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Natural polymer-based food packaging: paving the way to a greener future – a review

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Food packaging materials play a major role in the current plastics industry. To pursue environmental protection and sustainability, the search for alternatives to replace conventional plastics has emerged as an industry-wide imperative. This article offers a comprehensive comparison of different food packaging materials, analysing both synthetic and natural polymers across key performance criteria. The analysis reveals that natural polymers demonstrate superior biodegradability, tensile strength, and oxygen barrier properties. Conversely, synthetic packaging exhibits significant advantages in elongation performance, mass production, and costs due to mature manufacturing technology. However, this review also highlights the need to overcome key challenges related to their production scalability, mechanical and barrier properties, and waste treatment. Realizing their full potential will require close collaboration among researchers, industry stakeholders, and policymakers to promote sustainable solutions.

Sustainability spotlight

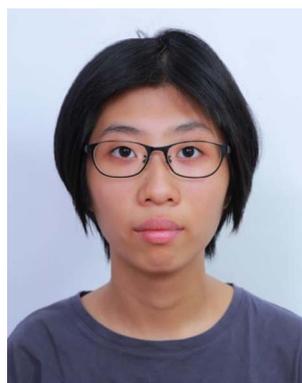
The widespread use of synthetic polymer-based food packaging materials has been a long-standing practice. However, growing environmental concerns have prompted increased scrutiny in recent times. As the global community recognizes the need for sustainable practices, research into eco-friendly alternatives has gained momentum. One area of focus is natural polymer-based food packaging materials, which have shown promise as a viable replacement for synthetic polymers. Nevertheless, significant challenges remain to be overcome in terms of post-processing. This article provides a comprehensive analysis of the advantages and disadvantages of current natural polymer-based food packaging materials, with a particular emphasis on their production, usage, and treatment. Through comparing various materials, we assess the feasibility of replacing synthetic polymer-based materials with natural polymers, providing a valuable resource for decision-makers and stakeholders.

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renewable alternatives and address environmental pollution problems.

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activities, collaborating with experts from various fields to enhance her understanding. With her background and eagerness to learn, Chong is committed to contributing to innovative solutions in materials science.

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1. Background

The food packaging industry plays a crucial role in ensuring the quality and safety of food products. Packaging acts as a critical shield for preserving food. It protects against moisture, oxygen, and carbon dioxide, thereby helping to maintain its flavours, aromas, nutrients, and colors.¹

Historically, natural materials like gourds, shells, and leaves were used to contain food in ancient civilizations.² However, with the advent of paper packaging in the 17th century, a lightweight and versatile alternative emerged. This innovation offered printability, portability, and disposability, but it struggled to ensure product quality preservation due to limitations in protection and durability. The 20th century marked a significant shift with the emergence of plastic packaging – a revolutionary development that reshaped the market. Plastics, mainly being synthetic polymer, began to replace conventional packaging materials due to their lightweight, flexible, and water-resistant properties, as well as their exceptional polymeric elongation and tensile strength. Furthermore, the stable chemical structure and non-biodegradable nature of plastics led to a significant extension of shelf life.

The environmental costs associated with plastic packaging are multifaceted and far-reaching, stemming from its durability and persistence in the environment.³ Rapid development and population growth have significantly increased the demand for single-use plastics, driven by our preference for convenience. However, the lack of effective global waste management systems has created a stark imbalance between supply and demand, leading to improper disposal and exacerbating plastic pollution.⁴

Plastic manufacturing relies heavily on finite petroleum resources, generating toxic byproducts such as phthalates, bisphenols, alkylphenols, and biocides.⁵ To address these complex challenges, a holistic approach is necessary, balancing convenience with sustainable practices and effective waste management solutions.

The widespread use of plastic food packaging has led to a significant annual increase in plastic waste discard, with single-use packaging plastic waste constituting approximately 40% of the market by weight.⁶ Removing this persistent waste from the environment is incredibly time-consuming and energy-intensive. To accelerate decomposition, common approaches include physical, thermal/chemical, and biological treatments.^{7–9} Natural degradation can be extremely slow, with plastics decomposing as little as 10 micrometers per year. In contrast, according to industry standard EN 17033, biodegradable plastic mulches must decompose in soil by at least 90% within two years. However, few plastic alternatives have successfully achieved a balance between performance and cost.^{10,11}

Physical treatment methods for plastic waste include polymer size reduction and UV/photo-oxidative treatment,¹² with some processes utilized in material recycling to create new products from used plastics. However, recycling efforts have struggled to achieve widespread success due to policy enforcement challenges.¹³ Thermal treatment approaches like incineration, pyrolysis, and gasification demand advanced processing systems and meticulous waste sorting for optimal efficiency. This exportation increases the risk of improper waste management practices, a problem often exacerbated by the widespread reliance on plastic packaging.¹⁴

Given these challenges, the development of natural polymer-based materials (NPMs) is emphasizing biodegradability, compostability, and a reduced carbon footprint. As consumer demand for sustainable solutions grows, the market for biomaterial-based food packaging is expanding. This growth is driven by a focus on replacing traditional single-use plastic packaging with recyclable and biodegradable alternatives, reflecting a broader shift towards a more sustainable future.¹⁵

Despite its potential, the market growth of NPMs has fallen short of expectations.¹⁶ A major hindrance is the need for industrial-scale investment and practical differentiation from synthetic polymer-based materials (SPMs) in terms of environmental impact.¹⁷ Some commercially available NPMs promote



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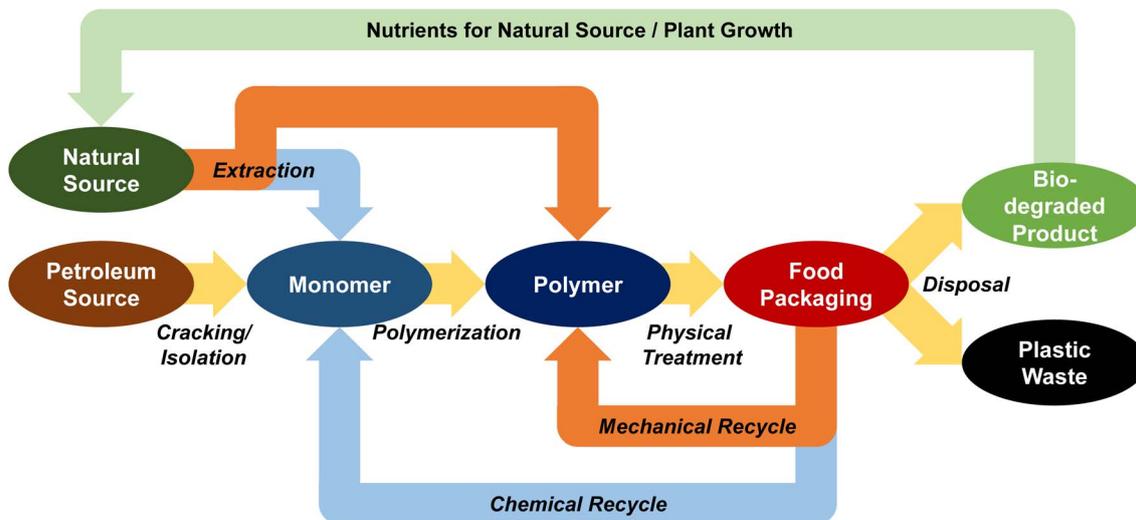


Fig. 1 Overview of the lifecycle of food packaging materials.

biodegradability but require specific waste treatment processes. This necessitates waste sorting and collection to meet the conditions necessary for degradation. Conversely, soil degradation may be a more viable option depending on the availability of suitable NPMs and landfill space.¹⁸ However, comprehensive studies on the soil and aquatic decomposition of these materials are still lacking,^{19–22} which has limited their adoption as a common solution. Therefore, it is crucial to analyse the complete life cycle of bio-based food packaging materials when considering the potential of bioplastics.

Fig. 1 illustrates the typical lifecycle of food packaging materials derived from natural and petroleum sources. Although both types undergo processes like extrusion, moulding, or lamination, SPMs cannot be repurposed as nutrients for new natural resources after disposal. Conversely, NPMs can reintegrate into the lifecycle due to their characteristics, highlighting their significant potential as sustainable materials. This capability has garnered considerable attention in recent years.

Biodegradable films formed by natural polymers have emerged as a promising alternative to traditional plastic packaging, offering a viable solution to address the growing issue of plastic pollution. Despite their potential benefits, including reduced environmental impact and increased sustainability, biodegradable films also present several challenges, including resource utilization, production processes, material properties, and biodegradability. This review aims to critically evaluate the current state of biodegradable films, highlighting their strengths and limitations, and exploring future directions for their development and implementation in the food packaging industry.

2. Introduction of common food packaging materials (FPMs)

FPMs can be classified into two main types: synthetic polymer and natural polymers, sourced from either petroleum-based or

bio-based sources that adjusted chemical and physical properties. Synthetic polymers are man-made polymers created through chemical reactions, typically involving the combination of monomers. They are produced through industrial processes and have unique properties such as strength, flexibility, and resistance to heat. Natural polymers are a type of macromolecule that occurs naturally in the environment, or can be produced through biological processes. These polymers are often found in living organisms such as plants and animals, or can be derived from renewable biomass sources. They are biodegradable and renewable, and often exhibit unique structures and properties derived from their natural sources. Fig. 2a illustrates the production process of FPMs from these two sources. Also, Fig. 2b presents the outlook of these natural polymer based materials.

2.1. Synthetic polymer-based materials (SPMs)

2.1.1. Polypropylene (PP). PP is a widely used synthetic thermoplastic in food packaging applications. Its chemical structure, $(C_3H_6)_n$, makes it a thermoplastic with high chemical resistance.³³ The US produced 16 829 million pounds of PP in 2022, ranking second after polyethylene.³⁴ Traditional PP is derived from petroleum-based sources, but researchers have developed alternative methods to produce propene monomers from plant or biomass sources.³⁵ This approach creates bio-polypropylene (Bio-PP), which reduces environmental impact.³⁶ However, both PP and Bio-PP exhibit non-biodegradable characteristics under natural conditions, making further research necessary to address technical and economic challenges associated with sustainable production of PP.

2.1.2. Polystyrene (PS). PS is a widely used polymer for FPMs, consisting of a long-chain hydrocarbon with an attached phenyl group. Its desirable properties include transparency, low thermal conductivity, and good elasticity. Expanded polystyrene (EPS) is particularly well-suited for thermal insulation, with



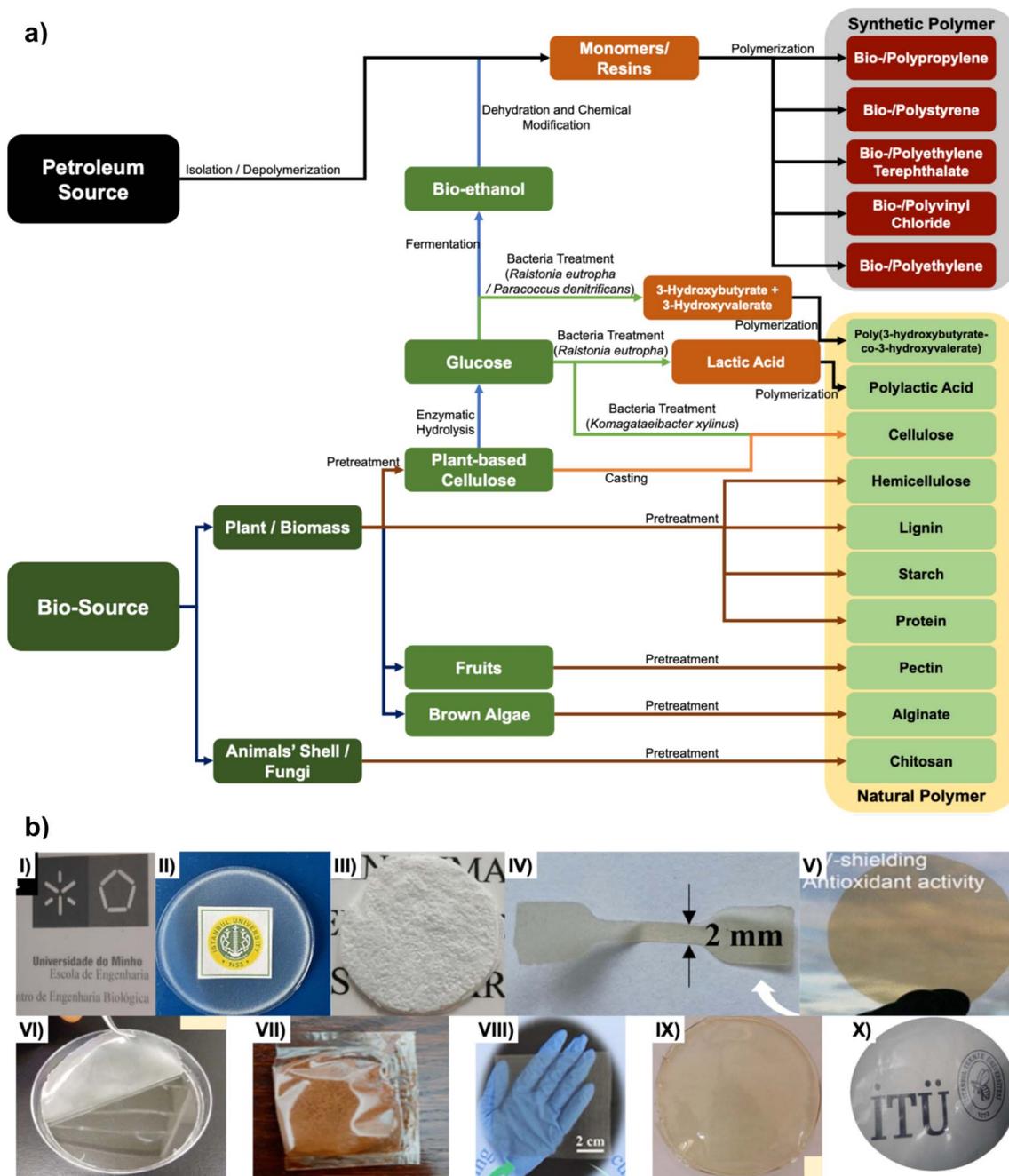


Fig. 2 (a) The production routes of different food packaging materials, and (b) appearance of a (I) poly(3-hydroxybutyrate-co-3-hydroxyvalerate) film²³ (Reprinted with permission from Elsevier), (II) polylactic acid film²⁴ (Reprinted with permission from Elsevier), (III) cellulose-based film²⁵ (Reprinted with permission from SNCSC), (IV) hemicellulose-based film²⁶ (Reprinted with permission from Elsevier), (V) lignin-based film²⁷ (Reprinted from with permission from SNCSC), (VI) starch-based film²⁸ (Reprinted with permission from SNCSC), (VII) protein-based film²⁹ (Reprinted with permission from SNCSC), (VIII) pectin-based film³⁰ (Reprinted with permission from Elsevier), (IX) alginate-based film³¹ (Reprinted with permission from MDPI), and (X) chitosan-based film³² (Reprinted with permission from Elsevier).

a higher melting point of 240 °C.³⁷ However, PS exhibits non-biodegradable characteristics and is traditionally produced from the petroleum-based monomer styrene.³⁸ Recent research has explored the use of bio-ethanol from biomass as a feedstock for PS production.³⁹ Despite benefits, both types face challenges in recycling due to the need to separate them from other waste materials.

2.1.3. Polyethylene terephthalate (PET). PET is a prevalent synthetic polymer used to produce transparent and amorphous thermoplastics. Its chemical structure, $(C_{10}H_8O_4)_n$, makes it highly transparent and barrier-proof. PET has excellent properties for packaging materials like bottles and lunch boxes.^{40,41} Traditionally, PET is produced from petroleum-based feedstocks: terephthalic acid and ethylene glycol. However,



researchers have explored the use of biomass as an alternative feedstock for PET production.⁴² This bio-based approach, known as Bio-PET, uses fermented corn stover to produce bio-ethanol and isobutanol, which serve as starting materials for PET production.⁴³ Despite its sustainability benefits, Bio-PET still exhibits non-biodegradable characteristics, making it a significant challenge to environmental sustainability.

2.1.4. Polyvinyl chloride (PVC). PVC is a thermoplastic material formed through the addition polymerization of chloroethene. It has a relatively low melting point range of 102 °C to 210 °C and is often used as a commercial cling film for food packaging applications due to its low price and high chemical resistance.⁴⁴ PVC is produced from the precursor chloroethene, which is derived from natural gas or crude oil.⁴⁵ Despite its widespread use and market ranking as the third-highest plastic produced in the US, PVC has significant environmental concerns associated with its production.³⁴ However, its production is associated with significant environmental concerns, particularly during the manufacture of 1,2-dichloroethane, which can generate dioxins posing toxicity risks to humans and the environment.⁴⁶ Researchers have explored a bio-based approach to mitigate these concerns by converting bio-ethanol from sugarcane into bio-ethylene, which can be chlorinated to form vinyl chloride monomers. While this approach reduces environmental concerns, PVC retains its non-biodegradable properties and recycling challenges, making it an unsuitable option for truly sustainable applications.

2.1.5. Polyethylene (PE). PE is a thermoplastic material that dominated production in the US in 2022.³⁴ There are two main types of PE: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). LDPE is produced at high temperatures and pressures, resulting in a branched structure with a melting point range of 80 °C to 110 °C. HDPE, on the other hand, is produced at lower temperatures and pressures, resulting in a linear structure with a higher melting point range of 120 °C to 135 °C.⁴⁷ Both types are suitable for different applications, such as plastic containers (HDPE) and cling film (LDPE). Both conventional PE and bio-based PE can be derived from bio-ethanol, making it a more sustainable option.³⁹ However, despite its sustainability benefits, PE retains its non-biodegradable characteristics, and poses an environmental challenge and highlights the need for sustainable alternatives to traditional plastics.

2.2. Natural polymer-based materials (NPMs)

2.2.1. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). PHBV is a biodegradable, non-toxic, and biocompatible thermoplastic produced by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.⁴⁸ PHBV can also be produced by the bacterial fermentation of glucose and propionic acid to obtain (*R*)-3-hydroxybutyryl-CoA and *D*- β -hydroxyvaleryl-CoA with PHBV as the final product.⁴⁹ It has a melting temperature of 176 °C,⁵⁰ making it recyclable. PHBV is commonly used in food packaging materials, and manufacturing bottles, drugs, and medical implants due to its unique properties. Its biodegradability and non-toxicity make it

an attractive alternative to traditional plastics, reducing environmental concerns. However, it showed a low thermal stability compared with synthetic polymers, which limited its application.⁵¹

2.2.2. Polylactic acid (PLA). PLA is a versatile and renewable thermoplastic polymer that is derived from renewable feedstocks like corn starch, sugarcane, and other plant-based materials.⁵² The production of PLA involves a multi-step process. Cellulose or starch is extracted from plants and then undergoes enzymatic hydrolysis to obtain glucose, and glucose is then treated by *Ralstonia eutropha* bacteria to form lactic acid.⁵³ The optical purity of lactic acid is a key factor in determining the crystallinity and biodegradation of the final PLA polymer. Therefore, it is important to carefully manage the downstream processing of lactic acid, as the fermentation broth typically contains significant levels of impurities. Due to the chirality of lactic acid, there are three forms of lactide that can be produced: *L*-lactide, *D*-lactide, and *D,L*-lactide.⁵² Producing optically pure, high molecular weight PLA requires close monitoring and control of the entire production process in real-time.

PLA exhibits good transparency and mechanical strength, which are comparable to those of traditional plastics like PE and PP.⁵³ However, PLA has a relatively low melting point, limiting its use in high-temperature applications. One of the key advantages of PLA is its biodegradability.⁵³ Under suitable composting conditions, PLA can break down into naturally occurring substances such as carbon dioxide and water.⁵² This makes PLA an environmentally friendly alternative to conventional SPMs, such as PET, which is commonly used for bottles, cups, trays and films of disposable cutlery.⁵⁴

2.2.3. Cellulose. Cellulose is a naturally abundant linear polymer that is predominantly produced by plants such as rice bran, sugarcane bagasse, cotton, and coconut fibers.⁵⁵ After purification, it is found to be a sustainable, recyclable, and biodegradable natural polymer with a natural white color.^{56,57} Meanwhile, the potential applications of cellulose have been explored through various modifications, including esterification, acetylation, and etherification.^{58–60} These modifications allow for the derivation of cellulose with different degrees of substitution, resulting in adjustable processing temperatures. Although the use of cellulose-based composites and coatings has led to a reduction in plastic consumption, these composite materials present challenges in terms of recycling and natural degradation, in contrast to pure paper packaging, which is typically easier to recycle and naturally degrade.^{61,62} Furthermore, food residue within food packaging requires additional clean-up efforts, which is undesirable for both consumers and the recycling industry.²⁷ While cellulose holds promise in reducing the environmental impact of synthetic polymer-based packaging, optimization of sourcing and efficient extraction processes must be addressed to facilitate its industrialization.^{63,64}

2.2.3.1. Cellulose nanofibers (CNFs). Nanocellulose can be produced through chemical, biological and mechanical approaches.⁶⁵ Regardless of the method employed, the resulting CNFs typically undergo high-pressure homogenization during



pretreatment and post-treatment to achieve desirable functionalities and fiber sizes.⁶⁶

Traditionally, CNFs have been extracted from wood cellulose through kraft pulping treatment. This process requires pretreatment to remove lignin and hemicellulose components, which are then discharged into the black liquor waste stream.⁶⁷ TEMPO-oxidation is an energy-efficient approach to chemically obtain CNFs from the plant sources, which oxidises cellulose hydroxyl groups, enabling easier subsequent treatment under basic and neutral conditions.⁶⁸ Other common downsizing methods include soft acid hydrolysis, enzymatic treatment, and mechanical beating. Studies have shown that TEMPO-oxidized CNFs offer the highest yield in nanofiber content compared to the other types of CNFs.⁶⁹ In recent years, there has been growing interest in using non-wood sources for CNF production, as they can offer rapid generation and a lower starting value. Aside from their high aspect ratio and nano-scale dimensions, the residual elements in CNFs have demonstrated potential to enhance fibrillation efficiency. As a result, maintaining an optimal level of residual elements is an ongoing area of research.

On the other hand, CNFs possess several desirable properties, including a high specific surface area, high compressive strength, low density, a small expansion coefficient, and an easily modifiable polyhydroxy surface structure.⁷⁰ These characteristics make CNFs attractive for various applications. To obtain specific desired properties, such as antibacterial, emulsifying, and stabilizer properties, CNFs are often grafted with new functional groups.⁷¹

2.2.3.2. Cellulose nanocrystals (CNCs). CNCs are rod-like or needle-shaped particles with dimensions less than 100 nm and high crystallinity. Similar to other cellulose derivatives, CNCs possess desirable properties such as high strength, stiffness, mouldability, and transparency, making them suitable for applications in the transparent packaging market.^{72–74} The preparation of CNCs typically begins with acid hydrolysis, but other methods like enzymatic hydrolysis, mechanical refining, ionic liquid treatment, subcritical water hydrolysis, and oxidation methods are also employed.⁷⁵ The goal of these processes is to cleave the glycosidic bonds between cellulose fibers, resulting in CNCs with a high surface-to-volume ratio, which facilitates surface functionalization.⁷⁶ Through composition and chemical modifications, CNCs can acquire drug delivery capabilities,⁷⁷ aerogel and foam production,^{78,79} and maintain food quality with PHBV and PLA composites.⁸⁰

2.2.3.3. Bacterial cellulose (BC). BC is a newly developed bio-based material synthesized by using specific bacteria, notably *Komagataeibacter xylinus*. Although BC exhibits the same chemical structure as plant cellulose, it exhibits higher crystallinity, which imparts superior physical and mechanical properties. Like typical plant cellulose, BC comprises a linear chain of β -1,4-linked D-glucose units, represented by the molecular formula $(C_6H_{10}O_5)_n$. It forms a three-dimensional network of ultrafine fibers characterized by high yield, purity, biocompatibility, and biodegradability. These attributes position BC as a promising material for diverse applications, particularly in food and biomedical engineering.⁸¹

However, the abundance of hydroxyl groups in BC results in high water sensitivity, low barrier properties, a complex structure, low solubility, and an unpleasant odor that depends on the medium.⁸² These drawbacks reduce the performance of BC films under humid conditions and limit their application for oxygen-sensitive foods, such as strawberries and meat.⁸³ To address these challenges, various strategies have been developed to modify the surface or structure of BC films, including blending, cross-linking, coating, or grafting with different agents or polymers, in order to introduce new properties, such as antimicrobial, antioxidant, or bioactive effects.^{84–86}

The production of BC films from a carbon source involves three main steps: hydrolysis, fermentation, and oxidation. This process can be classified as a typical bottom-up production method. The quality and quantity of BC films depend on various factors, such as the type and concentration of tea, the duration and temperature of fermentation, and the strain and inoculum size of bacteria.⁸⁷ Recently, several studies have investigated the potential applications of BC films for food and biomedical purposes,^{82,83,88,89} reassuring their potential in use as FPMs.

2.2.4. Hemicellulose. Hemicelluloses, comprising 20–35% of lignocellulosic biomass, are the second most common polysaccharide in nature, found in both annual and perennial plants.⁹⁰ The composition varies due to plant type and extraction methods. They are categorized as xylans (composed of 1,4-linked D-xylose units), mannans (1,4-linked D-mannose units), arabinans (1,5-linked L-arabinose units), and galactans (1,3-linked D-galactose units).⁹¹ Xylans, the predominant hemicelluloses, have drawn attention for their practical applications due to their high strength and adhesive properties, showing potential in bioplastic,⁹² coating,^{13,93} and film forming applications.⁹⁴ Furthermore, xylan films can be formed by casting or extrusion methods and can be tailored to exhibit specific properties such as transparency, mechanical strength, and gas barrier properties like plastics.

2.2.5. Lignin. Lignin is a complex organic polymer found in plant cell walls, primarily derived from lignocellulosic biomass sources such as wood, bark, and agricultural residues, where it acts as a binding agent. Through processes like acid hydrolysis, steam explosion, and organosolv treatment, extracted lignin can exist in either the liquid or solid form; however, its dark brownish color may vary depending on the wood source.⁹⁵ Currently, approximately 95% of industrial lignin is utilized as fuel in heat and power plants due to its challenging structure for direct industrial applications. Only about 5% of lignin undergoes modification for various applications.⁹⁶ Chemically, lignin is a complex three-dimensional polymer composed of phenylpropanoid units, featuring various functional groups. The mechanical properties of lignin are influenced by its chemical structure and the degree of polymerization.⁹⁶ Lignin exhibits excellent binding and elongation properties, typically found in synthetic polymers, while maintaining high biodegradability, presenting significant potential for development.⁹⁷ It is also known for its rigidity, strength, and resistance to degradation, with a high glass transition temperature that makes it thermally stable and suitable for applications



requiring heat resistance.⁹⁸ Examples of its potential uses include dietary fiber, a natural antioxidant in food, and thermoplastic biodegradable packaging materials.^{99–102}

2.2.6. Starch. Starch is a carbohydrate polymer commonly found in plants and serves as a major source of energy. It is derived from various plant sources such as corn, wheat, and potatoes.¹⁰³ Starch extraction typically involves grinding plants and separating proteins and fibers. The obtained powder has gel forming properties when heated in the presence of water, and exhibits thickening and binding properties, making it useful in a wide range of food applications.¹⁰⁴ Mechanically, starch has unique properties such as shear thinning behavior and thermal plasticity and has gained interest from industries.

Thermoplastic starches (TPSs) have been investigated with blends of PVA and LDPE.^{105–107} By replacing water with glycerol, sugars, and glycols, the gelatinization temperature will vary according to viscosity, diffusion, and hydrogen bonding.¹⁰⁴ Although TPSs have many benefits and applications, without modification, they are water-soluble and have poor mechanical properties. Therefore, reinforcement with different biopolymers to enhance strength and reduce water absorption has become a common approach for TPS blends.¹⁰⁸

2.2.7. Pectin. Pectin is a natural polysaccharide extracted from citrus fruits, apples, and other pectin-rich fruits. The extraction process typically involves juice extraction and concentration through evaporation, followed by enzymatic hydrolysis.¹⁰⁹ Resulting from the network structure of pectin, covalent and non-covalent intra- or intermolecular linkages are available, providing a vast variety of gelling, thickening, and stabilizing properties that make it useful in the food industry.

Pectin is typically a white to yellowish powder that dissolves in pure water and at high concentration showcasing pseudo-plastic characteristics.¹¹⁰ It offers good compatibility with different polymers, and pectin films are mainly prepared with glycerol as the plasticizer and formed through solution casting.^{111,112} Additionally, pectin-based nanocomposites films can be used in packaging to provide barriers against water, gases and contaminants.¹¹³ These films are biodegradable, renewable, and customizable with additives or other biopolymers to enhance specific properties, aligning with sustainability goals. However, stability and mechanical properties still have to be addressed.¹¹⁴

2.2.8. Alginate. Alginate is a type of polysaccharide that occurs naturally in brown algae and is also synthesized by certain bacteria. It is commonly extracted and refined from various types of brown algae, including *Laminaria hyperborean*, *Macrocystis pyrifera*, and *Ascophyllum nodosum*.¹¹⁵ It is typically found as a white to light yellowish-brown powder¹¹⁶ and exhibits strong gelling properties characteristic of alginates. It is ideal to create gels and dessert jellies, and encapsulate flavours in the food industry.¹¹⁷ Additionally, alginate can be processed into films with excellent film-forming properties. These films are typically transparent, flexible, and can vary in thickness and mechanical properties based on the formulation and processing conditions.¹¹⁸ Although alginate has vast applications in industries and as individual food packaging, its stability and

mechanical properties are still challenges that need to be addressed.¹¹⁹

2.2.9. Protein. Soy protein isolate (SPI) is a highly refined form of soy protein derived from soybeans, which accounts for 35% of the total composition. The manufacturing process involves the removal of fats and carbohydrates from soybeans, resulting in a light yellow or off-white powder that possesses solubility, emulsification, gelation, water binding, foaming, and viscosity properties, making it a valuable ingredient in various applications.¹²⁰

One of the notable applications of SPI is in food packaging, as it is also considered safe for food contact. It can be utilized to produce edible films and coatings that act as a barrier between the food and its surrounding environment, thereby extending the shelf life of perishable food items. Studies have shown that SPI possesses polymerization properties, and blending with collagen can enhance hydrophobicity.¹²¹ Combined with plasticizers and antimicrobial nanoparticles, the composite films made from SPI offer protection against moisture, oxygen, and microbial contamination, ensuring the quality and safety of packaged food.¹²²

In addition to SPI, another natural protein with unique properties and various applications is zein, which is derived from corn (maize). It is obtained through a process called wet milling, which involves separating the corn protein from other components such as starch and fiber. Zein has exceptional hydrophobicity due to its non-polar amino acids.¹²³ Through electrospinning, zein polymer solutions are prepared as fibers that possess antimicrobial properties.¹²⁴ Moreover, blending with other biopolymers can achieve thin, flexible films that serve as coatings or packaging materials.¹²⁵

2.2.10. Chitosan/chitin. Chitin is a naturally occurring biopolymer derived from the exoskeletons of crustaceans, such as shrimp, crabs, and lobsters. It is a linear polysaccharide composed of β -(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine units.¹²⁶ It exhibits antimicrobial activity, is edible, and possesses gas and moisture barrier properties. Chitin can be extracted from crustacean shells and fungal cell walls using efficient acid or enzyme extraction methods; however, current challenges include the collection of chitin biomass from food waste, and the persistent yellowish color resulting from structural light absorption and deacetylation hinders the use of related products.¹²⁷ Despite the production cost, chitosan films have been manufactured for food packaging, and multiple functionalities are obtained in simple ways such as direct casting, coating, dipping, layer-by-layer assembly, and extrusion.^{128–130} These films demonstrate great potential, exhibiting remarkable antibacterial properties, sensitivity, water resistance, thermal stability, and mechanical strength.¹³¹

As discussed in the previous sections, various NPMs and SPMs have been explored for their potential use in food packaging. These polymers exhibit distinct properties and characteristics that can impact the performance of food packaging materials. To better understand the extent to which these polymers can replace SPMs, a comparison of their properties has been provided in the section below.



3. Comparison of different FPMs

3.1. Production and cost

The global production of thermoplastics has experienced significant growth, with a compound annual growth rate (CAGR) of 8.4% from 2 million tons in 1950 to 159 million tons in 2023.¹³² The production of NPMs is driven by increasing demand and investment, which currently account for a global production capacity of 4 Mt and has a CAGR of 17.04%.^{133,134} This highlights the great potential of biodegradable packaging in the market, driven by increasing attention to severe plastic pollution and restrictions on plastic use.¹³⁵

While both legislative and non-legislative actions have been found to be effective in reducing single-use plastic consumption, finding suitable alternatives to single-use plastics remains a challenge. The production of such alternatives is often considered complex and small-scale, with high costs, but their performance still does not compare to that of conventional synthetic polymers.

Table 1 illustrates that SPMs have mature manufacturing techniques, resulting in a larger production scale and lower costs. However, their CO₂ emissions remain significantly higher, and despite efforts to recycle and reduce energy consumption, the recycling rate remains low.¹³ The production scale refers to the total annual production volume, while energy consumption is influenced by factors such as viscosity, dissolution, and drying, which impact polymer processing costs.¹⁵⁹ In a cradle-to-gate analysis of plastics with an annual consumption exceeding 1 million metric tons, energy consumption was assessed.

Although NPMs have achieved adequate reduced CO₂ emissions compared with some SPMs, challenges persist in scaling up and cost reduction of the production process. NPM sources struggle to secure a stable resource chain, affecting material quality and limiting their application fields, particularly in terms of moldability and elasticity. Despite the success of PLA, its flexibility remains relatively low compared to plastics

without additives.¹⁶⁰ Therefore, scientists are focusing on other naturally occurring elastic materials, such as starch and chitosan, which are projected to reach a global production of 225.82 and 365 tonnes in the coming decade, respectively, with a compound annual growth rate (CAGR) of 7.10%, and 11.93% respectively.^{161–163} New generations of these materials have been developed, but their inherent fragility and instability have led to the introduction of composites such as cellulose, fibers, waxes, lignin and metal oxides.^{164–168} Among them, bacterial cellulose (BC) has gained popularity due to its non-wood source and rapid growth, which proves to be economically feasible, with a predicted CAGR of 12.6%.^{169,170}

Currently, the production cost of NPMs is primarily limited by small-scale production and immature manufacturing technology. This results in NPMs lacking a clear cost advantage compared to traditional SPMs, which have undergone decades of development.

A similar situation exists regarding CO₂ emissions. Consequently, at this stage, NPMs' primary advantage lies in energy consumption, particularly for bio-based NPMs like cellulose and starch, which benefit from established production methods. However, due to cost and production constraints, NPMs have yet to fully replace traditional SPMs.

To achieve significant reductions in production and treatment costs associated with SPMs, it is crucial to allocate more resources towards improving development procedures. Prioritizing the development of natural resources is essential to advance NPMs and realize cost-reduction goals. Furthermore, addressing the challenges related to transparency and water resistance in NPMs has the potential to attract further investment and drive progress in this field. The production and recycling of bio-based plastics pose significant challenges due to their complex production processes and limited recyclability.

3.2. Mechanical properties

The mechanical properties, specifically tensile strength and maximum elongation, are critical in determining the

Table 1 Production process, cost, CO₂ emission, and scale of different FPMs

Type of food packaging material	Cost (USD per kg)	Annual energy consumption (PJ per year)	CO ₂ emission (kg kg ⁻¹)	Scale	Reference
PP	0.32–1.12	560	0.63	Industrial, kiloton	136 and 137
PS	0.32–1.33	270	0.98	Industrial, kiloton	138
PET	0.13–1.17	340	5	Industrial, kiloton	139 and 140
PVC	0.27–0.91	340	2.82	Industrial, kiloton	141 and 142
HDPE	0.01–1.21	830	2.5	Industrial, kiloton	142 and 143
LDPE	0.21–0.74	—	3	Industrial, kiloton	142 and 144
PHBV-based	2.05	10	2	Industrial, kiloton	145–147
PLA-based	12–15	587	1.8	Industrial, kiloton	148–150
Cellulose-based	1300	0.22	1.2–3.7	Industrial, kiloton	69 and 151–153
Hemicellulose-based	—	—	—	Lab scale	—
Lignin-based	—	—	—	Lab scale	—
Starch-based	4081	6.2 × 10 ⁻⁷	1.14	Industrial, kiloton	154 and 155
Protein-based	—	—	—	Lab scale	—
Pectin-based	—	—	—	Lab scale	—
Alginate	2358–5623	—	2.6	Lab scale, kg	156
Chitosan	20	0.03–0.16	0.7	Lab scale, kg	126, 153, 157 and 158



effectiveness of food packaging materials in separating and protecting food from the surrounding environment. Specifically, the tensile strength and elongation at break are vital parameters.¹⁷¹ A higher elongation results in a higher possibility of achieving close contact between the food and packaging, thereby enhancing protection and enabling denser packaging. Fig. 3 illustrates a comparison of the tensile strength and elongation at break for various FPMs, including materials with additives or modifications.

Observations reveal that typical SPMs are distributed in a region characterized by lower tensile strength and higher elongation at break (blue region). NPMs primarily occupy the low-elongation region, with some displaying higher tensile strength than typical SPMs (green region). This clear distinction highlights the distinct functional characteristics of these material types.

It is essential to note that, at the current stage, NPMs cannot fully replace SPMs. In contrast, historical applications of cellulose have primarily involved composites, relying on other elastic polymers to expand its utility.⁶⁵ Government policies promoting sustainability have led to a review of paper-plastic composites and coatings like PE, PP, and PVC, which enhance water, oil, and grease resistance, and durability in paper packaging.

The development of BC presents a possible solution to break the limitation, as demonstrated by Jiang *et al.*'s study on BC films modified with long-chain alkenyl succinic anhydrides.⁸³ This material exhibited impressive tensile strength (115.6 MPa), which is twice that of a PET film and nearly three times higher than that of a neat BC film. However, its stretchability falls short

compared to conventional SPMs, limiting the applicability of BC in certain applications such as plastic wraps that demand high elasticity.

Apart from the ultra-performance in terms of tensile strength for modified BC, the lignin-poly polyethylene glycol polyurethane bio-plastic developed by Chen *et al.*⁹⁸ has shown an extremely high elongation compared to other NPMs. Its elongation property closely resembles that of synthetic polymers. The biodegradable semicrystalline polyester, polyethylene glycol, acts as a soft segment, contributing to the material's high elongation performance. This method enhances the elongation of certain NPMs, although it may not be suitable for those that can form films independently.

It is noteworthy that the elongation at break of the PLA/PBAT/Plasticizer film (315.4%), developed by Slezak *et al.*¹⁷⁹ exhibits a staggering 44 times higher value compared to that of a pure PLA film (7%). The addition of a plasticizer has significantly improved its mechanical properties, aligning them closely with those of typical SPMs and providing an exceptionally high elongation compared to other NPMs. This factor has contributed to making PLA a common material for food packaging in recent years. It is important to point out that this method improves the elongation performance of the material through the additive, which differs from lignin-poly polyethylene glycol polyurethane discussed above, where the material can form a film without an additive. Hence, the method of additive addition will be suitable for most film formations of different natural polymers. Apart from this, PHBV is found to be another promoting bioplastic other than PLA in recent years; however, it showed a weak tensile strength and elongation at break compared with other NPMs.

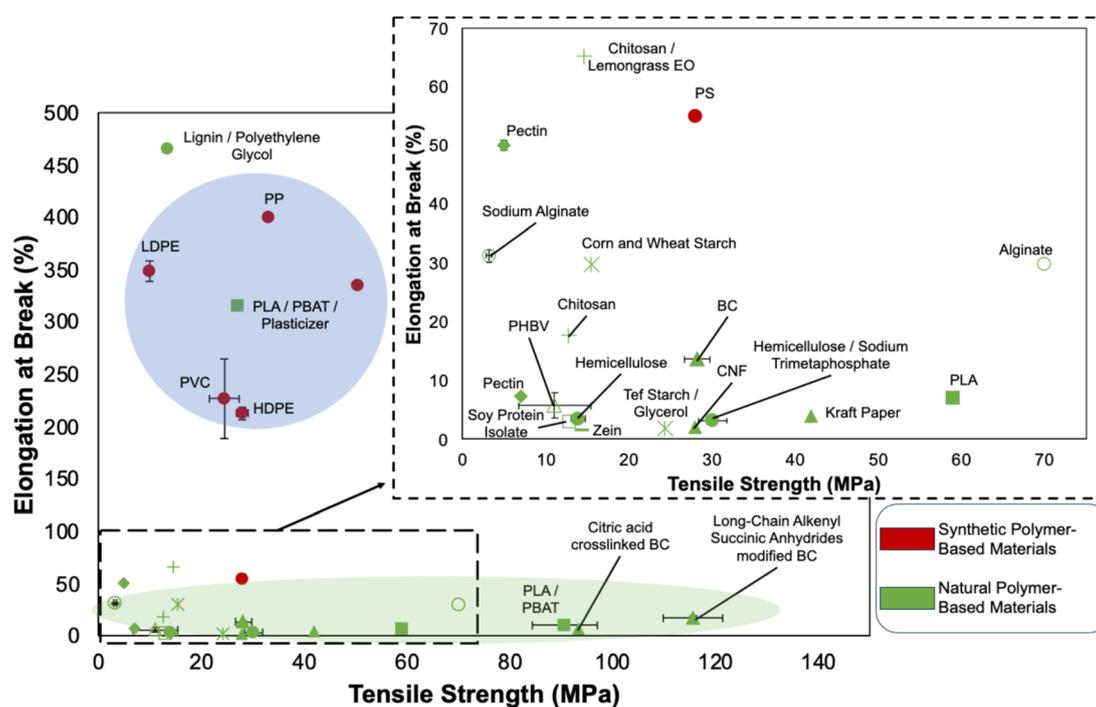


Fig. 3 The comparison of tensile strength and elongation at break of different film-based materials.^{83,98,172–195}



This limited its application, and additives will be necessary in future development to enhance the tensile strength and elongation at break, similar to PLA.

This underscores the possibility that, through continuous development, the extensibility of natural source materials can be further enhanced, ultimately leading to the replacement of outdated SPMs. This aligns more closely with the characteristics and practical requirements of existing NPMs, marking a promising evolution in the field.

3.3. Oxygen and water vapor permeability

Food spoilage poses a significant threat to food safety, characterized by undesirable changes in food quality due to chemical processes. Chemical oxidation, arising from the interaction between food and oxygen, emerges as a primary pathway for food spoilage.¹⁹⁶ Additionally, mold, yeast, and other harmful fungi thrive in oxygen-rich and high-humidity environments,¹⁹⁷ underscoring the importance of isolating food from oxygen and water vapor in the atmosphere to preserve both food quality and safety.^{198,199} Fig. 4 illustrates some examples of biobased materials used as food packaging, designed to prevent food spoilage.

Table 2 presents the oxygen and water vapor permeability of various packaging materials, with lower permeability values indicating superior barrier properties. For NPMs, raw forms without modification are selected, while for SPMs, additives or cross-linkers are included.

The permeability of materials to water vapor and oxygen is influenced by several factors, including their chemical composition, structure, crystallinity, and cross-linking level at the raw

material level, as well as the content of additives and fillers during the manufacturing process. The literature suggests a direct correlation between crystallinity and permeability: materials with higher crystallinity demonstrate lower permeability.^{221,222} Conversely, materials with lower crystallinity feature greater internal spaces, which facilitate the passage of oxygen and moisture, leading to a high permeability.²²³

Apart from crystallinity, the hydroxyl group may form hydrogen bonding with the water molecules passing through the materials,²²⁴ the interaction provided the ability of water molecule catching and further, a very low water vapor passing rate for the materials. Thus, the permeability characteristics of different raw materials are complex and multifactorial.

In Table 2, we can observe that synthetic materials generally have relatively low permeability, especially in terms of water vapor. The performance of NPMs in terms of water vapor permeability is not as good as that of most synthetic materials, such as PP and HDPE. Crystallinity is not the only factor affecting water vapor permeability in these film materials; additives and fillers in synthetic materials also play an important role.

The hydrophobic nature and chemical structure of the polymer are found to be other key factors in determining the water vapor barrier properties,²²⁵ with most synthetic polymers not containing hydroxyl groups in their chemical structure. The more hydrophobic the polymer, the lower its water vapor permeability.²²⁶ Unlike “catching” by hydroxyl groups, the impermeability of these materials prevents water from passing inside the material, resulting in low water permeability.

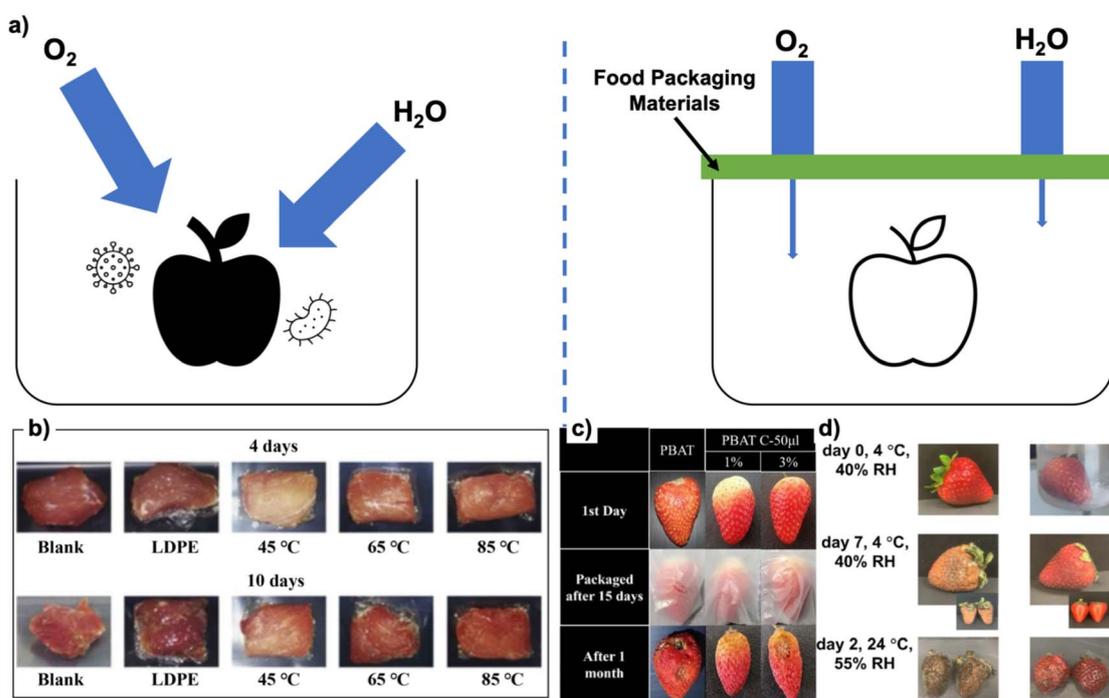


Fig. 4 (a) The use of food packaging materials to prevent quality changes in food, and the example of using (b) chitosan-based²⁰⁰ (Reprinted with permission from MDPI), (c) PLA²⁰¹ (Reprinted with permission from Springer Nature), and (d) bacterial cellulose-based food packaging materials⁸⁵ (Reprinted with permission from American Chemical Society).



Table 2 Oxygen permeability and water vapor permeability of different packaging materials^a

Materials	Oxygen permeability (mL per mm ² per day per Pa)	Condition	Water vapor permeability (g per mm ² per day per Pa)	Condition	Reference
PP/Bio-PP	4.94×10^{-7}	50% RH, 23 °C	8.24×10^{-11}	85% RH, 23 °C	22 and 202
PS/Bio-PS	9.87×10^{-7}	50% RH, 23 °C	4.12×10^{-10}	85% RH, 23 °C	22 and 202
PET/Bio-PET	9.80×10^{-5}	50% RH, 23 °C	6.14×10^{-10}	50% RH, 23 °C	22, 175 and 203
PVC/Bio-PVC	1.97×10^{-8}	20 °C	4.12×10^{-10}	90% RH, 38 °C	22 and 202
HDPE/Bio-HDPE	7.13×10^{-7}	25 °C	1.46×10^{-10}	90% RH, 38 °C	22 and 204
LDPE/Bio-LDPE	4.48×10^{-8}	25 °C	2.25×10^{-5}	100% RH, 38 °C	22 and 175
PHBV-based	7.88×10^{-3}	0% RH, 23 °C	9.78×10^{-4}	100% RH, 37.8 °C	205
PLA-based	8.64×10^{-9}	0% RH, 23 °C	1.56×10^{-6}	50% RH, 25 °C	206 and 207
Cellulose-based	1.12×10^{-9}	50% RH, 25 °C	1.72×10^{-3}	50% RH, 23 °C	208 and 209
BC-based	5.87×10^{-8}	54% RH, 25 °C	8.79×10^{-7}	—	82, 83, 89, 210 and 211
Paper	—	—	6.96×10^{-9}	38 °C	212
Hemicellulose-based	3.72×10^{-9}	50% RH, 23 °C	2.46×10^{-5}	100% RH, 20 °C	191
Lignin-based	5.28×10^{-7}	—	3.14×10^{-7}	—	213
Starch-based	1×10^{-3}	75% RH	7.41×10^{-3}	75% RH	214 and 215
Protein-based	5.37×10^{-8}	—	3.14×10^{-2}	20% RH, 24 °C	216 and 217
Pectin-based	3.39×10^{-7}	53% RH, 25 °C	1.33×10^{-6}	25 °C	181 and 218
Alginate-based	1.11×10^{-10}	0% RH, 25 °C	1.09×10^{-5}	—	219
Chitosan-based	6.21×10^{-9}	55% RH, 25 °C	8.50×10^{-5}	55% RH, 23 °C	220

^a RH = relative humidity.

Therefore, apart from LDPE, which has a high water vapor permeability due to its low density, other synthetic polymers exhibit a lower water vapor permeability than NPM.

Apart from the synthetic materials, we can also observe that paper, lignin-based materials, and BC have outstanding performance in preventing water vapor penetration (6.96×10^{-9} g per mm² per day per Pa, 3.14×10^{-7} g per mm² per day per Pa, and 8.79×10^{-7} g per mm² per day per Pa respectively). For Kraft paper and BC, the crystallinity was found to be 69.81% and 74%, respectively;^{227,228} the high crystallinity of cellulose creates a highly ordered, three-dimensional framework that traps water molecules. This limits the ability of water to penetrate the material. Besides this, the free hydroxyl group inside the film, provided water molecule capture ability, ultimately leading to a lower water permeability.²²⁹ Apart from this, the abundance of aromatic rings and various non-polar functional groups led to a high hydrophobicity of lignin, resulting in a high water vapor barrier ability of the materials.²³⁰ Therefore, the water vapor permeability of these materials can become lower than that of other NPMs.

Apart from the interaction between a hydroxyl group and water molecules, lignin-based materials have a different mechanism to lead to a low water vapor permeability. Lignin has a unique three-dimensional long chain network structure, consisting of aromatic rings, benzene groups, and ether bonds; this led to a highly branched and heterogeneous structure of the lignin-based material, which creates a complex network of molecules. This complexity limits the ability of water molecules to penetrate the material and disrupt the hydrogen bonding network. This decreases the interaction between lignin and water, resulting in hydrophobic properties and low water vapor permeability.^{231,232}

Interestingly, we can observe very different situations in terms of oxygen permeability. NPMs such as PLA ($8.64 \times$

10^{-9} mL per mm² per day per Pa), alginate (1.11×10^{-10} mL per mm² per day per Pa) and chitosan (6.21×10^{-9} mL per mm² per day per Pa) show better oxygen barrier properties than traditional SPMs in the table. This is probably due to the molecular linear structure, which has no branches and allows each layer of molecules to be arranged neatly giving these materials a certain degree of hydrophilicity; the tighter crystal structure reduces the chance of oxygen passing through the film, so they can have a better performance for the oxygen barrier. Starch-based materials have the opportunity to contain a branched chain structure of amylose and amylopectin,²³³ which leads to large numbers of alternating layers of crystalline and amorphous areas in the hydrogen bonding network, forming holes that allow oxygen to pass through the film. A similar situation occurs due to its water permeability. Additionally, protein-based materials have relatively high oxygen and water vapor permeability due to their unique three-dimensional structure. The unique structure prevents the proteins from arranging themselves neatly, leading to the formation of voids during film generation. Generally, similar to starch-based materials, this may also weaken the interaction between the polymer backbone and increase permeability.²³⁴ Hence, oxygen and water vapor can pass easily through those voids, resulting in a high oxygen permeability and water vapor permeability.

Therefore, understanding a packaging material's permeability properties is crucial for designing effective food packaging solutions that preserve food quality and safety. While synthetic materials generally exhibit lower permeability, exceptions exist among natural materials, highlighting the importance of considering material-specific characteristics.

The properties of packaging materials play a significant role in determining their effectiveness in preserving food quality and safety. NPMs, such as lignin-based materials, Kraft paper, and chitosan, exhibit high water vapor barrier properties and



potential low oxygen permeability. In contrast, SPMs, such as PP and HDPE, generally possess lower permeability to water vapor and oxygen. The hydrophobic nature of synthetic materials contributes to their low water vapor permeability, while additives and fillers can impact the material's overall performance. Material-specific characteristics are crucial for designing effective food packaging solutions, and further investigation can lead to innovative developments. Further investigation into these factors will enable researchers to contribute to the development of innovative packaging materials that tackle the challenges of food spoilage and improve food preservation techniques.

3.4. Waste treatment

The waste treatment of FPMs after use plays a crucial role in their life cycle. Currently, there are three major waste treatment methods: recycling, landfilling, and incineration, which accounted for treatment of 9%, 79%, and 12% of FPM waste dominated by plastics in 2015, respectively.⁹ It is worth noting that natural polymer-based materials exhibit distinct differences in comparison to synthetic polymers and polymers with natural building blocks. This led to the different results between SPMs and NPMs after they have undergone these treatments, specifically landfilling. This underscores the importance of considering material-specific characteristics when designing effective food packaging solutions.

3.4.1. Recycling. The recycling of FPMs is a crucial aspect of maintaining sustainability. Recycling aims to collect used FPMs and regenerate new materials, thereby reducing energy consumption and the carbon footprint in the process. There are two prominent methods for recycling packaging materials: mechanical recycling and chemical recycling.

Mechanical recycling involves washing, shredding, melting, and remolding waste into a new product. However, only materials that exhibit thermoplastic-like properties, such as polyethylene (PE) and polyethylene terephthalate (PET), can undergo mechanical recycling.²³⁵

Natural polymers, like starch-based films, also demonstrate thermoplastic-like characteristics, making them suitable for mechanical recycling.²³⁶ For example, PLA can be mechanically recycled, but the process may lead to depolymerization, altering its mechanical properties.^{237,238}

Chemical recycling offers an alternative method that converts waste into valuable products, often involving depolymerization. Pyrolysis, pyrolysis-reforming, and gasification are examples of chemical recycling methods that selectively produce gases, fuels, or waxes through catalysed thermo-processing. Chemolysis, also known as chemolytic depolymerization, is a specific method suitable for PET, where the waste yields monomers of the polymer, allowing them to be reused in polymerization.^{239,240}

Both synthetic polymer and natural polymer-based FPMs can undergo recycling through these two methods. However, NPMs follow a distinct path. Xia's group reported a lignocellulosic bioplastic produced through the casting method, using deep eutectic solvent (DES) as a dispersing medium for cellulose-

lignin-based materials.²⁴¹ This bioplastic can be recycled and reformed using DES as the solvent without changing its chemical structure. On the other hand, Cibinel presented alginate composites using ethylenediaminetetraacetic acid as a solvent, demonstrating the ability to produce and recycle new composite materials.²⁴²

Ren *et al.* introduced a pectin-based film that follows a similar method of production and recycling.³⁰ It is noteworthy that for NPMs, the use of solvents is a critical aspect of both casting and recycling, distinguishing them from synthetic polymers. However, it's essential to highlight that recycling NPMs requires careful selection methods. Each material must be matched with a suitable recycling method based on its manufacturing process.

This is in contrast to traditional synthetic polymers, which commonly use heat as a generic recycling method following the separation of different types of synthetic polymers. As a result, the recycling of NPMs presents increased complexity, leading to a low recycling rate in today's society.

3.4.2. Biodegradability. Biodegradability is a crucial factor in selecting future food packaging materials. This process can be broken down into three stages: biodeterioration, biofragmentation, and assimilation. Biodeterioration refers to the degradation of a material's surface under environmental stressors such as pressure, light, temperature changes, and chemical exposure. Biofragmentation involves the breakdown of long-chain polymers into low-molecular-weight fragments or monomers, while assimilation is the absorption of these fragments by microorganisms.²⁴³

Typically, ideal biodegradable materials require specific environmental conditions such as temperature, light, moisture, and oxygen along with the addition of enzymes or bacteria to enhance biodegradation rates. However, incorporating functionalized materials into FPMs to achieve desired properties such as water resistance, flexibility, and anti-barrier characteristics often hinders the degradation process.^{244,245} This can affect the formation of final fragments and raise concerns about the overall reliability of biodegradable FPMs.^{246,247} But generally bio-based modified FPMs have higher degradability than conventional plastics under natural terrestrial composting.^{248,249}

Recent studies have shed light on the biodegradation rates of various natural polymer-based materials. Fig. 5a illustrates the time required for biodegradation and the resultant degradation products in different environments with various additives. The results show that, excluding SPMs, most other biobased materials tend to decompose into substances with a lower environmental impact within a year, provided that ideal and suitable conditions are met.

Additionally, Fig. 5b and c demonstrate the degradation of bacterial cellulose and lignin-based materials in soil, where biofragmentation can be observed. The materials break down to become smaller in size and undergo assimilation, making them unobservable in the soil. Chitosan-based, HPBV-based, and hemicellulose-based materials have been shown to be highly biodegradable, taking as little as 0.8–2 weeks to degrade in the soil.



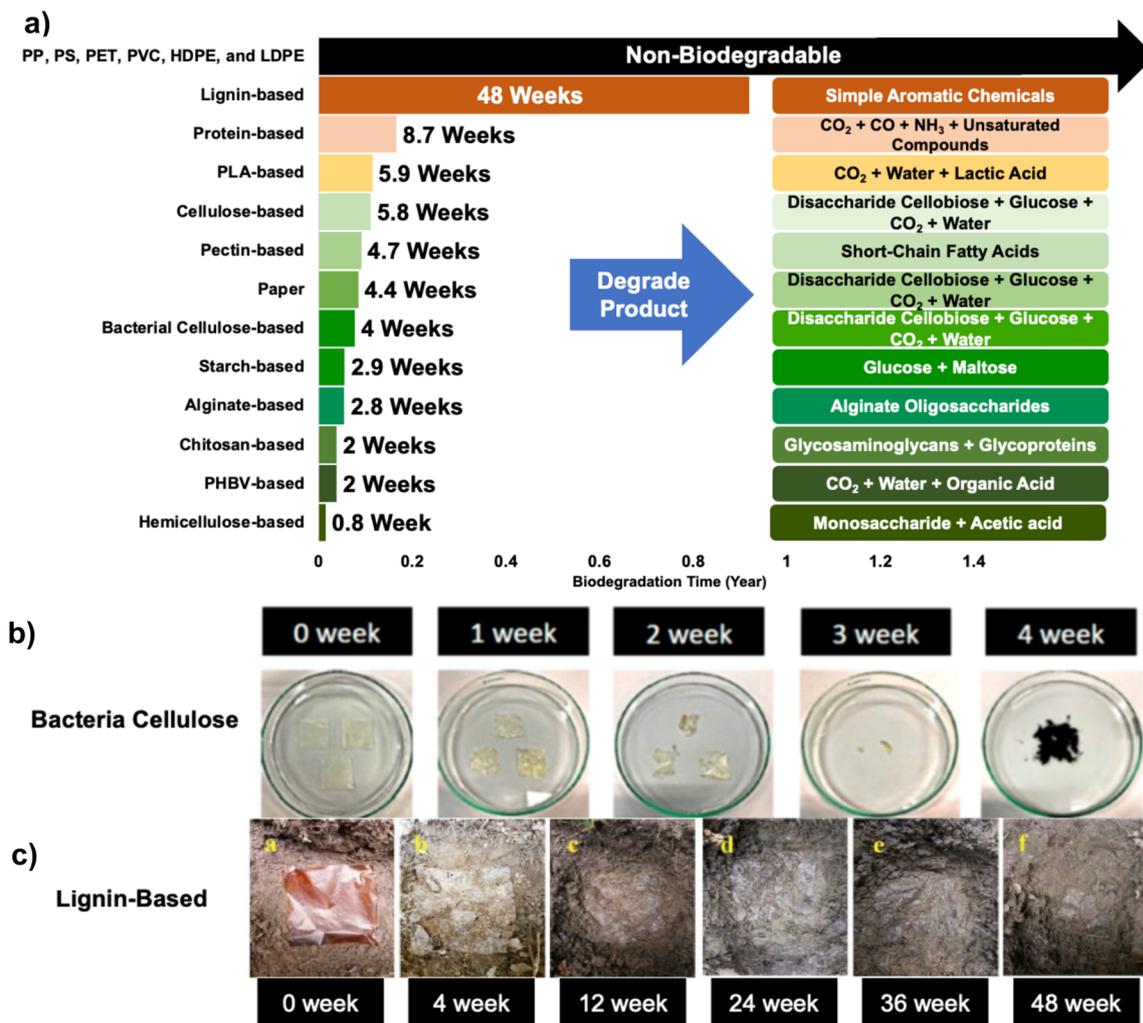


Fig. 5 (a) Biodegradation time of different FPMs,^{10,26,82,111,178,179,250–263} (b) degradation of bacterial cellulose²⁶⁴ (Reprinted with permission from MDPI), and (c) degradation of lignin-based films²⁵⁵ (Reprinted with permission from Elsevier).

These findings highlight the potential of natural polymer-based materials as alternatives to traditional synthetic plastics. Paper, a common food packaging material, has significant advantages in terms of biodegradability but is limited by its inherent characteristics. Despite these limitations, natural polymer-based materials demonstrate remarkable biodegradability and environmental benefits.

Table 3 provides details on the biodegradation conditions required for various FPMs, including environmental conditions and whether enzymatic additives can enhance the degradation rate. Upon examining the table, it becomes clear that PLA requires relatively stringent conditions to achieve complete biodegradation within six weeks. Specifically, a temperature of 58 °C and a relative humidity of 55% are necessary for swift degradation. However, temperatures between 20 °C and 25 °C fail to meet these environmental conditions, restricting the process to controlled factory or laboratory environments.

In contrast, typical cellulose, BC, pectin, SPI, and alginate-based materials exhibit more favourable biodegradation conditions, at temperatures closer to room temperature (20–25

°C). It is important to point out that for some types of NPMs, the addition of enzymatic additives can enhance the degradation rate, providing a more outstanding biodegradability. Among these materials, cellulose and BC stand out due to their lower humidity requirements. When supplemented with enzymes, these materials can biodegrade under normal environmental conditions, highlighting their significant biodegradability.

This finding underscores the importance of considering environmental factors and additives when designing sustainable packaging solutions for the future. The challenging biodegradation conditions and rates for various FPMs emphasize the need for solutions that meet current environmental needs.

4. Discussion, challenges and future developments

Understanding the lifecycle of FPMs requires considering their production methods, usage characteristics, and post-use



Table 3 Biodegradation conditions and additives of different FPMs

Material	Condition	Additive to enhance the biodegradation rate	Reference
PP/Bio-PP	Nonbiodegradable	Nonbiodegradable	265
PS/Bio-PS	Nonbiodegradable	Nonbiodegradable	265
PET/Bio-PET	Nonbiodegradable	Nonbiodegradable	265
PVC/Bio-PVC	Nonbiodegradable	Nonbiodegradable	265
HDPE/Bio-HDPE	Nonbiodegradable	Nonbiodegradable	265
LDPE/Bio-LDPE	Nonbiodegradable	Nonbiodegradable	265
PHBV-based	Soil, 25 °C, 80% moisture content	Esterases, lipases, cutinases, peroxidases, and laccases	266 and 267
PLA-based	Soil, 58 °C, and 55% RH ^a	Proteinase K	247 and 268
Cellulose-based	Soil, 25–45 °C, 12% moisture content	Cellulase	258
BC-based	Soil, 35.1 °C, 10–20% moisture content	Cellulase	264
Paper	Soil, 40 °C	Cellulase, mannanase, xylanase, and β -glucosidase enzyme	269
Hemicellulose-based	Soil	—	26
Lignin-based	Soil	White-rot fungi	255
Starch-based	Soil, 27 °C, 70% moisture content	Amylase	270 and 271
Protein-based	Aerobic soil with volatile, pH 6–6.5, 25 °C, and 40% RH ^a	Proteases	272 and 273
Pectin-based	Soil, 28 °C, 50% RH ^a /sea water, 25 °C	Polygalacturonase, pectinesterase, and pectin lyase	111, 253 and 274
Alginate-based	Soil, 25 °C, and 75% RH/beach sand, 25 °C, and 75% RH ^a	Alginate lyase	178, 250 and 275
Chitosan-based	Vineyard soil	Lysozyme	254

^a RH = relative humidity.

treatment strategies. Each material possesses unique features, which we have thoroughly evaluated and scored, resulting in the summarized findings presented in Fig. 6.

The primary feature of NPMs is their biodegradability. When degraded, these products typically form monomer materials that can be utilized as nutrients for plant growth, fostering the production of new natural polymers within the plant. This allows them to quickly re-enter the lifecycle. For instance, starch-based materials can degrade into glucose and maltose within 5.4 weeks, serving as nutrients for soil bacteria and enhancing bacterial activity, thereby perpetuating a sustainable lifecycle for natural polymers.^{276,277} In contrast, synthetic polymers are difficult to biodegrade and often break down into microplastics due to UV radiation, water, and earthworms.

In contrast, synthetic polymers are difficult to biodegrade and often break down into microplastics due to UV radiation, heat, and water.²⁷⁸ These microplastics can have a detrimental impact on the surrounding environment, inducing functional changes in soil and affecting the growth of soil microorganisms and bacteria.

Despite the readily biodegradable nature of NPMs under composting conditions, factors such as form, size, and the type of additives used can influence the degree of biodegradability. This variability may lead to incomplete degradation.^{249,279} However, studies have shown that composites containing additives are gradually compostable in natural terrestrial environments, landfills, and water bodies. Notably, temperature plays a crucial role in this process, as optimal temperatures allow for complete cellulose degradation, enhancing the suitability of NPMs for various applications.²⁴⁹

Conversely, introducing additives has proven complex due to their overall impact on biodegradability. For example, studies have shown that antimicrobial thermoplastic starch composites exhibit high antimicrobial efficacy. However, there is limited evidence regarding their biodegradation impact.^{280–282} Furthermore, Carmen *et al.* highlighted that while some enzymatic activities may be disrupted by phenolic additives, the overall enzymatic biodegradation of these composites under laboratory conditions generally remains unaffected.²⁸³ Therefore, it is crucial to assess the biodegradation rates of polymers modified with biodegradable agents before making any claims about their environmental sustainability.

Furthermore, NPMs exhibit notable tensile strength, with nearly half exceeding that of conventional synthetic materials. While products like plastic wrap and food boxes have relatively modest strength requirements, synthetic polymers often struggle in this domain. However, achieving optimal elongation performance in NPMs remains a challenge that must be addressed before they can fully replace unsustainable SPMs as food packaging in the future.

NPMs also exhibit exceptional oxygen barrier characteristics, which are crucial for food preservation. Maintaining a balance between oxygen and water vapor barrier properties is essential when selecting materials to effectively replace SPMs.

Upon reviewing the material properties, we conclude that lignin-based materials possess mechanical attributes comparable to current SPMs, notably exhibiting the highest elongation among all NPMs discussed. However, their extended biodegradation duration remains a notable limitation, warranting further research focus in this area.



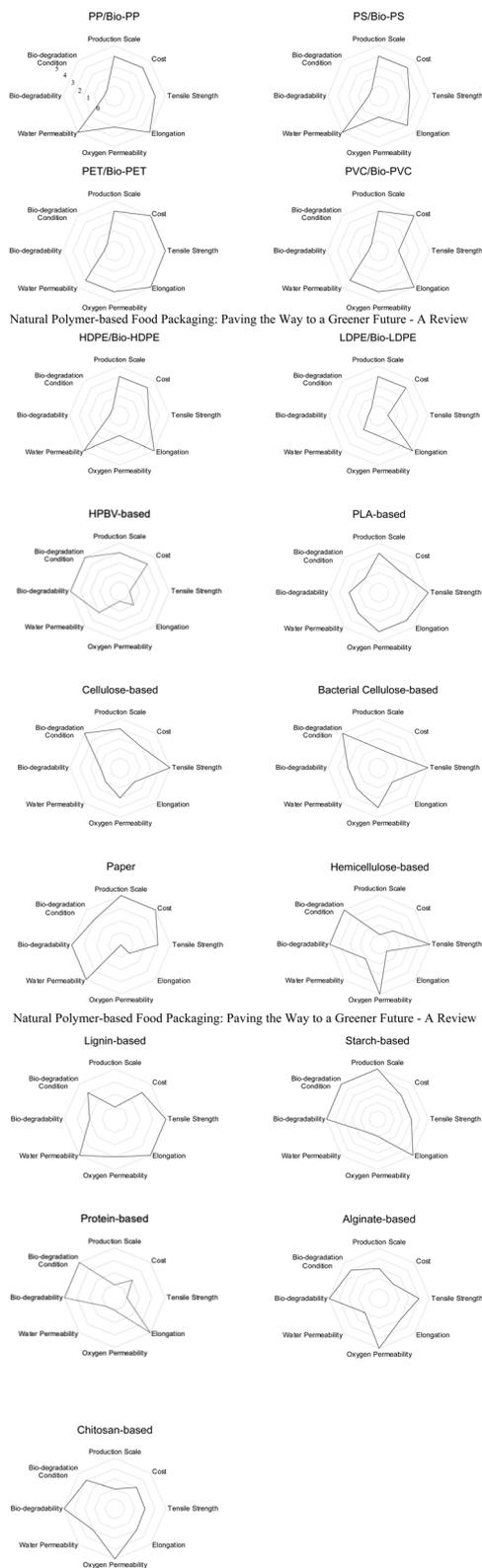


Fig. 6 Summary of comparison (1 = least preferable and 5 = most preferable).

Conversely, BC presents another promising avenue. Cellulose-based materials can exhibit excellent tensile strength after modification and possess good oxygen and water vapor

barrier properties. Their relatively short biodegradation time and environmentally friendly biodegrade conditions, with only the addition of enzymes needed, make them a potential candidate for future development.

HPBV, one of the NPMs gaining attention in recent years, exhibits significant biodegradability. However, its mechanical properties, water vapor barrier properties, and oxygen barrier properties lag behind those of existing SPMs and other NPMs. These limitations hinder its widespread practical application and development. Future research will likely focus on expanding the functional capabilities of HPBV to overcome these challenges and propel it into mainstream use.

While we have identified three potential alternatives to SPMs, scaling up material manufacturing presents a significant obstacle to their complete replacement. A primary hurdle in NPM production is establishing large-scale manufacturing processes. Currently, limited production capacity hinders this development.

The production capacity of green materials is significantly lower than that of conventional plastics. This limitation stems from factors such as the availability of raw materials, specialized equipment, and unique processing requirements.

Producing green materials often incurs higher costs due to limited economies of scale. For example, extracting chitosan from food waste can be both challenging and inefficient, requiring effective extraction methods.¹²⁶ However, as the demand for sustainable alternatives grows, advancements in production techniques and the achievement of larger economies of scale are expected to reduce costs and facilitate wider adoption.

Similar to cellulose, the production of green materials typically involves a series of extraction processes, including pulping, dissolution, film formation, purification, drying, coating, and sheeting. This results in NPMs being weaker than SPMs in terms of production costs and production quantities. Furthermore, after pre-treatments, these materials are often limited to bottom-up film production methods, which can compromise their strength and barrier properties, such as in solution casting and solvent dissolution of starch, pectin, alginate, and cellulose.^{284–286} Additionally, modifications are required to improve processability but this may lead to the reduction of their biodegradability as observed in cellulose acetate at high degrees of modification,²⁸⁷ which changed the properties of biodegradability, making complete biodegradation and disposal challenging.

Despite the diverse chemical properties of NPMs, there is a strong demand for solutions that minimize plasticizer content and ensure compatibility with existing machinery. Improving transparency, controllable smoothness, thickness, color, and high-speed operation will make NPMs more competitive with conventional plastics. Adjusting the fiber size and molar mass of bio-based materials used in NPM production is necessary. These adjustments are closely related to pretreatment methods, morphology control, functionalization strategies, and the feasibility of pelletization for applications in the packaging field.^{288,289}

In the future, producing multilayer structures may be a promising method for minimizing the need for extensive



modification.²⁹⁰ This can be achieved by utilizing plant-based materials and tailoring structure–function relationships through pretreatment and fibrillation to achieve desired properties. Conversely, enhancing NPM processability with existing machinery and reducing toxicant usage are crucial parameters.²⁹¹ Exploring the impact of surface energy on moulds and drying surfaces can help address issues such as film shrinkage, adhesion during the drying process, and challenges posed by solid content in sample preparation.²⁹²

In conclusion, while NPMs offer several advantages compared to SPMs, their production, usage characteristics, and end-of-life treatment require careful consideration. Addressing practical considerations like regulatory barriers, industry resistance, and consumer acceptance will necessitate collaboration among stakeholders.

5. Conclusion

The food packaging industry is currently dominated by SPMs. These materials are widely adopted due to their well-established manufacturing processes, high production volumes, and relatively low costs. However, the environmental impact of SPMs, including their significant contribution to greenhouse gas emissions and limited recycling rates, underscores the urgent need for more sustainable alternatives.

In contrast, NPMs, such as starch-based and cellulose-based materials, offer promising properties with the potential to meet industry demands. NPMs, like BC films, exhibit promising biodegradability and tensile strength compared to SPMs. However, challenges remain in scaling up production, securing resources, and expanding application fields.

Recent advances have been made in thermoplastic starch, chitosan, and lignin-based composites; however, issues such as fragility and instability persist, necessitating further research and development. The mechanical properties, as well as oxygen and water vapor permeability, of materials play crucial roles in food packaging effectiveness. SPMs excel in these areas, but NPMs, such as BC and lignin-based materials, show potential for enhancing mechanical strength and barrier properties. Achieving a balance between strength, elasticity, and barrier properties remains a challenge.

SPMs and NPMs differ in their waste treatment methods, including recycling and biodegradation. SPMs can be recycled mechanically or chemically. NPMs, however, may require specific solvents, such as deep eutectic solvents (DESs), to dissolve them and be reformed. While the biodegradability of NPMs presents a key advantage, challenges remain in achieving rapid degradation under diverse conditions.

Several regulatory barriers and industry resistance must be addressed to enable the widespread adoption of NPMs. For example, infrastructure changes are needed to support recycling programs for NPMs, potentially requiring specialized equipment and facilities. Industry stakeholders must be willing to invest in developing new production lines and manufacturing processes that can efficiently scale up NPM production. It's crucial to note that most NPMs are still under investigation; further research on mass production, energy

consumption, and cost reduction is necessary for their future promotion.

Consumer acceptance is crucial for the commercial success of NPMs. Studies indicate that consumers often favour traditional SPMs due to familiarity and perceived performance. To overcome this resistance, industry stakeholders should invest in education and awareness programs highlighting the benefits of NPMs, such as reduced waste and environmental sustainability.

The authors hope that this review will provide an overview of different FPMs by analysing various material performances and manufacturing conditions. This analysis aims to provide momentum and direction for future research on NPMs, ultimately enabling NPMs to replace traditional SPMs and contribute to a more sustainable and environmentally friendly future.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

We declare that we have no financial or personal relationship with other people or organizations that could inappropriately influence our work. Furthermore, we have no professional or personal interests of any nature in any product, service or company that could be perceived as influencing the position presented in, or the review of, the manuscript entitled "Natural Polymer-based Food Packaging: Paving the Way to a Greener Future - A Review".

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