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Biodegradable polyester thin films and coatings in the line of fire: The time of polyhydroxyalkanoate (PHA)?

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Summary

From sustainability standpoint, bio-based resins are of crucial importance nowadays rather than fossil-based resins, but the former has lower flame retardancy. Bio-based coatings are in their early stages; therefore, a long way must be gone to make them resistant against flame. Polylactic acid (PLA)-based biodegradable coatings have been in the core of attention, but one can rarely find reports on flame retardancy of bio-based thin films and coatings. Attention should also be paid to the fact that first-generation biodegradable polyesters, PLAs, are hooked on crop consumption. On the other hand, polyhydroxyalkanoates (PHAs) with more or less similar structure, but different physical properties arising from their lower glass transition temperature compared with PLAs, are known as the second-generation of bio-polyester. Overall, we highlight here that PHAs might a better candidate for thin film manufacturing thanks to their synthesis by microorganism. Though mass production of PHAs is not cost-effective these days and their market just entered into the growth phase, we suggest study on flame retardancy of PHA-based resins, thin films, and coatings. This short communication deals with the current status and future ahead of PHA-based flame retardant thin films and coatings.

Keywords: Bio-based coating; Fire retardancy; Polyhydroxyalkanoate (PHA); sustainability

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1. INTRODUCTION

Bio-based and biodegradable polymers such as chitosan [1], agarose [2], gelatin [3] and silk [4] have received a considerable attention in recent years, even more than what an optimistic could hope, due to ever increasing sustainable development. Environmental threats and resource limitations are the main issues accompanied by the use of fuel-based polymers [5-9]. Such debates have aligned the developed countries in the need of replacement of unsustainable routes in manufacturing advanced materials and systems as well as developing modern technologies to draw a green horizon of opportunities upon material design [10-13]. Synthesis of bio-based and biodegradable resins still experiences early stages of development; therefore, a long road should be paved to make bio-based resins directed toward global plastic market [14-19]. Research on naturally driven, bioengineered, and synthetic biopolymers gained from bacteria, conventional biotechnology, and biomass has undergone an accelerating trend just in between 1993 and 2012 by ca. 35-fold and 15-fold rise in the number of scientific papers and patents, respectively [20-22]. Synthesis of polylactic acid (PLA) as the first-generation biodegradable polyester opened hope tracks beyond commercialization of bio-resins for widespread uses [23]. PLA known as the most promising bio-resin comes from fermentation *via* conventional chemistry followed by polymerization of lactic acid [24]. Undesirably, however, a large volume of corn, the main food supply in developing countries, must be utilized in the synthesis of PLA, which remains big challenge over future ahead of PLA production [25, 26]. An elaborate analysis of patents unraveled that long-term research and development on PLA aligned it in the line of maturity, but its limited potential of commercialization was recognized for further PLA market progression [27].

Despite promising aspects of bio-resins for a sustainable future, they are highly flammable as well as they show poor mechanical properties; hence, they should be modified/reinforced with additives [28]. Pursuing instructions on the ban of usage of some halogenated flame retardants, substantial attempts were directed toward development of bio-based additives to meet low toxic product emission requirements [29-32]. Fire retardancy of bio-based resins filled with minerals, biofillers, biofibers, as well as bio-based composites composed of both bio-matrix and biofillers has been the focus of a wide variety of surveys over the past decade [33-38]. PLA-

based flame retardant systems from metal oxide source were extensively studied, but the use of phosphorous-based and nanoclay flame retardant additives, alone or combinatorial, still remains in a long research road with a trace of hope in resolving poor mechanical properties of PLA composites[39].

The advent of polyhydroxyalkanoate (PHA) as second-generation fully biodegradable polyester resin through synthesis from a wide range of microorganisms and bacteria has eliminated the need for fermentation of crops [40-42]. This biogenic resin has just entered the market, but rapidly experienced growth period [43]. PHA family resins are appropriate candidates for energy storage and intracellular carbon purposes. They can be classified into short-chain length (C_3 - C_5) and medium-chain length (C_6 - C_{14}) groups with poly(3-hydroxybutyrate) (PHB) as the first widespread resin [44, 45]. Thanks to their compatibility to blood and tissues and low permeability against H_2O , CO , and O_2 , PHAs have been used in a wide variety of fields ranging from food packaging industry to tissue engineering (**Figure 1**) [46-49]. Nevertheless, high production cost and poor mechanical properties were recognized as major drawbacks that have limited large-scale application of PHA [50]. In this sense, modification of PHA by the aid of plasticizers, its blending with the second polymer, and its chemical modification with different functional groups/chains were examined[51, 52].

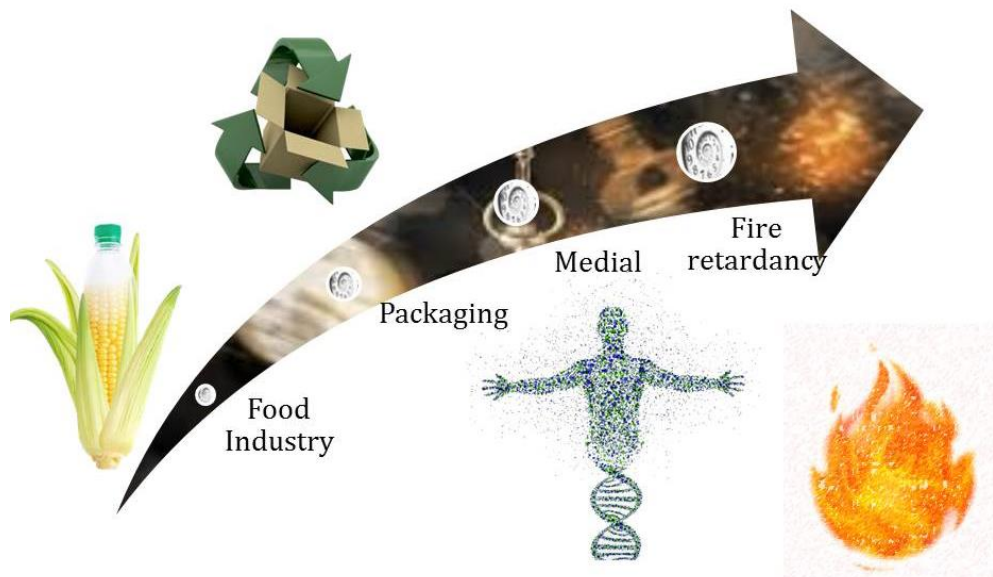


Fig. 1. Developments in application of biodegradable polyesters, PHA in the line of fire.

Bio-based thin films and coatings have opened new era of research for widespread uses. Fu et al. synthesized and fully characterized bio-based waterborne polyurethane dispersions starting from castor oil by the use of chain extender, and obtained good thermal and hydrophobic properties[53]. Turkenburg et al. developed highly thermos-reversible self-healing coatings by incorporation of high amounts of bio-based precursors and reported acceptable abrasive wear and solvent resistance together with mechanical properties [54]. There have also been some attempts to synthesis of bio-based UV-curable resins for applications in waterborne coatings [55-58] in the quest of adhesion, flexibility, mechanical and anti-corrosion properties. Biodegradable coatings based on waterborne polyester [59, 60] as well as vegetable oil-derived nanocomposite coatings were also investigated [60]. The open literature suggests that bio-based polyurethane resins were quite often the subject of studies in this field [60, 61].

There are several reports on PLA-based coatings. Active PLA films used in packaging containing bergamot, rosemary, lemongrass or clove essential oils were developed by Qin et al., where acceptable antimicrobial and mechanical properties were obtained [62]. Elsewhere addition of equivalent weight of acrylic polyol and PLA ended in packaging films resistant against humidity

and the cured films revealed good hydrolytic degradation resistance in humid media [63]. Durable hydrophobic PLA coatings obtained from pulsed plasma polymerization [64], fast-formed microporous PLA coatings [65], nanostructured composite coatings based on PLA and amorphous magnesium phosphate with anti-corrosion and bioactivity characters [66], and PLA-based nanocomposite coatings from electron beam with substantial antibacterial features [67] were also subjects of research. There were also some works on the use of blends of PLA or PHB with other polymers, e.g. thin films and bio-coatings based on PHB and cellulose showing improved tensile properties [68]. Biodegradable smooth coatings based on polycarbonate and PLA [69] were among limited reports on the use of second-generation PHA coatings. It is worthy of note that the blend of PHA and PLA lacks miscibility; hence, chain extenders make possible formation of compatible bio-based coatings with acceptable thermal and mechanical properties thanks to intensified intermolecular entanglements [70, 71].

The quantity of research on flame retardancy of PLA thin films and coatings containing flame retardant additives is indeed limited. Solution casting PLA films containing phosphorous flame retardant were examined for thermal stability and flame retardancy performance in terms of the limiting oxygen index (LOI), UL-94, and thermogravimetric analysis (TGA) [72]. There are some works on the individual or combined use of conventional flame retardants with nanoparticles in PLA thin films. Shi et al. used nanoparticles of metal-organic framework (MOF) in PLA solution film casting having thickness of ca. 140 μm for electronic devices [73]. The LOI value for neat PLA film was ca. 20%, which was indeed low. The neat sample failed in UL-94 test and continued to burning for about 21 s, implying high flammability of PLA. The surprising point was that by incorporation of just 0.2 wt.% of MOF into PLA films the LOI value increased to 23.5%, and nanocomposite sample burned in a very shorter time of ca. 16 s. Increase of MOF content to 1 and 3 wt.% in the PLA film caused rise in LOI to 24.5 and 26.0%, respectively. In the same direction, burning times were decreased to 4.3 and 2.9 s. Film-stacking method was also used to obtain PLA films containing 10:1 ratio of polyphosphorous: montmorillonite (MMT), where self-extinguishing PLA films were achieved at 16 wt.% flame retardant content [74]. Having met V-0 rating UL-94 as well as up to 50% decrease in the value of peak of Heat Release Rate (pHRR) in cone calorimetry measurements and the Total Heat Release (THR) were

signatures of a superior fire retardancy performance. The combined use of a phosphinic acid-contained precursor and layered double hydroxide (LDH) [75] and a hybrid containing di(phenyl phosphate) (RDP), MOF, resorcinol, and graphene oxide (GO) [76] in PLA solution-casted films was successful in achieving good fire retardancy performance. Investigations also unraveled high potential of PLA nonwoven mats with intumescent features when ammonium polyphosphate (APP) was blended with lignin and starch carbohydrates [77].

In the light of above discussion, this short communication intends to place stress on the importance of research on flame retardancy of PHA-based family as potential era of survey in the field. Though kinetic study on thermal degradation of PHB was addressed in two reports, flame retardancy of neat PHA has never been reported. Except a work on the blend of PHB with poly(butylene adipate-co-terephthalate) (PBAT) filled with combination of nano-iron oxide and antimony oxide with emphasis being placed on superiority of additives [78, 79], no report is available in the literature on flame behavior of PHA-based systems. This is why we pictured here a potential framework for research on flame retardancy of PHA-based composites, looking at present from the future window. **Figure 2** provides a comprehensive comparison of some physical and structural characteristics of PLA and PHA [80]. Although the density of PLA and PHA are the same, glass transition temperature (T_g) of PLA is well above room temperature, notifying suitability of PHA for usage in moderate temperature. PHA behaves like ductile materials at room temperature due to low T_g , however, its T_g can be changed for lower or higher levels by incorporation of additives and plasticizers. Moreover, PHA is a semi-crystalline biodegradable polyester; while PLA possesses somehow an amorphous structure. Water permeability of PHA stands lower than PLA, due to the presence of crystalline domains, which offers PHA as a potential candidate for packaging industry. Thus, comparison between thermal stability and flame retardancy performances of PHA and PLA would be motivating.

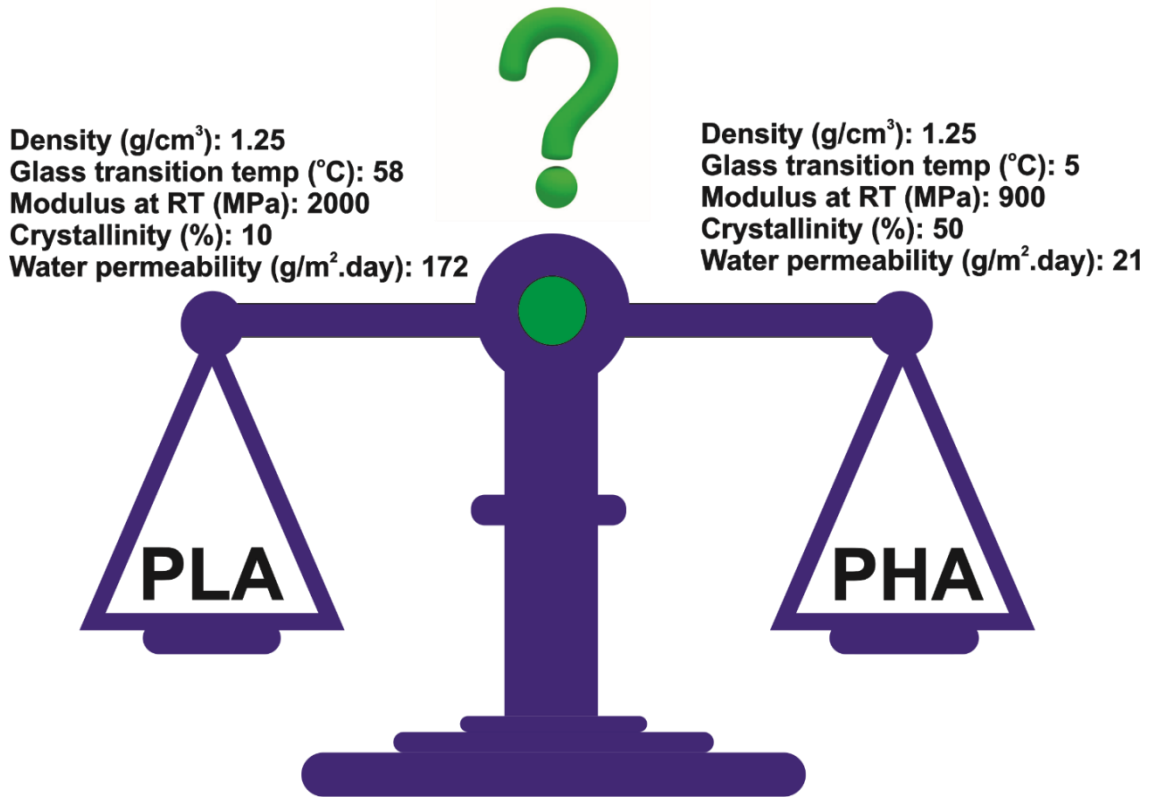


Figure 2: General comparison of final properties of PLA and PHA

2. CONCLUSION

Biodegradable polymers appeared as candidates for wide variety of fields thanks to their environmental-friendly and almost respectable properties. However, inadequate flame retardancy and mechanical strength of biopolymers have opened doors to substantial research in recent years to tackle their drawbacks. In the meanwhile, some promising outcomes have positioned them in the way commercialization. PLA belongs to the first generation of biodegradable polyesters, which is produced from food supply resources, mainly corns. However, substantial volume of corn is required in synthesis of PLA, which remains an unsolved problem in their large-scale production. Furthermore, PLA products suffer from very high flammability, along with insufficient mechanical properties-what suggests blending them with additives to reimburse their defects. These severe drawbacks highlights the need for synthesis of PHA as the second generation of fully biodegradable polyesters through microorganisms to

eliminate the usage of corn. PHA has been found many potential applications in wide variety of fields thanks to biocompatibility, biodegradability, and low permeability against H₂O, CO, and O₂. Though researchers and technologists alike have addressed flame retardancy of PLA, no report is available on flame retardancy of PHA. This communication intends to underline the importance of research in this field and seeks to encourage researchers working on flame retardancy of biobased polymers to take direction towards PHA.

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