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# Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH): synthesis, properties, and applications - A Review

Kerim Eraslan<sup>1</sup>, Clizia Aversa<sup>2</sup>, Mohammadreza Nofar<sup>\*1,3</sup>, Massimiliano Barletta<sup>\*2</sup>, Annamaria Gisario<sup>4</sup>, Reza Salehiyan<sup>5</sup>, Yonca Alkan Goksu<sup>3</sup>

*1: Polymer Science and Technology Program, Institute of Science and Technology, Istanbul Technical University, Istanbul, 34469, Turkey*

*2: Dipartimento di Ingegneria, Università degli Studi Roma Tre, Via Vito Volterra 62, 00146, Roma, Italy*

*3: Sustainable & Green Plastics Laboratory, Metallurgical & Materials Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, Istanbul, 34469, Turkey*

*4: Dipartimento di Ingegneria Meccanica e Aerospaziale, Sapienza Università degli Studi di Roma, Via Eudossiana 18, 00184, Roma, Italy*

*5: International Institute for Nanocomposite Manufacturing (IINM), WMG, University of Warwick, CV4 7AL, UK*

\*Corresponding authors: [nofar@itu.edu.tr](mailto:nofar@itu.edu.tr) and [massimiliano.barletta@uniroma3.it](mailto:massimiliano.barletta@uniroma3.it)

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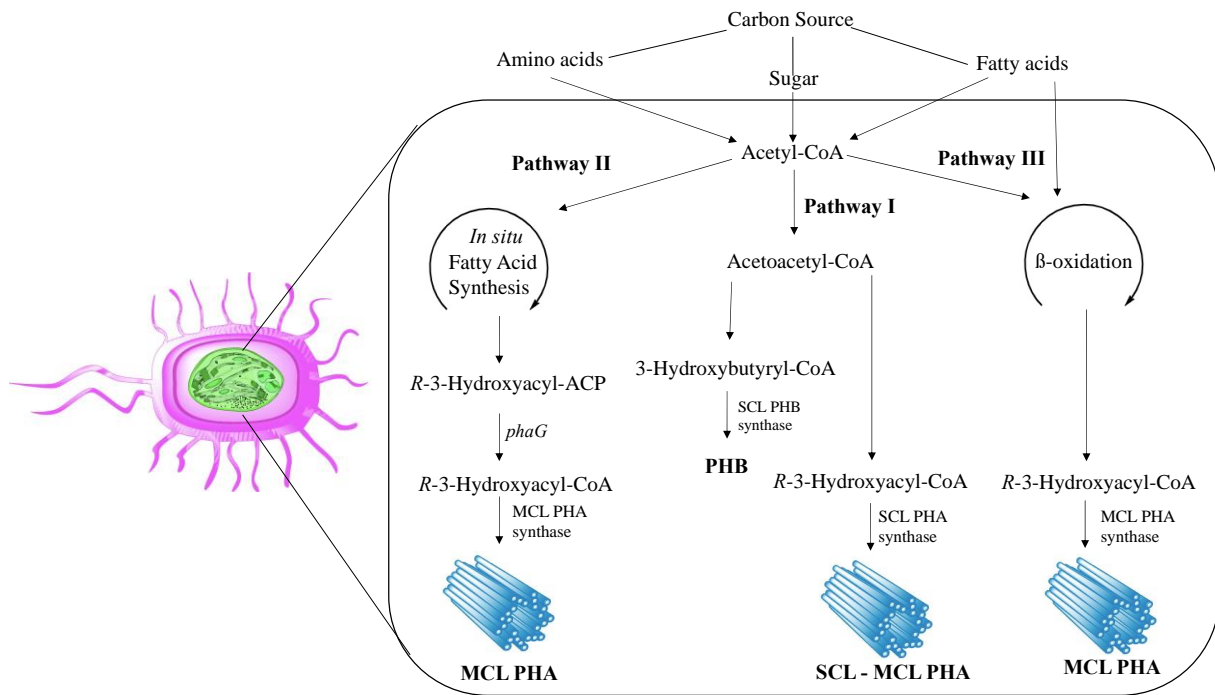
## **Abstract**

The development of biobased and environmental-friendly polymeric materials to replace petroleum-based plastics is one of the main global challenges nowadays. Among biopolymers, polyhydroxyalkanoates (PHAs) have gained increasing attention due to their compostability under environmental conditions. Copolymers of poly(3-hydroxybutyrate) (PHB) with comonomers belonging to PHA types have been developed to tackle better processability, higher ductility, and better impact properties. These common copolymers could be listed as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH). Compared to PHB and PHBV, PHBH has revealed a wider processing window with better thermal stability and more promising mechanical performance due to its tailorable composition of both highly crystalline (3HB) and elastomeric (3HH) units. The increase in 3HH unit content decreases the crystallinity and the melting temperature, which broadens the processing window with minimized thermal degradation. Therefore, PHBH could be employed in applications where both flexibility and room temperature compostability are required. However, PHBH has received minimal attention due to its low availability in the market, high cost, strict confidentiality of the polymer manufacturers, and continuous evolution in the synthesis stage. This article reviews the achievements in PHBH synthesis and the dependency of PHBH thermal, mechanical, and physical properties on the 3HH content. It also explores PHBH compostability and degradation behavior and the attempts made to develop PHBH based blends and composites. It further discusses the challenges and future perspectives for the usage of PHBH in various industrial applications.

**KEYWORDS:** Poly (3-hydroxybutyrate-co-3-hydroxyhexanoate), PHBH, PHBHHx, review

## Introduction

Polyhydroxyalkanoates (PHAs) are biobased, biodegradable, and biocompatible polyesters that could be adapted to a wide range of applications. They are synthesized within the cellular structure (*in vivo*) of different microorganisms [1]. PHAs could be accumulated as granules up to 90 % of the dry cell weight (DCW) of microorganisms under appropriate growth conditions [2,3]. Depending on **the number of carbon atoms present in the monomer**, they could be classified into short-chain PHA (SCL PHA) and medium-chain PHA (MCL PHA), which are, respectively, made up of 3-5 and 6-14 carbon atoms. The synthesis of SCL and MCL PHAs within a microorganism generally occurs through the following steps: First, carbon source diffuses through the cell membrane. Then, the anabolic and/or catabolic reactions convert the carbon source into hydroxyacyl coenzyme A, which is the substrate for the enzyme (i.e., PHA-synthase or PHA-polymerase) required to catalyze the polyesterification reaction [4,5]. Schematic representation of three essential PHA synthesis pathways, including the acetoacetyl-CoA (Pathway I), *in situ* fatty acid synthesis (Pathway II), and  $\beta$ -oxidation (Pathway III), is given in Figure 1 [6]. Metabolic engineering and synthetic biology approaches could also generate other synthetic pathways for PHA synthesis [7].

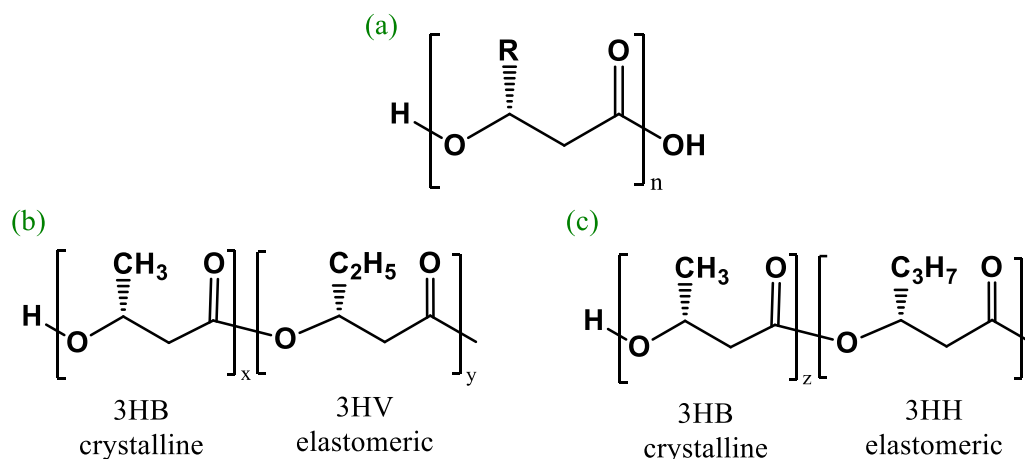


**Figure 1.** Schematic representation of three essential PHA synthesis pathways including the acetoacetyl-CoA (Pathway I), in situ fatty acid synthesis (Pathway II), and  $\beta$ -oxidation (Pathway III) [6]

Figure 2a shows the general structure of PHAs, composed of 3-hydroxyalkanoic acid units within which **number of monomer units**,  $n$ , ranges between 100 to 30,000. The  $R$  groups within the structure depend on the type of microorganism or physiological stress conditions [3,8]. So far, around 150 different PHA structures have been introduced using different microorganisms, cultures, and environmental conditions; however, only a few of them have been more commonly studied [9,10]. Table 1 illustrates the common  $R$  groups within the PHA structure and the resultant PHA polymer type.

Among the PHAs shown in Table 1, poly (3-hydroxybutyrate) (PHB) homopolymer has been the most commonly studied grade as it could be synthesized within the microorganisms without requiring further modification [11]. However, due to certain drawbacks of PHB, such as its brittleness and low toughness, copolymers of PHB with a comonomer belonging to the PHA types have been developed to tackle better processability, higher ductility, and better impact properties. These common copolymers could be listed as poly (3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV) or PHBV] and poly (3-hydroxybutyrate-co-3-

hydroxyhexanoate) [P(3HB-co-3HHx), PHBHHx or PHBH] [12]. Figures 2b and 2c illustrate the chemical structures of PHBV and PHBH copolymers where  $x$ ,  $y$ ,  $z$  and  $t$  subunits represent the number of monomeric units in the copolymer structure that could be tailored to obtain defined macromolecular structures



**Figure 2.** Chemical structure of (a) a general PHA, (b) PHBV and (c) PHBH

**Table 1.** Common  $R$  groups and the corresponding polymer names

$R$ group type	Polymer name
Hydrogen (-H)	Poly (3-hydroxypropionate) (PHP)
Methyl (-CH <sub>3</sub> )	Poly (3-hydroxybutyrate) (PHB)
Ethyl (-C <sub>2</sub> H <sub>5</sub> )	Poly (3-hydroxyvalerate) (PHV)
Propyl (-C <sub>3</sub> H <sub>7</sub> )	Poly (3-hydroxyhexanoate) (PHH)
Pentyl (-C <sub>5</sub> H <sub>11</sub> )	Poly (3-hydroxyoctanoate) (PHO)

Compared to PHB and PHBV, PHBH has revealed a wider processing window with better thermal stability. PHBH has also shown more promising mechanical properties compared to PHB and even PHBV due to its tailorable composition of both highly crystalline (3HB) and elastomeric (3HH) units [13]. As the presence of propyl groups in PHBH reduces the regularity of the polymer, the increase in 3HH unit content decreases the degree of crystallinity and the melting temperature, which broadens the processing window with minimized thermal degradation [14]. Therefore, among PHAs, PHBH with more promising properties could be employed in applications where both flexibility and room temperature compostability are required [15–17]. In this context, PHBH can be employed for processing routes such as

injection molding [18,19], extrusion [20,21], thermoforming [22–24], foaming [25], non-woven fabrics and fibers manufacturing [26,27], 3D printing [28,29], paper and fertilizer coating [30].

However, PHBH has received minimal attention due to the low availability in the market, high cost, strict confidentiality of the polymer manufacturers, continuous evolution in the synthesis stage, and production effort of different PHBH copolymers. In addition, the technical development and experimental results of PHBH have been dependent on the characteristics of the insufficient number of raw materials available. This study reviews the research and technical understanding of PHBH and its compounds developed mainly during the last two decades. In particular, PHBH synthesis and the dependency of PHBH features on the copolymer type, composition, and the general thermal, mechanical, and physical properties of PHBH and its blends and composites are comprehensively reviewed. Lastly, the most relevant industrial applications and prospects are discussed.

## **1. PHBH synthesis and preparation**

PHBH synthesis occurs within the cellular structure of several microorganisms. Depending on the microorganism type, environmental conditions, and carbon sources (amino acids, sugar, and fatty acids) required for bacterial growth, one of the forementioned pathways in Figure 1 could be employed. The effects of both related (*i.e.*, valeric acid, propionic acid, levulinic acid,  $\gamma$ -butyrolactone, etc.) and unrelated (*i.e.*, glucose, fructose, sucrose, etc.) carbon sources on the PHBH-producing microorganisms under different stress conditions have been studied by several researchers. *Rhodospirillum rubrum* was the first reported microorganism in 1989 that could produce PHBH in the presence of butyrate or hexanoate as the only carbon source [30]. Later, in 1993, *Aeromonas caviae* FA440 was isolated from soil, and it was found that this strain could harvest a random copolymer of 3HB and 3HH by using fatty acids, natural fats, or oils as a carbon source [31]. *Aeromonas punctata*, a synonym of *Aeromonas caviae*, could successfully synthesize PHBH up to 27 wt. % of its DCW with 10-25 mol % 3HH fraction [32].

*Aeromonas hydrophila* 4AK4 [33–35], *Aeromonas hydrophila* WQ [36], *Aeromonas hydrophila* CGMCC 0911 [37] and *Aeromonas* sp. KC014 [38] are the other wild microbial strains that could produce PHBH in between 27-68 wt. % of their DCW with different 3HH compositions (5.5 – 25 mol %) (Table 2). In addition to those pure strain fermentation strategies, activated sludge was also used in PHBH production, and 6.34 mol % 3HH content was obtained by adjusting the environmental conditions [39].

**Table 2.** Composition of PHBH produced by pure *Aeromonas* wild strains.

Microorganism	PHBH content (wt. %)	3HH composition (mol%)	Carbon source	Reference
<i>Aeromonas caviae</i>	27	25	Alkanoic acids (C <sub>12</sub> to C <sub>18</sub> ) and olive oil	[32]
<i>Aeromonas hydrophila</i> 4AK4	50	11	Glucose and lauric acid	[33]
<i>Aeromonas hydrophila</i> WQ	49	6	Lauric acid	[36]
<i>Aeromonas hydrophila</i> CGMCC 0911	49	5.9	Lauric acid	[37]
<i>Aeromonas</i> sp. KC014	40	16	Dodecanoic acid	[38]

Recent advances in bioengineering techniques also allowed scientists to construct novel PHA-producing microorganisms through genetic modifications. Since *Cupriavidus necator* shows a relatively high PHB productivity, several processes have been examined to modify its metabolic pathway for PHBH synthesis [40–42]. It has been reported that by replacing PHA-synthase with PHBH-synthase (derived from *Aeromonas caviae*) in *Cupriavidus necator*, 3HH coenzyme A could be recognized as a substrate to copolymerize with 3HB [43,44]. The effect of both related carbon sources such as palm oil [45], crude palm kernel oil [42,46], soybean oil [47], and plant oil [48] and unrelated carbon sources such as sucrose [49] and fructose [40,50] on the synthesis of PHBH by using recombinant *Cupriavidus necator* have been evaluated in the literature and are summarized in Table 3.

Besides *Cupriavidus necator*, *Escherichia coli* was also genetically engineered to obtain PHBH polymers. Recombinant *Escherichia coli* could provide several advantages over wild-



type PHA-producing microorganisms, such as fast growth rate, ease of purification of obtained polymers, and lack of intracellular depolymerase enzymes that could degrade PHAs [51]. Lu *et al.* manipulated the fatty acid  $\beta$ -oxidation pathway of *Escherichia coli* and obtained PHBH with 3HHx composition of 15-20 mol % by using lauric acid as its carbon source [52]. Wang *et al.* also designed new metabolic pathways and synthesized PHBH with 10 mol % 3HH fractions in *Escherichia coli* directly from glucose [53]. *Aeromonas hydrophila* and *Pseudomonas putida* are also other genetically engineered microorganisms to produce PHBH using gluconate and glucose [54].

**Table 3.** Production of PHBH from genetically engineered strains.

Mutant strain	PHA content (DCW) (wt%)	3HH composition (mol%)	Carbon source	Reference
<i>Cupriavidus necator</i>	33 - 68	0.9 – 1.6	Fructose	[40]
	40 - 87	5	Palm oil	[45]
	61 - 77	41 - 62	Palm kernel oil	[42]
	30 - 82	3 - 25	Soy bean oil	[47]
	NA*	22	Fructose	[50]
	74 - 78	4.2 – 13	Palm kernel oil + butyrate	[46]
	8 - 22	2.8 – 10.7	Plant oil	[48]
	56 - 74	0.07 - 27	Sucrose	[49]
<i>Escherichia coli</i>	NA	15 - 20	Lauric acid	[52]
	12.9	13.2	Glucose	[53]
<i>Aeromonas hydrophila</i>	10.7 – 14.7	12.8 – 19.2	Gluconate	[54]
<i>Pseudomonas putida</i>	12.5 – 24.2	4 – 6.8	Glucose	[54]

\*Information is not given.

Although recent advances in synthetic biology provide feasible technologies for developing PHBH-producing microorganisms, the large-scale production of PHBH is still limited due to the high production cost. Unless economic feasibility is provided, biological engineering approaches could not be noteworthy [55]. Culture conditions (pH, temperature, carbon, nitrogen, and phosphorus ratio), microorganism feeding regimes, feedstock pretreatment (substrate breakdown for fermentation), and reactor sterilization are several parameters that

affect the overall economy of the PHBH synthesis [55]. There is ongoing research to increase productivity and reduce the cost of PHBH production. Kaneka Corporation (Japan) is nowadays known as the producer of commercial PHBH grades. When required enhancements are provided, larger-scale PHBH production for industrial applications could be available, and the number of commercial grades and perhaps producers could be expected to increase.

## 2. Properties of PHBH

PHBH comprises two distinctive monomeric units of 3HB and 3HH. These monomers, which differ in thermal and mechanical properties, can be copolymerized to achieve significant enhancements in material properties. Upon copolymerization, the effect of each monomer on the properties of the final product has to be considered carefully. Therefore, individual material properties and characteristic behaviors of 3HB and 3HH must be well understood.

3HB is a short-chain length (SCL) monomeric unit obtained from 3-hydroxybutyric acid and comprises four carbon atoms [56,57]. Natural and aliphatic PHB could be dissolved in some organic solvents but not in water. It shows thermal properties close to polypropylene (PP) or low-density polyethylene (LDPE). PHB has recently received great industrial attention due to its fully biodegradable and highly hydrophobic character [58]. However, PHB suffers from poor processability since its degradation temperature is around 200 °C [59] which is close to its melting point (~ 180 °C) [60]. Thereby, further modification such as blending with other polymers or copolymerization is inevitable for its production and usage.

On the other hand, 3HH is a medium-chain length (MCL) monomeric unit obtained from 3-hydroxy hexanoic acid comprised of six carbon atoms with a longer side chain (-C<sub>3</sub>H<sub>7</sub>) group than 3HB (-CH<sub>3</sub>) monomeric unit of PHB [56]. PHB is a semicrystalline, stiff, brittle thermoplastic with high crystallinity, strength, and modulus. Therefore, it could be copolymerized with 3HH to obtain PHBH with improved flexibility and toughness. The developed PHBH copolymer could also be processed at lower temperatures (below the thermal

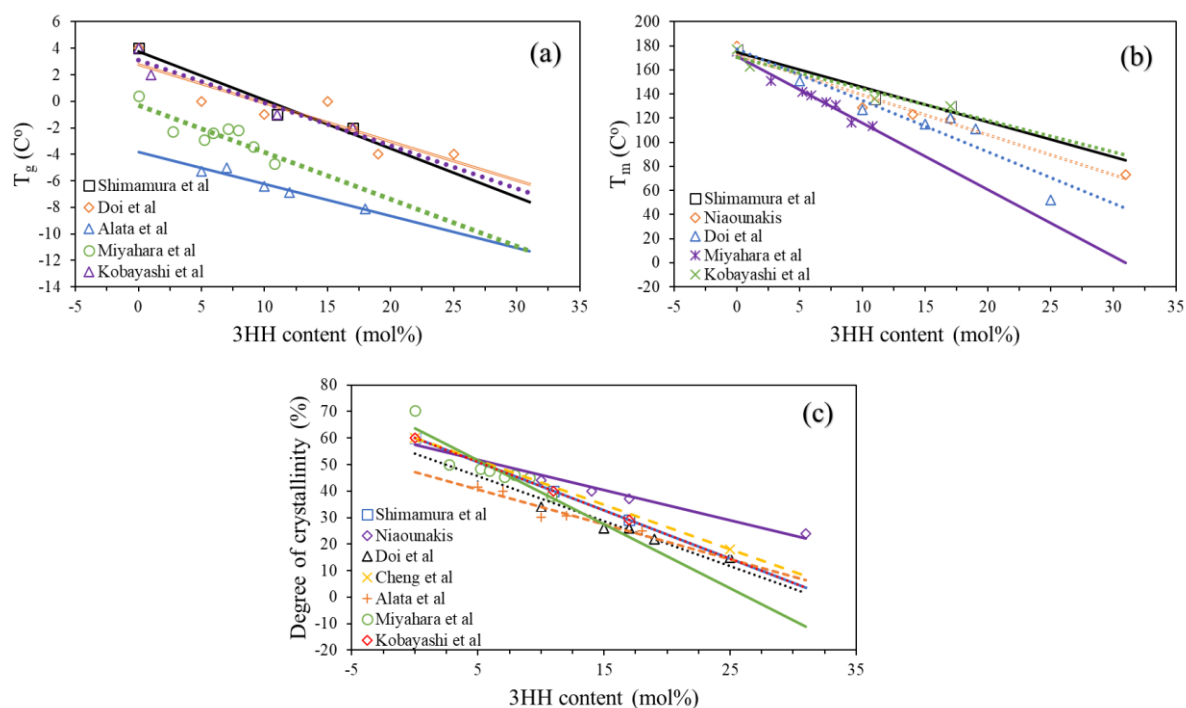
degradation threshold) as its crystallinity, and melting temperature are reduced compared to PHB. Furthermore, in PHBH, the 3HB and 3HH differ in size and shape and are not isodimorphous because 3HH is sterically hindered. Therefore, such copolymerization results in a material with enhanced mechanical properties and processability than PHB homopolymer or even PHBV copolymer.

PHBH copolymer could also be in the form of random (most commonly used) and block. Hence its properties could be different depending on the type of copolymerization. In block copolymer of PHBH with 42 mol. % 3HH monomeric unit, two  $T_g$  values of around  $-16\text{ }^\circ\text{C}$  and  $3\text{ }^\circ\text{C}$  could be observed [61], which correspond to the  $T_g$  of 3HH and 3HB blocks, respectively. Compared to the  $T_g$  values of PHB ( $\sim 3\text{ }^\circ\text{C}$ ) and PHH ( $\sim -28\text{ }^\circ\text{C}$ ) homopolymers, the  $T_g$  of 3HH block increased most likely due to the inevitable interactions between individual chains in the block changing points. Since the PHH originally possesses an amorphous structure, the PHBH melting temperature belongs to the melting of crystals of 3HB blocks. Compared to those of PHB, the mechanical properties of this PHBH block copolymer (with 42 mol. % 3HH) revealed that Young's modulus reduced from 1470 MPa to around 7.6 MPa, elongation at break improved from 3 % to 207 %, and the tensile strength reduced from 18 MPa to around 1.4 MPa. As seen in such copolymer, while the flexibility dramatically increases, the suppression of modulus and strength are also pronounced [61].

In random copolymer PHBH counterpart with 21 mol. % 3HH monomeric unit, it was observed that the resultant  $T_g$  appears around  $-18\text{ }^\circ\text{C}$  while Young's modulus, elongation at break, and tensile strength are about 23 MPa, 75 %, and 1.8 MPa, respectively. As seen, compared to PHB, the modulus and strength of such random copolymer significantly reduced with even lower 3HH comonomer content [61].

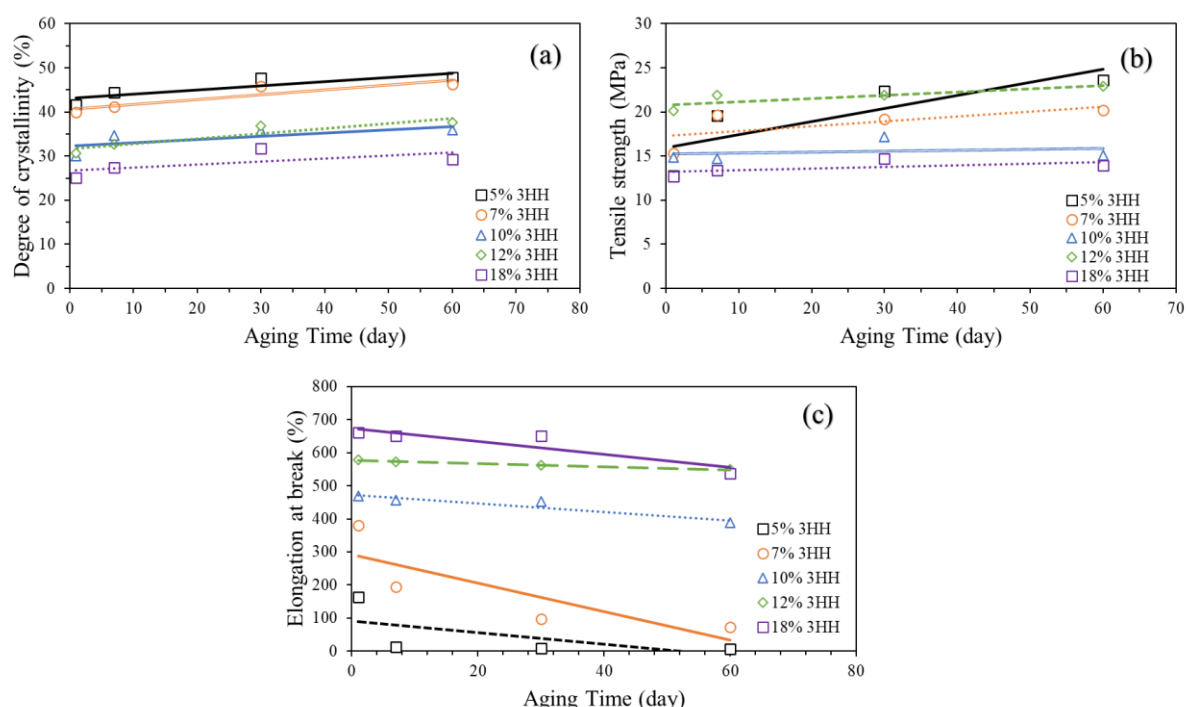
## 2.1 Thermal and crystallization behavior

A few studies have explored the crystallization behavior of PHBH through differential scanning calorimetry (DSC), wide-angle x-ray diffraction (WAXD), and infrared spectroscopy (IR) [62–69]. While only one melting point could be appeared for PHB at around 170 °C, random copolymers of PHBH with various 3HH mol % may reveal two close melting points at lower temperatures. Figure 3 illustrates that with the increased 3HH comonomer content, the  $T_g$  of the random copolymer PHBH suppresses while the  $T_m$  and the final degree of crystallinity significantly reduce. As seen, for each 10 mol % 3HH comonomer content increase, the  $T_g$  could reduce around 4 °C. This is while the reduction of  $T_m$  and the degree of crystallinity are around 40 °C and 20 %, respectively. These thermal behaviors are due to the incorporation of longer side-chains of 3HH comonomers into the short side-chained 3HB which further hinders the molecular mobility and reduces the packing efficiency of the crystallites. In this context, to enhance the crystallization of PHBH, the incorporation of crystal nucleating agents could be helpful [70].



**Figure 3.** Glass transition temperature (a), melting temperature (b), and degree of crystallinity (c) of various PHBH grades with different 3HH mol. % contents [60,71–75]

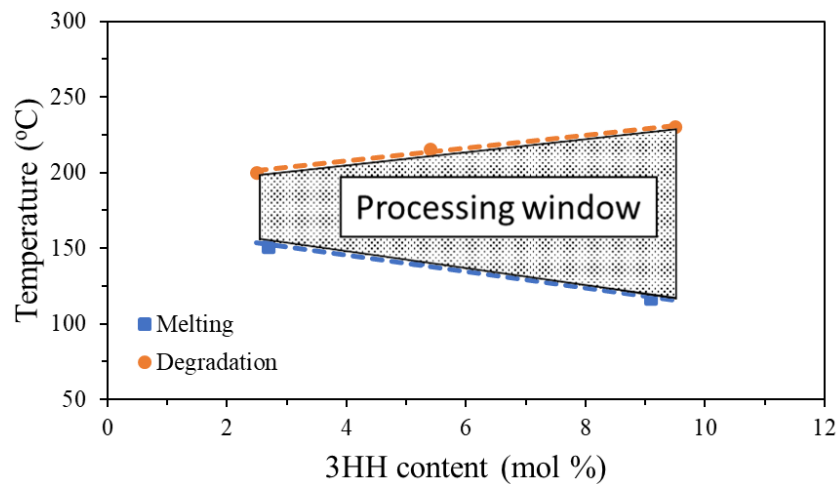
Due to the slow crystallization of PHBH and its  $T_g$  far below the room temperature, PHBH samples could undergo a secondary crystallization at room temperature as a consequence of aging, which could also be considered a cold crystallization phenomenon [76]. The increase in the degree of crystallinity after aging for specific periods could remarkably influence the final mechanical performance of the PHBH copolymer. The  $T_g$  of the aged samples also increases due to the increased total degree of crystallinity [74]. Figure 4 shows how aging could affect the degree of crystallinity and the resultant mechanical performance of PHBH with various 3HH comonomer contents.



**Figure 4.** Effect of aging on the degree of crystallinity (a), tensile strength (b), and elongation at break (c) for various PHBH grades with different 3HH mol. % contents

The thermal degradation temperature of PHBH copolymers have also been shown to be highly dependent on the 3HH comonomer content. The increase in 3HH comonomer content further postpones the thermal degradation to higher temperatures. It has been shown that when the 3HH content increases from around 2.5 to 9.5 mol%, the thermal degradation temperature of PHBH also extends from around 200 to 230 °C, respectively. Therefore, while the 3HH comonomer could reduce the melting temperature of PHBH and thereby its processing

temperature (see Figure 3b), the gap between the processing and thermal degradation temperatures further expands with the increase in 3HH content (Figure 5) [77].



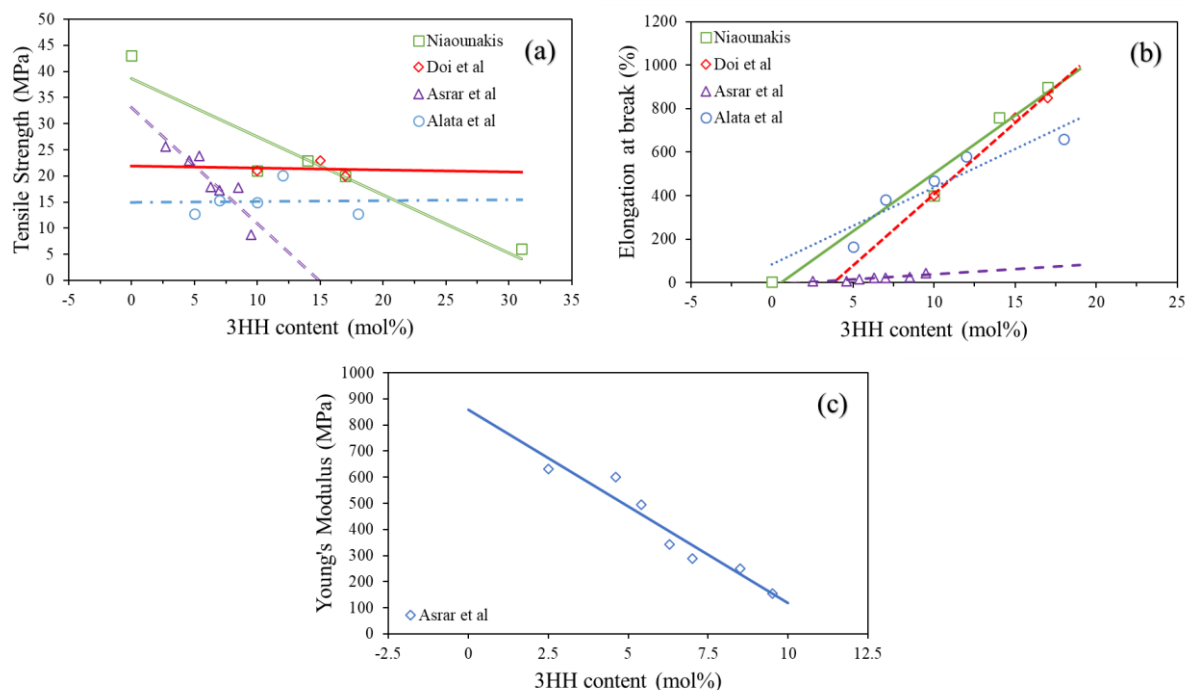
**Figure 5.** PHBH processing window variation with 3HH content

## 2.2 Mechanical properties

The 3HH content variation could significantly influence the mechanical performance of PHBH copolymers. The mechanical properties of various PHBH types have been studied in several works. Figure 6 illustrates the dependency of tensile strength, elongation at break, and stiffness on the 3HH comonomer content in various PHBH grades. Most of these studies have elucidated a similar trend with 3HH content variation. With the 3HH content increase, while the elongation at break increases, the strength, and modulus values decrease due to more flexible 3HH content in PHBH molecules [77–80].

In contrast, Niaounakis et al. [60] and Doi et al. [72] showed barely an increase in tensile strength until almost 17.5 mol. % 3HH content. As Figure 6 shows, although the increase in 3HH content could significantly enhance the ductility of the samples, the suppression of modulus and strength are also noticeable. This indicates that incorporating flexible PHBH polymers with high 3HH contents may require further reinforcement additives such as fibers or micro-/nano-sized fillers to compensate for the destructive role of 3HH content on the modulus and strength reduction of PHBH products. The use of nanoparticles could, for instance, not only enhance the suppressed modulus and strength of PHBH with high 3HH content but could also

improve its slow crystallization through heterogeneous nucleation and melt strength. Consequently, the processability and the final mechanical performance of PHBH products could be improved by incorporating well-dispersed nanoparticles.



**Figure 6.** Tensile strength (a), elongation at break (b), and Young's modulus (c) of PHBH samples with different 3HH mol. % contents [60,72,74,82].

### 2.3. Compostability and degradation behavior

Biodegradable polymers are generally capable of being composted under various conditions, depending on their thickness. As Table 4 shows, PHB and its copolymers, including PHBH, are compostable bioplastics under various ambient environments. This advantage makes them suitable candidates for commodity applications where they could be degraded in the environment without requiring industrial composting. Therefore, although their price is still not convincing, the development of PHBH copolymers could be considered a future alternative for many extensively used petroleum-based plastics. In an anaerobic environment, PHBH could be degraded into methane and carbon dioxide, whereas in an aerobic environment, it could be degraded into water and carbon dioxide [83]. Biodegradation of PHBH occurs in a two-stage

process similar to that of PHAs. The first degradation occurs outside of microbial cells on the surface of the polymer, where enzymes are released [60,84,85].

**Table 4.** Compostability behavior of various bioplastics in different environments. Adopted and represented from [86].

		Compostability in Different Environments						
		Marine	Fresh Water	Soil	Home Composting	Industrial Composting	Anaerobic Digestion	Landfill
<b>Biodegradable Polymers</b>	<b>PHB &amp; its copolymers</b>							
	<b>Starch</b>							
	<b>Cellulose (Lignin &lt; 5%)</b>							
	<b>Cellulose Acetate &amp; other derivatives</b>							
	<b>PBAT</b>							
	<b>PBSA</b>							
	<b>PCL</b>							
	<b>PLA</b>							
	<b>PBS</b>							

The presence of ester bonds in the chemical structure enables hydrolysis degradation where chain scission occurs; hence the polymer would be segregated into oligomeric or monomeric species. Oligomer hydrolase enzymes can break down molecules into smaller pieces, whereas for monomeric species, dehydrogenase enzymes transform them into acetoacetate [87]. After hydrolysis, smaller species can then be transferred into microbial cells for the mineralization of carbon species. Amorphous regions are observed to be first degraded, and degradation propagates along the crystalline regions as it proceeds [88,89]. The biodegradation kinetics is affected by several factors such as temperature, humidity, material concentration within the degradation environment, hydrophilicity, crystallinity, and chain flexibility [83,90–92]. Although much research has explored the biodegradation behavior of PHB and PHBV and its



dependency on the above-noted parameters, not many studies have yet been conducted on PHBH.

As noted, the biodegradation rate could vary with the crystallinity content. In PHBH copolymers, with the increase in 3HH comonomer content, the amount of crystallinity of PHBH decreases, and hence the degradation rate of PHBH could be expedited. Volova et al. [90] confirmed that the biodegradation rate of PHBH is more pronounced than that of homopolymer PHB and even copolymer PHBV. Shimamura et al. [93] and Morse et al. [94] also elucidated how the biodegradation rate increases with increased 3HH content in various PHBH copolymers.

Along with these studies, Doi et al. [72] and Wang et al. [95] illustrated that although the biodegradation rate of PHBH increases with the increase in 3HH content up to 15 mol. %, they revealed that such degradation is retarded in samples with 3HH contents beyond 15 mol. %. It was explained that in PHBH samples with 3HH contents below 15 mol. %, the increase in 3HH content facilitates biodegradation due to the increased amorphous regions in the samples. However, it was also claimed that the increase in 3HH content reduces the surface roughness/imperfections of the PHBH samples. Such an increase in surface smoothness (with increased 3HH content) would hamper the surface adhesion of enzymes and their diffusion required for degradation. Therefore, while in samples with 3HH content below 15 mol. %, the reduced crystallinity expedites the degradation, the further increase of 3HH content beyond 15 mol. % retards the degradation of the PHBH samples as the decreased surface imperfections hinder the degradation rate more dominantly [95].

Since the density of PHBH ( $1.24 \text{ g/cm}^3$ ) is relatively higher than that of water, Kato et al. [96] studied the PHBH degradation behavior by deep-sea sediment bacteria to demonstrate the biodegradability in the ocean, especially at the deep-sea bottom. The researchers demonstrated the biodegradation of PHBH by *Bacillus* sp. MH10, *Alteromonas* sp. MH53, *Psychrobacillus*

sp. PL87 and Rheinheimera sp. PL100 is very active under both high pressure and low temperature of the deep-sea bottoms.

Comparing the microbial degradation behavior of polyester blends based on PHBH (with 11 mol. % 3HH) with other polyesters [poly(butylene adipate-co-terephthalate) PBAT, poly(butylene succinate) PBS, and poly(lactic acid) PLA], it was shown that PHBH revealed an excellent degradation behavior in seawater [97]. Sashiwa et al. demonstrated that increasing the PHBH content in its corresponding blends with other polyesters promotes the degradation behavior of the blend system. In PHBH blends with PBAT, PBS, and PLA, it was revealed that although pure PBAT, PBS, and PLA possess similar biodegradation behavior, their influence on the biodegradability of PHBH based blends is different. While PBS and PBAT incorporation revealed similar degradation responses in PHBH blends, employing PLA further accelerated the degradation of the corresponding PHBH based blends. Therefore, PHBH could be considered an excellent candidate for improving the marine biodegradability of polyester blends, especially those with PLA. This is while the incorporation of PLA with PHBH could boost the modulus and strength of the PHBH. Therefore, their corresponding blends can feature a good compromise between stiffness and toughness, offer good thermal resistance, and quickly biodegrade in a natural environment.

In PHBH composites, Dehouche et al. [98] demonstrated that adding hydrophilic constituents (e.g., cellulose or natural fibers) inside the PHBH matrix can facilitate water absorption, which further accelerates polymer degradation in natural environments. Xu et al. [99] studied the biodegradation effect of regenerated cellulose addition. Cellulose accelerated the PHBH degradation in the soil environment, especially when water molecules invade material in high cellulose concentrations. **The mass loss percentage of pure PHBH was increased from 10.3 to 55.5% with the addition of 90 wt% regenerated cellulose after 30 days.**

In contrast, the hydrophobicity of PHBH significantly affects biodegradability because it is difficult for water molecules and microorganisms to penetrate through the surface.

## 2.4 Melt rheology

Melt rheological behavior of PHBH grades is rarely explored in the literature. In a study, it has been stated that PHBH exhibits shear thinning behavior typical for non-Newtonian polymer melts [100]. It has been stated that the ratio between the characteristic relaxation time  $\lambda$  and the zero-shear viscosity  $\eta_0$  depends on the 3HH content in the PHBH copolymer and slightly increases with 3HH content. But it should be noted that the PHBH grades with various 3HH contents used in this study possessed various molecular weights and a solid conclusion on the 3HH content effect on the rheological behavior of PHBH is not accurate.

## 2.5 Gas permeability

Vandewijngaarden et al. [101] studied the permeability of PHBH (with 10.5 mol % 3HH) where oxygen permeability was  $8.3 \pm 0.2 \text{ cm}^3 \text{ mm m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ , carbon dioxide permeability was  $54 \pm 1 \text{ cm}^3 \text{ mm m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ , and water vapor permeability was  $1.42 \pm 0.04 \text{ g mm m}^{-2} \text{ day}^{-1}$ . The values are very close to the typical ranges for PLA and slightly worse than those found for PET. An Arrhenius-type dependency of the oxygen permeability on temperature was also emphasized for PHBH. Vandewijngaarden et al. [102] further studied the influence of ultrafine talc on the gas permeability of PHBH. Although ultra-fine talc was previously proven to be an effective nucleating agent, the increase in crystallization rate did not reflect a corresponding improvement to oxygen, carbon dioxide, and water vapor permeability.

# 3. Blends of PHBH

## 3.1. Commonly used blending polymers

As noted earlier, PHBH is a promising candidate for packaging applications; however, this goal has not been fully met due to the series of drawbacks associated with PHBH. The physical

properties of this thermoplastic polyester can deteriorate over time since it is pretty sensitive to aging [103–105]. As a result of aging and secondary crystallization, its ductility and overall mechanical properties drop quite substantially [106].

One attractive approach to overcome the shortcomings related to PHBH is to blend with other polymers. Although the literature is still not rich on PHBH-based blends investigations, some studies have considered a few blend systems of PHBH. This is while blending could reduce the final cost associated with the use of expensive and scarcely available PHBH. So far, blends of PHBH have been considered with PLA [107–109], polycaprolactone (PCL) [110–114], polycarbonate (PC) [115], poly(methyl methacrylate) (PMMA) [116], poly (vinyl alcohol) (PVA) [117] and polystyrene (PS) [118]. Blends of PHBH with PLA and PCL, however, have been the most commonly used systems. It should be noted that the more frequent use of other biodegradable polymers such as PCL and PLA could be related to the preservation of the biodegradable characteristics of the final blend. It should be considered that PCL with  $T_g$  of around  $-60\text{ }^\circ\text{C}$  is a good candidate for enhancing the ductility of PHBH, although the final service temperature should be noted for the potential applications. In contrast, PLA with higher  $T_g$  ( $\sim 60\text{ }^\circ\text{C}$ ) possesses less flexibility and low toughness. Therefore, blending PHBH with PLA could not be intended to enhance the elongation at break and toughness, but rather the stiffness, strength, and higher service temperature of PHBH, specifically when PLA possesses a reasonable amount of crystallinity. PVA is another water-soluble polymer with good thermal, physical, and barrier properties that have been blended with PHBH [117]. PHBH/PVA blend was immiscible in the crystalline phase and compatible in the amorphous state due to the hydrogen bond that can both form. Thus, the combination of PHBH with PVA was influencing on the change of the morphology against water, improving the degradation rate of the blend with respect to as-is- PHBH.

### 3.2. Miscibility in PHBH blends

It is worth noting that blending of polymers with different solubility parameters, crystallinity, and polarity would not necessarily lead to forming a homogeneous structured final material. Most polymer pairs are either partially or entirely immiscible, meaning that the final mixture exhibits phase-separated structures. However, the extent of the segregated structures in partially miscible blends depends on the blend ratio [119], temperature [120], and volume of the amorphous regions in the polymers. Cheng et al. [121] demonstrated that PHBH/PLA blends are immiscible in the entire blending ratios. In this blend, PLA did not have any influence on the crystallization of PHBH. Another study conducted by Zhang et al. [122] revealed that PHBH/PBAT blends are immiscible in various compositions and showed droplet-matrix morphology. Similarly, Tamiya et al. [114] have recently shown that PHBH/PMMA blends are immiscible at a wide range of examined compositions. Several studies have also demonstrated the immiscibility between PHBH and PCL phases at different blending ratios [110,111,114]. Lim et al. [124] studied the miscibility of PHBH with methoxy poly(ethylene glycol) (MPEG) and poly(ethylene glycol) (PEG). All the blends investigated had a single glass transition temperature, which evidenced their excellent miscibility in the molten state. Strong hydrogen bonding between PHBH and MPEG makes this blend more miscible than PHBH/PEG blend. In addition, MPEG was found to enhance the crystallization rate of PHBH by acting as a nucleating agent. More recently, Chen et al. [125] studied the PHBH (with 3.9 and 13 mol. % 3HH)/PEG: (70/30) binary blends by varying the mol. % of the 3HH unit. The influence of PEG on PHBH (with 3.9 mol. % 3HH) is different from that of PHBH (with 13 mol. % 3HH). The experimental results suggested that neither PHBH composition forms strong hydrogen bonding with PEG. In the PHBH (with 3.9 mol. % 3HH)/PEG blend, PEG acted as an effective solvent; however, the influence of PEG on the properties of PHBH (with 13 mol. % 3HH) still needs clarification. Yu et al. [126] studied the miscibility of PHBH (with 11 mol. %)

3HH/poly(ethylene oxide) (PEO) binary blends. While 10 wt. % PEO in the amorphous state provides good miscibility, 20 wt. % PEO dramatically decreases the miscibility of the binary blends. While the yield strength remains almost constant, the elongation at break increase from 26.1 % to 436 %, and Young's modulus decrease from 6.4 to 4.7 MPa with 17.5 wt. % PEO addition. More specifically, PEO can be an effective plasticizer for PHBH without compromising its exceptional biodegradability and biocompatibility. In the same compositional range, PEO could also improve the crystallization of PHBH by acting as an effective nucleating agent. Cai et al. [127] studied the miscibility of PHBH and poly(vinyl phenol) PVPh blends. The two constituents were completely miscible over the whole compositional range due to hydrogen bonding between PHBH and PVPh. However, PVPh decelerates the crystallization rate of PHBH because crystallization regime changes from thermal nucleation for pure PHBH to athermal nucleation for PHBH/PVPh blends.

### 3.3. Compatibilization in PHBH blends

In polymer blends, improved properties depend on the homogeneity of the final blend morphology. It has been frequently reported that immiscible blends need further enhancement in their interface region to provide compatibility between the two polymer phases [128–130]. Therefore, compatibilizers are introduced into the immiscible blends to create a linkage at the interface and similarly stabilize the morphologies with surfactants in emulsions. Compatibilizers could be copolymers with each side compatible with one of the phases or a reactive component compatible with one phase and reactive with an opposite phase during processing at high temperatures [131]. Both approaches are shown to be effective in stabilizing the morphologies depending on the processing conditions and concentrations. As such, PHBH-based blends are no exception to this. For instance, Tamiya et al. [114] synthesized a graft copolymer of PMMA-*g*-PHBH to improve the interfacial properties of the PMMA/PHBH

blends. As a result of such compatibilization in PHBH/PMMA blends at the weight ratio of 90/10, the toughness values increased with increasing PMMA-*g*-PHBH content.

In another study, Oyama et al. [110] synthesized block copolymer of PHBH-*b*-PCL with different block architectures, e.g., AB, A<sub>2</sub>B, AB<sub>2</sub>, ABA, and A<sub>2</sub>BA<sub>2</sub>, with A being the PHBH and B the PCL polymer. The efficiency of the block copolymers on the compatibility of the blends is highly proportional to the block architecture of the copolymers. The different PCL domain sizes were discussed due to the major positioning of the block segments in the blends. For instance, in the case of A<sub>2</sub>B and A<sub>2</sub>BA<sub>2</sub>, the majority of the PHBH segment of the block copolymer is on the PHBH matrix side, which leads to the increased curvature at the interface and hence, smaller PCL droplet sizes. However, A<sub>2</sub>B was found to be more effective despite the same reasoning explained earlier. This was due to the more symmetric block ratio of the A<sub>2</sub>B, which led to interfacial localization of the copolymer and thus smaller PCL sizes. It was also demonstrated that the increase in toughness and elongation at break is proportional to the PCL size reduction. This suggests that the mechanical properties of the blends can be tuned by varying the architecture of the copolymers.

As mentioned earlier, another approach for compatibilizing the morphologies is through reactive compatibilization during melt blending. Zhou et al. [107] utilized a reactive epoxy compatibilizer (REC), a copolymer of glycidyl methacrylate and styrene, to compatibilize PHBH/PLA blend (80wt./20wt.). It is believed that the epoxy group would, on the one hand, react with the hydroxyl group of PHBH and, on the other hand, with hydroxyl and carboxyl groups of PLA which eventually could compatibilize the blend. The study revealed a significant stabilization of the morphologies with the addition of REC to the blends where PLA sizes reduced dramatically with more uniform morphology. The results were interesting since not only was there an enhancement in toughness with minimal loss of stiffness, but the onset degradation temperature of the blends significantly increased from 256 °C at zero REC to 293

°C at 4% of REC. The main positive effect of REC and compatibilization was on the elongation at break and impact strength of the blends where tensile strengths and moduli of the blends did not show a remarkable loss.

### 3.4. Achieved enhancements

The summary of the tensile properties of the compatibilized system is shown in Table 5. PHBH/PLA has by far the largest moduli of the investigated systems, owing to the higher modulus of PLA, although the lowest elongation at break was also in this system as expected. The most remarkable alterations at the constant ratio and compatibilizer content belong to PHBH/PCL blends. It is shown that the uncompatibilized PHBH/PCL blend and compatibilized blend with ABA copolymer (i.e., PHBH28k-b-PCL26k-b-PHBH28k) has relatively similar modulus and tensile strength values. This is while the toughness of the ABA-compatibilized blend is 10 times higher than that of the neat blend. That again enlightens the critical role of compatibilization and molecular architecture of the compatibilizer on the final properties. Interestingly, this result was obtained while this compatibilized blend (ABA-blend) did not have the smallest PCL droplet size among the compatibilized blends. In PHBH/PMMA blends, tensile properties varied significantly depending on the blending ratio, indicating the importance of morphological evolution on the final mechanical properties. Overall, PHBH/PMMA blends show higher elongation at break than other investigated blends, specifically at lower PMMA contents. It is also seen that 5 % PMMA-*g*-PHBH is the optimum level of compatibilizer with relatively higher values of moduli amongst the PMMA-*g*-PHBH compatibilized blends at all ratios. Moreover, at 5% copolymer content, the toughness and elongation at breaks were the highest in PHBH-rich blends.

**Table 5.** Summarized tensile properties of the compatibilized PHBH-blends investigated. The values are adopted from references [107,110,116].

Blend type	Blending ratio	Compatibilizer type	Compatibilizer %	Young's Modulus (MPa)	Elongation at break %	Maximum strength (MPa)
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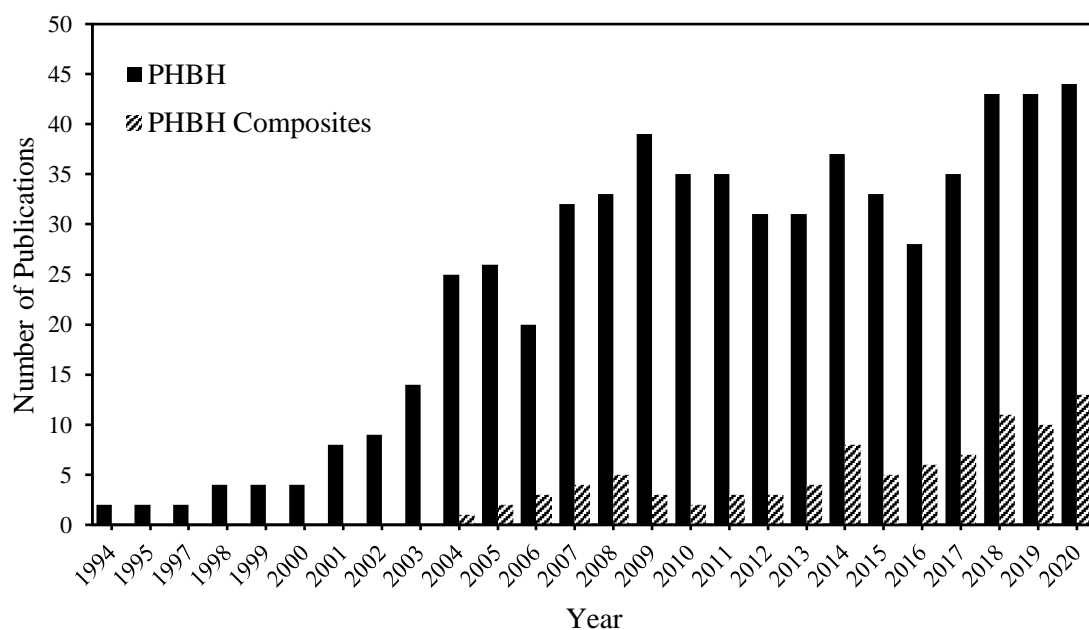


PHBH/PMMA	90/10	-	0	530±20	258	17.0±1.0
PHBH/PMMA	90/10	PMMA-g-PHBH	1	350±20	363	18.0±0.8
PHBH/PMMA	90/10	PMMA-g-PHBH	5	430±20	370	20.0±0.7
PHBH/PMMA	90/10	PMMA-g-PHBH	10	370±30	327	19.0±0.7
PHBH/PMMA	70/30	-	0	630±10	124	15.0±0.6
PHBH/PMMA	70/30	PMMA-g-PHBH	1	450±10	138	12.0±0.8
PHBH/PMMA	70/30	PMMA-g-PHBH	5	480±3	218	16.0±0.7
PHBH/PMMA	70/30	PMMA-g-PHBH	10	460±20	196	13.0±0.8
PHBH/PMMA	50/50	-	0	720±30	40	15.0±0.6
PHBH/PMMA	50/50	PMMA-g-PHBH	1	720±30	39.3	14.0±0.8
PHBH/PMMA	50/50	PMMA-g-PHBH	5	700±20	48.8	14.0±0.3
PHBH/PMMA	50/50	PMMA-g-PHBH	10	590±4	88.1	13.0±0.3
PHBH/PMMA	30/70	-	0	920±50	10.2	16.0±1.0
PHBH/PMMA	30/70	PMMA-g-PHBH	1	750±30	51.1	15.0±0.2
PHBH/PMMA	30/70	PMMA-g-PHBH	5	820±30	48.8	17.0±0.3
PHBH/PMMA	30/70	PMMA-g-PHBH	10	650±50	96	14.0±0.8
PHBH/PCL	75/25	-	0	534±8	11.2±0.2	27.2±0.6
PHBH/PCL	67/23	PHBH <sub>30k</sub> - <i>b</i> -PCL <sub>27k</sub>	10	220±24	28.3±3.3	22.2±0.1
PHBH/PCL	67/23	PHBH <sub>30k</sub> - <i>b</i> -PCL <sub>13k</sub>	10	473±9	6.6±0.6	23.5±0.8
PHBH/PCL	67/23	(PHBH <sub>27k</sub> ) <sub>2</sub> - <i>b</i> -PCL <sub>29k</sub>	10	181±27	32.8±1.8	22.2±1.2
PHBH/PCL	67/23	PHBH <sub>30k</sub> - <i>b</i> -(PCL <sub>13.5k</sub> ) <sub>2</sub>	10	367±30	16.8±2.6	24.2±0.9
PHBH/PCL	67/23	PHBH <sub>28k</sub> - <i>b</i> -PCL <sub>26k</sub> - <i>b</i> -PHBH <sub>28k</sub>	10	533±34	102.2±2.5	25.2±0.8
PHBH/PCL	67/23	(PHBH <sub>30k</sub> ) <sub>2</sub> - <i>b</i> -PCL <sub>27k</sub> - <i>b</i> -(PHBH <sub>30k</sub> ) <sub>2</sub>	10	417±14	50.6±5.5	19.5±0.9
PHBH/PLA	80/20	-	0	1076	5.0	19.4
PHBH/PLA	80/20	REC	1	1190	7.9	18.8
PHBH/PLA	80/20	REC	2	1034	7.9	19.0
PHBH/PLA	80/20	REC	3	997	10.7	19.8
PHBH/PLA	80/20	REC	4	1042	10.0	18.6

#### 4. PHBH based composites

As previously mentioned, PHBH is a random copolymer comprised of two distinctive monomeric units of 3HB and 3HH. Adding a 3HH monomeric unit softens the material, improves thermal properties, reduces the melting temperature, increases the degradation

temperature, and enhances the processing range. However, the increase in 3HH content decreases the modulus and strength of PHBH products. However, such suppression of modulus and strength could be compensated by developing its composite structures using different reinforcement types. This section reviews the studies that have been conducted on the achievements in PHBH-based fiber-reinforced or particulate-reinforced composites and nanocomposites. **Since 1994, there has been a significant increase in the number of publications based on pure PHBH and PHBH composites according to Web of science (Figure 7).** According to these research studies, the preliminary reported result has been the crystallization acceleration of PHBH through promoting heterogeneous crystal nucleation, specifically in nanocomposites. The enhancements in the mechanical properties of the composite structures were hence obtained through such reinforcements and the improved degree of crystallinity [132].



**Figure 7.** Number of publications related to PHBH and PHBH Composites since 1994 according to the Web of science.

#### 4.1. Fiber reinforced composites

Glass fiber is one of the most basic reinforcements used in many polymeric composites due to its high strength and stiffness. In a study, the properties of PHBH-based composites reinforced with glass fiber are investigated [133]. Two different types of PHBH with 3HH contents of 5.6 mol. % and 11.1 mol. % were reinforced with 5, 10, 16, and 23 vol% glass fiber. As the glass fiber content increased from 5 to 23 vol%, the composites transitioned from ductile to brittle behavior while the tensile strength and modulus of both PHBH grades significantly increased. This is during the PHBH grade with 11.1 mol. % 3HH content and its corresponding composite revealed a more ductile behavior than PHBH having lower 3HH content. On the other hand, the reinforcing efficiency (i.e., the strength and modulus enhancements) of glass fibers was more noticeable in PHBH grade with 5.6 mol. % 3HH content. It should, however, be noted that the increase in glass fiber over 10 vol% is less effective on the property enhancements of PHBH matrices. According to their DSC results, the thermal and crystallization behaviors of PHBH were not affected much by the incorporation of glass fibers. Even though the fiber addition could promote the resultant properties in a composite, the compatibility between phases and the presence of solid interfacial interaction is inevitable.

Mei et al. [134] studied the biocompatibility of PHBH (with 12 mol. % 3HH) reinforced by modified silk fibroin (i.e., degummed by alkaline solution). The presence of modified silk fibroin increases the hydrophilicity of the PHBH matrix, thus favoring its biomedical applications. Similarly, Zini et al. [135] studied the bio-composite of PHBH (with 12 mol. %) reinforced by vegetable (flax) fibers. The researchers noted that the addition of untreated short flax fibers did not significantly enhance the mechanical properties of biocomposites. Surface treatments of the flax fibers by acetylation led to better results. Another critical effect noted is the capability of the fibers to act as a nucleating agent, improving the crystallization kinetics of the PHBH.

The group of Bruzard [136,137] explored the effect of using 20 wt. % Aloe Vera Fibers (AVF) with different treatments on the thermal and rheological properties of PHBH. Untreated AVF (UNAVF), alkaline treated AVF (ALAVF), organosilanes treated AVF (SiAVF), and combined alkaline and organosilanes treated AVF (ALSiAVF) were used. The incorporation of UNAVF caused randomly distributed agglomerates due to the phase incompatibility between the AVF and PHBH. In the case of ALAVF, the fibers were distributed randomly, whereas holes and cracks were present in the surface of PHBH. The SiAVF showed fewer cracks and a decrease in void sizes. Finally, the ALSiAVF showed the most improved fracture surface with a minimal number of defects and aggregates, which resulted in better interfacial adhesion. Although the rheological experiments clearly illustrated such interfacial interaction enhancement through fiber treatment, the DSC and TGA results showed negligible differences.

More recently, Giubilini et al. [138] investigated the addition of silanized oat-hull fiber (8 vol. %) inside the PHBH (with 11 mol. % 3HH) matrix by melt blending. The fillers inside the polyester matrix favored improving the mechanical properties, as elastic modulus increased about 12 %. The embrittlement of the polymer matrix by the addition of the fibers resulted in a slight loss in elongation at break. However, the oat-hull fibers can be incorporated inside the PHBH matrix to significantly reduce the material cost without substantially altering the mechanical properties of the resulting composite.

#### 4.2. Particulate reinforced composites

The effects of calcium carbonate and talc reinforcements on the mechanical properties of PHBH were analyzed with different filler contents [139]. It was shown that Young's modulus of PHBH proportionally increases with increasing filler content, although the effect of talc sounds to be more dramatic on such modulus increase. This could be due to the higher aspect ratio of talc (20) than calcium carbonate (1). Moreover, while the addition of talc enhances the tensile strength, calcium carbonate reduces such value in its composite counterparts. It was

claimed that this difference could be due to the inadequate interfacial adhesion in PHBH-calcium carbonate composites which decrement the strength at the break with increasing calcium carbonate content. Both the strain and energy at break values decrease with increased filler content in both composites. They also illustrated that the impact resistance of PHBH and its composites with 30 wt. % fillers were quite similar.

Ivorra-Martinez et al. [140] investigated the biocomposites achievable by dispersion of almond shell flour (ASF) (10, 20, and 30 wt. %) and PHBH. A significant improvement in the mechanical properties of the composite was detected with increasing ASF content. Nevertheless, the addition of ASF inside the polymeric matrix caused significant embrittlement of the composite. The researchers clarified that the addition of a compatibilizer could improve the properties of the composites. In particular, adding an oligomer of lactic acid (OLA) could enhance the affinity between ASF and PHBH by acting as a plasticizer.

Nanni and Messori [141] investigated the dispersion of wine lees (WL) wastes (10, 20, and 40 phr) inside the PHBH to contract the cost of the final polymeric material. In addition, 3-methacryloxypropyltrimethoxysilane was tested as a coupling agent to improve the interfacial affinity between the natural filler and the polymer. The researchers found that WL can improve the overall properties of biopolymers without compromising their bio-based origin and reducing their production cost.

## **5. PHBH based nanocomposites**

### **5.1. PHBH- cellulose nanocrystal (CNC)**

Due to the abundance of cellulose in nature and its low density, biobased and biodegradable CNC has attracted more attention in the literature to develop PHBH nanocomposites [142–146]. However, due to its high hydrophilicity, the dispersion of CNC in various thermoplastics through melt mixing is still a serious concern [147]. Using the solution casting method, Xiaojun Ma [142] group showed that untreated CNC could enhance the strength and crystallization of

PHBH. Later, the same group studied the hybrid nanocomposites of PHBH with CNC and nanoclay through the solution casting method [143,144]. They proved that the incorporation of nanoclay could retard the degradation onset temperature of PHBH. At the same time, it could significantly increment the strength and modulus of PHBH up to 5 wt. % nanoclay content [144].

Li et al. [148] studied a novel biocomposite of PHBH reinforced with surface modified acetylated cellulose nanocrystals (ACN) prepared by solution casting. Acetylation of cellulose nanocrystals improved its dispersion inside the PHBH matrix and enhanced the tensile strength and Young's modulus. The addition of ACN was also proven to improve the gas permeability of the resulting composite. These improvements were attributed to the uniform dispersion of ACNs and solid interfacial bonding between filler and matrix.

In another study, CNC grafted with PHBH (CNC-g-PHBH) was developed to improve the CNC dispersion ability in PHBH [145]. They revealed that the crystallization rate of PHBH was enhanced with the use of CNC and, more importantly, with 1.0 wt. % CNC-g-PHBH. Meanwhile, they also proved that the spherulite nucleation of PHBH was significantly promoted with 1.0 wt. % CNC-g-PHBH. The grafting of CNC also noticeably enhanced the modulus and strength of PHBH, while no improvement was observed when ungrafted CNC was used.

## 5.2. PHBH-nanosilica (SiO<sub>2</sub>)

Few studies have also explored the thermal, crystallization, mechanical, and morphological properties of PHBH nanosilica nanocomposites [149–152]. It has been reported that the degradation onset temperature of pure PHBH was increased with the addition of nanosilica. This is while the strength and modulus of the nanocomposite increased with increasing nanosilica content. In contrast, the elongation at break and toughness of the nanocomposites decreased with nanosilica content.

More recently, Li et al. [152] studied a biocomposite of PHBH and nano-SiO<sub>2</sub> modified with 3-aminopropyltriethoxysilane (APTS) by solution casting. The addition of the silane agent improved the dispersion of the nano-silica inside the polyester matrix, improving the thermal stability and crystallinity of the resulting material and the elastic modulus and tensile strength. The significant improvement of the thermo-mechanical and physical response of the composite can be attributed to the effective dispersion of the nano-silica inside the PHBH, promoted by the surface treatment of the nano-particles with the silane agent.

Reports show that the oxygen and water vapor permeability of PHBH also decreases with an increase in nanosilica content. The crystallization rate of the PHBH could barely be improved with nanosilica particles, although some enhancements were observed in some composites with specific nanosilica contents [150,152].

### 5.3. PHBH carbon-based nanoparticles

Carbon nanotubes (CNTs) and graphene-based particles could be employed in nanocomposites to induce functional electrical properties further while improving mechanical properties. However, not many studies have explored the effect of using these nano-additives on the properties of PHBH [153,154]. Wu et al. [154] showed that while the CNTs could enhance the strength, modulus, and, interestingly, even the strain at break value of PHBH, it could significantly induce electrical conductivity into the final nanocomposite product.

Qui and Ma [155] studied the effect of graphene oxide (GO) in PHBH (with 11 mol. % 3HH) based biocomposites produced by solvent casting. The addition of GO increased the crystallinity and the number of spherulites of the polyester, which indicated that GO was an effective nucleating agent for PHBH. Compared to PHBH, the tensile strength and elastic modulus of biocomposites increased by 25% and 40%, respectively. Moreover, the oxygen permeability of biocomposites was almost 50% lower than PHBH. Lastly, the experimental results also revealed that GO/PHBH biocomposites are promising anti-ultraviolet materials.

In another study, graphene oxide (GO) was incorporated in PHBH [153]. It was observed that the onset of degradation temperature of PHBH was increased from around 230 °C to 260 °C with the addition of only 0.25 wt. % GO. Such low GO content could also enhance the crystallization rate of PHBH. While the addition of GO remarkably improved the barrier properties of PHBH, it did not have a significant influence on the final mechanical properties of PHBH composites. It was shown that the gas barrier values for nanocomposites were decreased to half for N<sub>2</sub> and one-sixth for CO<sub>2</sub>.

#### 5.4. PHBH-clay nanoparticles

Vandewijngaarden et al. [156] studied the nanocomposites of PHBH and organomodified montmorillonite (OMMT) with concentrations of 1, 3, 5, and 10 wt. %. The effectively dispersed and highly intercalated OMMT significantly improved the gas barrier properties of the resulting composites. While OMMT addition increases the stiffness of the composite, it also causes significant embrittlement and deterioration of ductility. Dong et al. [157] studied the composites of PHBH and MMT modified with a silane coupling agent, specifically 3-aminopropyltriethoxysilane. The crystallinity, thermal properties, mechanical properties, and barrier properties of the PHBH/silanized-MMT improved due to the optimal dispersion of the silanized MMT. Elastic modulus, tensile strength, and elongation at break of the PHBH/silanized-MMT composite increased by 220.05 %, 158.25 %, and 58.91 % compared to pure PHBH, respectively.

## 6. Industrial applications and future perspectives

The final achievable properties of PHBH compounds depend on copolymer composition and, eventually, their blending with other polymers (for example, with other polyesters and additives). However, industrial applications of PHBH are still at earlier stages. PHBH manufacturers must face two crucial issues: (i) the high cost of the polymer and; (ii) its difficult



processability, especially in case PHBH is not modified or blended with other polymers and additives.

PHBH has potential in industrial applications due to tailorable mechanical properties, processing behavior similar to other polymers, and superior barrier performance than most polymers. Nevertheless, PHBH particularly comes forward in several industrial applications because of its biobased character and high biodegradability in the environment, including soil, marine, and freshwater. In addition, PHBH can be composted in industrial and domestic composting equipment. Therefore, PHBH can be profitably applied in all those applications that require the disposal of plastic material at the end of life, especially when the life cycle is very short. Concerning this, there are some scenarios where PHBH application can be particularly advantageous: (i) manufacturing of garbage bags; (ii) manufacturing of packaging and single-serve items that come in touch with food or beverages like plastic containers, coffee capsules, disposable tableware; (iii) manufacturing of agricultural and horticulture technical solutions like mulch film, clips, plant pot; (iv) manufacturing of fishery items, like fishnets, fishhooks, fishing lines, screens. **Since this review mainly focuses on the PHBH use in packaging applications, biomedical and drug delivery applications are excluded from the present dissertation. However, when suitable production and processing conditions of PHBH is achieved with reasonable price for biomedical applications, its usage will also significantly increase in this area.**

**Kaneka announced a significant investment to increase the production capacity of PHBH from 1,000 ton/year to 5,000 ton/year. In addition, it is also declared by Kaneka that feasibility study to further expand PHBH production to 20,000 ton/year has been started [160]. In 2019, Kaneka Corporation and Seven & I Holding Co. Ltd. started to develop a variety of products based on PHBH. Specifically, they focused on developing low environmental impact straws for “Seven Cafe”, a business run by Seven-Eleven Japan Co. Ltd. Seven Cafè claimed the**

introduction of the newly developed straws in PHBH (100 % biodegradable) in approximately 10'000 stores in Japan [158]. In 2020, the PHBH usage in straws in Seven Cafè was further expanded to more than 21'000 stores, having 6 and 8 mm diameter straws suitable for both cold and hot [159].

Similarly, The North Face Company introduced PHBH straws in their stores [160]. Shiseido Company Ltd. has, instead, adopted PHBH for the fabrication of cosmetics packages. As of November 1<sup>st</sup>, 2020, Shiseido Global Flagship Store started using PHBH to manufacture a palette case's main body and lid [161]. Kaneka Corporation also employed foamed PHBH for packaging items (expanded PHBH box) as an additional application. These items are generally produced in **expanded** polystyrene (EPS) and are characterized by a very long persistence (even more than two centuries) in the marine environment, soil, and acute toxicity. They are mainly used in seafood packaging or takeaway food; therefore, they are often accidentally dispersed in the natural environment. Hence, replacing EPS with E-PHBH is crucial to mitigate the impact of such kinds of packaging solutions.

Capsul'in Professional has instead launched the world's first certified home compostable coffee capsule [162]. Although the technology behind the development of the capsule was not disclosed, PHBH is used to fabricate the capsule body, thus ensuring thermal stability, gas impermeability, and a good balance of stiffness and toughness to the packaging solution. These capsules should be available on the market by the end of 2021. The capsule is also able to ensure exceptionally long shelf-life of the coffee (i.e., 12 months) as a result of the good oxygen-barrier properties of the body and the top and bottom lids (made from cellulose-based materials), with a level of gas permeability equal or superior to conventional and industrial compostable coffee capsules.

## **Data availability**

Data not available / Data will be made available on request.

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