

Application of Poly(hydroxyalkanoate) In Food Packaging: Improvements by Nanotechnology

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Review

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The environmental impact of plastic usage is of critical concern and too great to repair. A shift toward biodegradable food packaging is one option. The aim of this review paper is the study of the potential of biodegradable materials for food packaging. The main characteristics in relation to food usage can be narrowed down to mass transfer (gas and water vapor), thermal and mechanical properties. Among several kinds of biodegradable polymers, poly(hydroxyalkanoate) is one of the favorable candidates for food packaging due to its physical and mechanical properties, biodegradability, with low permeability for O₂, H₂O and CO₂ without residues of catalysts and water solubility. The main focus of this article is to address poly(hydroxyalkanoate) as a potential candidate for food packaging. The need of applying biobased polymers in food packaging is presented in the introduction of this study. We also describe the most common biopolymers providing a brief overview of classification and application. This is followed by an outline of biopolymer production and a main section in which the properties of poly(hydroxybutyrate)-based nanocomposites of greatest relevance to food packaging are discussed. Furthermore, several approaches for improvement of poly(hydroxybutyrate) properties are described and the role of nanotechnology to improve its mechanical properties is presented. Finally, the article concludes with a summary as well as some possible future trends.

Key words:

poly(hydroxybutyrate), poly(hydroxyalkanoate), food packaging, properties, modifications, nanoparticles

Introduction

Food packaging is a main step of the food chain, the purpose of which is mechanical support, transition, extension of shelf life, and preservation of food. Petrochemical-based polymers have long been vital materials in food packaging due to several reasons, including their mechanical properties, easy processing, and cost. The common food-packaging polymers are polyethylene (PE) (cooking oil, milk and water containers), polyethylene terephthalate (PET) (applied in food, beverage, and other liquid containers); polyvinylchloride (PVC) and polypropylene (PP) (yogurt, spice ice tea, and margarine), polystyrene (PS) (eggs and mushroom), and polyamide (PA) (flexible packaging of perishable food, such as meat and cheese)¹. The cost, migration of toxic ingredients into food matrix, and the environ-

mental impacts are three main issues which should be identified in the concern of food packaging². The production of plastics is one of the largest manufacturing industries in the world. The aims of the recycling plants are reduction of the amount of plastic created each year, and their reuse. However, recycled materials can be used for food packaging only if they meet specific government standards. Such limitation leads to a cost- and time-consuming process. Despite a great amount of different recycling programs, in some places there is still no cohesive recycling program^{3,4}.

The food industry spends approximately less than hundred billion dollars a year on food processing⁵. Less than one tenth of the total food cost is spent on packaging and processing. At present, food and beverage packaging comprises about one half of food packaging in the United States. Innovation in food and beverage packaging is increased with the aim of reducing food preparation time and use

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of animal protein, as well as enhancing bioconversion of materials, and industrial processing⁵.

The packaging materials include fillers, plasticizers and stabilizers. Fillers tend to maintain barrier and mechanical properties, while filling the polymer with cheap materials reduces the cost. Plasticizers are applied to strengthen flexibility, ductility, and toughness of polymers while at the same time reducing hardness and stiffness⁶. Also, stabilizers are incorporated into the matrix to inhibit deterioration of mechanical properties due to UV light and oxygenation⁷.

There are still many concerns about food packaging materials and their possible interactions with food, especially when food plastics are reused⁸. Also, there are some issues about environmental problems due to slow degradation of polymers and the importance of consumption of renewable sources. Therefore, there is a growing interest worldwide to replace plastics with biodegradable plastics, particularly in packaging applications⁹. The use of biodegradable plastics and resources are seen as one of the many strategies to minimize the environmental impact of petroleum-based plastics. Plastic recycling is not often economically viable as there are problems of contamination of the food packaging¹⁰.

Biopolymer-based food packaging

Bio-based polymers can be categorized in three groups:

1. Polymers extracted directly from biomass e.g. proteins (whey, casein, collagen, soy), lipids (triglycerides), and polysaccharides (cellulose, starch, chitin gums)

2. Polymers synthesized from bio-derived monomers e.g. polylactides

3. Polymers produced by natural or genetically modified organisms e.g. microalgal and bacterial cellulose and other inclusion bodies, e.g. poly(hydroxyalkanoate)

Naturally occurring substances are partly or completely biodegradable, which may prove useful for food packaging¹¹. However, biodegradable polymers are expensive and exhibit poor mechanical properties¹².

Biodegradable polymers in food packaging

Biodegradable materials show some promising characteristics for many applications e.g. packaging, and the medical sector. Specifically, thermoplastic biodegradable polymers, such as polyhy-

droxyalkanoates (PHA), poly(lactic acid) (PLA), and polycaprolactones (PCL), which arise from renewable resources, present processability with conventional plastics machinery.

PCL is a biodegradable thermoplastic polyester synthesized by chemical conversion of crude oil. This biopolymer has good water, oil, solvent, and chlorine resistance, with a low melting point, glass transition temperature, and low viscosity, and processable using conventional melt blending technologies¹³. PCL is being investigated for its use in biomedical utensils, pharmaceutical controlled release systems, and in biodegradable packaging¹³. PLA is a thermoplastic biopolyester produced from L-lactic acid, which is usually produced from the fermentation of corn starch, and can be biodegraded by some bacteria (e.g. *Alcaligenes faecalis*) and fungi. Currently, PLA is the most commercially used biopolyester in food packaging applications commercialized in cups, containers and films for short shelf-life products¹². Incorporation of plasticizers for reduction of stiffness leads to a decrease in oxygen barrier and transparency. PLA, when compared to PET and polyolefins, presents easy processability¹⁴, availability in the market and transparency¹⁵, as well as printability¹⁶, biodegradability in compost¹⁷, but low thermal resistance, excessive rigidity, and high permeable properties. Conversely, the use of PLA films for food packaging has been strongly limited due to poor mechanical and barrier properties¹⁸. Moreover, for large-scale industrial production of PLA must guarantee adequate thermal stability or low thermal degradation during processing and use¹⁹.

Thus, melt blending PLA with another biopolymer may cause improvement of some characteristics, cost, and easy processing technology¹¹. Both PLA and PHB have a similar melting temperature. Therefore, melt blending for insertion of a highly crystalline poly (hydroxybutyrate) (PHB) to the PLA bulk has been considered as an easy way to moderate properties and enhance PLA crystallinity^{20,21}. About PLA, a great industrial interest is the enhancement of its thermal and barrier properties while maintaining its inherently good properties e.g. transparency and biodegradability.

Recently, a novel combination of PLA-PHB blends and functionalized CNCs for food packaging have been reported. This investigation indicates that this combination offers a new view for their industrial usage as short-term food packaging¹². There are some effective solutions for mechanical problems, but some problems exist for barrier and thermal properties^{11,12,22–26}.

PHA

PHAs are biopolymers which accumulate as a carbon/energy or reducing power storage material in various microorganisms, usually when there is a growth-limiting component such as O, N, P, S, or trace elements, e.g., Mg, Ca, Fe in the presence of excess carbon source^{27,28}. This family of bacterially synthesized biopolyesters is biodegradable, biocompatible, thermoprocessable, with flexible strengths. PHAs have found applications in the form of packaging materials, including films, boxes, coatings, fibers and foam materials, biofuels, medical implants, and drug delivery carriers. Two main limiting factors for large-scale applications of these biopolyesters are the costs and properties of PHAs. Over the past years, process development and metabolic engineering approaches have been adopted to develop recombinant PHA production strains for improving the strains' ability to produce PHA, and for changing the PHA structures to obtain better thermal and mechanical properties²⁷.

Three types of short, medium, and long chain length (*scl*, *mcl* and *lcl*) PHA may result from hydroxy fatty acids with 3–5, 6–14 and (more than 15) carbon atoms, respectively. The *scl*-PHA are synthesized by numerous bacteria e.g. *Ralstonia eutropha* (recently named *Cupriavidus necator*) and *Alcaligenes latus*, while *mcl*-PHA can be produced by fluorescent *Pseudomonas* like *Pseudomonas putida*. A few bacteria, including *Aeromonas hydrophila* and *Thiococcus pfennigii*, synthesize copolyester in the form of *scl*- and *mcl*-PHA^{27–29}.

PHB

PHB is the first discovered member of the PHA family and also the most widely studied and characterized. It is accumulated inside a membrane-enclosed inclusion in many bacteria at up to 80 % of the dry cell weight. PHB has properties very similar to conventional plastics. Although PHB can be extruded, molded, spun into fibers, made into films and used to make heteropolymer, typically, *scl*-PHA are highly brittle with poor elastic properties, while *mcl*-PHA are more ductile and easier to mold³⁰.

One copolymer, named poly(hydroxybutyrate-co-hydroxyvalerate), (PHBV), is less brittle than PHB, and therefore potentially more usable. Piezoelectric property of PHBV makes it applicable³¹. PHB has the advantageous property of being degraded in D-3-hydroxybutyrate (HB), which is a natural constituent of human blood. Thus, this homopolymer is biocompatible and applicable in biomedical usage, such as tissue engineering scaffolds and drug carriers^{32–34}. PHB has been used in small disposable products and in packing materials³⁵.

Bucci *et al.* 2005, investigated the use of PHB in food packaging, comparing it to PP⁹. The deformation value of PHB was about 50 % lower than that of PP. PHB is more rigid and less flexible than PP. The performance of PHB tends to be lower than those of PP under normal freezing conditions. Nevertheless, at higher temperatures PHB performed better than PP.

PHB production cost is dependent on several key factors, e.g., substrate, selected strain, cultivation strategy, and downstream processing. The utilization of inexpensive substrates^{36–42}, modeling⁴³, proper experimental design^{44,45} and development of new recovery method^{46–50} as well as opportunities for their competition in the global market has recently been addressed. Besides various application of PHB⁵¹, its advantages and disadvantages in food packaging have been also reported²¹ while little information can be found regarding PHB usage as food packaging.

The effect of different nitrogen (ammonium chloride, nitrate and sulphate as well as urea), and carbon sources (fructose, sucrose, glucose, cane molasses and glycerol), as well as culture conditions on production of biomass and PHA content of *Pseudomonas aeruginosa*⁵⁰ and *R. eutropha*^{44,45} has been investigated. The maximum PHA yield on sugar refinery waste (cane molasses) and urea was achieved in batch fermentation. Also, *Alcaligenes* sp. showed maximum PHA concentration of 70.8 % dried cell weight by supplementing palmitic acid in MSM at a concentration of 15 g L⁻¹. Shake flask cultivation scale-up in 7.5 L bioreactor (working volume 3.0 L) gave a PHB content of 78.0 % w/w with productivity of 0.14 g L⁻¹ h⁻¹. The present study clearly suggests that *Alcaligenes eutrophus* is the most widely used bacterial PHB producer. It grows easily and accumulates large amounts of PHB (up to 80 % of dry cell weight) in a simple medium⁹. In some bacteria, PHA monomers are derived by biotransformation of long-chain fatty acids^{51,52}. It has also been shown that plant and vegetable oil stimulate synthesis of polysaccharides^{53,54}, and *mcl*-PHA synthesis⁵⁵.

PHB properties

As mentioned above, PHB is a partially crystalline material with a high melting temperature, and a high degree of crystallinity. It is not water-soluble but is 100 % biodegradable and has optical activity, piezoelectricity, and good barrier properties³⁵. Young's modulus and tensile strength of PHB are comparable to those reported for PP, but the elongation at break (5±10 %) is significantly lower⁵⁶. Thus, stiffness of PHB is attributed to cracks within the PHB spherulites that form under conditions of non-externally applied stress^{57–60}. Long storage at

room temperature causes brittleness to increase. PHB does not have any residues of catalysts because the sources of production are microorganisms. It is isotactic and does not include chain branching. So it flows easily during processing^{58–60}.

PHA applications: From medical to food packaging

PHAs are known to have various applications in packaging, medical, and disposal usage⁶¹. PHBV could be applied for packaging of films, blow molded bottles, and as a coating on paper. Also, PHBV medical applications (potential in reconstructive surgery) result from its slow hydrolytic degradation and biocompatibility. *mcl*-PHAs are applicable in coatings and medical temporary implants e.g. scaffolding for the regeneration of nerve axons and arteries. Amphiphilic PHA copolymers have significant applications in drug delivery, tissue engineering and cardiovascular area, e.g., artery augments, vascular grafts, cardiologic stents, heart valves, implants, pericardial patches, microparticulate carriers, and dressing tablets⁶². PHB can be degraded to HB identified in high concentration in human blood. So, it is non-toxic for implanting in mammalian organs⁶³.

PHBV has showed effective application for disposable personal hygiene as the sole structural polymers or part of degradable composites. PHAs show comparable properties to petrochemical polymers so it can be used instead of them in composite material⁶¹.

As mentioned above, PHA-based films have attracted interest for food packaging application due to its renewability, biodegradability, and water vapor barrier properties. PHB acts as a better light barrier in the visible and ultraviolet light regions than PLA²¹. Despite the comparable properties of PHB with synthetic thermoplastics^{64,65}, its widespread usage has been limited by drawbacks of cost and narrow melt processing window due to brittleness and low thermal stability in the molten state^{63–68}. Its thermal stability is low during processing, which causes a decrease in the viscosity and molar mass.

The cost of the carbon source is approximately 40 % of the total operating cost^{69,70}. PHB production has been reported by various cheap carbon sources. Global trend in application of PHAs is application of the copolymer instead of the homopolymer due to its poor mechanical properties.

Main approaches to improve PHB properties for food packaging

PHA properties may be improved by modifying the surface or combining PHA with other polymers, inorganic materials, and enzymes. The incorporation of nanoparticles into PHA may cause improved

mechanical properties, thermal stability, machine cycle time and temperature (due to modification of the thermal properties)⁶⁷.

Interaction and dispersion of nanocomposites generated from PHB (or other biopolymer) in the matrix can modify the polymer characteristics. Different nanoparticles may lead to different improvement in structure of matrix, generating new materials with particular organizational properties. Incorporation of nucleating agents to the polymer may lead to decreased brittleness and melt during processing⁷¹.

Copolymers production

Some disadvantages of PHB for industrial applications may be overcome by copolymerization with hydroxyvalerate or hydroxyhexanoate. In PHA family, monomers can be combined in 150 different combinations to produce copolymers with different properties²⁸. Mechanical properties of copolymers depends on the composition of the monomer units and may differ from hard crystalline thermoplastic polymer (e.g., PHB) to elastomeric ones, such as poly(3-hydroxyoctanoate) (PHO)^{72,73}. Enhanced ratio of 3-hydroxybutanoic acid to 3-hydroxyvaleric acid leads to enhanced water permeability, melting point, tensile strength and glass transition temperature (T_g), but reduced impact resistance^{74,75}. The physicochemical characters of PHAs produced from different carbon sources is reported³⁴. Copolymer of PHBV, is not tough and stiff if compared to PHB, so it can be applied in packaging⁷⁶. Also, it possesses a lower melting point and therefore a wide melt-processing window^{76–79}. In fact, by enhancing fraction of hydroxyvalerate (HV), the copolymer becomes tougher (increased impact strength) and more flexible (reduced Young's modulus), with decreased tensile strength^{59,72,80–82}. As a rule, disadvantages of PHBV are low elongation at break, slow crystallization rate, and therefore difficult processing^{63,83–84}.

Among PHAs, copolymers of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate), PHBHx, with low 3HHx residue are identified as one of the most useful members (if compared to PHB) due to its suitable mechanical properties for application as flexible films⁸⁵. An investigation of Escapa et al. showed production of poly(hydroxy-6-acetylthiohexanoate-*co*-4-acetylthiobutanoate) produced by *P. putida* KT2442 on a mixture of 6-acetylthiohexanoic acid⁸⁶.

PHAs have good thermal stability (up to 200 °C), with improved mechanical properties and good processing ability. *mcl*-PHA with decreased T_g is soft and elastic, making it suitable for biomedical applications⁶². The chemical structure and monomer

composition are efficiently influence the material and physical characteristics of PHAs^{29,87,88}. Rigid *scl*-PHAs with decreased mechanical properties is not suitable for biomedical and packaging applications. However, elastomeric *mcl*-PHAs show low mechanical strength. Incorporation of hydrophilic groups in hydrophobic PHAs make it suitable for biomedical applications, e.g., as drug carrier. Graft copolymerization of the PHAs, which is another strategy of modification, shows the advantages of both synthetic and natural polymers to produce new diversified PHAs⁶².

Blending

To reduce brittleness of PHB or PHBV, they can be mixed with other biodegradable materials. For this purpose, the nucleating agents are added, and then smaller spherulites with improved mechanical properties are produced. The morphology, processing conditions, glass temperature transition and crystallinity influence the properties of the blend^{59,60}. As a rule, blending has been known as a strategy of tailoring the properties of PHAs while maintaining biodegradability⁶⁷. Blending of PHB and PHBV with other biopolymers including starch^{89–91}, thermoplastic starch, PLA⁹², PCL^{13,93,94}, and polyvinyl alcohol (PVOH)⁹¹ are reported.

In addition, there are some reports on PLA blending with different polymers e.g. PCL,⁹⁵ ethylene vinyl alcohol (EVOH),⁹⁶ ethylene copolymer⁹⁷. The increasing of compatibility of the blends is necessary to improve properties of polymer. In most systems, PLA and other polymers are immiscible.

In any case, limitation of blending with other polymers is chemical incompatibility. To improve the mechanical properties of PHB or PHBV, and to increase the rate of degradation of those polymers, they can be mixed with other polymers or additives^{98,99} including nucleating agents (e.g. plasticizers as glycerol, saccharin, tributyrin or triacetin) or processing lubricants (glycerol mono or tri stearate)^{59,60}. By obtaining plasticization, the PHBV properties are modified¹⁰⁰.

For application of blends in food packaging, polymer should protect foodstuff against light, water, or oxidative process¹⁰¹. The crystalline phase has an important impact on mechanical and permeation properties; thus, much research has been conducted on increasing crystallinity of polymers. For PLA, incorporation of high crystalline PHB to PLA matrix by melt blending is a way to increase PLA crystallinity and regulate its properties²⁰. PHB has also been proposed for application in short-term food packaging²¹. Because of similar melting temperature of PHB and PLA, these polymers can easily blend, which results in increased barrier proper-

ties against oxygen and water transfer, but reduces the inherent high transparency of PLA^{11,12}. Transparency is a significant issue in the development of materials intended for food packaging¹⁵. Moreover, packaging materials should protect food from ultraviolet light¹⁰². Therefore, the development of transparent films with increased UV protection is relevant in packaging industry¹⁰³. PHB acts as a better light barrier in ultraviolet and the visible light regions²¹ in comparison to PLA.

Also, functionalized PHAs have side-chain cross-linking and reduced crystallinity. Insertion of some particular monomer into the polymeric chains may lead to improved thermal stability and reduced melting temperatures²⁹. Hazer *et al.* (2012) reviewed functionalization and grafting reactions for improving the thermal, mechanical, and hydrophilic properties of PHAs⁶².

Nanocomposite film of PHA

Introduction of nanocomposites based on PHAs and inorganic or organic nanofillers may bring about improved opportunities for their application in food packaging¹⁰⁴. Incorporation of nanofillers into a polymer may efficiently modify biodegradation rate, crystallization behavior, morphology, stability, as well as mechanical, thermal, and barrier properties. A polymer composite is a mixture of particular organic or inorganic fillers (certain geometries e.g. flakes, fibers, particulates, and spheres) with polymers. For nanocomposite production, the fillers should have at least one dimension in the nanometric scale. Isodimensional nanoparticles (semiconductor nanoclusters or spherical silica nanoparticles) have three nanoscale dimensions. Two dimensions of nanotubes or whiskers are in the nanometer scale, while in the composites named polymer-layered crystal nanocomposites, only one dimension is in the nanometer. The latter case is usually obtained by the intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of layered host crystals¹⁰⁵.

Much research is involved in the incorporation of montmorillonite (MMT) clay as the nanocomponent in very different polymers, e.g., nylon, PE, starch and PVC. Additionally, some nanocomposites for food packaging (especially for beverage) applications are in the marketplace or being developed with the extraordinary benefits to improve food packaging⁵.

PHAs nanocomposites filled with layered silicates such as MMT, layered double hydroxides (LDHs), multi-walled carbon nanotubes (MWCNTs), and cellulose nanowhiskers (CNWs) are reported¹⁰⁶. The property improvement is in direct correlation with increased nanofiller dispersion. Cellulose

nanocrystal (CNC) is an ideal biodegradable and biobased nanoparticle¹⁰⁷ which showed suitable mechanical properties, high stiffness, biodegradability, low density¹⁷ and availability in nature with low cost¹⁰⁸. A novel combination of PLA-PHB blends and functionalized CNCs showed a new perspective for their industrial application as food packaging in short-term¹¹.

Other roles of nanotechnology in food packaging

Nanotechnology has potential for application in food industry¹⁰⁹ and processing as new tools for molecular and cellular biology, new materials for pathogen detection, disease treatment delivery systems, food packaging, and delivery of bioactive compounds to target sites.

Two main categories of nano-application in food industry is nanopackaging and nanoencapsulation via various vehicles like liposome¹¹⁰.

Nanotechnology efficiently influences the packaging industry and leads to some improvement in packaging properties (e.g. barrier properties, flexibility, and stability), shelf life (with antimicrobial or oxygen scavenging properties), food safety (nanosensors), and biodegradability¹¹¹. Recently, the ability of producing highly ionic metal oxide nanoparticles with different size and shape, have enabled the development of new antibacterial agents¹¹². Antimicrobial active packaging is made by incorporating metal high-performance nanoparticles into polymer films. The high ratio of surface area to volume is the main reason for enhanced antimicrobial activity of metal and metal oxide nanomaterials antimicrobial agents^{113,114} like Au, Ag, SiO₂, ZnO, Al₂O₃, MgO, TiO₂, Fe₃O₄ and Fe₂O₃. The nanoparticles of ZnO and TiO₂ compared to Ag are safer for food packaging¹¹².

Roles of nanotechnology for improvement of PHB properties for application in food packaging

Mechanical properties

For application of PHAs in food packaging, the lack of adequate flexibility is the main significant problem. Although blending may reduce brittleness, the incorporation of nanofillers into PHAs may result in higher Young's modulus. In order for these nanopackaging materials to compete with petrochemical-based polymers applied in food packaging, significant improvement of the flexibility of PHAs by means that will not compromise their other properties is necessary¹⁰⁸.

Permeability

Potentially positive properties of PHB and PHBV films with respect to food packaging applications are water vapor permeability (similar to that of PVC or PET^{115–119}), non-swelling behavior, and lower hydrophilicity (compared to other biopolymers e.g., cellulose, starch, chitosan and gluten)¹¹⁵. Besides, solubility and diffusivity of water in PHAs is a key factor for their degradation via enzymatic or non-enzymatic hydrolysis^{120–122}. The water transport properties of PHB and PHBV films and their blends with other biodegradable polymers in different process conditions are reported^{65,94,115–117,120,121,123–125}. PHAs can decrease the water sensitivity of other biopolymers⁹⁴. PHAs shows suitable barrier properties against different organic solvents^{115,116,126} and possess low oxygen and CO₂ permeability^{65,77,126–129}. Sanchez-Garcia *et al.* reported lower water vapour permeability for PHB compared to PHBV¹²². The impact of crystallinity on permeability properties of PHAs is discussed^{93,115,120,130,131}. As a rule, decreased oxygen permeability of PLA, PCL, PET and PP is reported by incorporation of nanoclays. Further investigation into the improvement of PHA barrier properties following incorporation of nanofillers is needed⁹³.

Thermal stability

A main limitation of PHAs in processing is their thermal instability^{83,132}. Various strategies for improvement of thermal stability have been reported using thermal gravimetric analysis, differential scanning calorimetry and pyrolysis GC/MS¹³³. The thermal degradation of PHAs near the melting temperature is the result of a non-radical random chain-scission reaction, and the depolymerization of the macromolecular chains is the controlling stage¹³³. Thermal instability is important at temperatures above 200 °C¹³⁴. As a rule, increasing the HV residues in a PHBV copolymer causes reduced melting point. So, the processing temperature is enhanced and degradation rates are maintained in an acceptable range¹³³. Blending as a technique for raising the thermal stability of PHAs has been reported¹³³.

Incorporation of inorganic nanofillers, including LDHs and MMTs, can improve thermal stability of PHAs^{11,12,64,68,78,79,132,134–139} attributed to the dispersed silicate layers acting as a barrier to volatiles and O₂ produced during thermal decomposition^{64,135,140} of PHAs. Thermal degradation of nanocomposites is affected by the degree of dispersion, because accumulation may lead to generation of local heat^{68,135}.

Migration from package to food

Migration is a key issue for selection of monomers or additives in PHA for food packaging purposes. Uncommon additives in contact with food materials may conceivably migrate into food. There is no report on the investigation of the migration of specific components from PHA packaging. The total migration from PHB films into different food models, e.g., distilled water, 15 % ethanol, 3 % acetic acid, and *n*-heptane is reported²¹. All samples showed a total migration less than the recommended limit of 8.0 mg dm⁻² or 50 mg kg⁻¹, which indicates safety of PHAs film for packaging of different food products.

In European legislation, some special issues have to be considered in bio-based food contact materials¹⁴¹. Biodegradability, migration and shelf-life of the product should be considered in food packaging. Degradation must be inhibited during storage, and should only start after discarding¹⁴². Pure PHB and PHBV are non-toxic, but further investigations are required regarding the potential migration of degradation products produced during either processing or biodegradation⁶⁴.

Additionally, migration of nanoparticles from PHA films into food matrix should be considered because they are much more reactive compared to macro-scale particles. The high value of surface area of nanoparticles leads to increased contact and higher capacity for absorption and migration¹⁴³. Migration from packaging material and toxicological effects of nanoparticles in food needs more investigation¹³¹. Šimon *et al.* reported the theory of particle migration from nanocomposites and suggest that nanoparticles with a diameter of about 1 nm may migrate¹⁴⁴. Migration of Fe, Mg, Si from biodegradable starch/nanoclay nanocomposite films to model system are reported^{145,146}.

Biodegradation

A reduced rate of biodegradation of PHB or PHBV has been reported by increasing nanoparticle content⁸⁴. Such observation can be attributed to the difficulty of penetration of microorganisms into the bulk of the material due to formation of a tortuous path caused by nanoparticles^{84,147}. Also, decreased water permeability and antimicrobial effect of nanoparticles, such as MMTs, influence the reduction in the biodegradation rate⁷⁷. However, an increased biodegradation of toughened PHB containing modified MMT are reported due to the terminal hydroxylated edge groups of the silicate clay layers that can absorb moisture from compost and act as initiation sites for polyester hydrolysis¹⁴⁸. As a rule, any factor which increases the hydrolytic tendency of PHAs may facilitate degradation¹⁴⁹.

Also, well-dispersed clay particles lead to more rapid fragmentation of the polymer and therefore increased degradation¹⁵⁰. The presence of 2 wt % organo-modified fluoromica¹⁴⁷ and low temperatures increased the biodegradation rate of PHB. Inhibition of growth of microorganisms may occur at high temperature (above 60 °C). In addition, crystalline polymer is important since the amorphous inter-spherulitic regions are prone to hydrolysis followed by microorganism attack.

Investigation of influencing factors on the rate of PHA nanocomposite degradation is the subject of future trends. It has been shown that tomatoes stayed fresh in PHB-coated paperboard trays if compared to those wrapped in perforated low-density PE bags¹⁵¹. In addition, Haugaard *et al.* explored packaging of an orange juice simulant in PHB cups. The results showed that the performance was as good as that of high-density, and superior when samples were stored under light¹⁵². Hermida *et al.* showed that there was no significant reduction in PHB properties when exposed to the levels of gamma radiation needed to sterilize food or packaging materials¹⁵³.

Conclusion

Conventional plastics for food packaging are not renewable and biodegradable, resulting in environmental problems. Plastic recycling is not often economical and practical due to contamination of the food packaging. A shift toward biodegradable food packaging is one option. In addition, polymer characteristics such as permeability to gases, humidity, and odours remain a concern.

The cost is the most important limiting factor of application of PHAs in food industry. Although PHAs are still relatively expensive compared to petroleum-derived plastics, application of mixed cultures using various waste streams and scaling up of the process are proposed as an effective way to reduce these costs.

For application of PHAs in food packaging, the lack of adequate flexibility is the main significant problem. Although blending them may reduce brittleness, the incorporation of nanofillers into PHAs may result in higher Young's modulus and increased toughness of PHB. Further investigation on the improvement of PHA barrier properties following incorporation of nanofillers is needed. Also, decreased water permeability and antimicrobial effect of nanoparticles, such as MMTs, reduce the biodegradation rate. Solutions for this limitation cannot be fixed without continuing research and development over the coming years.

Further investigations are required regarding the potential migration of degradation products pro-

duced during either processing or biodegradation. There are presently no data available concerning the migration of PHA packaging materials, e.g., degradation products, nanoparticles to food.

A new strategy is under development to design, create or model gas-barrier with efficiently optimized characteristics. Research has been focused on development of cost-effective scaled-up production. The incorporation of sufficient dispersed nanocomposite into packaging materials suggests a new strategy for preserving and extending the microbial shelf life of temperature-sensitive foods in refrigerator. The addition of active agents (e.g. antimicrobial, antioxidant, oxygen-scavenging, etc.) and/or combining pasteurization with antimicrobial nanocomposite packaging may result in the development of a cost-effective method to control microbial growth and preserve the desirable quality. Nanocomposite packaging are predicted to make up a significant portion of the food packaging market in the near future, providing multiple functionalities, i.e. combined physical reinforcement and active performance. Investigation of influencing factors on the rate of PHA nanocomposite degradation is the subject of future trends. Also, further genetic and enzymatic studies are needed to elucidate the relationship between metabolism and PHA biosynthesis.

Nomenclature

PHB – poly(hydroxybutyrate)
 PET – poly(ethylene terephthalate)
 PVC – poly(vinylchloride)
 PE – poly(ethylene)
 PP – poly(propylene)
 PS – poly(styrene)
 PA – poly(amide)
 PHA – poly(hydroxyalkanoates)
 PLA – poly(lactic acid)
 PCL – poly(caprolactones)
scl – short chain length
mcl – medium chain length
lcl – long chain length
 PHO – poly(3-hydroxyoctanoate)
 T_g – glass transition temperature, °C
 PHBV – poly(hydroxybutyrate-co-hydroxyvalerate)
 PHBHx – poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)
 3HHx – hydroxyhexanoate
 HB – hydroxybutyrate
 HV – hydroxyvalerate
 PVOH – poly(vinyl alcohol)
 MMT – montmorillonite
 LDHs – layered double hydroxides
 MWCNTs – multi-walled carbon nanotubes
 CNWs – cellulose nanowhiskers

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