micres.2022.127177.

[2] Guzik MW. Polyhydroxyalkanoates, bacterially synthesized polymers, as a source of chemical compounds for the synthesis of advanced materials and bioactive molecules. *Appl Microbiol Biotechnol*. **2021**; 105(20): 7555-7566. doi: 10.1007/s00253-021-11589-0.

[3] Vanheusden C, Samyn P, Goderis B, Hamid M, Reddy N, Ethirajan A, Peeters R and Buntinx M. Extrusion and Injection Molding of (PHBHHx): Influence of Processing Conditions on Mechanical Properties and Microstructure. *Polymers*. **2021**; 13(22): 4012. https://doi.org/10.3390/polym13224012.

[4] Vanheusden C, Vanminsel J, Reddy N, Samyn P, D'Haen J, Peeters R, Ethirajan A and Buntinx M. Fabrication of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) Fibers Using Centrifugal Fiber Spinning: Structure, Properties and Application Potential. *Polymers*. **2023**; 15(5):1181. https://doi.org/10.3390/polym15051181

[5] Ragaert P, Buntinx M, Maes C, Vanheusden C, Peeters R, Wang S, et al. Polyhydroxyalkanoates for Food Packaging Applications in *Reference Module in Food Science*, Amsterdam: Elsevier, **2019**.
[6] Muiruri JM, Chuan JC et al. Poly(hydroxyalkanoates): Production, Applications and End-of-Life Strategies – Life Cycle Assessment Nexus. *ACS Sustainable Chemistry & Engineering*. **2022**; 10 (11), 3387-3406. https://doi.org/10.1021/acssuschemeng.1c08631.
[7] Meereboer KW et al. Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chem*. **2020**; 22: 5519, https://doi.org/10.1039/D0GC01647K
[8] Tan C et al. Novel bio-based materials and applications in antimicrobial food packaging: recent advances and future trends. *Int J Mol Sci*. 2021; 22: 9663. https://doi.org/10.3390/ijms22189663
[9] Couto C & Almeida A. Metallic Nanoparticles in the Food Sector: A Mini-Review. *Foods*. **2022**; 11: 402.
[10] Relinque J et al. Development of surface-coated PLA/PHA nanocomposites. *Polymers*. **2019**; 11: 400.
[11] Kraśniewska K et al. Biopolymers-Based Materials Containing Silver Nanoparticles as Active Packaging for Food Applications. A Review. *Int J Mol Sci*. **2020**; 21: 698.
[12] Istiqola A & Syafiuddin A. A review of silver nanoparticles in food packaging technologies: Regulation, methods, properties, migration, and future challenges. *JCCS*. **2020**; 67, 1942–1956.
[13] Bruna T, Maldonado-Bravo F, Jara P, Caro N. Silver Nanoparticles and Their Antibacterial Applications. *Int J Mol Sci*. **2021**; 22(13):7202. https://doi.org/10.3390/ijms22137202.
[14] Zahoor M et al. A Review on silver NPs: classification, various methods of synthesis, and their potential roles in biomedical applications and water treatment. *Water*. **2021**; 13: 2216.
[15] Tiekstra S, Dopico A, Koivula H, Lahti J and Buntinx M. Holistic Approach to a Successful Market Implementation of Active and Intelligent Food Packaging. *Foods*. **2021**; 10(2):465. https://doi.org/10.3390/foods10020465.
[16] Yildirim S et al. Active Packaging Applications for Food. *Compr Rev Food Sci Food Saf*. **2018**; 17: 165–199.
[17] FAO. Sustainable development goals. https://www.fao.org/sustainable-development-goals/goals/goal-12/en/
[18] Lambré C et al. Safety assessment of the substance silver NPs for use in food contact materials. *EFSA Journal*, **2021**; 19.
[19] Proposal for a revision of EU legislation on Packaging and Packaging Waste, Nov **2022**. *Accessed April 2023* https://environment.ec.europa.eu/publications/proposal-packaging-and-packaging-waste_en
[20] European Green Deal: Putting an end to wasteful packaging, boosting reuse and recycling. *Accessed April 2023* https://ec.europa.eu/commission/presscorner/detail/en/ip_22_7155
[21] Global bioplastics production defies challenges by showing significant increase, Dec **2022**, *Accessed April 2023* https://www.european-bioplastics.org/global-bioplastics-production-defies-challenges-by-showing-significant-increase/
[22] EUBP's response on the proposal for rules on packaging and packaging waste. *Accessed April 2023* https://www.european-bioplastics.org/policy/revision-of-the-packaging-and-packaging-waste-directive/
[23] Revision of EU rules on food contact materials. *Accessed April 2023* https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12497-Revision-of-EU-rules-on-food-contact-materials_en
[24] Katsarova I. Members' Research Service. Proposal for a regulation revising EU legislation on Food Contact Materials In "A European Green Deal". *Accessed April 2023* https://www.europarl.europa.eu/legislative-train/theme-a-european-green-deal/file-revision-of-eu-legislation-on-food-contact-materials
[25] EFSA. Administrative guidance for the preparation of applications on substances to be used in active and intelligent materials and articles intended to come into contact with food. *EFSA Journal.* **2021**: 18(3): EN-6513. 32 pp. doi: 10.2903/sp.efsa.2021.EN-6513.
[26] EFSA Scientific Committee. Guidance on risk assessment of nanomaterials to be applied in the food and feed chain: human and animal health. *EFSA Journal.* **2021**;19(8):6768. https://doi.org/10.2903/j.efsa.2021.6768
[27] Misko GG. The Regulation of Active and Intelligent Food Packaging in the U.S. and the EU. *Food Safety Magazine*. April/May **2022**.