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Polyhydroxyalkanoates as Sustainable Agricultural Plastics: Processing Strategies, Performance, and Environmental Perspectives

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ABSTRACT

The widespread use of synthetic plastics in agriculture has significantly enhanced crop productivity and resource efficiency, but it has also generated severe and long-lasting environmental challenges, including microplastic accumulation and soil degradation. Developing bio-based and biodegradable alternatives that can perform effectively under agricultural conditions is therefore essential to advancing sustainable farming and environmental protection. This review critically examines polyhydroxyalkanoates (PHAs), a versatile family of biodegradable polyesters derived from natural sources, as promising substitutes for conventional agricultural plastics. Emphasis is placed on the relationships between polymer structure, processing behavior, and resulting mechanical and biodegradation properties that determine their suitability for key applications such as mulch films, seedling trays, and growth foams. Recent progress in blending strategies, additive incorporation and melt processing of PHAs, aimed at improving processability and mechanical performance, is discussed in detail. The review also identifies major challenges related to cost, scalability, and environmental performance under real-field conditions, and highlights future research directions toward optimizing PHAs for circular and climate-resilient agricultural systems.

1 | Introduction

As the global population continues to rise, the demand for food has driven significant advancements in agricultural technologies with the aim of maximizing productivity. A key component of modern agricultural practices is the use of plastic materials, such as mulch films [1], hydrophilic foams (growth foams) [2], or polymer coatings [3]. These products offer numerous benefits, including increased crop yield, more efficient water and nutrient use, protection against pests and weeds, earlier harvests and more sustainable use of fertilizers and agrochemicals [1]. However, most agricultural plastics are made from non-biodegradable, fossil-based polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinylchloride (PVC), and polystyrene (PS) [4]. Among these, polyethylene is the most widely used plastic in mulch production, with an estimated 2.5 million metric tons applied globally each year [5]. Their extensive use has led to growing concerns over plastic pollution, as these materials are difficult to recover and tend to accumulate in soils and ecosystems. When exposed to harsh weather and UV radiation, PE films often become brittle and fragment, generating microplastic particles that persist in soils even after the films are removed. It is estimated that 25%–33% of plastic mulch film residue could remain in agricultural soils after a single cultivation cycle [6]. This microplastic contamination is associated with decline in soil health, negatively affecting soil structure, microbial communities, soil biota, and ultimately, plant growth [7].

In 2019, the global use of agricultural plastics reached 12.5 million tons [3]. With climate change intensifying and global food demands continuing to rise, this figure is expected to grow significantly in the following decades. For instance, the demand for greenhouse, mulching, and silage films alone is expected to grow by 50%, from 6.1 million tons in 2018 to 9.5 million tons in 2030 [8]. This trend highlights the urgent need for sustainable alternatives to conventional plastics in agriculture. In this context, biodegradable polymers present a promising pathway toward sustainability. Among them, polyhydroxyalkanoates (PHAs) are strong candidates.

PHAs offer several advantages, including safety and complete biodegradability in diverse environments, making them particularly well-suited for agricultural applications [9, 10]. When compared to other bio-based polymers, such as poly-lactic acid (PLA) and poly-glycolic acid (PGA), PHAs stand out due to their superior biocompatibility and tunable mechanical properties. Despite these benefits, market adoption of PHAs remains limited, corresponding to only 1.2% of global bioplastic production [11]. Their commercialization is hindered by several challenges, such as high production costs and processing issues [12]. High production costs are primarily associated with expensive feedstocks and low extraction yields, while processing limitations arise from the inherent properties of PHAs, such as thermal sensitivity, low nucleation density, and low melt strength [13, 14]. Understanding these challenges and identifying possible research pathways to tackle them is key for future implementation of PHAs products in agriculture.

Several review articles on PHAs and biodegradable plastics have been reported in the literature, each addressing specific aspects of these materials. For instance, Lalonde et al. [12] provided a comprehensive analysis of structure–processing–property relationships in PHAs from a broad materials science perspective. However, while informative, their discussion of processing remains largely generic and lacks an application-oriented focus. Moreover, it does not address processing techniques for scalable film production or the fabrication of expanded structures such as foams. More general reviews [11, 15, 16] summarize the synthesis, extraction, characterization, and properties of PHAs. However, they do not explicitly link processing methods and structure to target application performance. Additionally, Merino et al. [16] present a perspective on biodegradable plastics in agriculture, discussing key materials such as PLA, PHAs, and other biomass-derived polymers, particularly in relation to microplastic generation in soil from applications such as mulch films, delivery systems, and soil conditioners. Nevertheless, their work does not focus on processing–structure–property relationships. Taken together, these limitations highlight a critical gap: the absence of an integrated, application-driven analysis that connects PHA processing methods and material structure with functional performance in agricultural applications.

To address this gap, this review examines the state of art on the development and processing of PHAs for agricultural applications. It begins with a brief overview of PHAs, outlining how their structure relates to their properties, and then discusses strategies aimed at improving their processability and performance. The review next explores the current role of plastics in agriculture, emphasizing high-impact applications such as mulch films and growth foams, where biodegradable alternatives are urgently needed. The core contribution of this work is the consolidation of melt-processing techniques and reactive-processing methods for producing PHA films and foams, a topic still insufficiently addressed in the existing literature. By highlighting recent advances, persistent challenges, and future research directions in integrating these processing pathways with application demands, this review aims to accelerate the implementation of PHAs as practical and environmentally responsible replacements for conventional agricultural plastics.

2 | Methodology

This review primarily focuses on literature published within the last decade (approximately 2015–present) in order to capture the most recent advances in PHA development, processing, and agricultural applications. However, earlier studies were included where necessary to acknowledge foundational and pioneering contributions, particularly in areas where recent research remains limited (e.g., foam processing and specific melt-processing techniques).

The literature was primarily sourced from major scientific databases, complemented by AI-assisted search tools (e.g., Scopus AI and Consensus). The selection of references was guided by their relevance to: (i) PHA production and strategies to reduce production costs; (ii) structure–property relationships, with particular emphasis on the influence of processing conditions; (iii) approaches to overcome key processing challenges associated with PHAs; (iv) processing strategies for PHA films and foams; and (v) the development of biobased films and foams.

3 | PHAs: Biobased and Biodegradable Plastics

PHAs are a family of polyesters naturally synthesized by a variety of microorganisms, such as *Cupriavidus necator* [17–19], *Pseudomonas putida* [20, 21], *Bacillus tequilensis* [22] and *Halomonas spp* [23]. Their commercial production involves several key steps, as illustrated in Figure 1. The process begins with selection, isolation, and cultivation of microorganisms, which are allowed to replicate until a sufficient starter culture is established. This culture is then transferred to a cultivation tank or bioreactor, where the microorganisms are supplied with a carbon-rich substrate [12]. Under specific stress conditions, they metabolize the substrate and accumulate PHAs as intracellular granules. Following fermentation, PHAs are extracted through cell lysis, most commonly using solvent extraction methods [11]. The resulting purified PHA powder is subsequently extruded into pellets, often by compounding with additives and other polymers. Finally, the pellets undergo further thermal processing to produce the final products.

The fermentation process strongly depends on the specific microbial strain employed and is often energy intensive. Depending on the selected strain, the process typically requires tightly con-

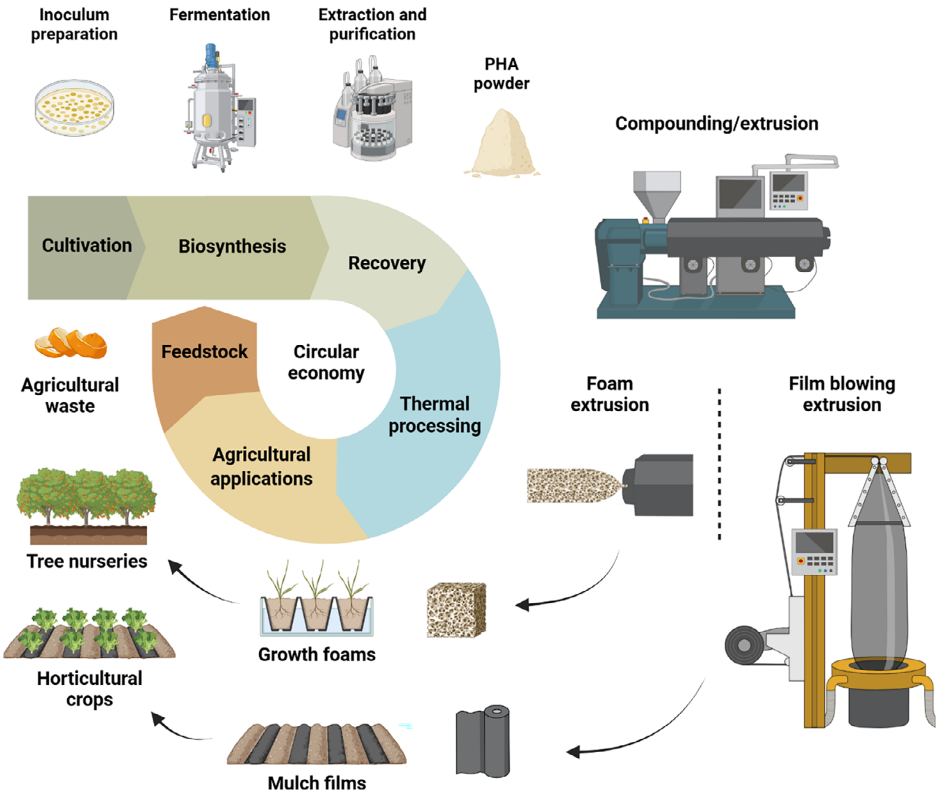

FIGURE 1 | Schematics of PHA production and processing into biodegradable agricultural plastics, highlighting microbial fermentation, polymer recovery, conversion into pellets, and shaping into end-products (e.g., growth foams, mulch films) using agricultural residues as feedstock within a circular bioeconomy framework. Created in BioRender. de Sousa, G. (2026) https://BioRender.com/zhb50go.

trolled conditions, including regulated temperature, pH, oxygen levels and monitoring of nutrient supply. In most cases, the fermentation also begins under sterile conditions to prevent contamination [24]. Recent advances include the development of novel bioreactor designs and the implementation of continuous fermentation processes, which can improve substrate utilization and reduce downtime between batches [24].

Another major challenge lies in downstream processing, particularly in the extraction of PHAs from microbial cells. This step can be performed using different approaches. One method involves treating the biomass with acidic, alkaline, detergent, or protease solutions, while another relies on solvent-based extraction [25, 26]. Chloroform is a commonly used solvent due to its high recovery efficiency. However, it poses significant environmental and health concerns [26, 27]. Life-cycle assessment (LCA) studies further highlight that, although PHAs generally exhibit lower greenhouse gas emissions and reduced dependence on fossil resources compared to petroleum-based plastics [28], these environmental advantages can be substantially offset by the energy-intensive nature of downstream processing and the use of hazardous solvents [29]. As a result, alternative systems such as cyclic carbonates, solvent mixtures, and hydrogenated solvents have been investigated. More recently, research has focused on non-halogenated or "green" solvents as more sustainable extraction options [30, 31].

In addition to extraction, disruption of the cellular structure is required to release the intracellular polymer. While chemical digestion has been widely used for this purpose, emerging approaches such as enzymatic digestion are being developed as potentially more selective and environmentally friendly alternatives [32].

Currently, PHA production costs range from \$4–8/kg, compared to \$1–2/kg for petrochemical plastics [33–35]. This price disparity reflects ongoing technology development challenges that limit large-scale production of PHAs [36]. It should be noted that conventional plastics result from highly optimized industrial processes (Technology Readiness Level 9, or TRL 9) that have been refined over several decades and enable competitive manufacturing [37]. In contrast, PHAs are still under development (TRL 5–8), with technologies demonstrated in relevant environments or approaching full qualification for deployment [38, 39]. Most PHA production facilities are currently transitioning from pilot-scale to early industrial-scale stages.

The main factors contributing to the high cost of commercially available PHAs are the high cost of feedstocks and relatively low production yields [12, 40]. It has been estimated that feedstocks alone account for 45%–50% of total manufacturing costs [11]. To address this, researchers have explored alternative feedstocks, such as lignocellulosic biomass, organic waste, and industrial by-products [41–45]. This strategy not only has the potential to lower production costs but also promotes the valorization of waste into high-value-added products, thereby supporting circularity

However, alternative feedstocks present their own limitations. For example, although lignocellulosic biomass is an abundant, low-cost, and renewable resource for PHA production, its resistance to direct bioconversion necessitates costly and time-intensive pretreatment processes to release fermentable sugars, ultimately increasing overall production costs [46, 47]. Table 1 summarizes the various feedstocks reported for PHA biosynthesis, including their key characteristics, advantages, limitations, pretreatment requirements, and industrial relevance. Among waste-derived feedstocks, fruit residues represent a particularly promising alternative due to their high content of fermentable sugars, which enables more efficient bioconversion with minimal pretreatment requirements [47].

Hou et al. [48] demonstrated that orange peels derived from food waste hold significant potential for cost-effective industrial PHA production. A strain of *Acidovorax diaphorobacter* ZCH-1, isolated from activated sludge, initially produced a poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) concentration of 0.39 g L^{-1}. Through optimization of fermentation conditions, this yield was increased by 138%, reaching a maximum concentration of 0.93 g L^{-1}. Similarly, Rao et al. [49] evaluated various types of kitchen waste as sole carbon and nitrogen sources for PHA production by *Bacillus subtilis* MTCC 144. Their results showed that watermelon rind and pulse peel were the most effective carbon and nitrogen sources, respectively, leading to poly(3-hydroxybutyrate) yields of up to 78 wt% (percentage of PHA relative to cell dry weight).

Genetic engineering is another key strategy to lower PHA production costs by increasing yield. For example, promoter engineering in *Pseudomonas putida* KT2440 enhanced PHA synthase expression and boosted yield by up to 90% [50]. Other promising approaches include genome editing, metabolic pathway optimization, and redox balance regulation [40, 51, 52].

These bio-based polymers are also biodegradable in a variety of environments, including soil, compost, and aquatic systems [12, 16, 53]. Compared to other commercially available biodegradable polymers such as PLA, poly(butylene succinate) (PBS), and poly(butylene adipate-*co*-terephthalate) (PBAT), PHAs generally exhibit faster degradation rates in soil, particularly at ambient temperatures and realistic moisture levels [54–56]. Table 2 summarizes comparative studies on the biodegradability of PHAs and other biodegradable polymers.

A key advantage of PHAs lies in their degradation products, which are non-toxic and therefore more suitable for agricultural applications than those of many other bio-based alternatives. PLA and PGA, for instance, degrade primarily through hydrolysis of ester bonds, producing lactic acid and glycolic acid, respectively [57]. These by-products can substantially lower soil pH, with negative impacts on plant growth, nutrient availability, and microbial activity [58]. By contrast, the main degradation products of PHAs are water-soluble compounds such as 3-hydroxybutyric acid, which are less acidic and non-toxic [59–61]. The pKa of 3-hydroxybutyric acid is higher than that of lactic acid, indicating weaker acidity [62]. Supporting this, studies have shown that weak acids with higher pKa values correlate with reduced toxicity and less inhibition of microbial growth [62].

In soil, a study [63, 64] evaluating six different PHA copolymers demonstrated that these materials could degrade under controlled conditions, reaching up to 90% biodegradation within 11 to 22 months. Importantly, the resulting degradation products showed no significant effect on cress seed germination. A more recent study further indicated that PHA degradation products may enhance soil health, although these benefits are dose-dependent. Specifically, the degradation products were found to increase soil microbial activity, organic carbon content, and enzyme activities. However, at higher application rates (≥1 wt% PHA), nutrient competition was observed, reducing the availability of essential nutrients for plants and ultimately leading to decreased crop productivity.

Overall, studies of PHA biodegradation remain limited in scope, highlighting the need for more comprehensive and long-term studies to better understand the environmental thresholds, variability across soil systems, and potential benefits and trade-offs associated with PHA degradation in soil health and crop productivity under real-world agricultural conditions.

Another factor hindering the widespread application of PHAs is the difficulty associated with their processing and the mechanical properties of the final products. The most extensively produced and studied PHA is poly(3- hydroxybutyrate) (PHB). While PHB exhibits excellent barrier properties against O_2, CO_2, and H_2O [97], its inherent brittleness severely limits its use in flexible applications. Moreover, PHB suffers from poor processability due to its generally low nucleation density and limited thermal stability. Its high melting point (around 170°C–180°C) lies close to the onset of thermal degradation, making processing particularly challenging. Changes in molecular weight due to thermal degradation have been reported as early as 170°C–190°C, while measurable weight loss occurs between 250°C and 300°C [98, 99]. The thermal degradation of PHB is highly sensitive to exposure time and can reduce melt viscosity, leading to processing issues such as discontinuous flow [14]. These factors significantly narrow the allowable processing temperature/time window, making melt-processing techniques such as extrusion, film blowing, or thermoforming particularly difficult [100].

In addition, PHB's sub-ambient glass transition temperature (approximately 4°C) allows secondary crystallization to occur at room temperature through lamellar thickening and/or the formation of new thinner lamellae [101, 102]. This phenomenon increases crystallinity and induces embrittlement over time, meaning the material's properties can continue to change even during storage at room temperature [102, 103].

To improve processability and expand applications, strategies such as copolymerization, blending, and additive incorporation have been explored [104–108]. Advancing the practical use of PHAs requires a clear understanding of how structure, properties, and processing interact with the sustainability criterion. The next subsection examines these relationships in detail.

3.1 | PHA Copolymers: Structure, Morphology and Properties

PHAs consist of hydroxyalkanoate monomers connected by ester linkages forming an aliphatic polyester with the general structure shown in Figure 2a. Their chemical structure can be tailored based on the carbon, nitrogen and phosphorous source and

TABLE 1 | Summary of feedstock types reported for PHA biosynthesis.

Feedstock source	Examples	Key characteristics	Advantages	Limitations	Pretreatment/processing considerations	Industrial relevance
Simple sugars and refined carbohydrates [65–67]	Glucose, sucrose, fructose	Water-soluble, high carbon purity	High yield and productivity, predictable kinetics, easy process control	High cost, competition with food supply, limited sustainability	Minimal pretreatment, sterilization and pH control required	Benchmark substrate for lab-scale optimization and metabolic studies
Lignocellulosic biomass [68, 69]	Corn stover, wheat straw, bagasse	Abundant, renewable, complex polymeric matrix (cellulose, hemicellulose, lignin)	Low-cost, non-food renewable resource	Requires costly pretreatment; generation of inhibitory compounds (furans, phenolics); compositional variability	Delignification and hydrolysis essential; detoxification often required	Strategic long-term substrate for integrated biorefineries
Agricultural residues [70–72]	Rice husk, corn cob, palm empty fruit bunch	Heterogeneous composition, high variability	Widely available, inexpensive, valorizes wastes	High ash content and heterogeneity hinder process control	Mechanical and enzymatic pretreatment may be necessary	Regionally relevant; strong potential for circular bioeconomy
Food waste [47–49, 73–75]	Fruit peels, bakery waste, dairy waste	Nutrient-rich, biodegradable, variable composition	Diverts organic waste from landfills, low/no cost	High compositional variability; contamination concerns	Homogenization, pH adjustment, nutrient balancing needed	Growing interest; viable with robust mixed microbial cultures
Plant oils [76, 77]	Palm oil, canola oil, soybean oil	Triglyceride-based, high carbon content	High PHA yield per carbon input, suitable for tailored copolymer synthesis	High cost, land-use concerns, limited sustainability	Emulsification and sterilization required	Used in specialty PHA production (e.g., mcl-PHA)
Waste cooking oils (WCO) [77–79]	Used frying oil, restaurant grease	Lipid-based, contains free fatty acids and impurities	Cheap, readily available, reduces waste burden	Variable quality; requires purification or treatment	Filtration, deacidification, and removal of particulates	Proven substrate in pilot-scale PHA production

(Continues)

TABLE 1 | (Continued)

Feedstock source	Examples	Key characteristics	Advantages	Limitations	Pretreatment/processing considerations	Industrial relevance
Glycerol [67, 80]	Crude glycerol from biodiesel production	Hydrophilic, byproduct of biodiesel, varies in purity	Abundant, inexpensive, carbon-rich	Impurities (methanol, salts) may inhibit growth	Filtration and partial purification desirable	Established feedstock; demonstrated at semi-industrial scale
Molasses [81, 82]	Sugarcane or beet molasses	High in sucrose and minerals, viscous	Widely available, low cost, nutrient-rich	Composition variability, potential microbial inhibition at high concentrations	Dilution and clarification required	Industrially explored for cost-effective PHA production
Dairy industry byproducts [83, 84]	Whey/permeate	Contains lactose and proteins	Revalorizes dairy waste streams, supports mixed substrate metabolism	Requires lactose-utilizing strains or enzymatic hydrolysis	Sterilization and enzymatic pretreatment commonly used	Demonstrated feasibility at pilot scale
Volatile fatty acids (VFAs) [85, 86]	Acetate, propionate, butyrate from anaerobic digestion	Readily assimilated as PHA precursors	Supports mixed culture processes; adaptable to wastewater valorization	Odor, acidity, substrate imbalance	pH control and buffering required; volatile losses must be managed	Central to mixed microbial culture (MMC)-based PHA processes from wastes
Wastewater-derived substrates [87–89]	Municipal and industrial effluents	Very dilute, heterogeneous, nutrient-rich	Abundant, enables negative-cost feedstock use	Low carbon concentration; high treatment demand	Concentration or enrichment often needed	Promising for coupling waste treatment and bioplastic production
Other industrial side-streams [90–92]	Pulp and paper black liquor, brewery effluents	Process-specific composition, residual organics	Utilization of sectoral residues, reduces waste discharge	Limited standardization, potential inhibitors	Filtration and adjustment of C:N:P ratios	Site-specific industrial symbiosis applications

TABLE 2 | Summary of comparative studies on the biodegradability of PHAs and other biodegradable polymers.

Comparison system	Biodegradation conditions	Metric	Main finding
PHA vs PLA (mulch films) [93]	Agricultural field and laboratory (composting at room temperature) for 7 months	Visual inspection, Fourier transform infrared (FTIR) spectroscopy, thermo-mechanical properties of the film	PHA mulch films disintegrated substantially in soil and under composting conditions; PLA showed much slower/limited degradation under real soil or farm composting conditions
PHB (multifilament yarns) vs PLA (films) [94]	Laboratory biodegradation (natural soil and soil amended with nitrogen sources) over 180 days	Amount of carbon dioxide (CO_2), sample evaluation (FTIR and scanning electron microscopy (SEM))	PHB completely degraded in 90 days in unamended soil; PLA only 6% in same period. Incorporation of nitrogen sources in the soil strongly increased PLA biodegradation (to 40%–45%), but slowed PHB as microbes preferentially decomposed other organic matter
PHB vs PLA, PBS, polycaprolactone (PCL) (discs with controlled thickness) [95]	Laboratory (commercial soil and compost) at $25^{\circ}C$, $37^{\circ}C$ and $50^{\circ}C$ for 10 months	Weight change, SEM, mechanical properties	PCL showed the fastest degradation rate under all conditions and was completely degraded when buried in compost and incubated at 50°C after 91 days. PHB discs also showed a significant reduction in weight under all conditions, and the rate of degradation at 37°C in compost and soil was equivalent to the PCL discs
PHA vs PBS, PLA (microplastic fragments) [96]	Laboratory (three agricultural soils) for 56 days	CO_2 partitioning	PHA microplastics biodegraded fastest and induced by far the strongest positive priming effect on native soil organic carbon, followed by PBS, then PLA

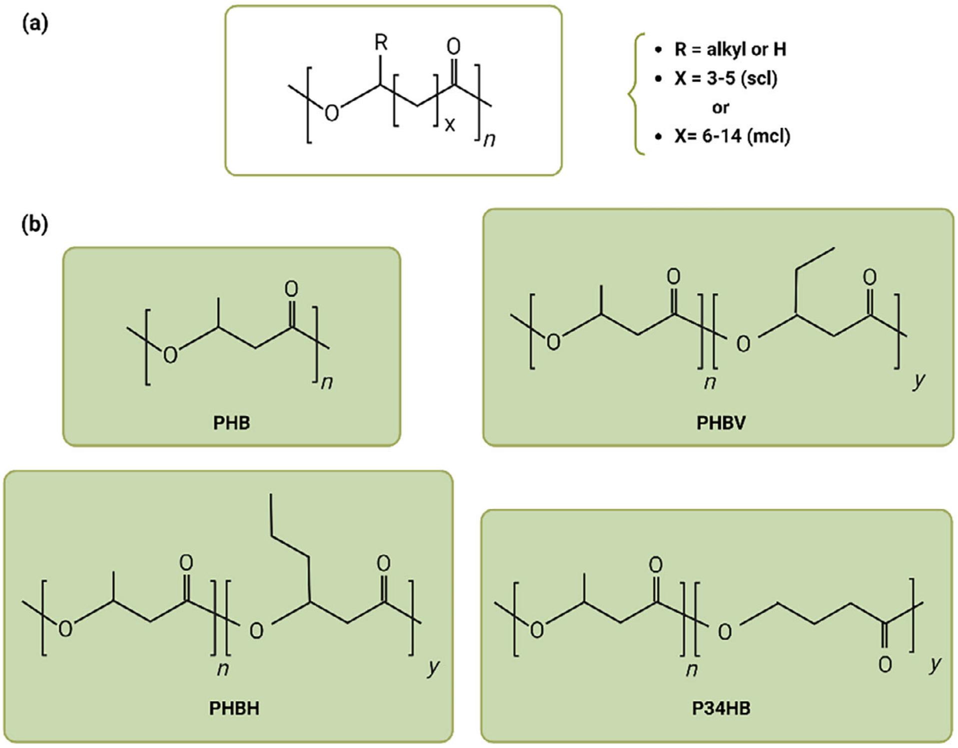

FIGURE 2 | (a) General chemical structure of PHAs and (b) chemical structures of PHB and common PHA copolymers, including PHBV, PHBH, and P34HB. "Application of Twelve Variables Gradient Method to the Study of Poly (β-Hydroxybutyrate) Crystallization," Created in BioRender. de Sousa, G. (2026) https://BioRender.com/laabxy9.

microbial strain used during biosynthesis [109]. Depending on the metabolic pathways specific to each microorganism, a wide range of homopolymers and copolymers can be synthesized [52]. They are typically categorized by the length of their monomer side chains: short-chain-length PHAs (scl-PHAs) containing 3–5 carbon atoms, and medium-chain-length PHAs (mcl- PHAs), containing 6–14 carbon atoms. In general, PHAs with short side chains exhibit thermoplastic behavior, while mcl-PHAs present elastomeric properties [16]. To date, over 150 structurally distinct PHA monomers have been identified, and this structural diversity strongly influences the polymer's mechanical, thermal, and degradation properties [110, 111].

As previously said, the most extensively studied PHA is PHB, a slc-PHA homopolymer with a highly regular structure and correspondingly high crystallinity (typically 60%–80%) [112]. However, its narrow processing window, limited flexibility, and structural instability constrain its practical applications. One effective strategy to address these challenges is the copolymerization of PHB with other PHA monomers. This approach improves processability and mechanical performance while preserving the material's biodegradability and bio-based origin, thereby supporting sustainability and circular economy goals.

The most commonly used PHA copolymers include poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P34HB), and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH) [113]. Their chemical structures are shown in Figure 2b. The morphology of PHAs is intricately influenced by their chemical composition. Incorporating different comonomer units modifies the polymer backbone, which affects morphological characteristics and, in turn, the material's processability and physical properties. These comonomers introduce irregularities that disrupt chain packing, typically resulting in reduced crystallinity and enhanced chain mobility. Consequently, the copolymers exhibit increased flexibility, higher elongation at break, and lower melting and glass temperatures [114, 115].

Depending on the specific combination and ratio of monomer units, PHAs can exhibit different crystal morphologies and polymorphic forms. It is also important to note that the crystal morphology is not only determined by composition but can be significantly influenced by the processing conditions and any post-processing treatments applied [116].

For PHB, depending on the crystallization conditions, different morphologies can be observed. In most industrial polymer processing techniques, such as extrusion or injection molding, crystallization occurs from the melt [117]. Herein, the formation of spherulites is observed. Upon rapid cooling, as adjacent spherulites grow, they impinge upon one another, with their final size and spatial distribution determined by the boundaries formed between them. Smaller and more uniform spherulites generally result in higher tensile strength due to better load distribution and fewer stress concentration points [118, 119].

Spherulite morphology is intrinsically dependent on crystallization kinetics, as illustrated in Figure 3. For PHB, non-banded spherulites form at both low and high crystallization temperatures, while banded spherulites appear within an intermediate temperature range (approximately 70°C–130°C) [120]. PHB is characterized by a low nucleation density, which often results in the formation of exceptionally large spherulites, sometimes on the order of several millimeters or even centimeters in diameter [121, 122]. Nucleation agents, such as boron nitride, talc, nano-clay, starch and lignin particles, are often incorporated to act as heterogeneous nucleation sites, leading to smaller and more numerous spherulites, which can improve the mechanical properties and thermal stability of PHB [123–127].

In copolymers, both the formation and spacing of banded structures are influenced by the type and concentration of the incorporated comonomer. For example, in the copolymer P34HB, increasing the 4HB content results in narrower band spacing and a lower melting temperature [128]. Similarly, Cai and Qiu [129] observed that band spacing decreased with increasing 3HH content and decreasing crystallization temperature. In PHBH with up to 18 mol% of 3HH, banded spherulites were observed over a wide range of crystallization temperatures. However, higher 3HH content significantly reduced the spherulite growth rate. A similar trend was found in PHBV: as the 3HV content increased, the crystallization process slowed considerably, and the crystallization curves shifted to lower temperatures [130].

While spherulites represent the microscale morphology formed during polymer crystallization, the underlying crystalline structures at the molecular level also play a crucial role in determining structure–property relationships. PHB can crystallize into two forms: α- and β-crystals. Crystallization from the melt occurs predominantly in the α-form. Upon cooling, the polymer chains adopt an antiparallel helical conformation, stabilized by dipole–dipole interactions within an orthorhombic lattice (Figure 4a) [122, 131, 132]. In contrast, the β-form consists of highly extended polymer chains in a planar-zigzag conformation, packed within a hexagonal or trigonal lattice [122, 131, 132].

The formation of β-crystals in PHB and PHBV can be induced under specific processing conditions such as uniaxial drawing during fiber spinning or film extrusion [133, 134]. A stress-induced phase transition from the α- to the β-form (Figure 4b) occurs through hot drawing near the melting point, followed by room-temperature drawing. During film processing, β-crystals primarily form due to high draw ratios under controlled temperature conditions [135–137]. These crystals emerge from the alignment of free molecular chains in amorphous regions and the stress-induced partial transformation of the α-form [132]. The presence of β-crystals significantly influences material properties, particularly mechanical strength and biodegradability [122]. Compared to the α-form, the β-form results in higher tensile strength [135] and superior structural stability. While the α-form tends to undergo secondary crystallization, the β-form remains largely unchanged for months at room temperature [122].

The effect of copolymerization on the crystal structure of PHAs depends on both the type and ratio of comonomer. Saito and Doi [138] reported that in P34HB, incorporation of low amounts of 4HB (< 10 mol%) did not alter the crystal structure of PHB, whereas higher comonomer contents significantly disrupted crystal packing, producing smaller and less perfect crystals. Similarly, Cai and Qiu [129] found that incorporation of up to 18 mol% of 3HH monomers into PHBH did not change the

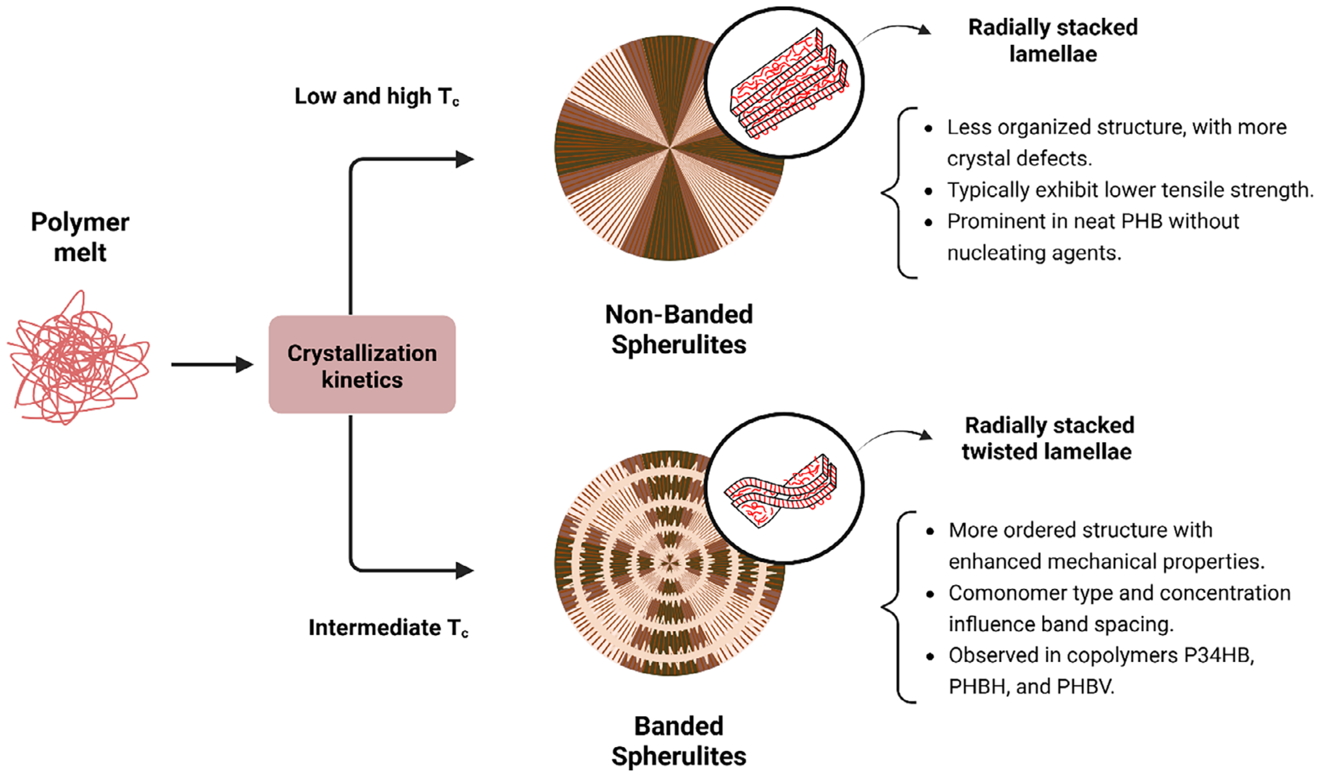

FIGURE 3 | Schematics illustrating the effect of crystallization kinetics on spherulitic morphology in PHB-based polymers. The diagram illustrates the optical patterns and internal lamellar arrangements of banded and non-banded spherulites formed at different crystallization temperatures (T_c).

crystal structure or unit cell parameters of PHB. However, the presence of comonomers interfered with crystalline packing, leading to reduced crystallinity and less stable crystals. The 3HH units, with their longer side chains (Figure 2b), act as molecular spacers, hindering the ability of polymer chains to organize into well-ordered crystals during cooling. This produces a thermodynamically unstable amorphous phase that can later crystallize upon reheating, a process known as cold crystallization. Such behavior has been reported for PHBH containing up to 20 mol% of HH units [129, 139, 140].

In the case of PHBV, co-crystallization occurs, meaning that the host PHB crystal lattice incorporates the 3HV units up to a critical threshold (above 40 mol%) [100]. When the 3HV content exceeds this threshold, a second crystalline phase emerges, resulting in the coexistence of both PHB and PHV crystal lattices [100, 141]. Notably, due to co-crystallization, the addition of 3HV has only a moderate impact on the overall crystallinity of the polymer, but it significantly affects the melting temperature. Wang et al. [55] reported an approximate 10% reduction in crystallinity and a nearly 70°C decrease in melting temperature as the 3HV content increased from pure PHB to 53 wt%.

In general, the melting temperature (T_m) of PHB-based copolymers decreases with increasing comonomer content until it reaches a pseudo-eutectic point. Beyond this point, the thermal behavior depends on the comonomer type and composition. For instance, PHBV exhibits a minimum T_m around 40–50 mol% 3HV. At higher 3HV contents, slight increases in crystallinity and T_m may occur under specific conditions, possibly due to co-crystallization or the formation of 3HV-rich crystalline sequences. However, overall crystallinity typically remains lower than that of the PHB homopolymer [141, 142]. In other systems, such as PHBH, the minimum T_m occurs around 60–70 mol% 3HH. At higher 3HH contents, the copolymer often becomes predominantly amorphous, exhibiting no distinct melting peak [142].

As previously mentioned, mechanical properties are also strongly influenced by comonomer incorporation. In general, the lower the crystallinity, the higher the flexibility. For example, while neat PHB exhibits a high Young's modulus (3.6 GPa) and low elongation at break (~3%), the addition of 55 mol% 3HV or 82 mol% 4HB can increase the elongation at break to 1200% and 1320%, respectively [143]. As flexibility increases, stiffness (modulus) decreases, with values as low as 0.05 GPa reported for copolymers with high 4HB content. Despite this trade-off, high tensile strength can still be maintained in optimized compositions. For instance, P34HB containing 82 mol% 4HB achieves a tensile strength of 58 MPa alongside 1320% elongation at break [138, 143].

The biodegradation behavior of PHAs is governed by their chemical structure and morphology, particularly crystallinity, lamellar thickness, and spherulitic organization. Microorganisms have been shown to preferentially attack amorphous regions before progressing to crystalline domains. The degradation rate of the crystalline phase is dependent on the morphology, with smaller spherulites and thinner lamellae degrading more rapidly [144]. Due to its high crystallinity and large spherulites, PHB degrades relatively slowly, whereas copolymers such as PHBV, PHBH, and P34HB, characterized by lower crystallinity, longer

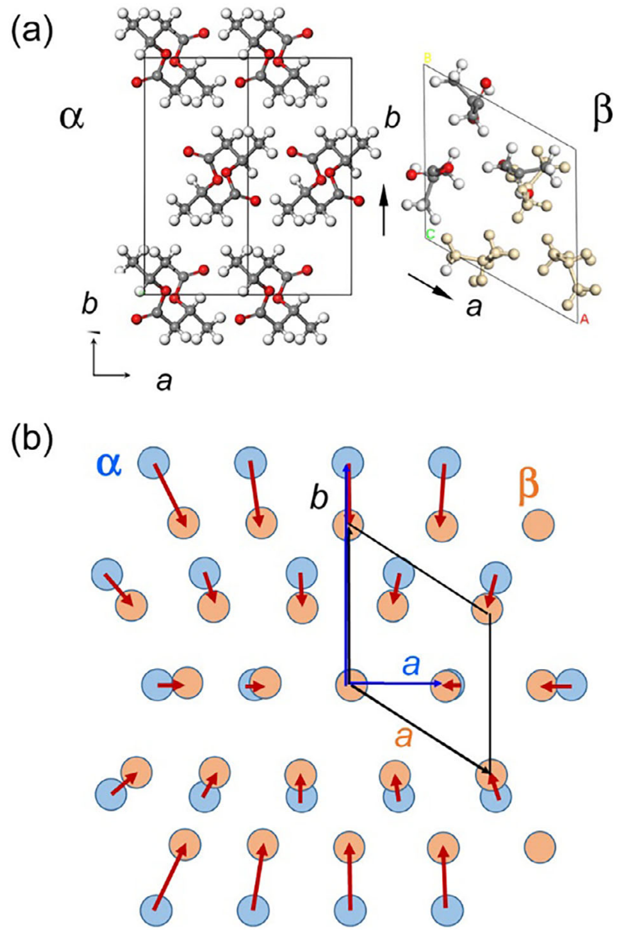

FIGURE 4 | Geometrical relation between PHB α- and β-forms: (a) the unit cell and (b) the positions of the chains. Reprinted with permission from Phongtamrug and Tashiro [132]. Copyright 2026 American Chemical Society.

side chains, and higher chain mobility, exhibit faster surface erosion and overall biodegradation [145–147]. These trends were observed in both soil and enzymatic degradation environments [128, 148, 149].

Overall, copolymerization is a valuable strategy for tailoring the properties of PHB, improving its compatibility with conventional processing methods and enabling sustainable customization of the mechanical and biodegradation properties for specific applications. However, compared to PHB homopolymer production, the biosynthesis of copolymers typically requires additional metabolic pathways, comonomer feeding strategies, tighter process control, and often incurs higher costs [150, 151]. According to the techno-economic review by Policastro et al. [150], enhancing the economic competitiveness of PHA copolymers requires a combination of low-cost waste feedstocks, engineered robust strains capable of efficiently converting these substrates into tailored copolymers, high productivity, and partially non-sterile fermentation strategies. In particular, integrating PHA copolymer production into biorefineries, through co-production with fuels, chemicals, or electricity, represents one of the most promising approaches to sharing infrastructure and reducing overall production costs.

3.2 | PHA Blends

Another common strategy to improve the processability of PHAs and tailor their properties is melt blending with other biopolymers. This approach enables tuning of mechanical and processing characteristics that are difficult to achieve with commercial PHA grades alone. PHAs are commonly compounded with more ductile biopolyesters, such as polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), polybutylene adipate terephthalate (PBAT), poly(ε-caprolactone) (PCL), and thermoplastic starch (TPS), which exhibit lower modulus and greater flexibility. These blends, when optimized, result in significant enhancements in overall technical performance [152].

Righetti et al. [153] demonstrated that although PHB, PBS, and PBSA are immiscible, PHB/PBS and PHB/PBSA blends exhibit mechanical compatibility. Even without compatibilizers, increasing the PBS or PBSA content led to improved ductility, with only a slight decrease in elastic modulus. This was attributed to the formation of a continuous morphology, resulting from the solidification of the two distinct crystalline phases, and to effective physical adhesion between the matrix and dispersed phase.

To preserve a fully bio-based composition while enhancing performance, PHAs are also frequently blended with PLA. The combination of PHA and PLA yields a synergistic effect, capitalizing on their complementary mechanical, thermal, and biodegradation properties [1]. The strongest synergistic improvement in mechanical properties is observed when PLA serves as the matrix and PHA as the dispersed phase, particularly at a 30/70 PHA/PLA blend ratio. A second performance peak is observed with the inverse composition (70/30) [154]. However, high PLA content can significantly slow the biodegradation rate of the blend. For example, Weng et al. [55] investigated P34HB/PLA blends with varying compositions and observed the following order of degradability: PHA-100> PHA-75> PHA-50> PHA-25> PLA. They also found that degradation mechanisms differ between the two polymers: PHA degrades primarily through bacterial surface erosion, whereas PLA undergoes hydrolytic degradation.

Additionally, blending PHB with other types of PHAs also shows promise in addressing its brittleness. Majka et al. [155] demonstrated that incorporating an amorphous medium-chain-length PHA (aPHA) composed of various monomers enhanced the flexibility of PHB without compromising thermal stability. Similarly, blending PHB with P34HB significantly improved the processability for melt spinning of biodegradable filaments [156].

Blends of PHB with other PHBV grades have shown satisfactory results, particularly when the 3HV content remains below 15 mol%. Blending PHBVs with different 3HV contents is also feasible, provided the differences do not exceed this threshold. Exceeding a 15 mol% difference in 3HV content can lead to issues related to crystallization kinetics. Specifically, mismatched crystallization rates may result in interpenetrating crystallization, where slower-growing crystals intrude into regions dominated by faster-growing ones [157, 158]. Such incompatibility between PHBV grades or between other

PHAs can lead to phase separation, which negatively affects mechanical consistency. This may manifest as localized variations in brittleness and flexibility, ultimately compromising the material's performance and reliability under mechanical stress [151].

3.3 | Additives

Another strategy to improve the processability of PHAs is the use of additives, particularly nucleating agents, plasticizers, compatibilizers and fillers. For instance, the incompatibility of PHA blends can be addressed using compatibilizers. One effective approach is reactive polymer blending, which involves the in situ formation of compatibilizing agents or the induction of chemical and physical interactions between polymer components [159]. Dicumyl peroxide (DCP), a free radical initiator, is commonly used in reactive extrusion to improve interface compatibility in blends by inducing branching and/or crosslinking in PHB. This results in a more uniform morphology, with improved toughness. Additionally, melt strength is enhanced, leading to better processability in applications such as blown film extrusion. Other organic peroxides, such as 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane (LUPEROX 101E), are also commercially available and can serve similar functions, with the added advantage of complying with food safety regulations [160].

Nucleating agents are class of additives that influence the crystallization kinetics of polymers. As discussed in previous sections, crystallization affects processability and can significantly alter the resulting mechanical properties [157]. Nucleating agents promote crystal formation within the polymer matrix by lowering the energy barrier for nucleation. When appropriately selected, they can raise the crystallization onset temperature, leading to earlier solidification during cooling. This can increase the apparent melt viscosity and improve melt strength, thereby enhancing processability in techniques such as blown film extrusion [161]. Additionally, they serve as sites for heterogeneous nucleation, therefore accelerating crystallization rates, and leading to smaller, more uniform crystals [162, 163]. These changes in crystalline structure directly impact key material properties, including barrier performance, biodegradability, and thermal, mechanical, and optical characteristics.

Various nucleating agents have been tested in PHBV, including boron nitride, talc, orotic acid, cyanuric acid, saccharin, theobromine, and xanthine [164–166]. Furthermore, the incorporation of reinforcing additives such as fibers has been shown to act as additional nucleation sites, further influencing crystallization behavior [162, 167]. Weihua et al. [127] has demonstrated that lignin particles function as an effective nucleating agent for PHB, increasing crystallization temperature and reducing cold crystallization. Polarized optical microscopy (POM) observations revealed that lignin enhanced the spherulitic growth rate, nucleation density, and the maximum temperature for spherulite formation. Although lignin altered the crystallization kinetics, it did not affect the crystalline structure or overall crystallinity of PHB. As a naturally abundant, biodegradable byproduct of the pulp and paper industry, lignin offers both economic and environmental advantages when used as nucleating agent for PHB [127]

The use of plasticizing agents can significantly enhance the processability and mechanical properties of PHAs. Their effect typically reduces the glass transition temperature and stiffness of the polymer by increasing the free volume and enhancing the mobility of the amorphous phases [160, 168]. The selection of an appropriate plasticizer depends on several factors, including its miscibility with the polymer, thermal stability under processing conditions, and compliance with relevant regulations, such as food safety. A range of plasticizers has been investigated for use with PHBV and PHB, including Licowax, soybean oil, epoxidized soybean oil, phthalates, polyethylene glycol, oligomers, and citrate esters such as triethyl citrate and acetyl tributyl citrate (ATBC) [160, 169]. Another important consideration in plasticizer selection is sustainability and environmental impact. In this context, there is growing interest in "green plasticizers" derived from renewable sources such as vegetable oils, fatty acids, and lignocellulosic biomass. Notable examples of these more sustainable alternatives include 1,2-cyclohexanedicarboxylic acid diisononyl ester (DINCH) and ATBC [169].

The incorporation of fillers, particularly nanofillers, has shown significant potential in tailoring the properties of PHAs for specific applications. For example, the dispersion of cellulose nanocrystals (CNCs) within the PHB matrix can enhance a range of properties, including physical strength, barrier performance, thermal stability, mechanical integrity, and rheological behavior, all while preserving the material's biodegradability. However, an optimal CNC loading of approximately 2 wt% is recommended, as higher concentrations may result in nanoparticle agglomeration or lead to polymer degradation during processing [170].

In agricultural plastic applications, various additives are commonly incorporated into both fossil-based and bio-based polymers to enhance functional and technical performance and extend service life. These additives include antioxidants, light and thermal stabilizers, lubricants, pigments, antistatic agents, and slip compounds. In the case of mulch films specifically, light stabilizers and UV absorbers are frequently employed to delay photodegradation by providing resistance to sunlight, heat, and agricultural chemicals [171, 172].

While these additives improve durability and functionality, their potential environmental impact must be carefully considered. Many of these substances can migrate from plastic materials into the surrounding soil during use, posing a risk of accumulation and contamination in soil, water, and even food systems [173]. Therefore, when developing PHA-based agroplastics, the selection of additives should prioritize not only technical performance but also environmental safety, favoring compounds with low ecotoxicological impact and minimal potential for long-term persistence in agricultural ecosystems.

Table 3 compares the principal strategies used to enhance the processability of PHAs, outlining their respective advantages and limitations. Among the approaches, copolymerization delivers the most substantial and intrinsic improvements in both processability and mechanical performance. However, it is also the most technically demanding and often the least economical access at scale. In contrast, blending represents the most industrially viable and cost-effective strategy due to its flexibility and compatibility with existing processing infrastructure. The use of

TABLE 3 | Strategies to improve the processability of PHAs.

Strategy	Main advantages for processability	Limitations
Copolymerization	Ductility enhancement; wider processing window	Process development cost, complexity
Blending	Tailored properties; flexible, scalable tuning; cost leverage	Compatibility, possible loss of biodegradability
Additives	Tailored properties; enhanced processability	Potential migration to soil, regulatory/ ecotoxicological constraints

plasticizers, fillers, compatibilizers, and processing aids can significantly enhance flexibility, strength, and overall processability. Nevertheless, their incorporation requires careful selection and optimization, as inappropriate choices may lead to issues such as additive migration, compromised biodegradability, or reduced material safety.

4 | Plastics in Agriculture Applications

Plastics have contributed significantly to the intensification and efficiency of agricultural practices. However, their reliance on fossil-based plastics and resistance to degradation has raised environmental concerns, particularly related to microplastic accumulation and long-term soil contamination. This has prompted a growing interest in bio-based and biodegradable alternatives, materials that not only perform essential agronomic functions but also degrade safely after use. In response, regulatory frameworks such as EU Standard EN 17033 for biodegradable mulch films and the EU Circular Economy Action Plan are driving innovation toward more sustainable solutions.

Within this context, PHAs are emerging as promising bioplastics for agriculture, offering biodegradability and tunable properties suitable for mulch films and growth-support media. However, scalable and efficient processing remains a challenge. The following subsections examine these two applications, focusing on PHA-based biodegradable alternatives.

4.1 | Mulch Films

Mulch films are used extensively across the globe, covering more than 18 million hectares and accounting for an annual consumption of over 1.45 million metric tons [174]. By modifying the soil microclimate, mulching enhances crop yields and enables cultivation in water-limited regions. In addition, these films reduce reliance on chemical herbicides and fertilizers by suppressing weeds and maintaining optimal soil moisture and temperature [175]. Commercial mulch films are primarily manufactured from low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), which are cost-effective, easy to process, and well-suited to the optical and physical requirements of agricultural applications. Their key properties include high puncture resistance, mechanical stretchability, long-term durability, and water impermeability [1, 176]. Mulch films are produced in a variety of colors, such as black and transparent, each providing distinct light transmission and heat absorption characteristics tailored to specific crops and climatic conditions [177].

An important limitation in the use of plastic materials for mulching is that plastic has to be removed after the harvest (Figure 5a), which is often labor-intensive, time-consuming, and costly. Mechanical removal typically recovers only about 75%–85% of the plastic, while the rest remain in the soil [178] As polyethylene mulch films are exposed to UV radiation and harsh weather, they gradually degrade, becoming brittle and fragmenting into small particles that can easily disperse. The persistence of residual agricultural film in soil leads to structural degradation, reduced root absorption of water and nutrients, and inhibited plant growth and development, ultimately resulting in decreased crop productivity [179]. In the EU alone, soil contamination from agricultural plastics is estimated at approximately 467 kilotons per year, with mulch film contributing around 36% (166 kt) of this total [178, 180, 181].

Recycling these plastics presents significant challenges, primarily due to two key factors: (i) high processing costs, mainly driven by heavy contamination with soil, stones, organic matter, and pesticide residues (contaminants can account for 30%–40% of the total weight). The cleaning processes required to remove these materials are complex and expensive. (ii) Low material value and limited market demand for recycled products. Plastic recovered from mulch films is generally of poor quality and has restricted applications [178]. Furthermore, recycling efforts are often hindered by inadequate regulatory frameworks and weak enforcement mechanisms [177]. In fact, conventional plastic mulch films with pollutant levels above 5% (e.g., pesticides, fertilizers, soil and debris, moist vegetation, and UV additives) are not recyclable. As a result, these films are typically sent to the landfill or incinerated, incurring high costs for local authorities and causing significant environmental problems [1].

4.1.1 | Biodegradable Plastics in Mulch Films Applications

Biodegradable plastic mulches (BDMs) offer a promising alternative to conventional polyethylene (PE) mulches, with the potential to reduce plastic pollution and soil contamination associated with plasticulture. First introduced in the 1980s, BDMs have seen significant advancements in recent years, with new formulations developed to address the challenges of agricultural plastic waste disposal. Unlike PE mulches, which must be removed after use, BDMs are designed to be incorporated into the soil after the growing season (Figure 5b), where they naturally degrade [1]. The growing market now offers a variety of BDMs made from different polymers and additives, as summarized in Table 4.

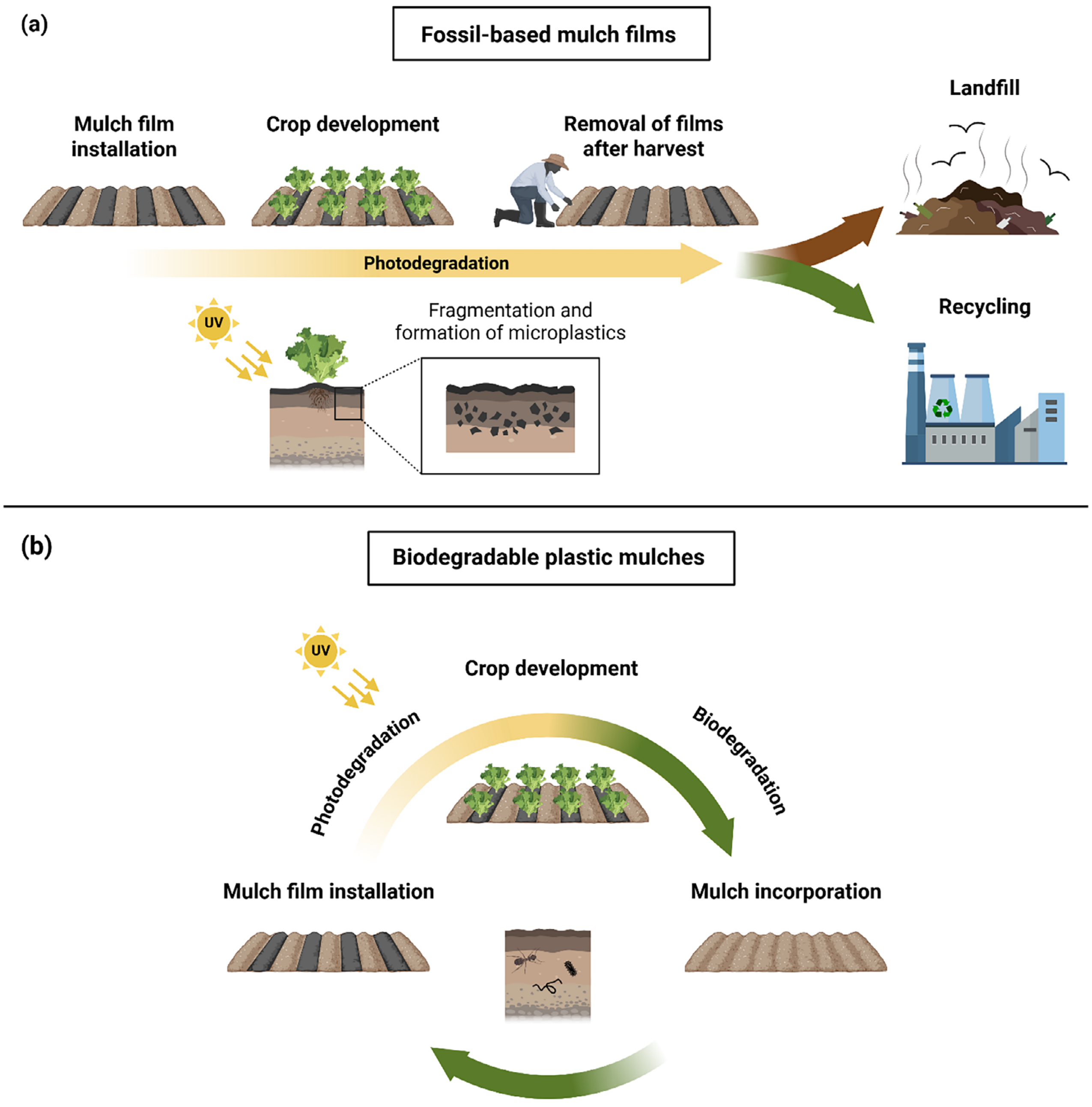

FIGURE 5 | Life cycle of (a) traditional fossil-based mulch films and (b) biodegradable mulch films. Created in BioRender. de Sousa, G. (2026) https://BioRender.com/xn6szvv.

Conventional plastics currently dominate the European agricultural market, accounting for approximately 99% of total usage, while biodegradable alternatives represent only about 1%. However, the biodegradable polymer sector is growing rapidly, with global production projected to reach 6.7 million tons by 2025 [182]. A wide range of biodegradable polymers is under investigation as potential substitutes for conventional plastics in agriculture, particularly for mulch films. These include starch blends, PBAT, PBS, PCL, PLA, PHAs, aliphatic-aromatic copolyesters (AAC), cellulose, and protein-based polymers. Among these, PHAs and PLA stand out, as they are both bio-based, derived wholly or partially from renewable feedstocks, and biodegradable. In contrast, PBS, PBAT, and PCL are petroleum-derived but still biodegradable.

The rate and extent of biodegradation of BDM films are strongly influenced by environmental factors such as climate, temperature, humidity, and soil characteristics. Agricultural soils often lack the microbial diversity and abundance required for complete degradation of BDMs, largely due to specific soil typologies and limited microbial activity [183]. As a result, many commercially available BDMs degrade at rates that do not align with the cropping cycle, particularly for short-cycle crops, where full degradation frequently does not occur within the necessary time frame.

In this context, PHA-based biodegradable films are gaining increasing attention due to their favorable attributes, most notably their ability to degrade rapidly in a variety of environ-

TABLE 4 | Examples of commercially available biodegradable mulch films, their composition and manufacturers.

Name	Composition	Company	References
BioAgri	Mater-Bi grade EF04P	BioBag Americas, Inc., Norway	[184]
BioFlex	PLA/PBAT	FKuR Kunststoff, Germany	[185]
Biopar	Starch and TPS, PLA, PBS, and PBSA	BIOP Biopolymer Technologies, Germany	[186]
Biosafe	PBAT/starch	Xinfu Pharmaceutical Co., China	[186]
Easter Bio	PBAT	Eastman Chemical, USA	[186, 187]
Ecoflex	PBAT	BASF, Germany	[188, 189]
Ecovio	PBAT/PLA	BASF, Germany	[188, 190]
Ingeo	Starch/PLA	NatureWorks, USA	[188]
Biomax	TPS/starch	DuPont, USA	[186]
Mater-Bi	TPS/PCL	Novamont, Italy	[184]
Bionolle	TPS/PLA/PBS or PBSA	Showa Denko Europe, Germany	[188]
EcoWorks	TPS/PBAT, PBS	Cortec Corporation, Germany	[191]
Biomer L	PHA	Biomer, Germany	[192]
ReNew	PLA	Futerro, Belgium	[193]

ments, including soil and compost, and their generation of non-toxic degradation products. In fact, PHA-based mulch films may contribute to improved soil structure, enhanced water retention, and reduced contamination from persistent plastics, ultimately supporting higher crop yields [194]. Nevertheless, the higher cost compared to fossil-based plastics and processability limitations, particularly for flexible mulch films, are major impediments to their widespread use. Further research is crucial to address these barriers by reducing production costs and enhancing processability, while ensuring the preservation of their excellent biodegradation properties in soil.

4.2 | Growth Foams

Polymeric foams are lightweight materials composed of a polymer-gas mixture that forms a microcellular structure, offering advantages such as low density, thermal insulation, energy absorption, and a high strength-to-weight ratio [195]. Foams can be categorized based on three main characteristics: (a) cell type, (b) wall stiffness, and (c) cell size. Structurally, foams may be open-cell, allowing the passage of fluids and air, commonly used in bedding, furniture, and acoustic insulation, or closed-cell, where the pores are sealed, providing greater rigidity and moisture resistance. Foams also vary in flexibility, with rigid foams typically used in construction, transportation, and thermal insulation, while flexible foams are found in cushioning, packaging, and footwear applications. Additionally, cell size allows classification into macrocellular, microcellular, ultramicrocellular, and nanocellular foams [196].

In agriculture, foams are widely used as insulating and shock-absorbing materials, helping to regulate temperature and noise, as well as protect delicate seedlings during packaging and transport. A particularly important application is growth-support foams, which are central to modern horticulture, hydroponics, and vertical farming. These foams function as synthetic root substrates, offering structural support, aeration, and moisture retention, features especially valuable in soilless systems, where conventional soil is absent. Common applications include seedling trays, nutrient delivery matrices, and plant propagation blocks, all of which enable high-density planting and significantly reduce water consumption, making them particularly valuable in arid and semi-arid regions [197]. For example, the use of foams in hydroponic lettuce production has allowed a reduction in water use by up to 90% compared to traditional soil-based methods [198].

From a materials engineering standpoint, growth-support foams must possess key properties such as low density, high porosity, strong water retention, and mechanical stability under wet conditions [199, 200]. Open-cell foams, due to their interconnected pore structure, are especially suitable for these applications, as they promote efficient water absorption, gas exchange, and root penetration, effectively replicating essential soil functions. Moreover, the microstructure and surface chemistry of foams can be engineered to incorporate active compounds like fertilizers, biostimulants, or microbial inoculants, enhancing their role as functional growing media. Beyond improving crop yields and water-use efficiency, these advanced foams support the development of controlled- environment agriculture and promote sustainable food production, particularly in regions affected by soil degradation or limited water availability [201].

Traditional growth-support foams are predominantly made from fossil-based polymers, such as polyurethane (PU), which, despite their excellent mechanical performance, are not biodegradable and contribute significantly to microplastic pollution and long-term soil contamination. In the European Union alone, PU foam production reaches nearly 900 000 tons annually, the vast majority of which is non-degradable, exacerbating environmental burdens [202].

4.2.1 | Biodegradable Plastics in Foam Applications

In response to these sustainability concerns, growing research efforts are focused on developing biodegradable alternatives derived from renewable feedstocks [203]. Bioplastics such as PLA, PBS, and various protein-based materials have emerged as promising candidates. However, most current applications of bio-foams are concentrated in non-agricultural sectors, such as insulation, purification, and absorption. For example, Li et al. [204] developed PLA/PBS open-cell foams for selective oil adsorption; Bettelli et al. [205] fabricated gluten-based foams for water absorption; and Gama et al. [206] produced PU foams using coffee waste as a sustainable filler for thermal insulation.

Among the most promising emerging alternatives are polyhydroxyalkanoate (PHA)-based foams, which are fully biodegradable in soil, compost, and marine environments [16]. Their thermoplastic nature also allows for processing into porous structures ideal for moisture retention and root support, making them suitable candidates for agricultural use. For instance, Zhang et al. [207] successfully produced foams from P(3HB-*co*-4HB) using supercritical CO_2 ($scCO_2$) extrusion, demonstrating that at 30 wt% 4HB, the foams could be processed at lower temperatures while achieving 100% resilience, suggesting strong potential for scalability. Similarly, Panaitescu et al. [208] explored the use of thermally expandable microcapsules in PHBV matrices, which effectively induced porosity and improved foam structure. These studies highlight a growing interest in expanding the role of bio-based foams in sustainable applications.

However, the foam processing of PHAs remains technically challenging due to their complex thermal and rheological behavior. Key challenges include achieving stable foam structures, maintaining mechanical strength, and optimizing processing conditions. Particularly, PHAs have poor melt strength and are difficult to foam uniformly, leading to inconsistent cell structures and densities [209]. Therefore, further research is needed to optimize formulations to address these issues, scale up processing methods, and fine-tune material properties to meet the specific performance requirements of agricultural and other sectors.

5 | Processing of PHAs for Agricultural Applications

This section outlines the primary industrial processing techniques used to convert PHAs into films and foams, with a focus on conventional manufacturing methods and recent advances in the processing of PHAs. Figure 6 provides an overview of the typical industrial processes involved, from initial compounding of PHA powder to the production of film and foam-based products.

The production of plastic products typically relies on melt processing methods, such as single- and twin-screw extrusion, blown film, cast film, and injection molding [210]. Twin-screw extrusion, or compounding, is commonly used to blend polymers with additives or other polymers, achieving homogeneous mixtures through the combined effects of shear from co-rotating or counter-rotating screws and applied heat. This step often serves as a preliminary process before further shaping techniques, such as blown film extrusion [211]. For bioplastics like PHAs, careful control of processing conditions is essential to minimize thermal and mechanical degradation. The use of twin screws increases the specific mechanical energy (SME) input compared to single-screw extrusion, which can reduce the molecular weight of PHAs [212]. Key factors influencing degradation during melt processing include residence time, temperature, and shear rate [213]. In particular, the combination of low screw speeds with high temperatures has been shown to accelerate degradation [213, 214]. Additionally, while less influential, screw configuration also plays a role: less dispersive and more distributive mixing is recommended during PHBV extrusion to help preserve polymer integrity [212, 213].

5.1 | Processing Methods for Film Manufacturing

Blown film extrusion is the primary method for converting plastics into thin films. The process begins with one or more single-screw extruders feeding molten polymer through an annular die. Air is then introduced to inflate the melt into a bubble, which is cooled and flattened before being wound onto a roll. This method inherently induces biaxial orientation in the film, circumferentially from bubble expansion, and longitudinally from stretching during winding. Both monolayer and multilayer films ranging from 10 to 100 µm in thickness can be produced [215]. The polymer's melt strength plays a critical role in determining the bubble's deformation behavior and the final film morphology. As such, the rheological properties of the polymer, along with carefully selected processing parameters, directly influence film quality. Key parameters include extrusion temperature and throughput, bubble diameter, and nip roll speed [216, 217].

Cast film extrusion is another method for producing plastic films and sheets. It typically involves a single-screw extruder feeding a flat die, followed by a calendering system. This process can produce films ranging from 10 to 200 µm in thickness, or thicker sheets up to 100 mm for more demanding applications. Both monolayer and multilayer films, with up to five layers, can be manufactured. Film characteristics are largely determined by the die geometry and width settings. During calendering, the film is stretched, resulting in a mono-oriented structure in the machine direction [217]. With additional equipment, bi-orientation can also be achieved in the transverse direction, though this adds complexity and cost to the process [215].

Overall, blown film extrusion is generally preferred for mulch film production due to its greater versatility in adjusting product parameters and its cost-effectiveness in producing wide films [215].

5.1.1 | PHA-Based Films

Despite their biodegradability, PHA-based films are not yet widely produced or commercially adopted, mainly because of their higher cost compared to fossil-based mulch films and their processing limitations, especially in flexible applications. Recent studies, however, have proposed effective strategies to address these challenges. For example, Genovesi et al. [218] developed blends of PHBH and P34HB using twin-screw and cast film extrusion. They found that increasing the P34HB content

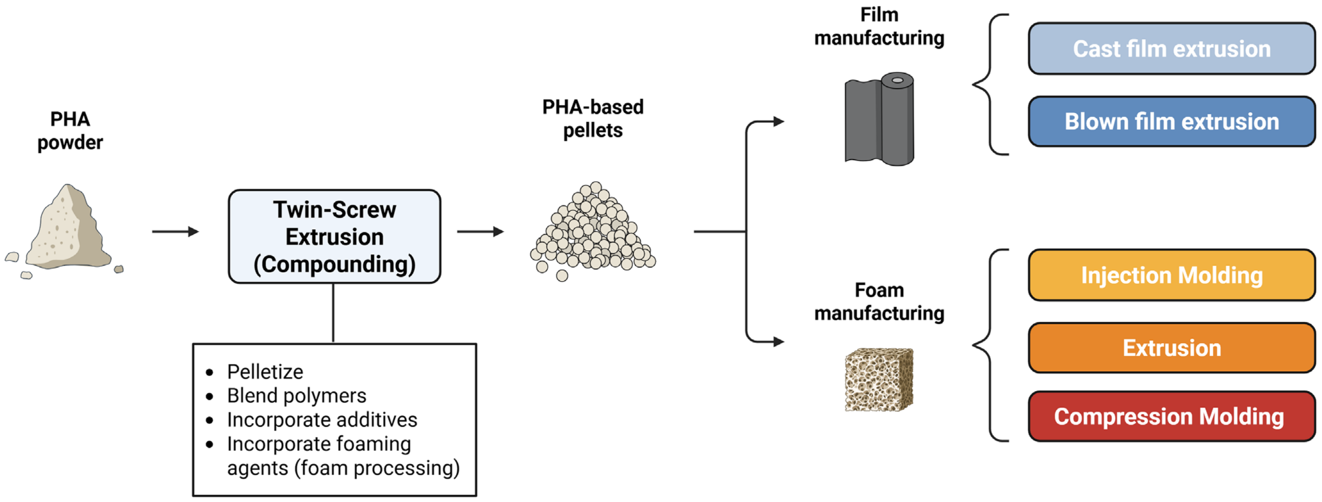

FIGURE 6 | Overview of common industrial processing methods for converting PHA powder into films and foams. Created in BioRender. de Sousa, G. (2026) https://BioRender.com/eoryj4c.

improved film flexibility (elongation at break) but reduced both maximum stress and elastic modulus. Higher P34HB content also increased gas permeability. Overall, these blends exhibited favorable mechanical, thermal, and barrier properties, highlighting their potential for low-impact packaging applications, such as films for fresh fruits and vegetables.

At the laboratory scale, solvent casting remains a widely used method for producing PHA films. In this technique, the polymer is dissolved in a suitable solvent, cast onto a flat surface or mold, and dried to allow solvent evaporation, forming a thin film. This process offers high control over film thickness and is commonly employed to investigate surface properties relevant to PHA biocompatibility [219, 220]

At the industrial scale, producing films from biodegradable polymers via blown film extrusion remains particularly challenging [221]. PHAs are characterized by rapid melt degradation, high crystallinity, low melt strength, and narrow processing windows. For PHAs such as PHBV, one of the primary limitations is low melt strength, which leads to excessive sagging and bubble instability or collapse during processing [222]. To address these limitations, the most effective strategies combine [1] modification of rheology through blending, copolymerization, or pre-treatments (e.g., acid washing); [2] reactive compatibilization to enhance interfacial adhesion and melt elasticity; and [3] precise control of processing parameters, including temperature, residence time, and cooling rate [223–225].

Larsson et al. [223] showed that mild HCl washing increased the PHA decomposition temperature by up to ∼50°C, thereby reducing molecular weight loss during extrusion and enabling more robust melt processing and blending. In addition, PHB/PBAT and P34HB/PBAT blends with improved processability (e.g., higher dynamic shear modulus) and enhanced interfacial adhesion were obtained via reactive extrusion using DCP.

Delliou et al. [13] developed a blend of PHBV and PBSA (70/30 wt%) using DCP as a compatibilizer. The addition of DCP promoted crosslinking and the formation of long-chain branched structures. An optimal formulation with 0.1 phr DCP significantly improved the melt strength, reducing the melt flow index from 90 g 10 min^{-1} (for neat PHBV) to 22 g 10 min^{-1}, enabling successful small-scale film blowing. Notably, the thermal properties of PHBV, including glass transition temperature and crystallinity index, remained unchanged.

Although the resulting films were more brittle and had a lower modulus than neat PHBV, they could be heat-sealed and retained their mechanical performance after 6 months of freezer storage, indicating potential for scalable film production [13]. In a follow-up study, Delliou et al. [160] investigated the use of acetyl tributyl citrate (ATBC) as a plasticizer to further enhance the processability and ductility of the PHBV/PBSA blend. While the incorporation of ATBC led to a reduction of over 50% in the melt flow index, only the non-plasticized films met the required food safety standards.

Teixeira et al. [226] developed PHB–PBAT co-extruded bilayer films. It was shown that the PBAT layer stabilizes the bubble, improves melt strength and drawability, and enables the production of films thinner than 50 μm, with elongation at break exceeding 500% at ≥50 wt% PHB [223]

In summary, improving the processability of PHAs for blown film extrusion relies on a combination of material design (e.g., blending and copolymerization), reactive modification, and precise control of processing conditions. While the production of PHA-based films via cast film and blown film extrusion has been demonstrated in lab scale, further research is essential to optimize PHA-based blends for adequate melt strength, which is critical for scalable manufacturing. Blends incorporating PHAs with PBAT or PBSA offer great potential for enhanced flexibility and processability. Achieving consistent film quality also depends on the careful selection of compatibilizers to prevent bubble collapse and ensure uniform thickness, as well as plasticizers to facilitate bubble formation and stabilize thickness during film blowing [160, 227]. For mulching applications, it is equally important to select polymer components and additives that comply with food safety and biodegradability standards, ensuring that the final materials meet both functional and regulatory requirements.

5.2 | Processing Methods for Foam Manufacturing

The foaming process typically involves two main steps: polymer saturation or impregnation with a foaming agent, followed by the formation of a gas phase that creates the foam's cellular structure. Foaming agents are substances responsible for generating the gaseous phase within the polymer matrix. The two primary categories of foaming agents are physical blowing agents (PBAs) and chemical blowing agents (CBAs). PBAs are usually gases or volatile liquids that generate gas through physical mechanisms, such as evaporation (boiling of a liquid) or phase separation caused by changes in solubility between the polymer and the blowing agent. In contrast, CBAs are compounds that produce gas chemically under specific processing conditions, either through chemical reactions or thermal decomposition [228].

Some of the most common industrially used polymeric foam processing methods are injection molding, extrusion, and compression molding. Injection molding can also be organized in low-pressure, high-pressure, and co-injection foam molding processes [228]. In polymer foam injection molding, a foaming agent is introduced into the polymer melt to create a polymer–gas mixture. This mixture is then injected, typically using a short-shot method, through a nozzle into a mold cavity under pressure. Upon contact with the colder mold surface, a solid skin layer forms, while the gas expands within the core, generating a cellular structure.

In low-pressure foam molding, foaming is initially suppressed due to maintained pressure during injection, with mold filling remaining incomplete. Foaming occurs only after pressure release, leading to relatively low-cost production. For this reason, low-pressure foam molding accounts for approximately 90% of global thermoplastic structural foam production. However, this method often suffers from non-uniform cell size distribution, poor surface quality, and limited density reduction (typically below 25%).

In contrast, high-pressure foam molding involves complete mold filling under elevated pressure. After the initial solid skin forms, the mold is allowed to expand, enabling the foaming agent to create a cellular core. This approach improves surface quality by minimizing surface swirl, increases density reduction up to 50%, and reduces overall processing time. An advanced variant, co-injection molding, utilizes two separate injection units to simultaneously inject a solid (non-foamed) polymer as the outer "skin" and a foamed polymer as the inner "core". This configuration enhances the final product's performance, providing improved cut-through resistance, higher modulus, better gas barrier properties, and superior printability [229].

Foam extrusion is a continuous manufacturing process used to produce polymeric foams with either open- or closed-cell structures. The process is illustrated in Figure 7. It begins by feeding a polymer (typically in pellet or granule form) into an extruder, where it is melted by the combined effect of external heaters and mechanical shear from rotating screws [230]. Once a homogeneous molten polymer is achieved, a blowing agent is introduced, either physical (e.g., $scCO_2$, supercritical N_2, or pentane) or chemical (which decomposes under heat to release gases like CO_2 or N_2). The blowing agent dissolves into the polymer melt under high pressure, forming a single-phase solution. This pressurized mixture then travels through the extruder to a die, where it is shaped and then rapidly depressurized as it exits to ambient conditions [231]. The sudden drop in pressure causes the dissolved gas to expand, creating bubbles within the polymer matrix, a process known as nucleation. These bubbles grow as the gas diffuses, and the melt continues to expand. As the material cools, solidification occurs, locking in the cellular structure. The cell morphology (size, density, and structure) is influenced by several factors, including the polymer's rheological properties, the blowing agent type and concentration, processing temperature and pressure, and post-extrusion cooling rate [232].

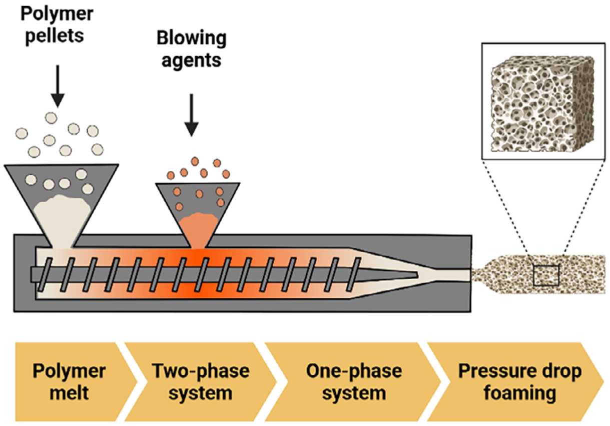

FIGURE 7 | Schematics of foam extrusion process with chemical blowing agents. Created in BioRender. de Sousa, G. (2026) https://BioRender.com/0ifxfxe Created in BioRender. de Sousa, G. (2026) https://BioRender.com/0ifxfxe.

Foam compression molding is a versatile method used for producing foamed thermoset or thermoplastic materials with well-defined geometries and controlled cellular structures [228]. This process can be carried out in one or two stages. In the two-stage approach, the first step involves using an extruder to thoroughly mix the polymer with the CBA, ensuring homogeneity of the compound. A precisely measured mass of this compound is then placed into a preheated mold, where it undergoes press-curing. During this initial molding step, the polymer is cross-linked, and the CBA is only partially decomposed to create a pre-expanded foam. The mold design typically allows for the evacuation of gases and initial foam expansion. In the second stage, this pre-form is transferred to a secondary mold of the final desired dimensions [233]. The temperature is raised further to fully decompose the remaining blowing agent, inducing rapid expansion and allowing the foam to fill the new mold cavity completely. This staged foaming process enables better control over foam structure and dimensions and is particularly advantageous when both high cross-link density and precise geometry are required [228].

5.2.1 | PHA-Based Foams

Despite their promising properties, PHA-based foams remain relatively underexplored compared to other biodegradable foam

TABLE 5 | Summary of PHA-based foams, foaming agents, processing methods, and applications.

PHA Composition	Foaming Agent	Processing Method	Application	References
PHBV/CNPS	$scCO_2$	High-pressure autoclave	Electromagnetic shielding	[234]
P34HB	CBA	Extrusion	—	[225]
PHBV	$scCO_2$	High-pressure autoclave	—	[235]
PHBV	CBA	Extrusion	Heat insulation	[236]
PHBV	CBA	Extrusion	Food packaging	[237]
P34HB	$scCO_2$	Compression molding	—	[207]
PHBV	TES	Compression molding	Insulation, packaging, biomedical applications	[208]
PHBV/Organo clays	$scCO_2$	Extrusion	Packaging, carriers of active ingredients	[238]
PHBV/PHBH	CBA	Extrusion	Insulating application	[239]
PHBV/cellulose acetate butyrate	CBA	Extrusion	—	[240]
PHBV/PBAT	scN_2	Injection molding	Food packaging, automotive applications	[241]

systems. Challenges such as the limited availability of commercial PHA grades, high production costs, and complex thermal and rheological behavior have hindered their broader investigation, particularly for porous applications. Consequently, only a limited number of studies have addressed the processing of PHAs into foam structures and evaluated their suitability for specific end-uses. These studies, summarized in Table 5, explore diverse strategies to foam PHA materials, mainly PHBV and its blends, with the objective of producing lightweight, porous, and in some cases, multifunctional foams. The foaming processes vary widely: some use PBAs like $scCO_2$ or thermally expandable microspheres (TES), while others rely on CBAs such as azodicarbonamide or endothermic gas-releasing mixtures (e.g., citric acid with sodium bicarbonate).

In the work of Luo et al. [234] PHBV/graphene nanoplates (GNPs) nanocomposites were foamed using a green $scCO_2$ batch process. This method provided good control over the pore structure and yielded a multifunctional foam with exceptional electromagnetic interference (EMI) shielding effectiveness, up to 27.4 dB cm^3 g^{-1}. In contrast, Panaitescu et al. [208], used TES in combination with nanocellulose and a peroxide crosslinker in a compression molding setup. This simpler, scalable melt-processing method yielded closed-cell foams with uniform pores and high energy absorption, making them suitable for insulation, packaging, and biomedical applications. In another study [225], the extrusion foaming of P34HB used endothermic CBAs, and incorporated chain extenders (CEs) and water-quenching. Here, CEs proved more effective than quenching in enhancing foamability, reducing density, and mitigating polymer degradation. As expected, mechanical properties were strongly dependent on foam density, with CE-modified foams showing slightly improved performance.

In terms of foam morphology, PHBV/GNP foams showed a decrease in pore size and volume expansion ratio (VER) with increasing GNP loading. Cell density exhibited a non-linear trend, initially increasing, then decreasing, due to GNP agglomeration [225]. Panaitescu et al. [208] also reported a closed-cell morphology in their foams, but the incorporation of nanocellulose significantly improved pore size uniformity and stabilized the cell structure. This effect was most notable in the samples containing both the nanocellulose and TES, which exhibited the highest porosity and the lowest density, over 2.7 times lower than that of pure PHBV. For P34HB, the addition of CE resulted in a coarser cellular structure but reduced degradation, reaching a balance between mechanical integrity and foam density.

When comparing the blends PHBV/PHBH or PHBV/cellulose acetate butyrate (CAB), the former allowed tuning of crystallinity and foaming behavior through compositional control. PHBV acted as a nucleating agent for PHBH and helped maintain higher cell densities, though PHBH achieved greater expansion ratios. PHBV/CAB blends, on the other hand, were able to withstand higher concentrations of the chemical blowing agent (activated azodicarbonamide—AZ) due to CAB's viscosity-boosting effects. However, this increase in viscosity reduced nucleation rates and cell density, resulting in more uniform but less porous foams. In both cases, temperature optimization was critical, with small changes (~10°C) in the extrusion profile significantly affecting foam morphology [239, 240].

From a rheological and thermal standpoint, several materials demonstrated enhanced viscosity and melt strength through the incorporation of additives. For example, the addition of GNP increased the storage modulus (G') and complex viscosity (η^*) of PHBV by up to 12 orders of magnitude [234]. Nanocellulose had a more moderate effect but still contributed to improved melt strength. Despite these enhancements, thermal degradation remained a persistent challenge across studies. Strategies such as supercooling (in the PHBV/CBA system) and CE addition (in P34HB) proved effective in mitigating degradation [240].

Reactive extrusion is widely reported as one of the most effective strategies to overcome the poor melt strength and thermal instability of PHAs during extrusion processing [13, 160, 223]. Because PHAs such as PHB and PHBV undergo rapid chain scission at temperatures only slightly above their melting point, several studies have incorporated chain-extending additives directly during extrusion to restore molecular weight and improve melt rheology [225, 236]. These additives react with hydroxyl (–OH) and carboxyl (–COOH) end groups formed during thermal degradation, leading to chain recombination, branching, or the formation of longer-chain structures [242, 243]. For example, a recent study on PHB showed that the addition of an epoxy-based multifunctional chain extender (Joncryl ADR) during melt processing significantly increased melt stability and partially reversed the molecular weight reduction caused by repeated processing, leading to improved rheological behavior and mechanical performance [97].

Similar approaches have been applied to PHBV, where reactive extrusion has been used both for chain extension and chemical modification. Nath et al. [242], maleic anhydride was grafted onto PHBV using a peroxide initiator, while a multifunctional epoxy chain extender (Joncryl ADR 4468) was simultaneously added to prevent chain scission and promote long-chain branching, resulting in improved thermal stability and higher melt viscosity. Earlier work, by Zheng et al. [243] also demonstrated that reactive extrusion could be used to prepare PHBV-g-GMA (glycidyl methacrylate-grafted PHBV), which improved compatibility in composites and increased melt strength, making the material more suitable for extrusion-based processing.

In foam processing specifically, extrusion foaming studies on PHB-based copolymers have shown that the addition of epoxy-functional chain extenders during extrusion significantly improves foamability by increasing melt strength and stabilizing the cellular structure [225]. Overall, the literature consistently shows that reactive extrusion combined with multifunctional chain extenders, particularly epoxy-based oligomers (e.g., Joncryl ADR), peroxide-initiated systems, and reactive monomers such as maleic anhydride or glycidyl methacrylate, represents a key approach for enabling stable extrusion of PHAs and expanding their use in applications such as films, blends, and foams [207, 225].

Despite these encouraging laboratory-scale results, the transition of PHA foams to industrial production remains highly challenging. A major barrier to scale-up lies in the broader constraints associated with large-scale PHA production [244–246]. Although progress has been made in reducing costs through the use of low-cost carbon substrates (e.g., food waste [47] or industrial side streams [247], several aspects still require further development, including microbial strain engineering, extremophile-based fermentation, and mixed microbial culture systems.

Furthermore, downstream processing, particularly extraction and purification, remains a significant bottleneck for scale-up, as solvent selection, usage, and recovery contribute substantially to both cost and environmental impact. Additional technical challenges arise from the need for precise control of process parameters such as temperature, pH, oxygenation, and cell density to ensure consistent polymer properties [244–246]. These factors not only affect PHA production efficiency but also influence key material properties, such as molecular weight.

Once produced, the intrinsic properties of PHAs, including brittleness and thermal sensitivity (as discussed in Section 3.1), further complicate their upscaling for foam applications. From an industrial perspective, certain processing routes, such as high-pressure foaming methods [234] or the use of non-sustainable CBAs [239, 248], may be limited in applicability or may not align with sustainability goals, particularly those related to responsible consumption and production [249].

Overall, the current body of work highlights that while significant progress has been achieved in tailoring the rheological behavior and foamability of PHAs, their successful transition from laboratory-scale demonstrations to industrial applications remains limited. Among the various approaches, strategies combining reactive extrusion, chain extension, and blending with more flexible polymers appear to be the most promising for improving melt strength and processing stability. However, these modifications often involve trade-offs, including increased formulation complexity, potential impacts on biodegradability, and regulatory constraints depending on the additives or processing aids used. In addition, the strong sensitivity of PHA systems to processing conditions, coupled with upstream production challenges and downstream purification constraints, continues to hinder scalability. Therefore, future research should focus on integrated approaches that simultaneously address material design, processing optimization, and sustainable production pathways. In particular, developing cost-effective feedstocks, robust microbial systems, and environmentally benign processing routes will be essential to unlock the full potential of PHA-based foams for large-scale and application-driven use.

6 | Conclusions and Future Prospective

Despite the significant progress achieved in recent years, the widespread industrial adoption of PHA-based materials for agricultural films and foams remains constrained by a combination of economic, processing, and material-related challenges. Future developments should therefore focus on integrated strategies that simultaneously address production cost, processability, and end-use performance.

From a materials design perspective, the combination of copolymerization, blending, and reactive extrusion is expected to play a central role in overcoming the intrinsic limitations of PHAs, particularly their low melt strength, high crystallinity, and thermal instability. Blends with flexible biodegradable polymers (e.g., PBAT, PBSA) and the use of multifunctional chain extenders have already demonstrated strong potential for improving processability in both film blowing and foam extrusion. However, these approaches must be further optimized to balance mechanical performance, biodegradability, and regulatory compliance, especially for agricultural and food-contact applications.

Economic and sustainability constraints further complicate the outlook for PHA-based materials. Although the use of low-cost or waste-derived feedstocks is frequently proposed as a solution, these approaches often introduce additional variability and require complex pretreatment steps, which can offset cost advantages. Similarly, downstream processing, particularly extraction and purification, remains a major bottleneck, with current methods still relying heavily on solvents that raise both economic and environmental concerns. Without significant advances in these areas, improvements at the material or processing level alone are unlikely to enable large-scale adoption.

For agricultural applications such as mulch films, future work must also critically address the gap between laboratory performance and real-world conditions. While many studies report promising mechanical or barrier properties, fewer evaluate long-term soil biodegradation, environmental interactions, or compliance with regulatory standards. Likewise, in foam applications, the development of lightweight and functional growth foams must be balanced against scalability and sustainability constraints, particularly when relying on non-environmentally friendly blowing agents.

Overall, the current literature suggests that the main barrier to the widespread adoption of PHA-based films and foams is not the lack of viable strategies, but rather the absence of integrated, scalable, and economically realistic solutions. Future progress will therefore depend on coordinated advances across the entire value chain, from microbial production to processing and end-of-life performance, rather than isolated improvements at the material level.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

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