Minireview

Best conditions and the main barriers for the biodegradation of PBAT, PLA and starch blends

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E02 Environmental risk of plastic materials

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Abstract

This minireview discusses the main barriers and best conditions for biodegrading PBAT, PLA, and starch blends, highlighting the importance of considering the material composition and environmental factors to improve biodegradation efficiency.

1. Introduction

In 2021, global plastic production reached 309.7 million metric tons, with 90.2% of this being derived from non-renewable fossil fuels. These fossil-based plastics are primarily utilized in the production of packaging materials for a variety of consumer goods, including food, beverages, cosmetics, and pharmaceutical products, accounting for 44% of plastic usage. An additional 18% of fossil-based plastics are used in the Building & Construction industry. The remaining 9.8% of plastic production is composed of recycled plastics at 8.3% and bio-based/bio-attributed plastics at 1.5%, according to data from [1].

Although the data above shows that the production of bio-based/bio-attributed plastics is not yet a significant proportion of global plastic production, there are positive signs of growth in the bioplastics industry. In 2022, the global bioplastic production capacity generated 1.1 million tons of materials that are considered biodegradable, representing 51.5% of total bioplastic production. Most of the bioplastics production is made up of starch blends, Polylactic acid (PLA), and Polybutylene adipate co-terephthalate (PBAT), which accounted for 20.7%, 17.9%, and 4.5% of production, respectively. It is projected that by 2027, the production of biodegradable bioplastics will increase to 56.5% [2], indicating a promising trend towards the use of more sustainable plastic materials.

The slow growth of biodegradable plastics production can be attributed to several factors, including high production costs, performance limitations such as lower strength and durability compared to traditional plastics, and stiff competition with established players in the industry. To accelerate the production of biodegradable plastics from starch blends, PLA, and PBAT by 2027, it is essential to identify and address the main production barriers and optimize production conditions. Therefore, we aim to share the best practices and strategies for overcoming these barriers in the short term, paving the way for the wider adoption of biodegradable plastics, and supporting the transition to more sustainable materials.

2. Structure, production, and applications

The relationship between the structure and bioplastic properties of starch blends, PLA, and PBAT is significant in determining their suitability for different applications. Starch blends, for example, consist of a mixture of starch and other polymers, which can significantly impact their mechanical, thermal, and barrier properties. Meanwhile, PLA is a linear aliphatic polyester derived from renewable resources and has excellent mechanical and barrier properties. PBAT, on the other hand, is a biodegradable polyester that is highly flexible and has good impact resistance [3].

2.1 Starch blends: are biodegradable polymers obtained from various botanical sources, such as cereal grains (corn, wheat, barley, and rice), grain legumes (pea, lentil, chickpea, and bean), and root tubers (cassava, taro, Canna edulis, and potato), can also be obtained from agricultural waste products and/or by-products of food processing, such as protein extraction from potato and legumes. Depending on geographical conditions it varies in amylose and amylopectin concentrations, thus, the abundant availability of starch polymer from renewable resources makes it the second most abundant biodegradable polymer in the world after cellulosic polymers [4].

Chemically, they are a semi-crystalline compound composed of amylopectin and amylose (see Figure 1 (a)). Depending on the source, the weight percentage of amylose components and amylopectin content varies between 20-25% and 75-80%, respectively. Amylose consists of α-D-glucopyranosyl molecules in linear or helical forms, whereas in the amylopectin macromolecule, the α-D-glucopyranosyl molecules are linked with α-D-glucopyranosyl molecules in an interval of approximately 20 units, which forms a highly branched, high molecular weight macromolecule.

Starch has become increasingly popular in the biodegradable polymer packaging industry due to its renewability, recyclability, film-forming ability, and low cost. It is an excellent alternative to petroleum-based single-use plastics and can be blended with other biopolymers to improve processability, heat resistance, and oxygen barrier properties. However, native starch lacks plasticity due to strong molecular H-bonding. Plasticization through the addition of low molecular weight molecules, such as water or sorbitol, is used to modify the molecular structure of starch and improve its processability. The plasticization process involves various chemical and physical interactions, including water diffusion, starch granule expansion, gelatinization, and polymer melting.

2.2 PLA: Polylactic acid is a biodegradable polymer made from renewable resources such as corn starch, cassava roots, or sugarcane. The glucose is then fermented to produce lactic acid, which is then polymerized to form PLA. The process typically involves three steps: purification of lactic acid, lactide formation, and polymerization [5]. Different manufacturing processes and conditions can be used to produce different types of PLA with varying properties.

PLA is made up of repeating units of lactic acid (See figure 1 (b)). Lactic acid can exist in two forms, L-lactic acid, and D-lactic acid, and these can combine to form three types of PLA: PLLA (poly-L-lactic acid), PDLA (poly-D-lactic acid), and PDLLA (poly-DL-lactic acid), which is a mixture of the two. PLA has a high molecular weight and can form crystalline structures, which affects its mechanical properties.

PLA finds a wide array of applications, such as in packaging, textiles, medical implants, and 3D printing. Its biodegradability makes it a highly desirable material for single-use products like food packaging and disposable cutlery. The textile industry uses PLA to produce clothing and fabrics. In the medical sector, PLA is used to create biodegradable sutures and implants that can break down in the body over time.

2.3 PBAT: is an aliphatic-aromatic polyester, obtained by polycondensation of diols and dicarboxylic acids. In its chemical structure, PBAT is a thermoplastic polyester formed by repeating units of adipic acid, terephthalic acid, and butanediol (see Figure 1 (c)). It has a flexible chain structure and a low glass transition temperature, which makes it suitable for use in applications requiring flexibility and toughness. has proved to be the most suitable combination, in terms of excellent properties and good biodegradability [6].

PBAT shows not only good biodegradability due to the aliphatic unit in the molecule chain, but also excellent mechanical properties due to the aromatic unit in the molecule chain, this makes it used in a variety of applications such as packaging, agriculture, and consumer goods. It is used to make biodegradable and compostable bags, films, and mulch sheets that can be plowed into the soil after use. In consumer goods, PBAT is used to manufacture toys, electronics, and other products that require flexibility and durability. PBAT is often combined with PLA to create blends that offer a wider range of properties and are used in sustainable packaging materials for food products and other consumer goods.

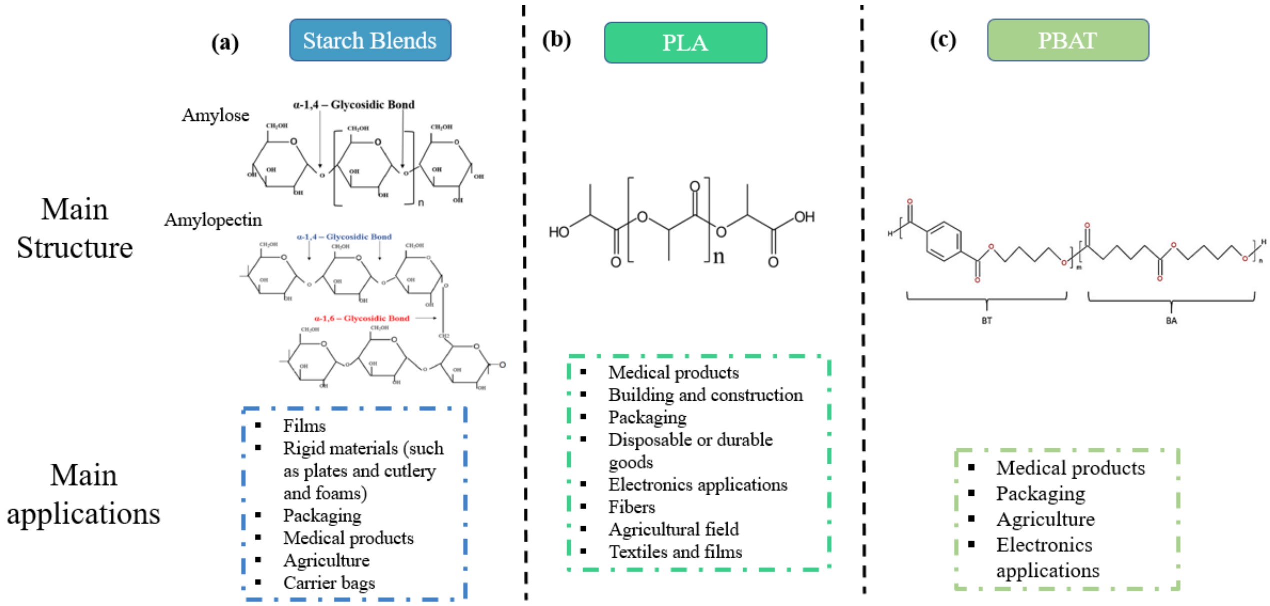

Figure 1. Main chemical structure and applications for (a)Starch blends (b)Polylactide (PLA) and (c)Polybutylene adipate terephthalate (PBAT)

3. Biodegradation conditions

Biodegradation is defined as the mineralization of organic material by microorganisms (e.g. fungi, archaea, and bacteria), which eventually results in the final products of carbon dioxide and water under aerobic circumstances, for this the ability to biodegrade under conditions existing in natural environments is a valuable property of bioplastics. The most important biodegradation processes for biopolymers, such as the hydrolysis of ester bonds to liberate the monomers are executed by extracellular enzymes that are excreted by microorganisms. In general, the biodegradation conditions for bioplastics such as starch blends, PLA, and PBAT depend on various factors such as temperature, moisture, pH, and the presence of microorganisms, but the overall process is described by three stages as described in Figure 2.

The process of biodegradation of the bioplastics

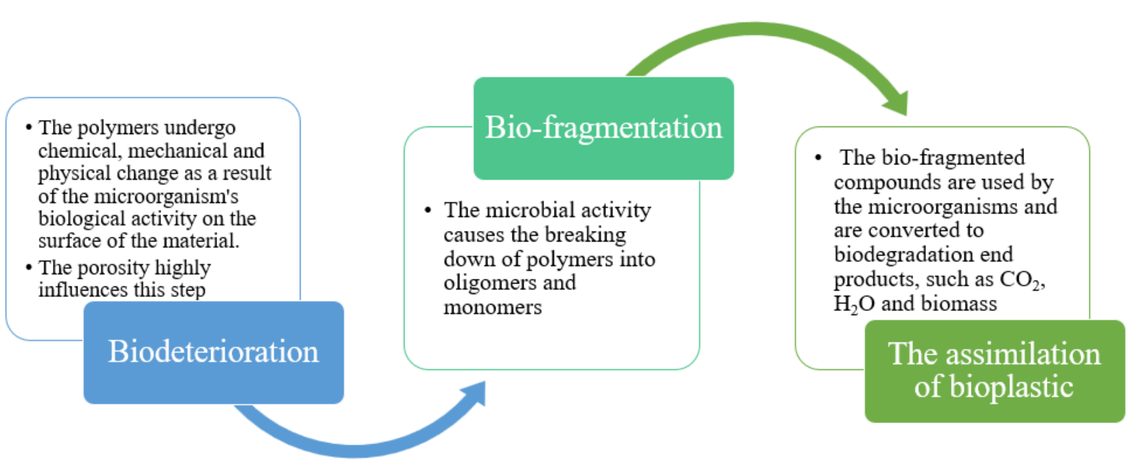

Figure 2. Stages of the bioplastics biodegradation process. Information adapted from [10]

The main biodegradation mechanism is explained below and the main methods and conditions for each of these bioplastics are summarized in Figure 3.

3.1 Starch blends biodegradation: Starch is mainly degraded by glycoside hydrolases, a large group of enzymes by the hydrolysis of glycosidic bonds. The enzyme α-amylase performs primary cleavage of long starch polymers, creating shorter fragments. These fragments are hydrolyzed by a series of enzymes such as β-amylase, glucoamylase, and α-glucosidase, all of which specialize in the hydrolysis of α-glycosidic bonds. The fungus Aspergillus oryzae and the bacteria Bacillus circulans, Klebsiella pneumonica, and Bacillus stearothermophilus produce various starch-degrading enzymes. In addition to glycoside hydrolases, lytic polysaccharide monooxygenases (LPMOs) are also capable of cleaving glucose bonds by catalyzing oxidative cleavage. LPMOs are copper enzymes produced mainly by bacteria and fungi. Another widely used method is gelatinization, which occurs when starch is dissolved in water at high temperatures and is an irreversible process that breaks intermolecular hydrogen bonds, causing the starch to lose its granular form. This increases the number of more easily degradable amorphous regions [7].

3.2 PLA biodegradation: The decomposition of PLA macromolecules occurs mainly at the end of the molecules by a zipper-like undoing mechanism, which is influenced by the molecular weight, crystallinity, purity, and stabilizers of the PLA. Also can biologically decompose into carbon dioxide and water under composting conditions [8]. The degradation leads to a drastic reduction in molecular weight and can be easily monitored by spectroscopic measurement of the -OH and -COOH groups.

3.3 PBAT biodegradation: The biodegradation of PBAT can be considered hydrolysis under the effect of microbial enzymes, during which the structure of butanedioic acid (BA) with a non-crystalline portion is degraded faster than the structure of BT (terephthalic acid and 1,4-butanediol) with a crystalline portion. PBAT undergoes hydrolytic degradation due to the cleavage of ester bonds and the reaction between water and carbonyl groups located in the vicinity of the benzene rings. Hydrogen transfer β-C-H reactions are assumed to occur randomly, even on the PBAT backbone.

Best conditions for biodegradation of starch blends, PLA and PBAT

Environmental conditions | By microorganisms

	Type of environment	Conditions	Biodegradability	% Biodegradability	Period of biodegradability (days)	Type of microorganism	Microorganism
Starch Blends	Compost	Aerobic, 58 °C	Weight loss	85	90	Fungi	Aspergillus sp, Aspergillus niger.
	Soil	60% moisture, 20 °C	Produced CO_2	14,2	110		
	Marine water with sediment	Room temperature	BOD biodegradability	68,9	236	Bacteria	Clostridium acetobutylicum
PLA	Compost	58 °C, pH-8.5, 63% humidity	Produced CO_2	84	58	Bacteria	Amycolatopsis sp., Amycolatopsis thailandensis,Thermomactinomyces sp.Bacillus licheniformis, Actinomadura keratinilytica.
	Soil	30% moisture, 20 °C	Weight loss	10	98		
	Sludge	Anaerobic, 55 °C	Produced CO_2	80	30-50	Fungi	Fennellomyces linderi, Fusarium solani, Purpureocillium sp
	Marine	30 °C	Produced CO_2	4.5-8.4	180-365		
PBAT	Soil	30 °C, in clay	Weight loss	80	180	Bacteria	Pseudomonas, Streptomyces sp.
	Compost	60 °C	Produced CO_2	95	90		
	Marine	20 °C	Weight loss	35	90	Fungi	Aspergillus and Penicillium sp.

Figure 3. Biodegradation of starch blends, PLA and PBAT in different environments and conditions (Adapted from [9-10-11]).

4. Main barriers

The manufacture and industrial use of polymer derivatives is one of the real challenges that we have today, it is necessary to recognize that any transformation requires a time of adaptation, in this case of new technologies, cost-benefit management, clarification of the need for more sustainable methodologies with the environment, among others. Some barriers that have been presented (Figure 4) for the use of Starch blends, PLA, and PBAT will be presented below and possible solutions for their implementation will be proposed.

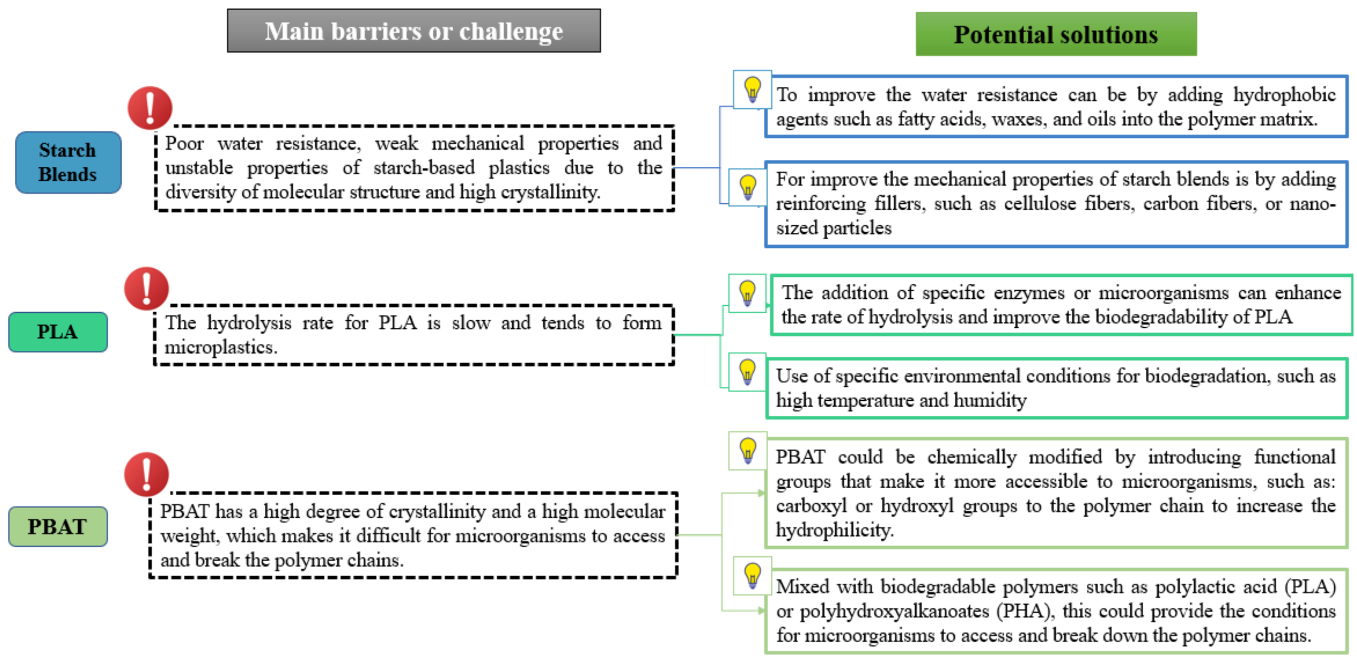

Figure 4. Compilation of main barriers for each type of bioplastic and potential solutions for their improvement.

5. Conclusion

Currently, the use of bioplastics is less than 2% and the highest percentage is found in the use of starch blends, PLA, and PBAT, but scientific production to improve biodegradation methodologies is increasing. Most of the literature talked about optimizing the process by changing the environmental conditions (such as moisture content, temperature, or pH) rather than modifying the physicochemical structure of the biopolymer (e.g., by pretreatment before the biodegradation process); on the other hand, some researchers have tried to improve the biodegradability of bioplastics by producing feedstocks that are easier to degrade.

Further research is needed to fully understand the long-term fate of bioplastics in natural and industrial environments, including the impact of environmental conditions on biodegradation. This research can help select appropriate feedstocks to minimize solid waste while ensuring the complete mineralization of biopolymers. However, bioplastics alone cannot solve plastic pollution because one of the main barriers is also the separation of these types of solvents to define their specific treatment, and other management strategies such as prevention, reduction, and reuse at the source must be considered.

6. References

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