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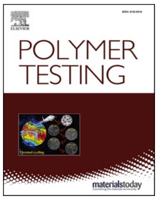

Extending biopolyesters circularity by using natural stabilizers: A review on the potential of polyphenols to enhance Poly(hydroxyalkanoates) thermal stability while preserving its biodegradability

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ABSTRACT

PHAs are polyesters synthesized by micro-organisms as an energy reserve from renewable, and possibly non-food, feedstock. They are non-toxic, biocompatible and quickly biodegradable in different natural environments, ensuring not to pollute and jeopardize our ecosystems unlike conventional plastics. They are good candidates to replace conventional plastics such as polypropylene for their functional properties during the usage stage of their life cycle. However, expanding their eco-efficiency and circularity by adding cycles, such as reuse or recycling, to their life-cycle requires to improve their thermal stability and mechanical properties. Here we offer to discuss on how improving their thermomechanical properties while preserving their crucial biodegradability. The review focuses on a well-known type of stabilizer, the polyphenols and their impacts on PHAs' thermomechanical properties and biodegradability. It has mainly been concluded that the presence of polyphenols, at a certain amount, contributes to the improvement of the physical-chemical properties of PHAs, whereas there is no evidence that polyphenols have an inhibitory effect on the biodegradation of PHAs.

1. Introduction

Plastic is omnipresent in our daily life. It is a low-cost, lightweight, resistant, hydrophobic and bio-inert material which has become almost indispensable in the packaging sector. It has replaced wood and metal in construction, and natural fibers in textiles. Today, the annual global production of plastics is about 360 million tons [1]. Between the abundance of packaging consumed in emerging and developing countries and the more sophisticated plastics in vogue in developed countries, this industry is growing steadily, despite the environmental challenges and increased regulation. In USA, the petrochemical industry announced investments of over 204 billion US dollars, driven by the shale gas boom, leading to an expected acceleration of virgin plastic production [2]. A report co-authored by Ellen Mac Arthur foundation states that by the year 2050, the annual production of plastic will amount 1124 million tons [3]. Meanwhile, the ecological disaster caused by plastic pollution is a reality that can no longer be denied. In 2016, approximately 19–23 million tons or 11% of plastic waste generated globally entered aquatic ecosystem [4]. Covid-19 pandemic has exacerbated the situation, as a recent estimate revealed that a monthly average of 129 billion face masks and 65 billion gloves were mismanaged worldwide [5,6]. So far, most attention has been focused on the more visible effects of large plastic objects, fueled by distressing images of marine animals sometimes fatally entangled by plastic objects. However, the invisible enemy is micro-plastics, which are less than 5 mm in size and can cause serious problems for a very wide range of species through ingestion or interaction. Today, it is estimated that there are over 5 trillion plastic particles in the world's surface waters [7]. Micro-plastics have been detected in foodstuffs such as seafood, sugar, salt, beer and honey, and also in drinking water and air [3]. Since they are hydrophobic with a high surface area-to-volume ratio, they are able to absorb and concentrate environmental pollutants [8]. To date, there is no clear evidence of the consequences of the uptake of micro-plastics or polluted micro-plastics on human tissue, but research in this area is ongoing.

Faced with this threat, a collective awareness is emerging. Commitments and initiatives are undertaken to reduce plastic emission such as the United Nations Environment Assembly resolutions on marine litter and micro-plastics from 2014 to 2019 [9]; goal 14 of United Nations on conserving and sustainably use of the oceans, seas and marine resources for sustainable development [10]; as well as the banning of single-use plastics by some governments [11]. Communities and

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non-governmental organizations are cleaning beaches and promoting zero-waste lifestyles, and the private sector is investing in plastic waste management. These initiatives are commendable and should be intensified, but they are far from curbing the exorbitant use of plastics today. One of the viable alternatives is to replace plastic and especially single-use-plastic by material that is degradable and compatible with the environment. Hence, the development of biodegradable plastics from renewable biomass has become a topic of great interest.

In 2020, 1.22 million tons of bio-based biodegradable plastics were produced in the world [12]. It may seem trivial compared to the production of conventional plastic, but the market of these plastics is continuously growing and diversifying. It is expected to grow with compounded annual growth rate (CAGR) of 11.28% from 2019 to 2025 [13]. Among the different groups of biopolymers, poly(hydroxyalkanoates) (PHAs) are naturally occurring polyesters synthesized by various microorganisms as energy and carbon reserves under nutrient stress conditions. They are nontoxic, biocompatible and biodegradable materials. They are highly crystalline, optically active, thermoplastics and hydrophobic. These features make them highly competitive with some petrochemical-derived plastics such as polypropylene [14,15]. As a result, over the last few decades, PHAs have attracted considerable commercial and research interest, as evidenced by the increasing number of publications on these polymers over the last 30 years. (Fig. 1). Today, there are several companies involved in the PHAs materials business, namely Metabolix Inc (USA), Shenzhen Ecomann Technology Co. Ltd (China), Meridian Inc. (USA), and Biomer (Germany), with maximum growth and developments for the two first mentioned companies [14]. The biodegradability and biocompatibility of PHAs make them prime candidates for medical and packaging applications. Initially, they were used to make shampoo bottles and packaging materials by Wella (Germany). They are now also developed for use as shopping bags, containers and paper coatings, as well as medical surgical garments, medical implants and drug delivery carriers, among others [16–18].

Despite this potential, PHAs are still far away from replacing petrochemical-based plastics in a competitive manner because of their limited thermal and mechanical properties. PHAs display a high degree of crystallinity, resulting in a stiff and brittle material, along with their very low thermal resistance [19].

To mitigate the brittleness of PHAs and to improve their thermal resistance, several strategies has been implemented such as plasticizing, chemical modification, polymer blending and additivation (Table 1).

These different strategies often involve the incorporation of non-biobased, non-biodegradable compounds into PHA matrices, which can cause them to lose their biodegradability. Thus, the move towards natural and biodegradable additives should be a priority in a sustainable and ecological approach.

In recent years, the use of natural polyphenols as thermal stabilizers for PHAs has begun to emerge. Polyphenols are biobased and biodegradable compounds with thermal stability and antioxidant properties that could allow them to ensure the thermal stability of PHAs while preserving their biodegradability. After providing a brief overview of the properties of PHAs and polyphenols, this review will attempt to shed light on the trade-off between the thermal stabilization effect of polyphenols and their impact on the biodegradability of PHAs.

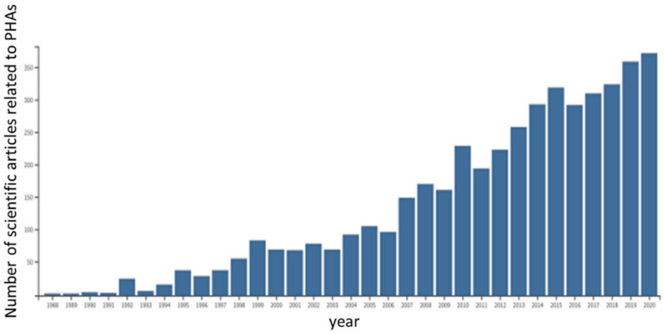


Fig. 1. Evolution of scientific literature in the field of PHAs over the last 30 years (Web of Science report. Thomson Reuters, New York, USA. 2021).

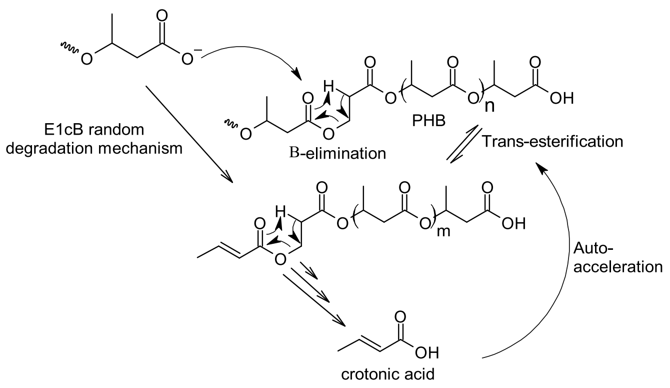
Table 1
Strategies for thermal stabilization and improvement of mechanical properties of PHAs.

Improvement strategy	Technique/Reagent/Polymer	Reference
Plasticizing (reduce PHAs brittleness)	Glycerol, 4-nonylphenol, acetyl tributyl citrate, salicylic ester, soybean oil, epoxidized soybean oil, epoxidized broccoli oil, fatty alcohols and polyethylene glycol …	[19,20]
Chemical modification	Grafting reactions, chlorination, cross-linking, epoxidation, hydroxyl and carboxylic acid functionalization …	[21]
Polymer blending	poly(ethylene oxide), poly(methyl acrylate), poly(vinyl acetate), poly(vinylidene fluoride), poly(epichlorohydrine), poly (butylenes adipate), epoxidized natural rubber, or poly(vinyl phenol), poly (ε-caprolactone) (PCL), poly(butylene succinate) (PBS), poly(butylene adipate-co-terephtalate) (PBAT), and poly(3-thiophene ethyl acetate) (PTAcET)	[22,23]
Additivation	zinc oxide (ZnO), cellulose nanocrystals, graphene nano-sheets, titanium dioxide (TiO_2), nanoclay, silane-treated-recycled wood fibers	[23–26]
Synthetic phenolic compound additives	Irganox 1010	[27]

2. Polyhydroxyalkanoates (PHAs) and their thermal degradation

Poly(hydroxyalkanoates) are a wide class of linear polyesters belonging to bio-based and biodegradable thermoplastic polymers. They are synthesized by a large number of microorganisms as intracellular carbon and energy stocks. Depending on microorganisms and carbon source used, 3-hydroxyalkanoic acid monomers of different length can be arranged to give rise to multiple congeners of PHAs. To date, about 150 different hydroxyalkanoate polymers have been reported [28], in which the pendant alkyl group of monomers can vary from methyl (C1) to tridecyl (C13) [14]. According to this, PHAs are classified into three classes of short, medium and long chain length (scl, mcl, lcl) polyesters, with different properties [29]. Poly(3-hydroxybutyrate) (PHB), Poly (3-hydroxyvalerate) (PHV) and their co-polymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) are typical examples of short chain length PHAs. In this class PHB and PHBV are the most common and intensively studied PHAs [30].

PHAs are completely biosynthesized and biodegradable. They are biocompatible with good barrier properties [19] which makes them good alternatives to some traditional fossil plastics. However, the applications of PHAs are limited due to some undesirable physical properties. These polymers suffer from their low glass transition temperature, slow crystallization rate, large spherulite size, and secondary recrystallization behaviors which result in their brittle products [15,16]. PHB and to a lesser extent PHBV are highly crystalline with ordered crystal structure, which leads not only to brittleness but also to the degradation at a temperature slightly above the melting point [31,32]. The thermal degradation mechanism of PHB and PHBV in isothermal and non-isothermal conditions has been widely investigated [33–36]. In their book chapter, Nishida et al. [37] summarized the main mechanisms involved in the thermal-induced chain scission of PHB (Scheme 1). It has long been considered that the reduction of polymer molecular weight is essentially generated by random chain scission process, induced by the β-elimination reaction, giving rise to crotonic acid and crotonyl end-group chains as degradation products. Then,



Scheme 1. Expected overall thermal degradation mechanism of PHB reported by Nishida et al.

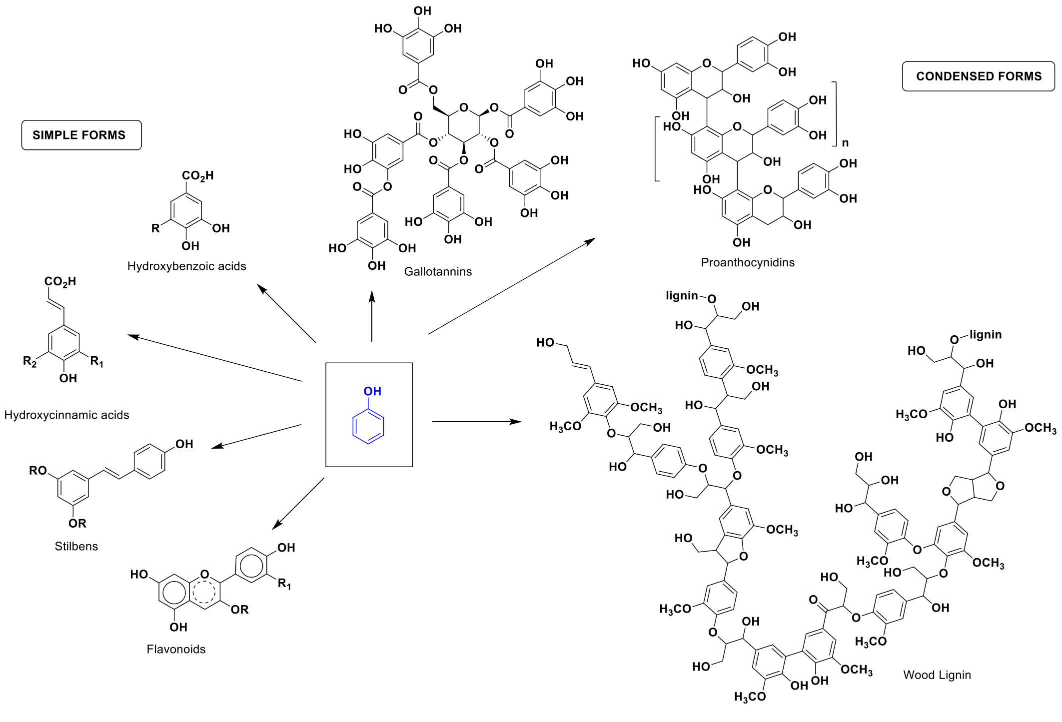
Kawalec et al. [38] proposed an α-deprotonation mechanism (E1cB) by a carboxylate anion, resulting in the same products. Oligomers bearing crotonate end-groups undergo subsequently an unzipping-β-elimination, accelerating the production of crotonic acid. Nuguyen et al. [39] have suggested that the crotonic acid thus produced induce the catalysis or the auto-acceleration of the random degradation by initiation trans-esterification reactions. The influence of oxygen on the thermal degradation of PHB was investigated by Michalak et al. [40]. It was observed that the process carried out in pure oxygen (flow of 90 L/h) at 140 °C led to a scission of the polymer backbone typical of a normal thermal degradation. The exposure of PHB to a mixture of oxygen/ozone was necessary to accelerate its degradation into 3-butyric acid and 3-malic acid units. They concluded that in the presence of oxygen, at temperatures above 100 °C, the PHB degradation does not respond to a thermos-oxidative mechanism.

3. Polyphenols and their properties

Polyphenols are a large family of secondary metabolites produced by higher plants, mainly for their protection from predators. Some academic experts on polyphenols claim that one can only call plant polyphenols the compounds having molecular weight ranging from 500 to 4000 Da and possessing 12 to 16 hydroxyl groups on five to seven aromatic rings per 1000 Da of relative molecular mass (definition of Haslam-Bath-Smith-Swain and White) [41]. Going beyond this very strict definition, the term “polyphenols” is widely attributed to organic compounds with one or more hydroxyl groups attached to a phenyl ring. According to that, polyphenols could be classified into two main categories. Polyphenols with simple chemical structures including flavonoids, hydroxybenzoic acids, hydroxycinnamic acids and stilbens; and complex polyphenols with polymeric structures comprising tannins (proanthocyanidins, gallotannins, ellagitannins), and lignin (Scheme 2) [42]. Lignin is a peculiar class of natural phenolic compounds. It is a cross-linked macromolecular material based on phenylpropanoid monomer structure, with molar mass ranging from 1000 to 20000 g/mol. Lignin isolation from lignocellulose materials is conducted under conditions that reduce progressively the molecular weight, resulting in structural modifications compared to native lignin. The major extraction processes are based on acid or base-catalyzed depolymerizations. The most common are sulfite, soda, kraft and organosolv processes [43,44].

The antioxidant capacity of polyphenols has been widely demonstrated. *In vitro*, they essentially act as free radical scavengers by donating the proton of their phenolic hydroxyls to free radicals. The aromatic radicals resulting from this proton transfer are then stabilized thanks to the delocalization of the π–electron system [45]. The antioxidant effect of polyphenols has been widely exploited in different domains. In food preservation, polyphenols mainly act as inhibitors of lipid oxidation [46–48]. In health, they are considered as good agents for the reduction of the oxidative stress by scavenging reactive oxygen species [49]. More recently, polyphenols have been studied for their ability to inhibit polymer degradation, if initiated by free radicals [50–52].

The involvement of polyphenols in polymer formulations requires the study of their capacity to maintain their structural integrity and activity in the different stages of polymer production and use. The thermal stability was mainly investigated for polyphenols with condensed structures such as tannins and lignin. Proanthocyanidins extracted from Radiata pine bark can withstand processing temperatures



Scheme 2. Chemical structures of the different polyphenol groups.

up to 200 °C if the carbohydrate content of the extract is below 5 wt% [53]. Proanthocyanidins from quebracho and hydrolysable tannins extracted from chestnut and tara pods showed similar degradation rates at temperatures ranging from 200 °C to 400 °C [54], which is above the melting temperatures of some biodegradable polyesters. Wheat straw and quersus lignin as well as birch lignin obtained respectively from klason and organosolv processes displayed maximum degradation at temperatures between 320°C and 380 °C [55]. On the other hand, the thermal stability of structurally simple polyphenols, such as flavonoids and phenolic acids, at elevated temperatures has hardly been studied. The majority of reported treatments were performed at temperatures not exceeding 100 °C [56–58], which does not correspond to the processing conditions of polymers.

4. Polyphenols as additives in PHAs and their effects on thermal stability

Although not yet widely studied, the incorporation of polyphenols into PHB or PHBV matrices to overcome their thermomechanical limitations has been reported in several studies. (summary in Table 2). The treatment of PHB film in rheometer at 190 °C during 2700 s led to a massive thermal degradation, corresponding to a drop of M_w to 20% of the initial value (200 KDa). On the contrary the M_w drop was slightly slower when 30 wt% of Klason lignin was added to neat PHB. In addition, polydispersity index of the blend was lower and storage modulus value and complex viscosity were higher, indicating an improvement in melt stability [59]. Loading of PHBV with 1–10 wt% kraft lignin by melt compounding resulted in an increase in Tg, improvement in E-modulus (from 19% to 58% depending on lignin concentration), stabilization of tensile strength value and change in crystallinity. Elongation at break values, stable up to 5 wt% lignin addition, showed a decrease of about 42% when lignin reached 10 wt% in the polymer [60]. When radical initiator such as dicumyl peroxide was used, kraft lignin was grafted to PHVB through C–C covalent bonds, leading to a better stabilization of the polymer. This resulted in higher modulus and viscosity, along with an increase of the tensile strength by 11% [65]. The same trend was observed when other types of polyphenols were used as additives. Solvent mixture of PHB with tannic acid up to 15 wt% led to the shift of the weight loss curves to higher temperatures, confirming the delay of thermal degradation process to longer times. The presence of tannic acid up to 20 wt% resulted in less ordered crystals [61] and increased the transition state and cold crystallization temperatures by 20 °C and 60 °C respectively. In addition, improvements were observed for the stress, tensile strength, elongation at break and fracture work. However, when the loading of tannic acid exceeded 20 wt%, all these parameters showed a significant decrease [32]. Flavonoids derivative, namely catechin was added to PHB at 15 to 50 wt% by solvent mixing. In blends with catechin content lower than 30 wt%, the melting temperature of PHB decreased from 179 °C to 164 °C and Tg shifted to higher temperatures, illustrating a higher viscosity and a better thermal stability of the blends. DSC analysis showed a disappearance of the melting point of catechin, suggesting that the miscibility of catechin in the polymer matrix suppressed its crystallization, but over 30 wt% of catechin loading, the double glass transition state appeared, attesting to the presence of two distinct entities [62]. Hydro-alcoholic extract from Cabernet wine pomace, containing 4 wt% of catechin-derivative compounds was mixed to PHB polymer in solution. Two films containing respectively 5 wt% and 15 wt% of pomace extract were produced by injection molding. The presence of phenolic compounds provoked an increase in both material viscosity and polymer molecular weight. Moreover, the thermal degradation of the blends occurred through a single weight loss at temperatures higher by about 15 °C compared to neat PHB. In this case, the thermal degradation was independent of the additive amount. However, the glass transition temperature (Tg) decreased when PHB was doped with 15 wt% of pomace extract, indicating the plasticizing effect of this amount of additive. This was reflected by the increase in elongation at break and the decrease of tensile strength, making the material more ductile [63]. Instead of phenolic

Table 2
Main thermomechanical effects induced by the addition of polyphenols to PHAs.

PHA	Polyphenol: amount		Blending process	Thermomechanical characteristics compared to neat PHA	Reference
PHB	Klason lignin: 30 wt%	LIGNIN	Solvent mixture	- M_w drop of 60% compared to 70% drop for neat PHB - Lower M_w/M_n - Higher storage modulus G_0' - Higher complex viscosity - Improvement of melt stability	[59]
PHBV	Kraft lignin: 1-5 wt%		Melt compounding	- Increase of Tg (−3.7 to −1.5 °C) - Nucleation of crystals with higher thermal stability - Improvement of E-modulus by 19–58% - Stable value of elongation at break - T_{onset} and T_{max}: shift to higher temperatures by 0.7–1.7 °C and 2.9–4.9 °C respectively	[60]
PHB/ PHBV	Tannic acid: 10-20 wt%	GALLOTANNINS	Solvent mixture	- Weight loss curves: shift to higher temperatures - Tg increase by 20 °C - Increase of cold crystallization T_c by 60 °C - Decrease of T_m by 17 °C - Hydrogen bonding (polymer/additive) - Improvement of stress, tensile strength, elongation at break and fracture work	[32,61]
PHB	Catechin <30 wt%		Solvent mixture	- Decrease of T_m from 179 to 164 °C - Shift of Tg to higher temperatures - Decrease of crystallization rate X_C about 20%	[62]
PHB	Cabernet wine pomace extract: 5-15 wt%	PROANTHOCYANIDINS	Solvent mixture	- M_w drop of 30% compared to 80% drop for neat PHB - Decrease of Tg from 1.8 °C to 0.8 °C (plasticizer effect) - Higher thermal degradation temperature by 15 °C - Increase of T_{onset} from 255 °C to 273 °C - Decrease of Young modulus from 2.84 to 1.95 GPa - Increase of elongation at break from 1.3 to 2.4% - Decrease of strength from 30 to 25 MPa	[63]
PHBV	Tea extract: 20-40 wt%		Solvent casting	- Increase of Tg by 54 °C - Increase of cold crystallization T_C by 66 °C - Decrease of T_m by 17 °C - Increase of elongation at break ratio of 2430%	[64]

extract of wine pomace, David et al. [66] tested the introduction of wine pomace fillers devoid of polyphenols into PHBV matrix. It was observed that the absence of polyphenols resulted in greater thermal degradation of the composites, confirming the thermal stabilizing role of polyphenols. Another catechin-based extract, namely tea extract was added to PHBV by solvent casting. Increasing the amount of tea polyphenols from 0 to 40 wt% resulted in the increase in both Tg and cold crystallization temperature by about 56 °C and 66 °C respectively. The melting temperature decreased by about 17 °C, indicating a disruption in crystallization behavior of the blends. Up to 20 wt% loading of tea polyphenols, the elongation at break increased with an increasing ratio of 2430%. The same trend was observed for the tensile strength and the strain. Beyond this amount of additive, a significantly decreased of these parameters was recorded [67].

PHA materials with polyphenol coating were also studied. Cellulose nanopapers were coated with mcl-PHA mixed with apple pomace extract at 1, 3 and 5 wt% content. The coating of these nanopapers with mcl-PHA alone provoked an improvement of 650% and 9700% in tensile strength and Young's modulus respectively. The incorporation of the phenolic extract resulted in a decrease in modulus as the amount of the extract increased. This was attributed to the plasticizing effect of apple pomace extract [68].

In the light of these different studies, it appears that the addition of polyphenols up to a certain amount to PHA matrices by solvent mixing or melt compounding generally leads to an increase in Tg, a shift in degradation temperatures towards higher values, an increase in tensile strength as well as a disruption of crystallization which results in lower temperatures and enthalpies of fusion. These stabilizing effects are largely attributed to the intermolecular hydrogen bonds linking the carbonyl groups of PHA and the hydroxyl groups of polyphenols, revealed by FTIR analyses [32,59,61,63,65,67,69,70]. It was shown that the band around 1720 cm^{-1} related to the carbonyl stretching of the ester group in PHA crystalline part shifts into smaller wavenumbers, while the small shoulder around 1740 cm^{-1} attributed to the carbonyl bond in the amorphous region becomes more intense [32,61,65]. Although the characteristic band shifts after the addition of polyphenols remain very small, FTIR remains the preferred method to support the hypothesis of the presence of hydrogen bonds between the polymer matrix and the polyphenols. These hydrogen bonds will contribute to the polymer stabilization by hindering the formation of the six-membered transition structure involved in the random chain scission of the polymer during the thermal degradation (Scheme 1) [33]. Their presence will also modify the crystallization through a significant increase in the number of spherulites in PHA, accompanied by a consequent reduction of their size [32,65,67]. In the presence of these uniform sperulites with small radius, the crystalline phase acts as cross-linking point, while amorphous area is in rubbery state, increasing thereby the blend toughness [32]. On the other hand, the opposite effect occurs when polyphenols loading exceeds a certain amount. This was mainly attributed to the heterogeneous distribution of the polyphenols in the polymer matrix [71] and the over reduction of PHA spherulites, leading to the formation of a continuous amorphous phase [32].

Aside from an excess additive, other factors may accelerate the polymer degradation. PHBV mixed with lignosulfonates by mechanical melt processing, showed a decrease in its degradation rate even with low amounts of lignin derivatives (10 wt%). The PHBV/lignosulfunate films presented a cracked appearance of the fracture surfaces caused by the formation of lignosulfunate domains which increased with its concentration. Despite the poor interactions between the two blend components, their degradation processes were not independent. At temperatures ranging from 210 °C to 260 °C, water and acids were released during the thermal decomposition of lignosulfonate, which provoked the hydrolysis of PHBV polymer chains [72]. Therefore, depending on the polyphenol used, its decomposition products may catalyze the degradation reaction of the polymer.

The use of polyphenols as additives to PHAs was not only to improve the thermal stability of these polymers. Some authors have studied the new functionalities that polyphenols could confer to PHAs such as barrier properties and antioxidant and antimicrobial activities.

In term of barrier properties modification, the 1-10 wt% PHBV/Kraft lignin blends exhibited lower O_2 and CO_2 permeability compared to neat PHBV, that decreased with the increasing amount of lignin. At only 1 wt % loading, the permeability of PHBV film to O_2 and CO_2 decreased by about 77% and 91% respectively. The gas permeability is a result of both sorption and diffusion processes. As sorption coefficient proved higher solubility of both gases in PHBV/lignin films, it was concluded that lignin inhibited the diffusion in the polymer [60]. Electrospun PHBV showed water vapor and limonene permeability of 4.05×10^{-14} kg m^{-2}. s^{-1}. Pa^{-1} and 3.75×10^{-14} kg m^{-2}. s^{-1}. Pa^{-1} respectively. These values decreased to 0.95×10^{-14} kg m^{-2}. s^{-1}. Pa^{-1} and 0.81×10^{-14} kg m^{-2}. s^{-1}. Pa^{-1} respectively, when 15 wt% of eugenol was added. The decrease in water vapor permeability is mainly due to the dispersion of the hydrophobic eugenol in the polymer matrix, which impairs the mobility of water molecules [73]. When eugenol was encapsulated in the pores of mesoporous silica nanoparticles, the water vapor and limonene permeability increased for a loading of 2–7 wt% of nano-particules, before decreasing above 7 wt% encapsulated eugenol. With the lower amount of additive, the plasticizing effect of eugenol reduced the barrier properties, but with the higher loading, the presence of a large amount of particles hindered vapor diffusion [74].

Depending on the polyphenols structure, their antioxidant activity was not always maintained when incorporated into PHA matrices. mcl-PHA with 5 wt% of apple pomace displayed a radical scavenger activity of 80% in the presence of ABTS radical cation [68]. However, green tea and rosemary extracts introduced in PHBV matrix by electrospinning and annealing lost approximately 50% of their DPPH scavenging activity. This decline in activity, which has continued over time, has been attributed to the release of volatile active compounds, although this release was not assessed by the authors [75].

When tested for their antimicrobial activity, some PHAs/polyphenols systems (containing eugenol and curcumin) exhibited strong to moderate activity against *E. Coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Pseudomonas aeruginosa* strains, among others [73,74,76]. The proven antimicrobial activity of polyphenols in these few examples raises the question of their general behavior towards microorganisms, and consequently their impact on the biodegradability of PHAs.

5. Effect of polyphenols on PHAs biodegradation

5.1. The antimicrobial activity of polyphenols

The antimicrobial activity of polyphenols has been widely reported. However, most articles have focused on pathogenic micro-organisms (bacteria, viruses and fungi) which are not representative of the enormous bacterial variety present in the environment. Table 3 is a brief compilation of the most cited bacteria in the three reviews of M. Daglia et al. [77], I. Gorniak et al. [78], and MC. Lima et al. [79] dealing with the antibacterial activity of polyphenols. It can be seen that all types of polyphenols are able to inhibit different strains of the 2 g-positive bacteria *Staphylococcus aureus* and *Listeria monocytogene*; as well as the gram-negative bacterium *Escherichia coli*.

The inhibitory effect of polyphenols on bacteria is not yet well established, but several modes of action have been described, especially for flavonoids. The most common are (i) the membrane disruption: The bacterial plasma membrane is responsible for different functions including osmoregulation, respiration and lipid synthesis. Some polyphenols have the ability to bind to the lipid bilayer and to inactivate or inhibit the synthesis of intracellular and extracellular enzymes; (ii) the inhibition of biofilm formation: thanks to the formation of biofilm, the bacteria become from 10 to 1000 times more resistant to antimicrobial agents compared to their planktonic cells. Polyphenols disrupt the formation of this biofilm by inhibiting the alginate formation or other

Table 3
Bacteria sensitive to the different types of polyphenols.

Polyphenol	Target bacteria/stains	Reference
Flavonoids	*E. coli, S. aureus, B. cereus, F. nucleatum, P. vulgaris, L. monocytogenes*	[77,78,80, 81]
Phenolic acids (hydroxybenzoic and hydroxycinnamic acids)	*E. coli, S. aureus, L. monocytogenes, P. aeruginosa, Salmonella enteritidis, B. cereus*, MRSA	[77, 82–84]
Condensed tannins (proanthocyanidins)	*S. mutans, E. coli, S. aureus, B. cereus, L. monocytogenes*	[77,83,85]
Gallotannins	Stains of: *Salmonella, Staphylococcus, Helicobacter, E. coli, Bacillus, Colostridum, Campylobacter, Lystria*	[77]
Ellagitannins	*B. subltilis, E. coli, L. monocytogenes, S. aureus, Salmonella enteriditis, Y. enterocolitica, P. aeruginosa, L. innocua, Enterococcus faecalis*	[86–88]
Lignin	L. *monocytogenes, S. aureus*	[89]

siderophore proteins, resulting in a declination in bacterial adherence and aggregation; and (iii) the neutralization of bacterial toxins: these toxins interact with host tissues or mask the bacterial surface from host's defense mechanisms. Due to their antioxidant activity, polyphenols are able to neutralize these toxins [77,78]. For example, condensed tannins and phenolic acids may induce damages at cell membranes by binding with enzymes, and flavonoids such as catechin can neutralize bacterial toxins. Other lesser-known inhibition mechanisms have been reported, including, among others, the inhibition of cell envelop and nucleic acid synthesis, and the inactivation of bacterial-metal enzymes [78] (Table 3).

5.2. *The microbial degradation of PHAs*

In the environment, several micro-organisms are able to degrade solid PHAs into water-soluble monomers and oligomers which are then used as nutrients. These microorganisms including bacteria and fungi have been isolated from various ecosystems such as soil, compost, aerobic and anaerobic sewage sludge, fresh and marine water, estuarine sediment, and air [90]. Fungi that were identified as dominant microorganisms colonizing the polymer's surface polymers, belong mainly to *Comycetes*, *Basidiomycetes*, *Deuteromycetes* (such as *Aspergillus fumigatus and Penicillium* sp), *Zygomycetes*, *Micromycetes* and *Ascomycota* groups [91–96].

In the case of bacterial degradation, Meereboer at al. reported that the dominant PHA degraders in aerobic and anaerobic environments are members of the genera of *Variovorax*, *Stenotrophomonas*, *Acinetobacter*, *Pseudomonas*, *Bacillus*, *Burkholderia*, *Cupriavidus*, *Mycobacterium* and *Streptomyces* [96]. Additional genera such as *Stenotrophomonas*, *Alcaligenes*, *Comamonas*, *Rhodococcus*, *Rhodocyclus*, *Xanthomonas*, *Syntrophomonas*, *Ilyobacter*, and *Ralstonia* have been mentioned by Fernandes et al. [94]. Among these genera, several strains have been isolated from soil or sludge. Luzier et al. [97] and Mergaert et al. [98] isolated different strains of soil bacteria including *Acidovorax facilis*, *Comamonas* spp., *Pseudomonas lemoignei* and *Variovorax paradoxus*. Shah et al. listed the main bacterial strains found in composts, and marine water, namely *Bacillus* sp. *AF3*, *Pseudomonas fluorescens*, *Nocardiopsis aegyptia*, *Streptomyces* sp. *SNG9*, *Streptomyces exfoliatus*, *Streptomyces venezuelae*, and *Actinomadura* sp. [99]. For more information, see the article of Bano et al. gathering the main microorganisms responsible for PHA degradation [100].

These bacteria have the ability to produce extracellular enzymes called hydrolases and depolymerases, which are capable of degrading PHA into small molecules that can penetrate the bacterial membrane and be used as carbon and energy sources. Most of PHA-depolymerases share several characteristics. They are highly stable at a wide range of temperature and ionic strength; they have relatively small M_W (<70 KDa) with most of depolymerases consisting of only one peptide chain; and they show maximum activity at pH between 7.5 and 9.5 [90,101,102]. For example, PHBV-depolymerases from both *Streptomyces* sp. *AF11* and *Acidovorax* sp. *HB01* strains showed a 100% activity at temperatures ranging from 35 °C to 55 °C and pH from 7.0 to 8.0 [91,103]. The depolymerases adhesion and adsorption on the polymer is largely influenced by the polymer surface properties (surface area, hydrophilicity and hydrophobicity) as well as its crystallinity, and crystal structure [102]. It was observed that the degradation rate decreased with the increasing degree of crystallinity. P(3HB-4HB) which had the lowest degree of crystallinity (50%) showed the highest degradation rate (1.63 mg/day), compared to P(3HB) (78% crystallinity) which degraded at a rate of 0.61 mg/day. In the case of PHA copolymers, the crystallinity decreases as the HV content increases, which accelerates the enzymatic degradation rate [104,105]. The amorphous region allows permeation of moisture and enzymes, and thus, its degradation would increase the surface area of available crystalline regions. Only enzymes A and B from *Pseudomonas lemoignei* stand out by displaying a similar degradation rate of both amorphous and crystalline regions indiscriminately [106]. To a lesser extent, the stiffness of the material may also affect the bacterial degradation by affecting the biofilm formation. In general, an increasing stiffness is favorable for bacteria attachment [107].

Most of the purified depolymerases are known to be scl-PHA-specific. Volova et al. [108]. submitted PHA films with different monomeric composition to the extracellular enzymes from different bacteria. It was reported that P(3HB) was degraded by bacteria of the genera *Acidovorax* and *Mitsuaria*, which were not active against P(3HB-3HV) and P (3HB-4HB) films. *Streptomyces gardneri* and *Cupriavidus* sp. were specific degraders for P(3HB-4HB), while P(3HB-3HV) was depolymerized by *Roseomonas massiliae* and *Delftia acidovorans*. Nevertheless, these three PHA types were degraded by *Streptomyces*. Again, *Pseudomonas lemoignei* is the exception, as it is able to degrade the homopolyester PHV while most other PHB-degrading bacteria are unable to. This bacterium is capable of producing at least five extracellular depolymerases, three of which (A, B and D) are specific for PHB and PHBV with a low HV content; and depolymerases C and poly(D-3-hydroxyvalerate(PHV)) depolymerase which degrade both PHB and PHV [101,109].

The availability of medium chain depolymerases is hardly reported. Only a few species have been described so far, mainly belonging to *Pseudomonas* and *Streptomyces* genera [110,111].

Research on chemical agents that inhibit scl-PHA-depolymerases is very limited. currently, reducing agents and serine hydrolase inhibitors such as diisopropyl-fluorophosphate are the most incriminated compounds [90,101,102]. Metal ions such as Fe^{2+} and Cu^2 were designated by Wang et al. as inhibitors of *Acidovorax* sp. *HB01* strain, due to their effect on the active site of the extracellular enzyme [103].

Since polyphenols are reducing agents, it is conceivable that they could contribute to the inhibition of PHA-extracellular depolymerases. Therefore, it is important to review the studies on the impact of polyphenols on the biodegradation of PHAs and bioplastics.

5.3. *Impact of polyphenols on polymers biodegradation*

Very little research has been done on the impact of polyphenols on polymers biodegradation. The most important findings are summarized in Fig. 2.

The delay in biodegradation caused by the presence of polyphenols was observed by Latos-Brozio et al. [112] when P(3,4HB) and PLA films containing curcumin and morin were home composted under controlled conditions (30 °C and 60% moisture), during 6 months. The carbonyl index was used as an indicator of degradation, since its increase is related to the breaking of polymer chains. The degradation of neat P(3, 4HB) was visible after the first month of composting, while the addition of morin retarded the degradation process by one month. The same trend was observed for PLA, with a one-month delay in degradation

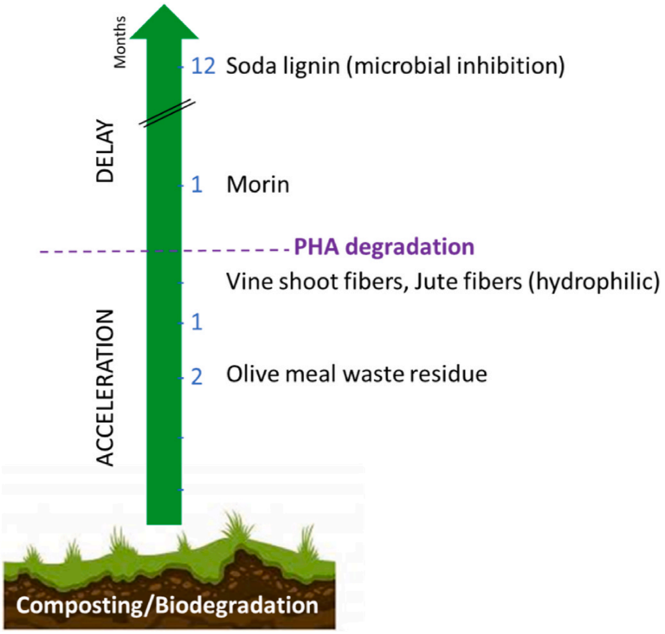


Fig. 2. Effect of some polyphenols on PHAs biodegradation.

between pure PLA and PLA/morin sample. At the end of composting, PLA/curcumin sample had a higher weight loss than PHA/curcumin. This was attributed to the difference of miscibility and solubility of the additive in the polymer matrices. Stronger were the interactions between the two components, slower was the polymer degradation. The same authors studied the impregnation of P(3,4HB) and PLA pellets by the ethanolic extracts of Cistus linnaeus (Cistus L.) and green husk of walnut Juglans regia Linnaeus (Juglans regia L.). The chemical composition of the extracts was not accurately determined, but the presence of phenolic acids, flavones and their glycosides, in addition to juglone and carotenoids was detected by FTIR. The microbial degradation of the impregnated polymers was carried out in the presence of mold fungus *Aspergillus niger*, *Paecilomyces varioti*, *Chaetomium globosum*, *Trichoderma viride* and *Penicillium funiculosum*. Unlike the previous study, polymers have preserved their biodegradation rates after the impregnation with phenolic compounds. This behavior was mainly attributed to the fact that during impregnation, small fragments of plant material were able to attach to the polymers, providing a carbon source that favors the growth of micro-organisms on the polymer surface [113]. However, as the biodegradation processes are different, it is not obvious to compare these two studies.

Vine shoot fibers, without polyphenols (after the extraction of proanthocyanidins), were biodegraded in soil according to NF EN 17033 standard at 28 °C. Compared to the virgin vine shoot fibers (still containing polyphenols) which degraded at 83% after 80 days, the exhausted fibers reached a final rate of biodegradation of 97% for the same period. Since the polyphenols extraction did not modify the fibers morphology and crystallinity, this delay was attributed to the removal of the antimicrobial polyphenols. Interestingly, PHBV polymer reinforced with these two types of fibers (virgin and exhausted) at 20 wt% loading, exhibited the same degradation behavior, indicating that the biodegradation process was mainly driven by the behavior of PHBV matrix [114].

The higher water vapor permeability induced by the introduction of natural fibers seems to favor the biodegradability of PHA-based composites, even if these lignocellulosic fibers contain a portion of lignin, which is recalcitrant to microbial attack. Indeed, PHB polymer reinforced with 30 wt% of jute and hemp fibers were placed in home compost during 12 weeks. PHB/jute fibers composite degraded at 84% between week 8 and 12, while PHB/hemp fibers composite and neat PHB underwent 68% and 50% weight loss respectively within the same period. Jute fibres with the highest lignin content (12–14%) were better able to promote the biodegradation of PHB thanks to the good dispersion of these hydrophilic fibers which led to a better water absorption and increased surface area for microbial attack [115]. The same finding was made by Carofiglio et al. when they assessed the soil degradation of PHB polymer reinforced with lignocellulosic material from olive mill wastewater residue (OMWR) [116]. After 8 weeks of soil burial, PHB/OMWR composite (with 40 wt% of fillers) recorded 20% of mass loss, while no evidence of biodegradation was observed for neat PHB.

Although lignin is part of lignocellulose composition, its effect on PHA biodegradation was not clearly demonstrated. Only Mousavioun et al. investigated the soil degradation of PHB films reinforced with soda lignin [117]. Thus, PHB films containing from 10 to 90 wt% of soda lignin were buried in soil, and their biodegradability was assessed over 52 weeks, according to ASTM D 4972 standard. Once lignin is present in the blend, the polymer degradation is inhibited. Indeed, the lowest amounts of lignin increased the crystallinity of PHB, and the highest amounts (over 30 wt%) reduced or prevented the accumulation of the microorganisms on the films surface, because of its antimicrobial property.

From these few studies, the inhibitory effect of polyphenols on the biodegradation of PHAs has not been clearly established. Despite the antimicrobial property of polyphenols, many other factors come into play, such as the chemical nature of the polyphenols (pure molecules or involved in a plant tissue), their amount, as well as the modification of the polymer structure induced by polyphenols (nucleating agent, plasticizer). In addition, the degradation conditions (temperature, time and microbial consortium) should not be neglected to make an accurate comparison.

6. Conclusion

Highly promising bio-based and biodegradable PHAs are struggling to replace conventional plastics in a wide range of applications, because of their brittleness and thermal instability. Many efforts are being made to address these problems, and one of the solutions to preserve the biodegradability of these polymers is the use of natural polyphenols as additives. It has been shown that regardless of the nature (pure or extract) or structure of the polyphenol, its addition to PHA matrices, up to a certain amount (generally <30 wt%) contributes to an improvement of their thermal and mechanical properties. This, is likely attributed to the hydrogen bonds between the phenolic hydroxyls of polyphenols and the carbonyl groups of PHAs. On the contrary, an excess of polyphenols leads to accelerate the thermomechanical degradation of the blends, due to their immiscibility and/or their plasticizing effect. The biodegradability of PHAs in the presence of polyphenols was then examined and no inhibitory effect was clearly established. Some studies claim that the presence of polyphenols delays the biodegradation of PHAs due to their antimicrobial effect (lignin), while others show an accelerated degradation of polymers loaded with polyphenols contained in fiber tissues or in extracts with other components. Indeed, the biodegradability is a complex process influenced also by the polymer properties, the environment and the bacterial consortium. To clearly establish the effect of polyphenols, all the biodegradation tests should be performed on similar polymers (in term of structure) and under the same conditions.

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