

Potential of polyhydroxyalkanoate (PHA) polymers family as substitutes of petroleum based polymers for packaging applications and solutions brought by their composites to form barrier materials

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Conference paper

Gülsah Keskin, Gülnur Kızıl, Mikhael Bechelany, Céline Pochat-Bohatier* and Mualla Öner*

Potential of polyhydroxyalkanoate (PHA) polymers family as substitutes of petroleum based polymers for packaging applications and solutions brought by their composites to form barrier materials

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Abstract: Today, there is an increasing concern about protection of ecological systems. Petro-based synthetic polymers are not biodegradable and cause environmental pollution. These polymers that are stuck in nature, affect wildlife adversely. Also, in future petrochemical materials will drain away and demand for eco-friendly plastics which can substitute synthetic plastics will increase. Biopolymers are products which can be degraded by enzymatic activities of various microorganisms, and the degradation products are nontoxic. They are attractive alternatives to non-degradable materials in short-term applications such as packaging. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a member of polyhydroxyalkanoate (PHA) family which is biodegradable and produced by microorganism. It has good gas barrier properties that make it convenient to use in different applications. The present paper gives an overview on PHAs and their composites, their main properties, with a specific focus on potential applications of PHBV in packaging.

Keywords: composite materials; materials science; nanocomposites; NICE-2016; polymers.

Introduction

Biopolymers are obtained from renewable and bio-sources. They are usually degraded biologically and they are nontoxic. Their mechanical, thermal and barrier properties are not as good as petro-based polymers. These problems have ensured to initiate improving of biopolymer properties [1–5].

Recently many efforts have been made to develop bio-based composite materials. "Green" composites originate from reinforcements of biodegradable polymer matrix by natural nano-fibers like plant and natural fibers present improved mechanical properties [1–5].

The advantage of composites is to utilize the properties of both the components in the system or to impart new properties to the component by adding suitable fillers. Polymer nanocomposites are mixtures of polymer and nanometer length scale particles, whereas, conventional polymer composites contain micrometer scale

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***Corresponding authors: Céline Pochat-Bohatier,** Institut Européen des Membranes, UMR 5635, Université de Montpellier, CNRS, ENSCM, Place Eugéne Bataillon, F-34, Languedoc-Roussillon, France, e-mail: Celine.Pochat@umontpellier.fr; and **Mualla Öner,** Yildiz Technical University Chemical-Metallurgical Faculty, Chemical Engineering Department, Istanbul, Turkey, e-mail: oner@yildiz.edu.tr; muallaoner@gmail.com
Gülsah Keskin and Gülnur Kızıl: Yildiz Technical University Chemical-Metallurgical Faculty, Chemical Engineering Department, Istanbul, Turkey
Mikhael Bechelany: Institut Européen des Membranes, UMR 5635, Université de Montpellier, CNRS, ENSCM, Place Eugéne Bataillon, F-34, Languedoc-Roussillon, France

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particles. The concept of nanocomposite is based on creating a very large interfacial area between the nano sized fillers and the polymer matrix, per unit volume of the material to enhance the polymer properties. The advantages of nanocomposites over macrocomposites include reduced filler amount and better properties than obtained for the conventional composites [5–7].

This paper deals with the potential interest of substituting petroleum based polymers such as polyethylene, polyethylene terephthalate by polyhydroxyalkanoate (PHA) polymers, by focusing especially on PHBV and gas barrier properties. We give an overview about bio-nanocomposites prepared with these bio-based polymers.

Polyhydroxyalkanoates and derivatives

In nature, the bacteria produce PHAs by fermentation of sugar or lipids with the aim to store carbon and energy. PHAs are member of biopolymers that consist of different kinds of monomers (3-hydroxybutanoic acid, 3-hydroxypentanoic acid). Development of biocomposite by combining PHA and various additives allows the applications of these biocomposites on various fields such as eco-friendly packing materials, fibers, biodegradable and biocompatible implants and controlled drug delivery carriers [1–5].

Polyhydroxyalkanoates are a biopolyester family that has a variety of structures. They can be synthesized from 30 % of bacteria which live in soil, in a wide range of environmental conditions and media. PHAs display very versatile materials that raise the attention of different industrial applications. As the best known application, PHAs are of interest for packaging purposes. The global demands for packaging are increasing, especially for safe covering and transportation of goods. Therefore packaging constitutes the most important application of PHAs in terms of quantity. Polyhydroxybutyrate and its copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are most known PHAs [8, 9].

Polyhydroxybutyrate (PHB) is a naturally occurring β-hydroxyacid produced by enzymatic synthesis of a large variety of bacteria kinds or different chemical ways. PHB is an isotactic semi-crystalline polymer resulting of breaking of hydrolytic ester linkage. Its melting point is between 160 and 180 °C. The brittleness is a major problem for PHB in processing. This problem limits PHB's applications. To improve PHB's properties, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) copolymers are produced by replacing methyl group in PHB's main chain with the ethyl group. These microbial copolymers are synthesized from the propionic or pentanoic acid by *Alcaligenes eutrophus* bacteria. The addition of polyhydroxyvalerate (PHV) in PHB matrix enhances the processability of the polymer due to reduced brittleness. PHB and PHBV have similar semi-crystalline properties with PHB but it also depends on 3-HV content (Fig. 1) [10–12].

The properties of PHBV with different HV contents are summarized in Table 1. Mechanical properties of PHBV are highly improved when compared to PHB. The melting point of copolymer reduces as the composition of HV increases. Copolymers can be processed by extrusion, injection molding and solution casting methods [10–12, 14].

Thus, the main advantages in using PHA, PHB or PHBV in industry lie on their thermoplastic properties while being biodegradable. However, whereas various biodegradable polymers can be directly extracted from biomass, PHAs are only produced by microorganisms. Their high manufacturing costs make these polymers rather used in areas where added value polymers are needed. Now, the points which could insure to PHBV

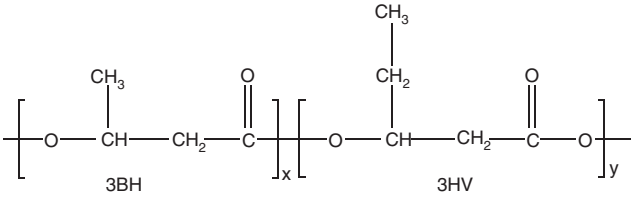

Fig. 1: Chemical structure of PHBV.

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Table 1: Thermal and mechanical properties in different PHV content (25 °C) [13].

HV content % (M)	Melting point (°C)	Glass transition temperature (°C)	Tensile stress (MPa)	Elongation (%)	Elastic modulus (GPa)
0	175	9	45	4	3.8
11	157	2	38	5	3.7
20	114	−5	26	27	1.9
28	102	−8	21	700	1.5
34	97	−9	18	970	1.2

large packaging applications are improved gas transfer properties compared to conventional polymers and optimization of the production costs coming from the necessary stages of bacterial culture and purification/separation procedures.

Applications of PHAs and related biocomposites

Biopolymers have many advantages when compared to synthetic polymers especially in tissue engineering. Biopolymers are used clinically in scaffolds, bone, skin and other parts in human [15]. Biopolymer composites have sensors, motion transducers, electromagnetic shielding materials and microwave absorbers applications in electronic industry [16].

Possible uses of PHA are very broad. PHAs are important materials for application in the medical field as a result of their biocompatibility. PHAs were successfully investigated as bone implant materials, for tissue engineering, as implants, surgical pins, screws, vein valves. The products used as carrier materials and degradable matrices can be produced from PHAs and are desired in many fields, such as agriculture, food technology, or pharmacy. Compounds can be released from these matrices at controlled rates include drugs, hormones, pesticides, antibiotics, dyestuffs, or flavors [17–19].

The gas barrier properties of PHBV in particular make it a good candidate for producing food packaging or plastic beverage bottles. Polyhydroxyalkanoate can be used in coated cardboard and film materials used in coated milk bottles in the same manner. PHB is also used as a plastic coating for sanitary napkins and towels to prevent moisture or gas permeability in medical area [20]. US based company Metabolix produced an elastomer using PHB and poly(3-hydroxyoctane) blend, and this elastomer was approved to use as a food additive. Another PHA type has been produced in order to make binders, flexible packaging, thermoform products, synthetic papers and medical devices in a project made in collaboration with BioTech, KAIST and P&G partnership. PHB is used in surgical threads or implants that do not require a secondary medical procedure due to its biodegradability, as well as in microcapsules or tablet packing areas [20, 21].

Gas barrier applications of biocomposites

In recent years, the number of scientific papers on bio-based polymers and products is still growing rapidly while it remains at a constant level for traditional fossil-based polymeric materials. Recently, production of bio-packaging materials is emphasized. These studies are particularly relevant to food packaging. The properties required for food packaging are listed on Fig. 2. Among these properties, next section will focus on gas barrier properties of PHAs. Actually, the most widely used bioplastic in the packaging industry is polylactic acid (PLA) [22]. However, polyhydroxyalkanoates (PHA) and particularly polyhydroxybutyrates (PHB) represent also good candidates especially when associated to nanofillers. The next section presents studies devoted to the preparation of composites with organic and inorganic fillers.

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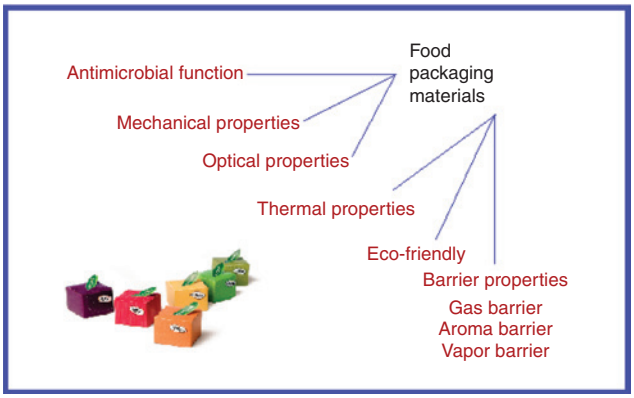

Fig. 2: General properties of bio food packaging materials.

Biopolymer composites with organic fillers or plasticizer

Hassaini et al. produced PHBV/olive husk flour (OHF) composites using melt blending technique. They investigated the effect of the filler and the surface modification on oxygen and water vapor permeability by using silane treated and untreated OHF. The results showed that silane treatment improved compatibility between the two components and decreased oxygen permeability of the biocomposite by almost 62 % when compared to untreated OHF. However, oxygen and water vapor permeability of the composites were similar to neat PHBV material [23].

Malmir et al. worked on PHBV/cellulose nanocrystal (CNC) composite and improved oxygen barrier properties. Oxygen transmission rate of PHBV was reduced significantly with CNC nanoparticles. This can explain by the positive effect of CNC on the crystallinity of nanocomposites and by more tortuosity in their morphology. They showed that good dispersion of CNC in PHBV could be obtained up to 4 wt.% and demonstrated the nucleating effect of CNC in PHBV matrix [24].

Pardo-Ibáñez et al. studied the improving of barrier properties of keratin/PHBV composites. Melt blending has been used for producing composites with different keratin contents. When compared to pure PHBV, 1 % keratin/PHBV composite has lowest oxygen permeability value. It decreased from 3×10^{-18} to 1×10^{-18} m^3 m/(m^2 s Pa) for 1 % keratin loading. Higher loadings have impacted adversely on permeability. The reason of these results was interpreted as the homogeneity of filler in the matrix and increasing tortuosity. But optimum content can change depending on chemical and size and shape of particles. Moreover, for more than 3 % keratin loadings, the crystallinity of materials has reduced and agglomeration has formed [25].

Kovalcik et al. [26] combined PHBV with lignin and investigated their oxygen, and carbon dioxide permeability. The gas permeability was decreased by combining PHBV with 1 wt.% lignin. The permeability reduction for oxygen by 77 % and by 91 % for carbon dioxide, respectively, was observed if compared to the neat PHBV specimens. Carbon dioxide permeability coefficient is higher than oxygen but it is compatible with the permeability of many polymers. The performance of oxygen and carbon dioxide barrier was associated with homogeneous dispersion of lignin [26].

PHBV-bacterial cellulose nanowhiskers (BCNW) nanocomposite with various hydroxyvalerate contents was studied and characterized by Martinez-Sanz et al. [27]. PHBV samples which contain 7.3 mol% valerate (PHBV7) and 40 mol% valerate (PHBV40) were used in the study. A significant decrease in the oxygen and water barrier properties of the PHBV films was observed with the increase in the content of the valerate. In general, barrier properties improved with the presence of 1 % BCNW. The oxygen permeability decreased from 8.16×10^{-19} to 5.24×10^{-19} (m^3 m/m^2 s Pa) from PHBV7 and 1 % BCNW composite; from 10.76×10^{-19} to 9.45×10^{-19} (m^3 m/m^2 s Pa) for PHBV40 and 1 % BCNW composite [27].

Jost and Langowski investigated the change in mechanical and barrier properties of PHBV with the use of various plasticizers. Propylene glycol, glycerol, triethyl citrate, castor oil, epoxidized soybean oil and polyethylene glycol were the plasticizers studied. The results showed that plasticizers increased crystallinity of PHBV

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and affected adversely on mechanical properties, but however some plasticizers improved barrier properties of PHBV. Plasticizers which contain ketone and ether groups found as suitable plasticizers for PHBV and they are capable of interacting with PHBV. Plasticizers with low molecular weight have no effect on PHBV. The most effective plasticizer for oxygen and water vapor permeability found was glycerol at 5 wt.% [28].

Shogren has studied the water vapor permeability of various biodegradable polymers. According to the results, water vapor permeability increased with temperature for all biodegradable polymers. There is an increase in permeability with the content of hydroxyvalerate for PHBV. Among the biodegradable polymers, PHBV have lowest water permeability [29].

Martínez-Abad et al. worked on PHBV-thermoplastic polyurethane (TPU) blends to improve mechanical and barrier properties. The addition of TPU has resulted in increased water vapor permeability of PHBV. This is due to the lack of interaction between the two phases and the increase in free volume during the formation of the mixture [30].

Boufarguine et al. have worked on improving the gas barrier and mechanical properties of PLA/PHBV films. PHBV has been used to improve the barrier properties of PLA, because PLA has very high gas permeability value when compared to PHBV. The composite production with multi-layer co-extrusion technique has been carried out. They measured only the helium permeability but results showed that compared to pure PLA it decreased in the presence of PHBV layers [31].

Zembouai et al. worked on the barrier properties of PHBV/PLA mixtures. In the study, PHBV was found to have better barrier properties than PLA. The crystal structure of PHBV is the main factor explaining this situation. The barrier properties improved with the increasing PHBV ratio in the prepared mixtures, while the oxygen permeability coefficient of PLA decreased. This suggests that PHBV supports the barrier performance for PLA even at minor proportions [32].

PHBV-functionalized graphene sheets (FGS) composites produced by Ambrosio-Martin et al. and their oxygen permeability property were investigated. A reduction in oxygen permeability was observed with the addition of FGS. And for PHBV and 3 wt.% FGS composite, 41.2 % permeability drop obtained [33].

Biopolymer composites with inorganic fillers

Castro-Mayorga et al. produced nanocomposites using zinc oxide (ZnO) particles as fillers for PHBV in various sizes and characterized these nanocomposites. According to the results obtained in the study, there was a decrease in the barrier properties of the PHBV with respect to the hydroxyvalerate percentage and the interaction of the ZnO particles with the PHBV matrix [34].

Öner et al. studied the boron nitride BN/PHBV nanocomposites. The gas barrier properties of PHBV were improved with BN particles. Polymer films were prepared by extrusion method. When compared to neat PHBV, oxygen barrier properties of composites decreased with BN addition and reached 0.12 cm^3 cm/(m^2 day atm) with 3 wt.% BN loading [35].

The steadily increasing numbers of studies on composites of PHAs have been developed in recent years. Corrêa et al. studied PHBV and clay composite to decrease their oxygen permeability. PHBV biodegradable bacterial copolyester and organomodified montmorillonitride (OMMT) clay and plasticizer were used and their thermal, mechanical, permeability and biodegradation properties have been investigated. Oxygen permeability values of PHBV and PHBV/OMMT composite without plasticizer were 0.47 and 0.41 cm^3 cm/(m^2 day), respectively. Plasticizer increases matrix mobility and free volume. So adding plasticizer has increasing the permeability. By contrast with this, adding nanofillers has decreased permeability due to increasing tortuosity. Oxygen permeability values of PHBV and PHBV/OMMT composite with plasticizer obtained as 2.57 and 1.70 cm^3 cm/(m^2 day), respectively [36].

Farmahini-Farahani et al. [37] worked on organomodified clay-PHBV composites and tested their barrier properties. The PHBV matrix with clay mineral additive showed a great improvement on water permeability (WVTR). The WVTR of PHBV/clay nanocomposite films reduced from 50 g/(m^2 day) (at 90 RH % and 38 °C) and 12.1 g/(m^2 day) (at 50 RH % and 23 °C) to 18.4 g/(m^2 day) and 4 g/(m^2 day) for 10 wt.% clay content [37]. The

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Table 2: Literature values of P_{O2} of PHBV.

%HV	T (°C)	RH (%)	P_{O2} (cm³ mm/(m² day atm))	Ref.
3	23	80	1.8	[34]
3	25	80	2.2	[39]
5	25	80	5.9	[40]
5	23	0	4.9	[41]
7	24	0	7.1	[27]
8	21	40	8.7	[42]
8	23	0	6.2	[41]
8	23	0	1.5	[35]
12	24	80	12.6	[43]
12	24	80	15.6	[44]
12	24	80	26.6	[25]
12	24	80	12.2	[25]
12	23	0	3.9	[41]

clay mineral causes an increase in effective path length for the diffusion of water vapor through the polymer matrix.

Sanchez Garcia et al. worked on barrier performance of poly(ethylene terephthalate) (PET), poly(lactic acid) (PLA), polyhydroxyalkanoates (PHB, PHBV), polycaprolactone (PCL) and their nanocomposites with montmorillonite (MMT). According to oxygen permeability results, PHB and PHBV nanocomposites have the lowest oxygen permeability compared to all other biodegradable polymer composites. Oxygen permeability values of PHB and PHB/5 wt.% MMT composite obtained as 2.24×10^{-19} and 1.78×10^{-19} m^3 m/(m^2 s Pa); PHBV and PHBV/5 wt.% MMT composite 15.7×10^{-19} and 11.5×10^{-19} m^3 m/(m^2 s Pa), respectively [38]. The oxygen permeation values of PHBV reported by different research group are shown in Table 2.

Overall, the reported studies emphasize the need for a good characterization of the fillers because their properties will directly influence the composite structure and therefore the gas permeability coefficient. The nature of the fillers may be organic or inorganic. The filler morphology (shape, size) and its concentration will affect its dispersion. Generally speaking, there is a threshold not to be exceeded to insure a good dispersion. Above it, agglomerates may be formed and lead to structure heterogeneity with higher permeation rates. The interest of using fillers at the nanoscale is to allow filler intercalation between polymer chains. One parameter of utmost importance is the surface chemistry which will govern the interactions between polymer and fillers. Preliminary treatment of fillers can positively favor these interactions and thus the fillers dispersion. Coating the surface of the fillers with an appropriate organic binding agent is an effective method for providing nanophase dispersion in the polymer matrix. Trimethoxyoctadecylsilane (TMOS) was successfully used for decreasing hydrophilic character of olive husk flour to favor the interfacial adhesion with PHBV [23]. The reduction of the gas transfer coefficients in the composite is generally attributed to a modification of the crystallinity and to morphology with more tortuosity. The reduction of the polymer chain mobility and of the free volume will reduce the gas diffusion coefficient. The gas permeability of composite materials will thus be reduced. It is difficult to predict to which extend one parameter can affect the permeability. At last, preparing a (nano)composite to improve gas barrier property must also be done by taking care of the mechanical properties. Antagonist impacts can be brought to the material. A bad dispersion of fillers can affect negatively the mechanical properties and thus a work on formulation, by adding plasticizer or binding agent for instance, may therefore become necessary. The increase in hydroxyvalerate content conducts to an increase in permeability values [27, 29] whereas it is needed to reduce material brittleness.

PHAs have properties close to traditional plastics such as low density polyethylene (LDPE), polypropylene (PP) which makes them suitable for industrial uses especially in packaging (see Table 3).

The increasing demand of environmentally friendly materials and of clean technologies for waste disposal suggests that PHAs can be rapidly accepted all over the world. Particularly the low gas permeability properties of PHAs and their composites' could lead to applications in food packaging. PHBV offers the suitable gas barrier properties for use in coated paper and films. Nonbiodegradable polyethylene coating is

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Table 3: Comparison of properties of PHB, PHBV with PP and PE [8, 26, 45, 46].

Properties (unit)	PHB	PHBV	PP	PE
Melting temperature (°C)	175	145	170	110
Glass transition temperature (°C)	4	−1	−10	−110
E modulus (GPa)	3.5	0.8	1.5	0.2
Tensile stress (MPa)	4	20	38	10
Elongation at break (%)	5	50	400	600
Crystallinity (%)	60	40–60	50	50
Oxygen permeability (cm^3 cm/(m^2 day MPa))	2	4.9–16.5	67.7	100.7
Carbon dioxide permeability (cm^3 cm/(m^2 day MPa))	3	144.0	228.9	789.5
Water vapor permeability (cm^3 cm/(m^2 day MPa))	1–5	1–3	0.2–0.4	0.5–2

currently used for this purpose preventing either biodegradation of the paper or recycling of the cellulose fibers. PHBV coated paper has been shown to be completely biodegradable and also easier to recycle compare to conventionally coated paper.

Conclusion and future perspective

In recent years, significant studies have been carried out on development and industrial applications of biodegradable polymer composites in terms of their inherent properties, biodegradability, accessibility, processability and physico-mechanical properties.

PHAs are suitable nominees for future replacement of synthetic plastics in future. The large scale use of these polymers' composites is limited due to their cost. Currently, many efforts have been made to develop the properties of the PHAs with different additives by lowering the production costs worldwide. Especially, PHA nanocomposites which are produced with nanosized fillers, have reached the level at which they can compete with the properties of petro-based plastics, making them usable in the packaging industry. PHAs are of enormous interest for producing packaging materials because of their high barrier properties towards oxygen permeation. Therefore usage of PHAs as packaging materials prevents the oxidative spoiling of products. Compared to the classical packaging material HDPE, food quality is at least as good when PHA is used. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) also received European approval for food contact use in 1996. We can conclude that important progress has already been achieved in terms of combining nanofillers with PHAs, regarding the high number of available data from literature.

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