Biotechnology Frontiers
An International Journal
OPEN ACCESS
ISSN 3117-5791
Review Article
Check for updates

Green Synthesis and Modification of Biodegradable Polymers Using Plant-Derived Catalysts and Solvents: Recent Advances, Challenges, and Future Perspectives

Emmanuel N. Ifedi[1], **Olayombo M. Banwo***[2], **Elizabeth T. Ajobo**[1], **Joy M. Adepoju**[1], **Oluwatosin Ale**[1] and **Christanah K. Oladoke**[1]

[1]*Department of Chemistry, Industrial Unit, Faculty of Science, University of Ibadan, Ibadan, Nigeria*
[2]*Department of Industrial Chemistry, Abiola Ajimobi Technical University, 200255, Ibadan, Nigeria*

Corresponding author: **Olayombo M. Banwo** | E-mail: **banwomargaret@gmail.com**

Citation: Emmanuel N. Ifedi, Olayombo M. Banwo, Elizabeth T. Ajobo, Joy M. Adepoju, Oluwatosin Ale and Christanah K. Oladoke (2026). Green Synthesis and Modification of Biodegradable Polymers Using Plant-Derived Catalysts and Solvents: Recent Advances, Challenges, and Future Perspectives. *Biotechnology Frontiers: An International Journal.* **DOI: https://doi.org/10.51470/BF.2026.6.2.01**

Received 06 July 2026 | Revised 04 August 2026 | Accepted 05 September 2026 | Available Online 08 October 2026

Abstract

Biodegradable polymers have drawn growing scientific and industrial interest as viable, environmentally responsible alternatives to conventional petroleum-derived plastics. These materials are derived from natural, renewable sources and include polylactic acid (PLA), polyhydroxyalkanoates (PHAs), starch, cellulose, chitin, and chitosan. These materials combine biocompatibility, tunable mechanical properties, and end-of-life degradability, making them useful in a wide range of applications, such as drug delivery, tissue engineering, biomedical implants, food packaging, and agriculture. However, to realise the sustainability potential of these materials, the polymers themselves must be bio-derived, and the catalysts and solvents used in their synthesis and modification must also move away from hazardous, petrochemical-based systems. This paper reviews recent advances in the green synthesis and chemical modification of biodegradable polymers using plant-derived catalysts and bio-based solvents. The polymers studied are starch, chitin and chitosan, sodium alginate, cellulose and its nanostructured derivatives, PLA, PHAs, Poly(butylene succinate) (PBS), Polycaprolactone (PCL) and Poly(butylene adipate-co-terephthalate) (PBAT). The catalytic and solvent strategies discussed include enzyme-based systems, organic acids from plant biomass, alkaloid organocatalysts, terpene-derived solvents, and natural deep eutectic solvents (NADES). The data indicate significant advances in reducing E-factors and greenhouse gas emissions compared to conventional routes, but important challenges such as scalability, production cost, mechanical performance, and end-of-life infrastructure still hamper widespread industrial implementation. Bridging these gaps will need coordinated progress in biorefinery integration, process engineering and material design, supported by policy frameworks that actively enable the transition from fossil-based to bio-based polymer systems.

Keywords: *Biodegradable polymers, green synthesis, plant-derived catalysts, bio-based solvents, deep eutectic solvents, circular economy.*

1. INTRODUCTION

1.1 Why Biodegradable Polymers Matter

The environmental costs of synthetic plastic pollution cannot be ignored. Globally, more than 400 million metric tonnes of plastic are produced each year, yet only 10% of all plastics ever produced have been recycled [1]. Unrecycled plastics end up in landfills, rivers, and oceans, where they break down into microplastics that have now been detected in human blood, breast milk, and placental tissue, prompting concern among the public and regulators about the long-term effects of plastics [2]. In this regard, biodegradable polymers have regained renewed importance as materials that, under appropriate end-of-life conditions, return carbon to natural cycles rather than persisting indefinitely in the environment.

The polymers examined in this paper span natural and synthetic categories. Starch, one of the most abundant plant-based polymers, has been explored for decades as a component of degradable films and agricultural mulches [3]. Chitin and chitosan, derived from crustacean shells and increasingly from fungal biomass, offer antimicrobial activity and biocompatibility valuable in medical and cosmetic applications [4,5]. Cellulose, the most abundant organic polymer on Earth, offers both structural utility and a rich surface chemistry for extensive chemical modification. PLA is the most-produced synthetic biodegradable polyester and is produced by fermentation of plant sugars [6,7]. PHAs are biologically synthesised in bacterial cells from plant-derived carbon sources [8].

© ***Authors:*** *Published in* ***Biotechnology Frontiers: An International Journal*** *under the CC BY-NC-ND 4.0 license (http://creativecommons.org/licenses/by-nc-nd/4.0/). No commercial use or modifications permitted.*

Other members of this family include PBS, PCL, and PBAT, which offer, respectively, mechanical properties, flexibility, slow controlled degradation, and toughness that complement the more brittle profile of PLA [9,10].

This diversity is reflected in the world market of biodegradable polymers. The sector is growing rapidly due to regulatory restrictions on single-use plastics in the European Union and other jurisdictions, and increasing demand in food packaging, biomedical devices and agricultural films, with projections pointing toward double-digit annual growth through 2030 [11]. Yet the sustainability case for these materials is more complicated than headline biodegradability figures suggest, and this complexity motivates the present paper.

1.2 The Production-Stage Problem

The challenge remains to develop sustainable large-scale biodegradable polymers. Even when the polymer backbone is bio-derived, the catalysts and solvents used in synthesis and downstream modification have traditionally relied on problematic chemistry. Tin (II) bis(2-ethylhexanoate) has traditionally been used for the ring-opening polymerization of PLA, an organotin compound whose metal residues require extensive purification before use in biomedical or food-contact applications [12]. The same tin catalyst is used to synthesize PCL, or aluminum triisopropoxide, usually in toluene or dichloromethane [13]. PBS is conventionally produced via polycondensation using titanium tetrabutoxide or stannous octoate [14]. Cellulose processing has relied on solvents such as N-methylmorpholine N-oxide, dimethylacetamide/lithium chloride, and N-methylpyrrolidone systems, which are non-renewable resources, energy-intensive to recover, and hazardous to handle. The consequence is that a significant portion of the greenhouse gas emissions and waste burden associated with biodegradable polymer production arises not from the bio-based feedstock stage but from the polymerisation and chemical modification steps, an irony the green synthesis literature has only recently begun to address systematically.

This effort is examined in the framework of green chemistry, as defined by [15] twelve principles. Key principles applied here include using catalytic rather than stoichiometric reagents, selecting renewable feedstocks, avoiding hazardous auxiliary substances, and maximizing atom economy. Atom economy measures how much reactant mass ends up in the desired product. For ring-opening polymerization of lactide and related lactones, atom economy approaches 100% because all monomer atoms are retained in the polymer chain. The E-factor (kilograms of waste generated per kilogram of useful product) is a practical mass-balance metric that allows the quantitative comparison of synthesis routes [16]. E-factors for conventional metal-catalyzed polymer synthesis in organic solvents are usually 15 to 30 at lab scale, while enzymatic bulk polymerisation with plant-derived lipases has been reported with E-factors below 3 [16].

1.3 Plant-Derived Catalysts and Solvents: The State of Play

Recently, research on plant-derived alternatives has increased significantly, driven by regulatory pressure, advances in enzyme immobilisation technology, and growing interest in biorefinery co-product valorisation. Lipases from plant and bio-production sources catalyze ring-opening polymerization of lactones and transesterification of polyesters under mild conditions, with excellent selectivity and recyclability [17]. Organic acids in plant biomass act as Brønsted acid catalysts and crosslinking agents in polysaccharide modification, including citric acid from citrus fermentation, tartaric acid from wine byproducts, and levulinic acid from lignocellulosic pyrolysis [18]. Alkaloids from plant secondary metabolism, including caffeine and cinchona alkaloids, act as effective organocatalysts for controlled polymerisation, providing stereochemical control over PLA crystallinity that metal catalysts cannot match [19,12].

On the solvent side, 2-methyltetrahydrofuran from furfural is a near drop-in renewable replacement for THF (Tetrahydrofuran) in polymer synthesis, with documented reductions of around 40% in cumulative energy demand compared to the petroleum-based analog. Natural deep eutectic solvents (NADES) are made from plant components like choline chloride with citric acid, glycerol, or malic acid, and they dissolve cellulose and chitin under mild conditions without the hazards of conventional ionic solvents. These developments suggest an integrated model for producing biodegradable polymers in which bio-based catalysts and solvents are co-products of existing biomass processing streams, lowering costs through system-level integration and avoiding direct competition with petrochemical commodities.

1.4 Objectives and Structure

This paper connects the renewable origin of biodegradable polymers from renewable feedstocks and the often non-renewable chemistry used for their preparation. The work is structured around four objectives: To provide context on the environmental and industrial motivation for the synthesis of green biodegradable polymers; To review the key plant-derived catalytic and solvent systems available for the synthesis of nine polymer classes; To critically evaluate the evidence for environmental performance, material quality, and scalability; and to identify the outstanding challenges for green synthesis routes to become industrially viable alternatives to conventional methods.

The paper does not claim that the shift to plant-derived systems is easy or imminent for all polymer classes and applications. Instead, it argues that the direction is clear, the scientific basis is strengthening, and the main barriers are now economic and infrastructural rather than fundamental.

2. Biodegradable Polymers

Biodegradable polymers can be categorised into two broad groups: natural polymers, which are directly extracted from biological sources, such as polysaccharides (starch, cellulose, and chitin),

and synthetic biodegradable polymers, which are synthesised via ring opening or condensation polymerisation (examples include: PLA, PHAs, PCL, PBS, and PBAT). Selection criteria for these materials in any given application include mechanical-degradation rate matching, biocompatibility, toxicity of degradation products, and manufacturability [20, 21].

2.1 Green Chemistry Metrics for Evaluating Synthesis Routes

The degree of greenness of a synthetic route requires assessment by quantitative measures. Atom economy measures the proportion of reactant mass converted into the desired product. For instance, ring-opening polymerisation of lactide has an atom economy close to 100% as all atoms in the monomer become part of the polymer chain with no by-products [16]. The E-factor, kilograms of waste per kilogram of product, measures a process's practical waste burden. Conventional metal-catalysed synthesis in organic solvents typically produces E-factors of 15 to 30, while enzymatic bulk polymerization with plant-derived lipases achieves values below 3 [16]. The third metric, Process Mass Intensity, is the total input mass per unit of product; this complements the first two metrics. Together they form the basis for data-driven comparisons of conventional and plant-derived routes for the polymer classes reviewed below.

2.2 Starch

Starch is one of the most abundant polymers derived from plants, mainly from corn, potato, and rice. Its granules consist of approximately 20 wt. % amylose, a largely linear crystalline fraction, and amylopectin, a highly branched water-insoluble fraction. Starch has been used in plastics since the 1970's, first as a biodegradable filler in LDPE films and later in starch-polyvinyl alcohol blends for agricultural mulch [22, 3].

2.2.1 Green Synthesis and Modification of Starch Using Plant-Derived Agents

Conventional starch modification has relied on formaldehyde-based crosslinkers and synthetic plasticisers that undermine end-product biodegradability. The most effective green alternative is citric acid produced by fermenting corn syrup with *Aspergillus niger*, which forms covalent crosslinks that improve mechanical strength and moisture resistance without compromising biodegradability [18]. Citric acid-crosslinked starch films show tensile strengths of 12 to 18 MPa and 40% lower water vapour permeability than unmodified starch, processed using only water as a solvent at temperatures below 120°C [18].

2.3 Chitin and Chitosan

Chitin is a natural biopolymer consisting of 2-acetamide-2-deoxy-beta-D-glucose linked by beta(1-4) glycosidic bonds. It is present in crustacean and insect shells and is degradable by chitinase [17].

Chitosan, the partially deacetylated derivative of chitin, is water-soluble and combines biocompatibility with antimicrobial activity and heavy metal ion adsorption capacity, making it valuable in cosmetics, wound healing, and drug delivery [17].

2.3.1 Green Modification of Chitosan Using Plant-Derived Solvents

Traditionally, chitin and chitosan processing has been done under harsh acidic conditions or in toxic solvents. Natural deep eutectic solvents (NADES), formed from plant-derived hydrogen-bond donors and acceptors, are a safe and effective alternative. Chitosan extraction from biowaste and in situ carboxymethylation were performed in one step using a ternary NADES formed by choline chloride, malic acid, and water, without pH adjustment or toxic reagents, reducing system viscosity by 60% while keeping the dissolution power. Citric and succinic acid, as plant-derived organic acids, have also been used as crosslinkers for chitosan films and hydrogels, replacing the toxic synthetic crosslinker glutaraldehyde with food-grade metabolites that maintain the material's full antimicrobial and biodegradable characteristics [23].

2.4 Sodium Alginate

Sodium alginate is a naturally occurring, water-soluble anionic polysaccharide extracted from the cell walls of brown seaweeds such as *Laminaria digitata*, *Macrocystis pyrifera*, and *Sargassum muticum*. It is a linear copolymer composed of β-D-mannuronic acid and α-L-guluronic acid residues in homopolymeric and heteropolymeric block sequences where the ratio of the two monomers varies according to the source species and harvest season [24]. Sodium alginate is widely used in food packaging, pharmaceuticals, wound dressings, and tissue engineering because of its biocompatibility, non-toxicity, biodegradability, and gel-forming properties.

2.4.1 Green Modification of Sodium Alginate Using Plant-Derived Solvents and Catalysts

Modification of Sodium Alginate Using Plant-Derived Solvents and Catalysts

Conventional industrial extraction of sodium alginate is chemical-intensive: seaweed biomass is pretreated with formaldehyde to remove pigments, treated with dilute hydrochloric acid to convert native alginate salts to insoluble alginic acid, then solubilised via alkaline extraction with sodium carbonate, precipitated with ethanol or calcium chloride, and dried. This pathway produces large amounts of acidic and alkaline wastewater and is energy- and time-consuming [25]. Ultrasound-assisted extraction has been proposed as an efficient green alternative; one study showed that ultrasound-assisted aqueous extraction of alginate from *Sargassum muticum* yields comparable to conventional acid/alkali extraction while significantly reducing chemical consumption, processing temperature, and extraction time [26].

For modification, researchers have reported using plant-derived organic acids as crosslinking agents instead of synthetic crosslinkers like glutaraldehyde.

In one study, crosslinked sodium alginate and pineapple-waste-derived pectin with citric acid, tartaric acid, and glycerol were used as a plasticiser in an entirely aqueous system, producing films with improved tensile strength and thermal stability that were edible in feeding trials and fully composted in soil [27]. Moreover, sodium alginate is a green and metal-free organocatalyst in its own right. A report by [28] shows that unmodified granular sodium alginate catalyses the synthesis of 2-amino-4H-pyran derivatives via hydrogen bonding by its hydroxyl and carboxylate groups. The catalyst can be recovered and reused several times with insignificant loss of activity.

2.5 Cellulose

Cotton and wood are the main commercial sources of cellulose, the most abundant organic polymer on Earth and the main structural component of plant cell walls [29]. The extensive hydrogen bonding between hydroxyl groups along the glucan chains gives cellulose remarkable mechanical stability but makes it insoluble in water and most common organic solvents [30]. Cellulose nanocrystals are derived from various sources such as coconut husk, bamboo, and corn straw with diameters from 4 to 55 nm [31, 32].

2.5.1 Modification of Cellulose Using Plant-Derived Solvents and Catalysts

Cellulose synthesis conventionally requires N-methylmorpholine N-oxide (NMMO), dimethylacetamide/lithium chloride (DMAc/LiCl), or N-methylpyrrolidone, all of which are energy-intensive, hazardous, and petrochemical-based. The NADES systems have changed this landscape. Cellulose derivative films prepared in NADES have a more uniform substituent distribution than heterogeneous counterparts, resulting in better film transparency and more consistent pharmaceutical dissolution profiles. Beyond NADES, 2-Methyltetrahydrofuran (2-MeTHF), derived from the catalytic hydrogenation of furfural from agricultural residues, is a near drop-in replacement for petroleum tetrahydrofuran (THF), with 40% lower cumulative energy demand and 35% lower global warming potential.

2.6 Polylactic Acid

Polylactic acid (PLA) was first synthesised in 1932 and is a biodegradable, bio-based aliphatic polyester derived from lactic acid monomers produced by fermenting plant sugars [33, 6]. PLA has three stereoisomeric forms: poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA), and poly-D, L-lactic acid (PDLLA). PLLA and PDLA are semi-crystalline, with a melting temperature of about 175°C and a glass transition temperature of 55-60°C, while higher D-isomer content in PDLLA produces an amorphous material [34, 35]. PLA exists as four crystalline polymorphs (alpha, alpha-prime, beta, gamma), with the alpha-phase being the most thermodynamically stable and predominant, obtained from melt or solution. It has a high modulus of 3 GPa and tensile strength of 50-70 MPa, but it is brittle, which is usually overcome by blending with flexible polymers [36, 7].

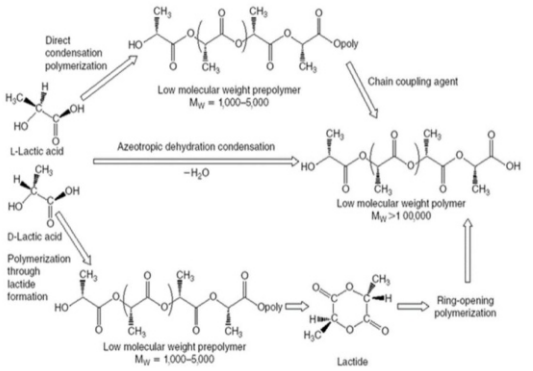


Figure 1: Conventional Synthetic routes of PLA synthesis, adapted from [7].

2.6.1 Green Synthesis of PLA Using Plant-Derived Catalysts

Conventional PLA ring-opening polymerisation uses Tin (II) bis(2-ethylhexanoate), leaving metal residues that require extensive purification. Cinchona alkaloids simultaneously activate the lactide monomer and the chain-end hydroxyl, providing stereochemical control that tin catalysts cannot match: quinine-mediated ROP yields PLA with isotacticity above 80% and a melting temperature of 178°C (vs 165°C for tin-catalysed material) without metal contamination [12]. Caffeine acts as a catalyst for ROP by activating N–H hydrogen bonds, giving polymers with molecular weights of 5,000 to 50,000 g/mol and dispersity lower than 1.3, and it can be recycled for five cycles [19].

2.7 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters synthesised by over 300 bacterial species as intracellular carbon storage granules [8]. They are classified by carbon chain length into short-chain-length (3-5 carbons, highly crystalline), medium-chain-length, and long-chain-length (15 or more carbons) forms. PHAs exhibit crystallinity ranging from 0 to 70%, UV stability, and mechanical properties comparable to polypropylene and polyethylene but more brittle, with Young moduli of 0.008 to 3.5 GPa and tensile strengths of 6.6 to 50 MPa [37]. Biodegradability and barrier properties make them suitable for food packaging, while biocompatibility makes them suitable for medical device and implant applications.

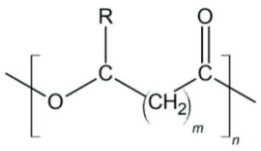


Figure 2: Structure of PHA

2.7.1 Plant-Derived Modification Strategies for PHAs

While PHA biosynthesis is inherently biological, the resulting poly(3-hydroxybutyrate) (PHB) is too brittle for many applications, with elongation at break below 5%.

Reactive blending of PHB with linseed and soybean oils in a twin-screw extruder increases elongation at break to over 150% through plasticisation and in situ epoxidation, building a network with covalent integration without any non-biodegradable component [38]. A more focused approach involves epoxidising pendant double bonds on medium-chain-length PHA with peracids derived from plant fatty acids, and then ring-opening with amino acid derivatives to introduce hydroxyl and amine functionality. These groups allow conjugation of plant polyphenols like quercetin and catechin, which have antimicrobial activity against Gram-positive and Gram-negative bacteria, for use in active packaging. Life cycle analysis revealed a 25% improvement in global warming potential compared with routes using synthetic reagents, confirming the environmental benefit alongside the functional gain [38].

2.8 Poly(butylene succinate) (PBS)

Poly(butylene succinate) is an aliphatic polyester with mechanical properties comparable to low-density polyethylene. It is flexible and can be processed well using conventional extrusion and injection molding equipment. This makes it attractive for film, mulch and rigid packaging applications [9].

2.8.1 Plant-Derived Modification Strategies for PBS

Polybutylene succinate (PBS) is usually prepared by polycondensation of succinic acid with 1,4-butanediol at 180–220 °C under reduced pressure catalysed by titanium tetrabutoxide or stannous octoate [14]. Historically both monomers have been petrochemical-derived. Hence conventional PBS, although biodegradable, has often not been bio-based in origin. Titanium and tin catalysts can leave residues that complicate food-contact use. Succinic acid produced by microbial fermentation of lignocellulosic sugars, and 1,4-butanediol increasingly available through fermentation routes, together enable PBS synthesis from entirely renewable starting materials [39]. Succinic acid itself, at sufficient purity, can catalyse its own polycondensation, removing the need for a separately added catalyst [40]. Enzymatic polycondensation with immobilised Candida antarctica lipase B has also been shown to provide good control over end-groups with no residual metals [39].

2.9 Polycaprolactone (PCL)

Polycaprolactone is a semi-crystalline aliphatic polyester widely used in drug delivery, resorbable sutures, and tissue engineering scaffolds, owing to its slow degradation rate, which extends from months to years [10]. Its low melting point of 59 to 64°C makes it attractive for 3D printing and as a compatibiliser in polymer blends.

2.9.1 PCL Modification By Plant-Derived Catalysts and Solvents

PCL is conventionally produced by ring-opening polymerisation of ε-caprolactone using Sn(Oct)2 or aluminum triisopropoxide as a catalyst, typically in toluene or dichloromethane at 110 to 150°C [13]. Residual tin or aluminum poses a regulatory obstacle for biomedical applications, and the solvents used are also hazardous, with dichloromethane restricted under REACH (Registration, Evaluation, Authorization and Restriction of Chemicals).

Lipase-catalysed ring-opening polymerisation is the most developed green alternative. Candida antarctica lipase B catalyses the same reaction at 60 to 70°C, eliminating toluene or dichloromethane when conducted in bulk or in 2-MeTHF, producing PCL with a molecular weight of around 45,000 g/mol and a dispersity of 1.15 [41]. Caffeine also catalyses ε-caprolactone polymerisation via N-H hydrogen-bond activation, achieving molecular weights of 5,000 to 50,000 g/mol with dispersity below 1.3 and recyclability across five cycles [19].

2.10 Poly(butylene adipate-co-terephthalate) (PBAT)

Polybutylene adipate-co-terephthalate is a biodegradable synthetic copolyester made by copolymerising adipic acid, terephthalic acid and 1,4-butanediol. It offers a good combination of the flexibility of aliphatic polyesters with the strength of aromatic polyesters, along with excellent toughness and elongation at break, unlike the often brittle PLA [42]. Conventional extrusion, injection molding, and film blowing can process PBAT, and it degrades by hydrolytic and microbial action under industrial composting conditions [42,43].

2.10.1 PCL Modification by Plant-Derived Catalysts and Solvents

PBAT is commonly blended with PLA for strength and flexibility, and with starch, cellulose fibres, and other natural fillers to reduce cost and increase renewable content. Researchers have incorporated natural fibres from agricultural residues, including rice husk, banana, coconut, and kenaf fibers, into PBAT matrices to improve tensile strength. Vegetable oil derivatives, including epoxidised soybean oil and castor oil-based plasticisers, serve as environmentally friendly modifiers that improve flexibility and thermal stability. Organic acids such as citric acid have been investigated as natural crosslinking agents, while bioethanol and limonene have emerged as green solvents for PBAT processing, reducing dependence on hazardous chemicals.

2.11 Recent Advances in Green Synthesis Methods

Across the nine polymer classes discussed in this paper, several advances in green synthesis have emerged that cut across polymer boundaries, rather than being specific to a single material. In enzymatic polymerisation, the immobilisation of Candida antarctica lipase B on lignin-based supports has greatly improved catalyst lifetime and cost, enabling PCL synthesis with a molecular weight of 45,000 g/mol and dispersity of 1.15 with over 85% activity retention after 15 reaction cycles, a performance that also applies to PBS polycondensation with precise end-group control [17]. For the polysaccharide classes: cellulose, chitin, chitosan, sodium alginate and natural deep eutectic solvents from plant-derived metabolites have enabled homogeneous dissolution and modification below 100°C, replacing hazardous

conventional solvents across all four materials.

The most important advances for PBS and PBAT have been the creation of complete bio-based monomer supply chains for lignocellulosic fermentation, meaning the green credentials can start at the monomer level, not only at the catalyst or processing stage [40]. At the systems level, the integrated biorefinery model, where bio-based solvents and catalysts such as 2-MeTHF, citric acid and choline chloride appear as co-products from existing biomass streams instead of isolated competing products, is still the most strategically important development to make green polymer chemistry economically feasible across all these polymer classes [44]. Machine learning-guided NADES formulation optimisation has also accelerated the discovery of best-suited solvent compositions for specific biopolymers. Microalgae are also emerging as a third-generation feedstock producing polymer building blocks at high biomass rates without competing with food crops.

2.12 Challenges in Plant-Derived Catalyst and Solvent Systems

Despite the advances documented above, several specific challenges remain for the widespread use of plant-derived catalysts and solvents across all nine polymer classes, beyond the general commercial challenges faced by biodegradable polymers. Firstly, catalyst reproducibility: plant-derived enzyme preparations vary 15–20% from batch to batch in activity, which leads to unacceptable variability in polymer molecular weight for precision applications such as medical devices and pharmaceutical packaging, and standardised quality assurance protocols for enzymatic polymer catalysts are not yet in place at an industry-wide level [45].

Secondly, NADES viscosity: binary solvent systems at working concentrations exhibit viscosities of hundreds to thousands of mPa, one to three orders higher than conventional solvents, making standard stirred-tank reactors insufficient for mixing and heat transfer, while anti-solvent precipitation for product isolation provides only 85 to 92% solvent recovery, a constraint that applies equally across cellulose, chitin, chitosan, and sodium alginate processing.

Thirdly, economic competitiveness: plant-derived solvents like 2-MeTHF carry price premiums of two to four times over petrochemical equivalents, bio-based succinic acid for PBS production remains more expensive than petrochemical succinic acid at current fermentation scales, and the immobilised lipase used in PCL and PBS enzymatic synthesis has not yet been shown to compete with cheap tin or aluminum catalysts on a per-kilogram-product basis at commodity scale.

Another challenge is reaction rate: enzymatic ring-opening polymerisation requires 12-48 hours for high conversion as opposed to 1-3 hours for metal-catalysed equivalents, a throughput disadvantage that affects PLA, PCL and PBS equally and is a major capital cost penalty at scale [17].

Additionally, feedstock variability for sodium alginate: the molecular weight and monomer composition of alginate differs significantly between seaweed species, harvest seasons, and geographic locations, indicating that green extraction processes optimised for one feedstock need to be reoptimised for another, adding complexity not present in the more uniform plant-based feedstocks used for other polymers [24,26].

Lastly, end-of-life constraints: green synthesis routes reduce environmental burden at the production stage but do not change end-of-life behaviour. PLA, PHAs, PBS, PCL, and sodium alginate-based materials all require industrial composting conditions for timely mineralisation and are essentially persistent in ambient soil or marine environments, meaning the environmental case for these materials depends equally on waste-infrastructure investment and green synthesis chemistry [46].

3. METHODOLOGY

This paper uses a critical systematic literature review. Instead of doing new experimental work, the aim was to find, evaluate and synthesise published evidence on the green synthesis and modification of biodegradable polymers by using plant-derived catalysts and solvents, for nine polymer types: starch, chitin/chitosan, sodium alginate, cellulose, PLA, PHAs, PBS, PLC, and PBAT.

We conducted the primary search across Web of Science, Scopus, ACS Publications, and Google Scholar. Search terms combined biodegradable polymer, green synthesis, bio-based solvent, plant-derived catalyst, enzymatic polymerisation, deep eutectic solvent, organocatalysis, ring-opening polymerisation, and the name of each polymer class with E-factor, atom economy, and life cycle assessment.

Studies were included if they reported experimental data on synthesis or modification of at least one target polymer using a catalyst or solvent of demonstrable plant-derived or enzymatic origin, with characterisation data sufficient to evaluate molecular weight, thermal properties, or mechanical performance. We excluded studies focused exclusively on biodegradation behavior without synthesis or modification data. The collected data were analysed using comparative performance analysis against established benchmarks, green metrics analysis (E-factor, atom economy, PMI), and thematic synthesis to identify common challenges and emerging trends.

4. DISCUSSION

4.1 Catalytic Performance across the Polymer Classes

The evidence reviewed indicates that plant-derived catalytic systems have moved well beyond proof of concept, delivering real performance benefits rather than simply giving equivalent outputs with a greener label. Cinchona alkaloids and caffeine provide stereochemical and molecular-weight control for PLA and PCL that traditional tin catalysts cannot achieve, and they eliminate metal residues that can cause regulatory problems for food-contact and biomedical applications [12]. For PHAs, reactive blending with plant oils increases the PHB elongation at break from less than 5% to over 150% through covalent network formation [38].

For PBS, succinic acid self-catalysis and enzymatic polycondensation remove the need for titanium or tin entirely when the monomers themselves are sourced from fermentation. For PBAT, plant-derived fibres and vegetable-oil-based plasticisers improve mechanical properties while increasing renewable content. For polysaccharides such as starch, chitosan, sodium alginate, and cellulose, citric and tartaric acid replace formaldehyde and glutaraldehyde crosslinkers without compromising biodegradability under mild aqueous processing conditions. Ultrasound-assisted extraction reduces the chemical burden of isolating these polysaccharides from their raw biomass in the first place [18,19].

4.2 Solvents: Readiness and Limitations

2-Methyltetrahydrofuran is the most industrially ready bio-based solvent, offering a near-drop-in replacement for THF with proven life cycle benefits of 35 to 40% [47]. A more transformative but earlier-stage development is natural deep eutectic solvents, which can dissolve cellulose and chitin at mild temperatures but are highly viscous and thus cannot be mixed and heated in a standard stirred-tank reactor, and product isolation by anti-solvent precipitation achieves only 85 to 92% solvent recovery. These are engineering problems with reasonable solutions that have not yet been demonstrated at pilot scale.

4.3 Environmental Metrics and Their Limits

The trend in E-factor from conventional metal-catalysed routes (15 to 30) to organocatalysed routes in bio-based solvents (5 to 12) and enzymatic bulk polymerisation (below 3) indicates up to a 10-fold reduction in waste per kilogram of product. Life cycle assessments report reductions in global warming potential of 25 to 70% [16]. These are real gains, but they have to be balanced against land use, freshwater consumption, and potential eutrophication from bio-based feedstock agriculture, particularly if first-generation food crops are used. The integrated biorefinery model addresses this by using catalysts and solvents from agricultural and forestry residues rather than primary crops. Demonstration-scale facilities are already in operation in Europe and North America [40,44].

4.4 Challenges That Require Honest Acknowledgment

Catalyst reproducibility remains a problem: immobilised enzyme preparations vary 15 to 20% batch to batch, which corresponds to polymer property variability that precision applications cannot tolerate, and standardised quality assurance protocols for enzymatic polymer catalysts have yet to be realised at scale [45]. Another important challenge is end-of-life behaviour: PLA, PHAs, PBS, PCL, and PBAT fully degrade under industrial composting conditions but remain essentially persistent in ambient soil and cold marine environments. Therefore, the environmental benefit of these materials depends on the availability of composting infrastructure, which is not yet available at sufficient scale in most markets.

A green synthesis route that reduces the carbon footprint during production is valuable, but a complete sustainability case requires green production and green end-of-life management [46, 48].

5. CONCLUSION

In this paper, we reviewed the green synthesis and modification of biodegradable polymers using plant-derived catalysts and solvents for nine polymer classes: starch, chitin and chitosan, sodium alginate, cellulose, PLA, PHAs, PBS, PCL, and PBAT. The evidence collected supports encouraging conclusions about the field's direction, while remaining honest about the distance still to be covered. Plant-derived catalytic systems now deliver genuine performance advantages in the applications where they are best suited. Cinchona alkaloid organocatalysts provide isotactic PLA with higher crystallinity and barrier properties than tin-catalysed equivalents. Immobilised lipases yield polyesters, including PCL and PBS, with narrower molecular weight distributions at E-factors below 3. Citric acid and other plant-derived organic acids efficiently modify polysaccharides under mild conditions, without compromising their biodegradability. Reactive blending of PHAs and PBAT with plant oils and natural fibres resolves brittleness and increases renewable content. In both cases, the green route is not a compromise; for the right application, it is the best route. Bio-based solvents have a wide range of industrial readiness. 2-MeTHF is effectively ready for adoption in existing infrastructure with confirmed life cycle benefits. NADES systems have created truly novel processing possibilities for cellulose and chitin, but dedicated process engineering development is needed before industrial implementation becomes realistic. The environmental case is quantitatively robust, but the benefits are most credible when bio-based feedstocks are derived from agricultural residues in an integrated biorefinery context, not primary food crops.

The main barriers to wider industrial uptake are now economic and infrastructural, not scientific ones. The chemistry works. What remains is scaling up enzymatic reactor configurations, standardising bio-based catalyst quality specifications, maturing bio-based solvent supply chains and building the composting infrastructure on which the end-of-life benefits of biodegradable polymers depend. The convergence of environmental urgency, increasing regulatory pressure, and a much stronger scientific basis than existed a decade ago makes this transition more favourable than at any previous point in the history of polymer science.

Declarations

Conflict of interest

The author declares no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Funding

No funding was received from any funding agency.

Data availability
No new data were generated or analysed to support this review.

Originality
This manuscript is original, has not been published previously, and is not under consideration elsewhere.

References

1. Garcia-Vaquero, M., Rajauria, G., O'Doherty, J.V., & Sweeney T. (2017). Polysaccharides from macroalgae: Recent advances, innovative technologies and challenges in extraction and purification. *Food Research International*, 99, 1011–1020.
2. Thompson, R. C., Swan, S. H., Moore, C. J., & Vom Saal, F. S. (2009). Our plastic age. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526), 1973–1976.
3. Otey, F. H., Westhoff, R. P., & Russell, C. R. (1975). Starch-based plastics and films, In Proceedings of the Technical Symposium. *Nonwoven Product Technology, INDA*.
4. Hosokawa, J., Nishiyama, M., Yoshihara, K., & Kubo, T. (1990). Biodegradable film derived from chitosan and homogenized cellulose. *Industrial & Engineering Chemistry Research*, 29(5), 800-805.
5. Muzzarelli, R. A. A. (1991). Modified chitosans and their chemical behavior. *ChemInform*, 22(11).
6. Ilyas, R.A., Sapuan, S.M., Harussani, M.M., Hakimi, M.Y.A.Y., Haziq, M.Z.M., Atikah, M.S.N., Asyraf, M.R.M., Ishak, M.R., Razman, M.R., Nurazzi, N.M., & Norrrahim, M.N.F (2021). Polylactic acid (PLA) biocomposite: Processing, additive manufacturing and advanced applications. *Polymers*, 13(8), 1326.
7. Li, X., Lin, Y., Liu, M., Meng, L., & Li, C. (2023). A review of research and application of polylactic acid composites. *Journal of Applied Polymer Science*, 140(7), e53477.
8. Sharma, V., Sehgal, R., & Gupta, R. (2021). Polyhydroxyalkanoate (PHA): properties and modifications. *Polymer*, 212, 123161.
9. Rafiqah, S.A., Khalina, A., Harmaen, A.S., Tawakkal, I.A., Zaman, K., Asim, M., Nurrazi, M.N., & Lee, C.H. (2021). A review on properties and application of bio-based poly (butylene succinate). *Polymers*, 13(9), 1436.
10. Woodruff, M. A., & Hutmacher, D. W. (2010). The return of a forgotten polymer—Polycaprolactone in the 21st century. *Progress in Polymer Science*, 35(10), 1217–1256.
11. Size, P. M. (2024). Share & Trends Analysis Report By Raw Material (Toluene Di-isocyanate, Methylene Diphenyl Di-isocyanate, Polyols). By Product, By Application, By Region, And Segment Forecasts, 2030.
12. Tempelaar, S., Mespouille, L., Coulembier, O., Dubois, P., & Dove, A. P. (2013). Synthesis and post-polymerisation modifications of aliphatic poly (carbonate) s prepared by ring-opening polymerisation. *Chemical Society Reviews*, 42(3), 1312–1336.
13. Labet, M., & Thielemans, W. (2009). Synthesis of polycaprolactone: a review. *Chemical Society Reviews*, 38(12), 3484–3504.
14. Platnieks, O., Gaidukovs, S., Barkane, A., Sereda, A., Gaidukova, G., Grase, L., Thakur, V.K., Filipova, I., Fridrihsone, V., Skute, M., & Laka, M. (2020). Bio-based poly (butylene succinate)/ microcrystalline cellulose/nanofibrillated cellulose-based sustainable polymer composites: Thermo-mechanical and biodegradation studies. *Polymers*, 12(7), 1472.
15. Anastas, P., & Warner, J. (1998). Green chemistry: theory and practice. Oxford University Press.
16. Sheldon, R. A. (2018). Metrics of green chemistry and sustainability: past, present, and future. *ACS Sustainable Chemistry & Engineering*, 6(1), 32-48.
17. Pellis, A., Cantone, S., Ebert, C., & Gardossi, L. (2018). Evolving biocatalysis to meet bioeconomy challenges and opportunities. *New Biotechnology*, 40, 154-169.
18. Reddy, N., Reddy, R., & Jiang, Q. (2015). Crosslinking biopolymers for biomedical applications. *Trends in Biotechnology*, 33(6), 362-369.
19. Zhang, X., Fevre, M., Jones, G. O., & Waymouth, R. M. (2018). Catalysis as an enabling science for sustainable polymers. *Chemical Reviews*, 118(2), 839-885.
20. Gunatillake, P. A., Adhikari, R., & Gadegaard, N. J. (2003). Biodegradable synthetic polymers for tissue engineering. *European Cells & Materials*, 5(1), 1-16.
21. Khan, W., Hosseinkhani, H., Ickowicz, D., Hong, P. D., Yu, D. S., & Domb, A. J. (2012). Polysaccharide gene transfection agents. *Acta Biomaterialia*, 8(12), 4224-4232.
22. Griffin, G. J. L. (1973). Biodegradable fillers in thermoplastics. *American Chemical Society Division of Organic Coatings and Plastics Chemistry*, 33(2), 88-96.
23. Xu, C., Nasrollahzadeh, M., Selva, M., Issaabadi, Z., & Luque, R. (2019). Waste-to-wealth: biowaste valorization into valuable bio (nano) materials. *Chemical Society Reviews*, 48(18), 4791-4822.
24. Fertah, M., Belfkira, A., Taourirte, M., & Brouillette, F. (2017). Extraction and characterization of sodium alginate from Moroccan *Laminaria digitata* brown seaweed. *Arabian Journal of Chemistry*, 10, S3707-S3714.
25. Saji, S., Hebden, A., Goswami, P., & Du, C. (2022). A brief review on the development of alginate extraction process and its sustainability. *Sustainability*, 14(9), 5181.
26. Flórez-Fernández, N., Dominguez, H., & Torres, M. D. (2019). A green approach for alginate extraction from *Sargassum muticum* brown seaweed using ultrasound-assisted technique. *International Journal of Biological Macromolecules*, 124, 451-459.
27. Singh, P., Baisthakur, P., & Yemul, O. S. (2020). Synthesis, characterization and application of crosslinked alginate as green packaging material. *Heliyon*, 6(1), e03026.
28. Dekamin, M. G., Peyman, S. Z., Karimi, Z., Javanshir, S., Naimi-Jamal, M. R., & Barikani, M. (2016). Sodium alginate: An efficient biopolymeric catalyst for green synthesis of 2-amino-4H-pyran derivatives. *International Journal of Biological Macromolecules*, 87, 172-179.
29. Felgueiras, C., Azoia, N. G., Gonçalves, C., Gama, M., & Dourado, F. (2021). Trends on the cellulose-based textiles: raw materials and technologies. *Frontiers in Bioengineering and Biotechnology*, 9, 608826.
30. Etale, A., Onyianta, A. J., Turner, S. R., & Eichhorn, S. J. (2023). Cellulose: a review of water interactions, applications in composites, and water treatment. *Chemical Reviews*, 123(5), 2016–2048.
31. Foster, E.J., Moon, R.J., Agarwal, U.P., Bortner, M.J., Bras, J., Camarero-Espinosa, S., Chan, K.J., Clift, M.J., Cranston, E.D., Eichhorn, S.J., & Fox, D.M. (2018). Current characterization methods for cellulose nanomaterials. *Chemical Society Reviews*, 47(8), 2609-2679.

32. Nargotra, P., Sharma, V., Tsai, M. L., Hsieh, S. L., Dong, C. D., Wang, H. M. D., & Kuo, C. H. (2023). Recent advancements in the valorization of agro-industrial food waste for the production of nanocellulose. *Applied Sciences*, 13(10), 6159.
33. Hamad, K., Kaseem, M., Yang, H. W., Deri, F., & Ko, Y. G. (2015). Properties and medical applications of polylactic acid: A review. *Express Polymer Letters*, 9(5), 435.
34. Zhao, X., Liu, J., Li, j., Liang, X., Zhou, W., & Peng, S. (2022). Strategies and techniques for improving heat resistance and mechanical performances of poly (lactic acid)(PLA) biodegradable materials. *International Journal of Biological Macromolecules*, 218, 115-134.
35. Raquez, J. M., Habibi, Y., Murariu, M., & Dubois, P. (2013). Polylactide (PLA)-based nanocomposites. *Progress in Polymer Science*, 38(10-11), 1504-1542.
36. Barkhad, M. S., Abu-Jdayil, B., Mourad, A. H. I., & Iqbal, M. Z. (2020). Thermal insulation and mechanical properties of polylactic acid (PLA) at different processing conditions. *Polymers*, 12(9), 2091.
37. Nigmatullin, R., Thomas, P., Lukasiewicz, B., Puthussery, H., & Roy, I. (2015). Polyhydroxyalkanoates, a family of natural polymers, and their applications in drug delivery. *Journal of Chemical Technology & Biotechnology*, 90(7), 1209-1221.
38. Tan, D., Wang, Y., Tong, Y., & Chen, G. Q. (2021). Grand challenges for industrializing polyhydroxyalkanoates (PHAs). *Trends in Biotechnology*, 39(9), 953-963.
39. Jiang, Y., Woortman, A. J., Alberda van Ekenstein, G. O., & Loos, K. (2013). Enzyme-catalyzed synthesis of unsaturated aliphatic polyesters based on green monomers from renewable resources. *Biomolecules*, 3(3), 461-480.
40. Bechthold, I., Bretz, K., Kabasci, S., Kopitzky, R., & Springer, A. (2008). Succinic acid: a new platform chemical for biobased polymers from renewable resources. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 31(5), 647-654.
41. Kobayashi, S. (2010). Lipase-catalyzed polyester synthesis–a green polymer chemistry. *Proceedings of the Japan Academy, Series B*, 86(4), 338-365.
42. Kijchavengkul, T., & Auras, R. (2008). Compostability of polymers. *Polymer International*, 57(6), 793-804.
43. Niaounakis, M. (2015). Biopolymers: applications and trends. William Andrew.
44. Llevot, A., Grau, E., Carlotti, S., Grelier, S., & Cramail, H. (2016). From lignin-derived aromatic compounds to novel biobased polymers. *Macromolecular Rapid Communications*, 37(1), 9-28.
45. Pellis, A., Acero, E. H., Ferrario, V., Ribitsch, D., Guebitz, G. M., & Gardossi, L. (2016). The closure of the cycle: enzymatic synthesis and functionalization of bio-based polyesters. *Trends in Biotechnology*, 34(4), 316-328.
46. Schick, S., Heindel, J., Groten, R., & Seide, G. H. (2024). Overcoming challenges in the commercialization of biopolymers: from research to applications—a review. *Polymers*, 16(24), 3498.
47. Slater, C. S., Savelski, M. J., Hitchcock, D., & Cavanagh, E. J. (2016). Environmental analysis of the life cycle emissions of 2-methyl tetrahydrofuran solvent manufactured from renewable resources. *Journal of Environmental Science and Health, Part A*, 51(6), 487-494.
48. Rujnić-Sokele, M., & Pilipović, A. (2017). Challenges and opportunities of biodegradable plastics: A mini review. *Waste Management & Research*, 35(2), 132-140.