ENVIRONMENTAL IMPACT ASSESSMENT AND PROPERTIES OF PHBH-ALUMINA AND GRAPHENE NANOCOMPOSITES

Julen Ibarretxe [1], Hugo Afonso [1,2], Amaia Orbea [3] and Maider Iturrondobeitia [1,2,*]

[1]eMERG Research Group, School of Engineering of Bilbao, Building II-I, University of the Basque Country (UPV/EHU), Rafael Moreno Pitxitxi 3, 48013 Bilbao, Spain; julen.ibarretxe@ehu.eus

[2]Life Cycle Thinking Group, Department of Graphic Design and Engineering Projects, University of the Basque Country (UPV/EHU), Plaza Ingeniero Torres Quevedo 1, 48013 Bilbao, Spain;

[3]CBET Research Group, Dept. of Zoology and Animal Cell Biology, Research Centre for Experimental

Marine Biology and Biotechnology PiE and Science and Technology Faculty, University of the Basque Country (UPV/EHU). Sarriena z/g, 48940, Leioa, Spain: amaia.orbea@ehu.eus

*****Correspondence: maider.iturrondobeitia@ehu.eus; Tel.: +34-946014311

Keywords: Biopolymers, biodegradable, PHBH, biocomposites, Life Cycle Assessment.

ABSTRACT

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is a bio-based polyester with the potential to replace some common polymers of fossil origin. However, PHBH presents serious limitations, such as low stiffness, tendency to undergo crystallization over long time periods and low resistance to thermal degradation during processing. In this work, we studied the use of alumina nanowires and graphene to generate PHBH nanocomposites, modifying the properties of PHBH to improve its usability. Solvent casting was used to produce the nanocomposites. Then, their mechanical properties and aquatic toxicity were measured. Finally, LCA was used to evaluate and compare the environmental impacts of several scenarios relevant to the processing and end of life (EoL) conditions of PHBHs. It was observed that, at low concentrations (3 wt.%), the alumina nanowires as well as graphene nanoparticles have a positive impact on the stiffness and young module. The toxicity measurements showed that PHBH alone and in combination with nanoparticles (10 wt.%) did not produce any impact on the survival of brine shrimp larvae after 24 and 48 h of exposure. The 18 impact categories evaluated by LCA allowed the comparison of PHBH-related impacts to those of some of the most common fossil-based plastics.

1 INTRODUCTION

The marine pollution produced by plastic materials is considered one of the greatest dangers of the 21st century as it seriously threatens plant and animal species, and several economic sectors such as tourism, shipping and fishing. As partial solution, the use of biodegradable plastics has been largely studied, supported and criticized. In this work, bio-plastic based nanocomposites, their processing and end of life have been studied thermo-physically and from an environmental point of view.

Polyhydroxy alkanoates (PHAs) are a family of polyesters that can be obtained from re-newable resources, can be biodegradable and biocompatible [1], and have physicochemi-cal properties similar to those of some of the nowadays most used commodity polymers [2–4]. Therefore, despite their relatively high price, they have gathered the interest of the industry and the research community.

A very common method to improve the properties of thermoplastics is mixing them with particles of other materials. Many studies have centered on improving further those properties, demonstrating that adding both inorganic and organic fillers to PHB and PHBV can significantly reduce their permeability (see references in [3]). In the present work PHBH, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)-alumina nanowire and graphene composites were prepared by solvent casting. Solvent casting is very convenient to probe new materials and hence it is relevant to assess the feasibility of the developed composites by this technique.

The recent interest on PHBH (and PHAs in general) is clearly driven by environmental and sustainability reasons. Hence, an acute toxicity assay using brine shrimp larvae as test organisms and a Life Cycle Assessment (LCA) of the developed materials is included in this study.

2 METHODOLOGY

Kaneka PHBH grade X151A (which has a 6 mol % hydroxyhexanoate and a molar mass of 6.1·105 g/mol) was reinforced with Sigma Aldrich alumina nanowires (product number 551643, with a diameter of 2-6 nm and a length of 200-400 nm) and graphene nanoparticles also from Sigma Aldrich. To dissolve the polymer chloroform (Sigma Aldrich ⩾ 99%, containing 0.5-1.0% ethanol as stabilizer) was selected.

The samples were prepared by means of solevent casting. Samples containing 0, 3, 5, and 10 wt. % of alumina nanowires and graphene were prepared.

Properties were analyzed by mechanicals testing in an Instron Universal tensile test machine (solvent casting). Additionally, the environmental viability of PHBH nanocomposites was assessed by acute toxicity assay using brine shrimp larvae and LCA according to ISO14040, as follows:

The functional unit selected for the LCA was the use of 1 Kg of polymer from production to processing, use and End of Life (EoL). Cradle to Grave boundaries were used. Recipe 2016 Midpoint € methology is used, obtaining 18 impact categories. OpenLCA and ecoinvent 3.9 and Gabi 2019 databases were used.

The studied scenarios were the following:

a-PHBH polymer: production, processing by melt blending and EoL biodegrada-tion in seawater.

b-Petroleum-based polyamide (PA), polypropylene (PP), polyethylene terephthalate (PET) and polyethylene (PE) production, processing by melt blending and pro-cessing and Landfill EoL.

c-PHBH alumina nanocomposites produced by solvent casting, EoL biodegradation in seawater.

d- PHBH graphene nanocomposites produced by solvent casting, EoL biodegradation in seawater.

Brine shrimp larvae were obtained by adding dry cysts (Artemia Koral GmbH, Ger-many) to 30‰ salt water prepared from commercial salt (Sera, Heinsberg, Germany), us-ing a hatching dish in a temperature-controlled room at 26 °C and under continuous il-lumination. Larvae of 24 h post hatching (hph) were harvested and selected for the test under a stereoscopic microscope (Nikon smz800, Tokyo, Japan). Larvae immobilization at 24 and 48 h of exposure was used as a criterion for acute toxicity, the methodology was set up in previous studies [5].

3 RESULTS

3.1 Mechanical test

Concerning the stiffness of the composites, significant increases are observed: approximately a 20 % increase in the storage modulus by adding 3 wt. % alumina and a 50 % increase of Young's modulus by adding 3 wt. % graphene. As the reinforcing percentage, increases the properties do not show the same tendency. Extra addition of alumina nanowires results in a decrease of the young module, which indicates the presence of large agglomerates of the particles. The tendency is similar when adding graphene, but the properties do not decrease below the neat polymer. Hence, the more content of graphene, the more difficult it turns to exfoliate it.

Material	**kaneka 151-Al2O3**				**kaneka 151-graphene (wt%)**			
wt %	**0**	**3**	**5**	**10**	**0**	**3**	**5**	**10**
Elongation$_{(Máx)}$ (%)	0.98	1.74	1.18	1.28	0.98	1.38	1.31	0.94
Young Module (Mpa)	524.63	649.16	458.23	379.28	524.63	1068.12	960.21	920.18

Table 1: Results from the tensile test.

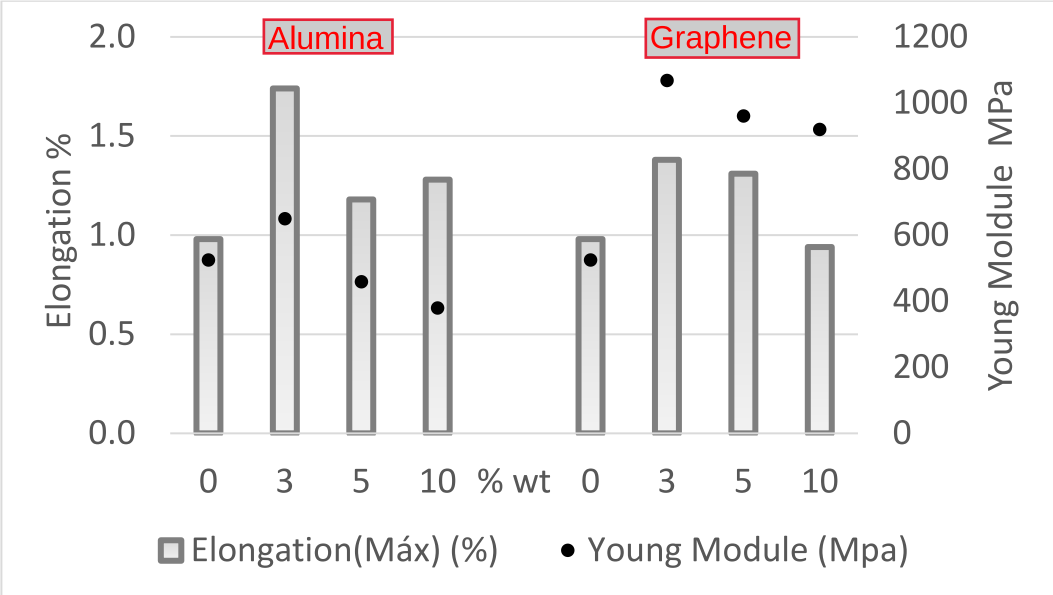

Fig.1. Relative elastic modulus and elongation at break as measured by tensile tests, taking as reference the sample that does not contain alumina.

3.2 Environmental assessment

In this section, environmental impacts of the scenarios “a” and “b are analysed.

In general, as Figure 2 shows, 14 out of the 18 categories indicate that the most polluting scenario is that related to the production and end of life of PA (of petrochemical origin). For the category of “Land Use”, the composting scenario has the greatest influence. To clarify that result, it should be mentioned that the land use is not taken into account in the landfill end of life scenario in ecoinvent 3.9; in fact, the process is carried out in industrial units. For “stratospheric ozone depletion” and “fresh water ecotoxicity”, the environmental impacts are larger for PHBH production and end of life. This is due to the emissions (methane, for instance) during its biodegradation process, which happens in open land and therefore the emissions are emitted to the air and ground directly.

The global warming category is a relevant impact indicator with regard to the transition to a low-carbon economy and to the fulfilment of the Paris Agreement, according to which a 55% emission reduction must be achieved by 2030. As Figure 3 shows, the use of petrochemical-based and non-biodegradable PA has severe effects in this category, in which the resulting impacts increase from 1.66 Kg CO2-eq. for PHBH, up to 24.5 Kg CO_2-eq. for PA (which scores the highest global warming impact among petrol-based polymers). Up to 50% of the contribution to the global warming effect comes from the production process of PA, where the emissions of carbon dioxide and dinitrogen monoxide are high.

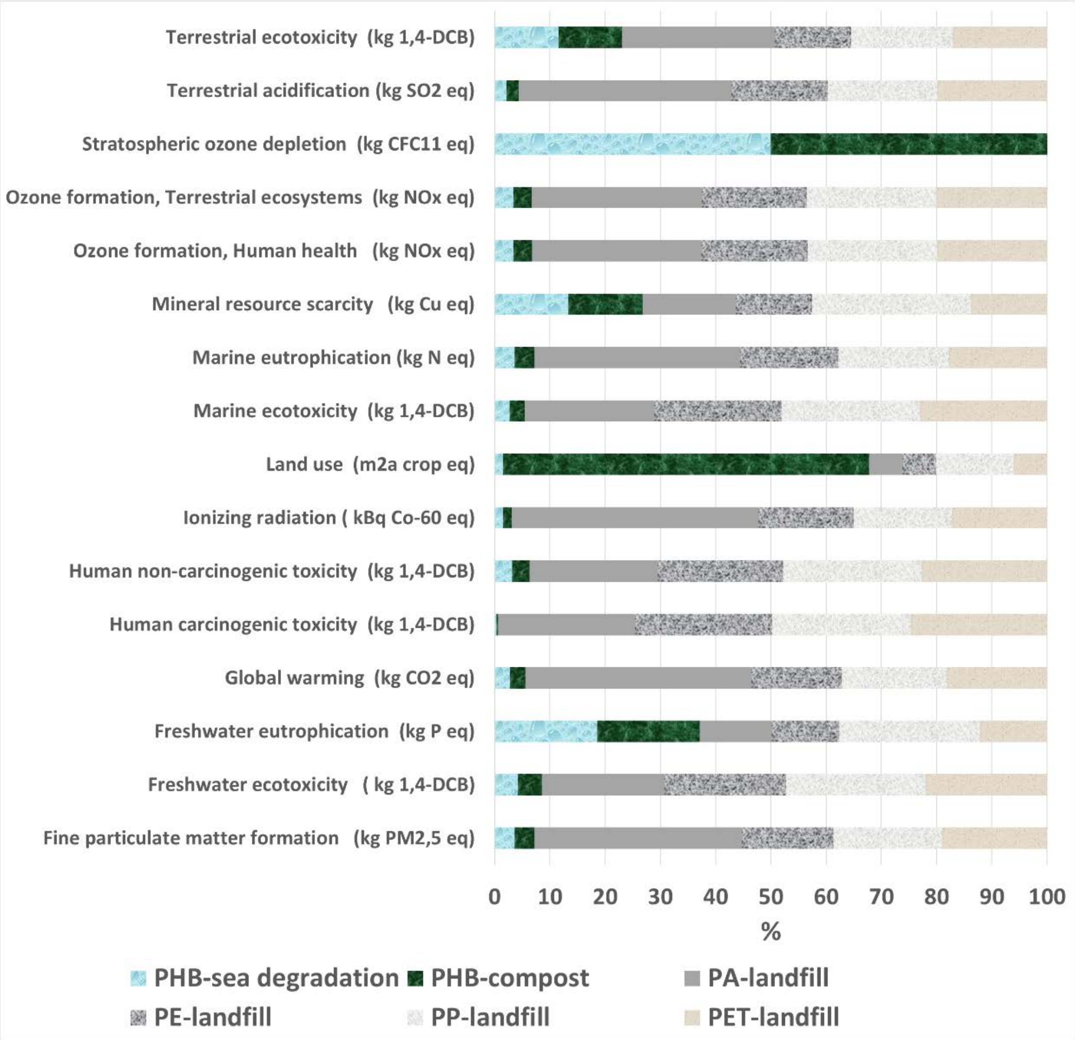

Fig.2. Relative contribution of cases “a” and “b” (%) to the quantified environmental impacts ob-tained using Recipe 2016 Midpoint.

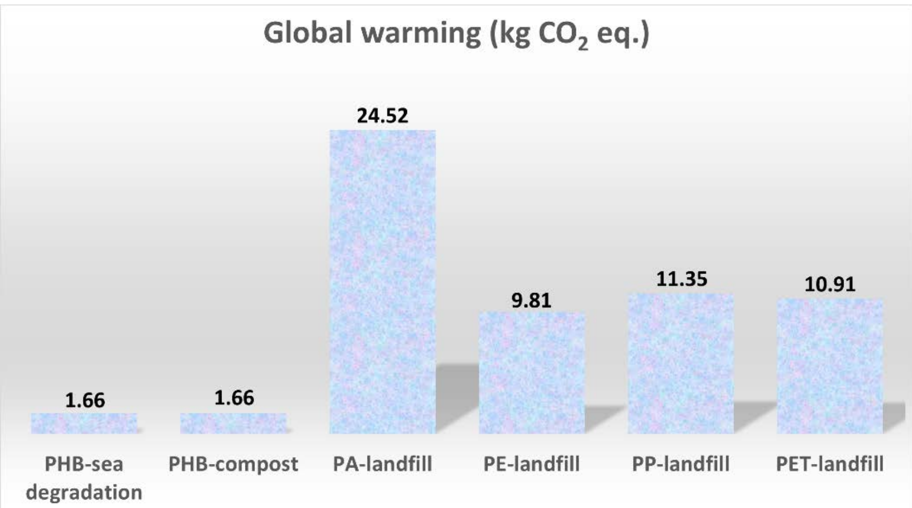

Fig.3. Global warming category for the studied cases “a” and “b”.

The analysis of the reinforcing particles is shown in Figure 4.As presented, results clearly show that the environmental impacts are not sensitive to the addition of such small amounts of different reinforcements.

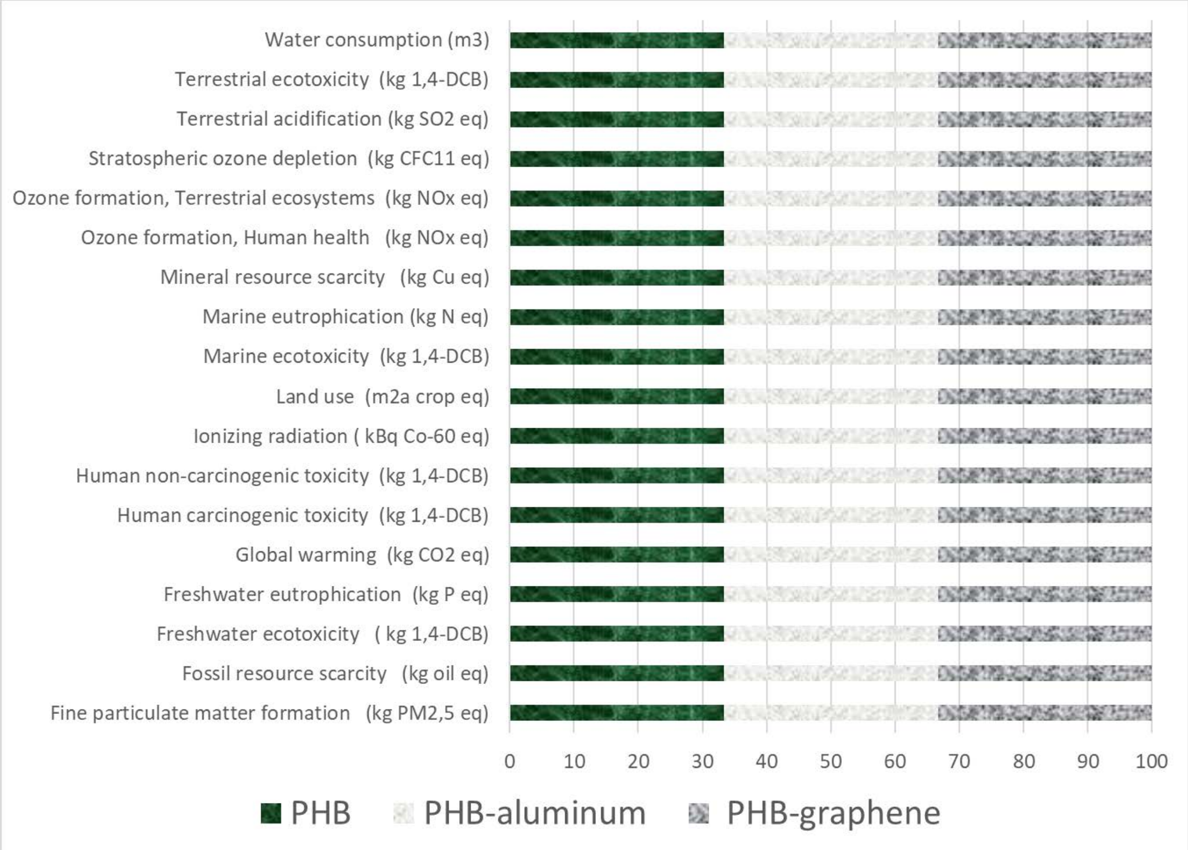

Fig.4. Relative contribution of cases “a”, “c”, and “d” (%) to the quantified environmental impacts obtained using Recipe 2016 Midpoint.

However, the LCA methodology does not take into account the size and geometry of the reinforcing particles. It is well known that nanometric particles can be harmful to the environment, as well as to humans. In this regard, toxicity tests showed that the exposure of brine shrimp larvae of 24 hph for 24 and 48 h to films of PHBH and PHBH–composites (10 wt.%) composites prepared by solvent casting has no impact on the survival of the organisms. After 48 h of exposure, 100% survival was registered in control animals (salt water treatment), as well as in animals exposed to both film types.

4 CONCLUSIONS

As stated before, from the environmental point of view, PHBH is an interesting potential alternative for some of the most used commodity polymers. However, PHBHs’ tendency to undergo aging, their low stiffness and low thermal stability pose a significant barrier for their adoption by the plastic industry. In this work, we studied the effect of mixing PHBH with a reinforcing material (i.e., alumina nanowires and graphene).

According to the LCA, using PHBH instead of any of the petrochemical-origin plastics that have been assessed here (i.e., PA, PE, PP, and PET) results in a reduction of most of the 18 environmental impact categories that have been assessed, even if the PHBH ends up as sea waste. LCA was also applied to study the environmental implications of the selected reinforcing nanoparticles. Alumina and graphene were used as reinforcement in the experimental part of this work. The corresponding LCA results show almost identical impact values for all considered materials (PHBH and nanocomposites) processed by solvent casting.

However, the performed LCA is based on the ecoinvent 3.9 database that does not take into account the effect of the nanometric dimensions of the alumina nanowires. Some studies have been already done to test the potential impact of PHB on aquatic organisms, but the experimental designs are diverse and controversial results have been reported. In this work, we studied the effect of the 48 h exposure to PHBH films produced by solvent casting on the viability of brine shrimp larvae. The results show no effect under the assayed conditions.

Environmentally speaking this work has proofed no harm and the existing benefits of using PHBH biopolymer. Next step should be enhancing properties for future applications in medical, electronic or fishing industry. As a preliminary work to future ongoing research, tensile tests have been performed to determine mechanical behavior of the composites. The addition of alumina nanowires meets a maximum of 3 wt% to enhance young module, which drastically decreases above. Using graphene, young module can be improved in 50 % adding 3 wt% and 40 % with the addition of 5 and 10 wt %.

REFERENCES

[1] K. W. Meereboer, M. Misra, and A. K. Mohanty, “Review of recent advances in the biodegradability of polyhy-droxyalkanoate (PHA) bioplastics and their composites,” Green Chemistry, vol. 22, no. 17. Royal Society of Chem-istry, pp. 5519–5558, Sep. 07, 2020. doi: 10.1039/d0gc01647k.

[2] T. Gurunathan, S. Mohanty, and S. K. Nayak, “A review of the recent developments in biocomposites based on natural fibres and their application perspectives,” Compos Part A Appl Sci Manuf, vol. 77, pp. 1–25, Jun. 2015, doi: 10.1016/J.COMPOSITESA.2015.06.007.

[3] G. Keskin, G. Klzll, M. Bechelany, C. Pochat-Bohatier, and M. Öner, “Potential of polyhydroxyalkanoate (PHA) polymers family as substitutes of petroleum based polymers for packaging applications and solutions brought by their composites to form barrier materials,” in Pure and Applied Chemistry, Nov. 2017, vol. 89, no. 12, pp. 1841–1848. doi: 10.1515/pac-2017-0401.

[4] J. Y. Boey, L. Mohamad, Y. sen Khok, G. S. Tay, and S. Baidurah, “A review of the applications and biodegrada-tion of polyhydroxyalkanoates and poly(Lactic acid) and its composites,” Polymers, vol. 13, no. 10. MDPI AG, May 02, 2021.

[5] J. Ibarretxe, L. Alonso, N. Aranburu, G. Guerrica-Echevarría, A. Orbea, and M. Iturrondobeitia, “Sustainable PHBH–Alumina Nanowire Nanocomposites: Properties and Life Cycle Assessment,” Polymers, vol. 14, no. 5033. MDPI AG, Nov 20, 2022.