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Overview of biodegradable polymers: synthesis, modification and application

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<p>Received: January 8, 2024 Peer-reviewed: February 1, 2024 Accepted: February 13, 2024</p>	<p>ABSTRACT Biodegradable polymeric represents a growing field. Owing to their wide-ranging properties, both synthetic and natural polymeric materials perform a vital and ubiquitous role in everyday life. Amended natural polymeric materials such as starch, cellulose, lignin, chitosan, cottonseed shell (CTS), and cotton gin trash (CGT) have enhanced properties, while synthetic Biodegradable polymeric materials such as poly (vinyl alcohol) (PVA), biodegradable plastics, biodegradable foams. Bioplastics are a kind of polymers able to be degraded by different microorganisms to small molecules (e.g., H₂O, CO₂, and CH₄). Bioplastics are observed to solve waste materials and biodegradability is just a new material to be exploited at the end of its life in specific terms. They should be used for applications that require cheap methods to dispose of items after it has fulfilled their job (e.g., for food packaging, agriculture, or medical products).</p>
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Introduction

Biodegradable polymers were raised as promising eco-friendly, but they are susceptible to enzymatic cleavage. Many BPs developed until now, and microorganisms capable of degrading them have been found in nature [1]. Plastic objects become part of the present society because they possess many properties [6]: light-weight, flexible and elastic, easy to shape and colour, and electric insulation. These properties are rewardingly

exploited for various applications. Some include containers with hard form as well as flexible films for application packaging, sell sheets, fibres for textiles, ropes, and mattresses or most kinds of coverings surface, and assembling agents such as coatings; elastomers; sealants and adhesives. These different applications demand different combinations of properties. Particularly required applications can be reached by reinforcing polymers with glass or carbon fibres, for forming composites [2]. Biodegradable plastic degradation is caused by

bacteria as well as fungal enzymes. The biodegradability of plastic bags depends on different factors including sand, water, humidity, and temperature. Also, plastics can be degraded by organisms to CO₂, methane, water, and edible compost. Many commercial plastics are converted into compost rather than gaseous products. For plastic to be compostable, the organic matter formed should be harmless to animals or plants.

The compost can form an industrial compost at room temperature with waste food, in industrial facilities at controlled temperatures (typically 58 °C)[3]. So, classification of biodegradable polymers: Natural and biodegradable polymers

– *e.g.*, poly(saccharides), like starch, lignin, cellulose, chitosan, guar gum, collagen, albumin, etc.

Synthetic biodegradable polymers

– *e.g.*, aliphatic polyesters like polyvinyl alcohol (PVA), poly(orthoesters), poly(anhydrides), poly(phosphazenes), poly (amino acids), trimers, BDMPs, etc.

Natural Biodegradable polymeric materials (BPMs)

Starch(S)

Starch is a natural polysaccharide, and is a homopolymer of Glucopyranose units with the molecular weight $(C_6H_{10}O_5)_n$. Amylose and amylopectin are two different forms of polymer chains that make up starch. While amylopectin is a branching polymer consisting of -1,4-glycosidic with branched-chain linked by-1,6-glycosidic bonds, amylose is a straight chain -1,4-glyco-sidic links. Each of these polymers receives unique features as a result of this conformational change. For instance, the crystalline area of the granules is caused by the short branching of amylopectin at the-1,6-glycosidic linkages [4].

For example, authors studied PVA with corn starch (CS) at a 70/30 weight per cent proportion, arranged utilizing an answer projecting technique, and integrated attapulgit at different sums (0.0-1.0 grams). The review is expected to evaluate the effect of attapulgit on the biodegradability and ductile properties of the PVA/CS lattice, contrasting all outcomes and the control test (PVA/CS). The presence of attapulgit blocked the debasement cycle in enzymatic, soil, and manure entombment conditions. Water sorption content expanded with longer inundation times. The PVA/CS with 0.2 grams of attapulgit content showed the most noteworthy rigidity and stretching at break among the tried examples [5].

Another study, revised the effect of PVA and nano-SiO₂ on the enzymatic hydrolysis of thermoplastic starch (TPS) mixes utilizing α -amylase and amyloglucosidase catalysts [6]. Mixes with 5 wt.% nano-SiO₂ displayed a critical decrease in the rate and degree of starch hydrolysis, proposing communications among starch and nano-SiO₂ that obstructed enzymatic assault — the absolute solids staying following 6000 minutes diminished with expanding nano-SiO₂ content. The pace of glucose creation diminished with nano-SiO₂ expansion: 226 μ g/ml h (TPS: PVA), 166 μ g/ml h (TPS: PVA:1% nano-SiO₂), 122 μ g/ml h (TPS: PVA:3% nano-SiO₂), and 94 μ g/ml h (TPS: PVA:5% nano-SiO₂). The review laid out that nanoparticles block debasement, and the weakness to enzymatic corruption follows the request: TPS: PVA > TPS: PVA: nano-SiO₂.

, Domene-López *et al.* [7] made biodegradable coatings by dissolved blending potato starch and PVA with various centralizations of rosin. Glycerol was utilized as a plasticizer. Rosin, an inexhaustible item, went about as a handling help and support specialist because of its moderately high sub-atomic weight. The expansion of 8% rosin to starch/PVA mixes brought about films with rigidity surpassing 10 MPa and stretching at a break near 2000%. These qualities are practically identical Iskalieva *et al.* [8] united mix copolymers (PVA/S) with polyethylene glycol methyl methacrylate (PEGMA) in different proportions to concentrate on the effect on biodegradability. The mix copolymer was made out of poly (vinyl alcohol) (PVA) and starch (S). FTIR spectroscopy uncovered hydrogen bond connections between PVA, S and PEGMA. The chemical structure of the (PVA/S)-g-PEGMA obtained. TGA and SEM investigations portrayed the subsequent polymers (PVA/S/PEGMA). Mechanical properties of the mix films were fundamentally affected by PEGMA, with film corruption time expanding with higher PVA and S contents and atomic weight (MW) of PEGMA. The M8 test (PVA/S/PEGMA in a 3:1:2 proportion, separately) with an MW of 950 g/mol displayed the most minimal extension at break (67.5%), while M1 (PVA/S/PEGMA in a 1:1:1 proportion, separately) with a MW of 300 g/mol had the most noteworthy (150%). Uniting PEGMA onto the mixing polymer further developed film rigidity and stretching at the break. The glass progress temperature (T_g) and softening temperature (T_m) expanded with higher PEGMA MW, recommending that expanded chain and atomic weight be added to raised T_g and T_m in the copolymers.

Cellulose

Cellulose is a renewable polymer found in trees, bacteria, algae, plants as well as tunicates. The structure of cellulose is a linear called homopolysaccharide with highly ordered β -1.4-linked anhydro-D-glucose units, which aggregate to form cellulose fibrils. Cellulose results from the extraction of the crystalline from the amorphous portion by acid hydrolysis [9].

For instance, Ong *et al.* [10] examined PVA composite coatings with the consolidation of microcrystalline cellulose (MCC), commercial-grade cellulose nanocrystals (NCCA), and nanocellulose (NCCB) from oil palm fiber. The nanofillers showed uniform scattering in the PVA lattice, with shifting molecule sizes. The expansion of 5 wt.% microcrystalline cellulose worked on extreme elasticity (UTS) and yield strength however decreased greatest lengthening. Integrating 5 wt.% nanocellulose from oil palm fibre expanded UTS, yield strength, and flexible modulus while keeping up with the greatest prolongation. Adding business-grade cellulose nanocrystals (up to 10 wt.%) improved UTS, yield strength, and most extreme extension while keeping up with flexible modulus. Soil internment tests uncovered sped-up corruption with dampness, and the coatings were completely disintegrated following 7 days. Under controlled conditions, the heaviness of coatings remained generally unaltered following 28 days. The created PVA composite coatings displayed better mechanical execution and biodegradability looked at than a financially accessible biodegradable plastic pack (Bio-PB), recommending their true capacity as harmless to the ecosystem options.

In another study, Haque *et al.* [11] presented a financially savvy strategy for creating bio-plastic from a mix of PVA and cotton gin junk (CGT) as a possible option in contrast to non-biodegradable plastics in bundling. The effect of plasticizers (diethylene glycol, glycerol, and urea) and the covering specialist ethyl cellulose (EC) was examined. Urea displayed the best execution as a plasticizer, giving adaptability, decreased crystallinity, and further developed dampness ingestion, transmission, and warm security. The composite coatings, with properties equivalent to business LDPE, showed higher elasticity and water opposition. The expansion of EC upgraded water opposition and UV obstruction, making the coatings cloudy. The assessed cost of power and synthetic substances per gram of film creation was viewed as financially reasonable. Generally speaking, this

study presents a functional strategy for delivering water-safe adaptable bioplastic with the possibility to address flow plastic contamination issues.

Lignin

Lignin is the second renewable biomass polymer and has potential as a sustainable material because of its abundance and high concentration of aromatic, complex lignin with poor chemical structure and excessive reaction sites limit its applications [12].

For instance, Su *et al.* [13] studied improving the presentation and decreasing the expense of PVA films for biodegradable mulch applications. The synergistic impact of sodium alginate and quaternary lignin was recognized as a key element. The composite coatings showed further developed water maintenance, UV obstruction, heat assortment, light transmission, mechanical properties, and soil combination. Lignin expansion guaranteed total UV obstruction, while sodium alginate synergistically improved mechanical strength and water-holding properties. The coatings exhibited better soil drooping, and their water fume porousness came to 109.2 g/m². day. The self-corruption properties of sodium alginate and lignin worked with film debasement, with a 55% debasement seen following 50 days. In general, the review features a promising methodology for creating practical and elite execution biodegradable coatings for mulch applications.

Synthetic biodegradable Polymeric materials Polyvinyl alcohol (PVA)

PVA is sold form dissolved in water and biodegradable polymer which is used in various biological applications. PVA has high aqueous phase solubility and biodegradable properties due to its polymeric nature. PVA and its derivatives have demanded great recent attention [14].

For example, Belay [15] tends to the natural worries related to customary plastics and features the rise of biodegradable plastics as another option. Specifically, it centres around agar and PVA as promising biodegradable materials that don't add to deforestation or affect food supplies. Nonetheless, these materials show impediments like high water ingestion and moderate rigidity. The survey examines physicochemical change strategies utilized by scientists to upgrade the properties of biodegradable polymers, with a particular accentuation on agar and PVA. Points covered incorporate the rudiments of polymers, the science

of biodegradation, the ecological effects of biodegradable polymers, and endeavors to work on their properties for different applications.

Authors revised [16] the impacts of glycerol and sorbitol as plasticizing specialists on the properties of biodegradable polyvinyl alcohol (PVOH)/rambutan skin squander flour (RWF) films. Glycerol-plasticized films showed higher extension at break, yet lower rigidity and Young's modulus contrasted with sorbitol-plasticized films. The expansion of plasticizing specialists expanded the water fume transmission rate (WVTR), with glycerol-plasticized films showing higher WVTR, demonstrating glycerol's more prominent water partiality than sorbitol. In biodegradability tests, unplasticized PVOH/RWF films displayed lower weight reduction contrasted with glycerol-and sorbitol-plasticized films.

In another study, Li *et al.* [17] explored the effect of phytic corrosive (PhyAc) on the intermolecular hydrogen-holding, structure, chain elements, and mechanical properties of PVA in a biodegradable PVA/PhyAc composite. Sub-atomic element recreations and trial strategies were consolidated for the investigation. The quantity of PVA-PhyAc hydrogen bonds per PhyAc atom and complete hydrogen bonds show various conditions on PhyAc content. The composite with 1.9 wt% PhyAc shows diminished free volume and a more modest dissemination coefficient. The glass progress temperature (T_g) of PVA arrives at its greatest at around 1.25 wt % PhyAc. Remarkably, the expansion of 10 wt % PhyAc brings about the most elevated elasticity and great antibacterial capacity in PVA. The review gives experiences into how little atoms impact the construction and mechanical properties of polymers, extending the likely utilization of PVA/PhyAc in different businesses.

Panda *et al.* [18] in their survey centres around the new improvements in PVA and normal polymer-based films for applications in food bundling. PVA-based materials are esteemed for their biocompatibility, biodegradability, antimicrobial properties, non-harmfulness, and simplicity of film arrangement. While past writing has focused on manufactured PVA or PVA-based nanomaterials, there is a developing interest in normal polymers because of their harmless to the ecosystem nature. The survey features the utilization of PVA/regular polymer-based films in food bundling and examines the joining of bio-waste and organic product strips in composite coatings. Furthermore, research patterns in PVA films are investigated, giving bits of

knowledge into the measurements of distributions in this field.

Authors researched and successfully created and analyzed environmentally friendly materials for the first time. These materials are made of a fully biodegradable substance called PVA and belong to a category known as single polymer composites (SPC) [19]. Through various tests, they demonstrated the feasibility of producing these composites within a suitable temperature range. Microscopic images showed that the desired reinforcement structure was maintained only when using high melting temperature fibres like WN8. The addition of PVOH fibres significantly enhanced the stiffness, yield properties, and Vicat softening temperature of the original PVA matrix, depending on the number of fibres added. However, as the fibre content increased, there was a decrease in the material's ability to stretch, and it became more prone to breakage. The introduction of fibres had a positive impact on the stability of the composites, leading to notable improvements in their viscoelastic properties. The storage modulus and glass transition temperature increased compared to the pure PVA, while the creep compliance values decreased significantly across all tested temperatures.

Rahman and Goswami *et al.* [20] studied the mechanical as well as barrier properties of PVA, which are useful for packaging purposes. The influence of bioactive elements added to the PVA matrix was also studied, particularly their ability to protect food from pathogens and prevent rapid expiration. Furthermore, an examination has been conducted on mitigation measures, specifically focusing on the biodegradability of industrial wastes generated by various manufacturing facilities.

Biodegradable foam (BF)

For instance, in Hendrawati *et al.* [21], the influence of PVA on the production of biodegradable foam from sago starch was determined. The production of biodegradable foam occurs at 125°C during the baking process, with a duration of one hour. The concentrations of PVOH varied from 0 to 50 wt. %. According to the results of the water absorption test, biodegradability test, and tensile test, an increase in PVOH concentration has a positive impact on water absorption, biodegradability, and tensile strength. The ideal state was achieved through the incorporation of 30% PVOH, resulting in water adsorption, biodegradability, and tensile strength values of 29.42%, 25.13%, and 2.22 MPa, respectively.

Authors studied that mixing of microfibrillated cellulose (MFC) suspension and polyvinyl alcohol results in the formation of MFC-based thin membrane-like biodegradable composites. The desired MFC content within the composites could be easily achieved by adjusting the concentration of the PVA solution [22]. To enhance the mechanical and thermal properties of the composites and render PVA partially water-insoluble, chemical crosslinking of PVA was conducted using glyoxal. Examination of the composite surfaces and fracture topographies revealed a strong bond between MFC fibrils and PVA, with uniform distribution. Infrared spectroscopy demonstrated the formation of acetal linkages in the MFC–PVA composites through glyoxal crosslinking.

Chemically altered waxy corn starch is a promising substance for creating biodegradable bioplastics. Yahia *et al.* [23] have studied the performance of films made from chemically modified waxy corn starch, along with their degradation by microbial enzymes. The effects of pre-gelatinization and the addition of cardanol oil as a mixed plasticizer with sorbitol were investigated. Biodegradable films were produced by blending waxy maize acetylated di-starch adipate (WADA) and waxy maize pregelatinized acetylated di-starch adipate (PWADA) with polyvinyl alcohol polymer using sorbitol and cardanol oil as plasticizers. The biodegradability of the films was studied through enzyme mixture testing and soil burial tests. The results showed that PWADA had a weight loss of 96% and a degradation percentage of 95.5%, which were significantly lower than WADA. The degradation was also evident from an increase in osmolality and the physical appearance of the film after 21 days. Various techniques were used to analyze the film's morphology, chemical structure, crystallinity, transparency, and thermal stability. Under an electron microscope, PWADA films had a more uniform surface. The film's infrared spectra indicated similar chemical structures. The X-ray diffraction analysis revealed that WADA had an A-type crystalline structure, while after thermoplasticization, PWADA showed a V-type crystal pattern. The addition of cardanol oil resulted in UV absorber films. Furthermore, thermal stability was improved with the addition of cardanol oil. The water uptake rate and water vapor permeability increased after the pre-gelatinization of WADA films but slightly decreased after the addition of cardanol oil. Additionally, pre-gelatinization decreased the film's elongation but increased its strength. Overall,

the chemically modified waxy maize starch film has the potential to be a biodegradable, thermally stable, and UV absorber film for packaging materials.

Liu *et al.* [24] explored how different amounts of polyvinyl alcohol (PVA) and its hydrolysis degree could improve the properties of the foams. By diving into the complex relationship between melt viscoelasticity and foam characteristics, we discovered some intriguing results. Increasing the hydrolysis degree of PVA had a significant impact on the foams, making them more suitable for various applications. The improvements observed in their foaming behaviors, viscoelastic properties, thermal stabilities, and mechanical performances were all linked to the interactions between starch and PVA chains, like hydrogen bonding and intermolecular entanglements. Additionally, incorporating PVA led to an impressive reduction in water absorption capacity. The foam that comprised 20% PVA with a hydrolysis degree of 98% demonstrated exceptional properties, including minimal water absorption, low density, excellent foaming ratio, and remarkable porosity. These qualities were on par with those of commercially available expanded polystyrene (EPS). Moreover, the addition of 20% PVA resulted in the highest compressive strength and recovery, hinting at its great potential for diverse cushioning applications. In conclusion, this research sheds light on the extensive possibilities for using starch-based foams in large-scale industrial settings, opening exciting avenues for their wider application.

There have been questions and misunderstandings surrounding the impact of liquid detergent capsules on the issue of environmental microplastics. To clarify, the film used in these detergent capsules is highly soluble in water, including cold water, as it needs to fully dissolve during the washing process. The film is typically made from water-soluble grades of polyvinyl alcohol, which is a recognized biodegradable material. Byrne *et al.* [25] conducted tests to confirm the biodegradability of various polyvinyl alcohol films commonly used in detergent capsules. The results showed that these films are readily biodegradable. Moreover, their high water solubility means that these detergent capsule films do not fall within the category of microplastics. Additionally, their biodegradability ensures that there are no concerns regarding persistence or accumulation in the environment.

In the world of packaging, there is a growing need for biodegradable composite plastics that can outperform synthetic polymer materials. Su *et al.*

[26] studied the use of a solvent-casting method to create different combinations of composite plastics using polyvinyl alcohol (PVA), esterified starch, and gliadin. Comparing these to pure PVA plastics, we found that the PVA/starch/gliadin composites exhibited lower hydrophilicity, superior tensile properties, and higher biodegradability. Although the elongation at break was lower, these composites showed promising characteristics. Through various analytical techniques, such as scanning electron microscopy, atomic force microscopy, X-ray diffraction, Fourier infrared spectra, and light transmittance measurements, we observed that the PVA/starch/gliadin plastics exhibited good compatibility due to hydrogen bonding. Interestingly, the different ratios of components in the plastics led to varying colours. Additionally, as the content of esterified starch increased, the melting and crystallization enthalpies of the composite plastics increased. Notably, at a ratio of 25% PVA and 75% starch/gliadin, the composite plastics had the lowest hydrophilicity, surpassing that of pure PVA plastics. When PVA comprised 50% and the ratio of starch to gliadin was 75%/25%, the ternary composite plastics demonstrated the highest tensile properties. Furthermore, when PVA accounted for 75% and starch accounted for 25%, the elastic modulus of the PVA/starch plastics reached its peak. Moreover, composite plastics showed higher biodegradability compared to pure PVA plastics. These environmentally friendly PVA/starch/gliadin plastics, with their versatile composition ratios, have great potential for various applications, including packaging water-sensitive goods and bearing heavy objects in real-world production scenarios.

To combat the pollution caused by mishandling petroleum-based plastics, there has been a significant interest in green composites that utilize biodegradable plastics and biomass waste. However, there is still a challenge in finding the right balance between mechanical performance and biodegradability. Tian *et al.* [27] proposed a novel concept for water-soluble composite materials using PVA and biomass waste. Unlike conventional degradation into small molecules, the PVA matrix in our composites can dissolve in water when in contact with soil. To enhance the mechanical and thermal properties, we utilized solid-state shearing milling (S3M) technology to composite PVA with waste cottonseed shell (CTS). This resulted in impressive performance, with the PVA/CTS composites achieving a maximum tensile strength of 10.3 MPa and a degradation temperature of

approximately 250 °C. Furthermore, our soil burial test demonstrated that even if the PVA matrix does not degrade in the environment in the short term, its water-soluble nature ensures environmental friendliness. Within just 10 days, the PVA matrix dissolves in the soil without causing any adverse effects on plants (specifically wheat) or animals (particularly earthworms). This research not only presents the development of a range of eco-friendly PVA/biomass composites but also contributes new insights into the environmental compatibility of PVA-based materials.

Starch-based biodegradable films (S-BFs)

S-BFs are not ideal for food packaging due to their weak mechanical strength and limited barrier properties. However, by combining two or more polymers, there is a possibility to create innovative materials with enhanced functionality. Gómez-Aldapa *et al.* [28] explored various proportions (ranging from 0% to 60%) of polyvinyl alcohol (PVOH) in potato starch films to examine the impact on water absorption, water vapour permeability (WVP), mechanical properties (elongation at break and tensile strength), and thermal properties (Tg). Throughout all the formulations, the two polymers demonstrated excellent compatibility during processing and in the resulting material. The inclusion of PVA significantly improved the functional properties, gas permeability, and mechanical strength of the potato starch films. Notably, the formulation containing 60% PVA (S4P6) showcased the greatest resistance to water vapour, lower density, enhanced solubility, and superior mechanical performance. PVA proved to be a valuable addition to potato starch films, rendering them suitable for potential use in food packaging and as an eco-friendly alternative to synthetic packaging materials.

In response to increased environmental awareness and regulations, the plastic industry has been making efforts to develop environmentally friendly products and processes. For example, authors [29] make an overview of the advancements made in thermoplastic starch, polyvinyl alcohol blends, and nanocomposites. These materials offer a wide range of physical properties and other benefits, all at an acceptable cost and rate of biodegradation, making them suitable for various applications. To further enhance their properties, such as mechanical strength and moisture resistance, innovative techniques like cross-linking and the incorporation of new nanoparticles have

been explored. These advancements have enabled the creation of materials with diverse property profiles that can even rival synthetic polymers in terms of both price and performance in different applications.

Authors [30] conducted a study to analyze how additives affect the properties of biodegradable films composed of PVA and tapioca starch. Three additives, specifically glycerol (GLY), polyethylene glycol (PEG), and glutaraldehyde (GLU), were utilized in the research. The PVA/tapioca starch blend films were produced through a mixing process followed by casting. Higher levels of GLY and PEG resulted in increased elongation at break for the blend film. However, the tensile strength decreased therefore. Additionally, the inclusion of a plasticizer improved the blend film's biodegradability, water absorption, and water vapour transmission. Interestingly, contrasting outcomes were observed when GLU was incorporated into the blend film.

Patil *et al.* [31] aimed to enhance the properties of starch-based biodegradable films through polymer blending. To achieve this, composite films were created by incorporating different proportions of PVA (ranging from 10% to 90% of starch weight) using the solvent casting method. Several aspects, including mechanical behaviour, barrier properties, water solubility, water contact angle, and biodegradability, were examined for all the films. The addition of PVA to the starch polymer had a significant positive impact ($p < 0.05$) on the mechanical and barrier properties of the composite films. Notably, the highest improvement in mechanical behaviour was observed in the SP90 composite film, which contained a higher percentage of PVA. This film demonstrated a remarkable 1.93-fold increase in tensile strength (TS), a 3.74-fold increase in elongation (E), and a 1.72-fold increase in breaking strength (BS) compared to the pure starch film. In terms of barrier properties, the maximum incorporation of PVA resulted in a 52% decrease in water vapour permeability (WVP) and a 57% decrease in oxygen permeability (OP) in the composite films, making them effective barriers against moisture and oxygen gas. The Fourier-transform infrared spectroscopy and scanning electron microscopy analysis of the films confirmed the excellent compatibility between starch and PVA polymers. Interestingly, these composite films degraded rapidly when subjected to moistened soil, with complete degradation occurring within three weeks of burial. The biodegradability study revealed the promising

potential of starch-PVA composite films as environmentally friendly materials for food packaging applications.

Alonso-López *et al.* [32] examined the potential impact of polyvinyl alcohol (PVA)-based polymers upon release into the marine environment, focusing on biodegradation in seawater (evaluated by the percentage of Theoretical Oxygen Demand, or % ThOD, for each compound) and aquatic toxicity using the standard toxicity test with *Paracentrotus lividus* larvae. Three materials were tested, including two PVA-based ones with glycerol and another made from pure PVA. The biodegradation of PVA under marine conditions without an acclimated inoculum appears negligible, but it shows a slight improvement when combined with glycerol, achieving 5.3% and 8.4% ThOD after 28 days. The toxicity of pure PVA is also minimal (<1 toxic unit, TU), but it increases slightly when glycerol is included in the material (2.2 and 2.3 TU). These findings contribute to a more comprehensive understanding of the behaviour of PVA-based polymers in marine environments. Despite the low biodegradation rates observed, further research is necessary to develop PVA polymers that are genuinely degradable in real marine scenarios.

Pérez-Blanco *et al.* [33] prepared blends using ethylene-vinyl alcohol samples containing 27% and 38% ethylene, incorporating 30% and 50% thermoplastic starch (TPS) plasticized with glycerol. The biodegradability and cytotoxicity of these blends were examined using various techniques (XRD, DSC, TGA, CA, ATR-FTIR, SEM). The presence of TPS had a notable impact on copolymer behaviour, evidenced by the emergence of O-H IR bands at $1000\text{--}1170\text{ cm}^{-1}$ and an overall reduction in ethylene-vinyl alcohol crystallinity, melting point, thermal stability, and hydrophobicity. Biodegradation was more effective in the presence of TPS, leading to the formation of a resilient biofilm by a consortium of three bacteria.

Lower ethylene content facilitated biodegradation, rendering the material more easily metabolizable. Mineralization percentages reached up to 66% (EVOH- 27/TPS 50:50) after a 40-day bioassay at $45\text{ }^{\circ}\text{C}$. In vitro, cytotoxicity assays showed no cytotoxicity both before and after biodegradation. EVOH/TPS blends are proposed as a potential environmentally friendly substitute for pure synthetic polymers.

Julinová *et al.* [34] investigated the biodegradation of blow-molded films composed of poly(vinyl alcohol) (PVA)/protein hydrolysate (PH),

incorporating starch (S) and lignin (LI) as biodegradation enhancers. The goal was to enhance the biodegradation rate of PVA while maintaining or improving the technical and usage properties of the blends. The objective was to achieve the maximum breakdown rate, facilitating rapid disintegration of PVA at a wastewater treatment plant. Activated sludge from a municipal wastewater treatment plant was chosen as the biological material. The preparation of blends involved the use of glycerol (G) as a plasticizer, enabling successful processing but extending the lag phase of PVA breakdown and reducing its final biodegradation percentage. The influence of G, in this regard, remained unaffected by the inclusion of PH. While S and LI mitigated the impact of the plasticizer, they caused a breakdown rate comparable to PVA alone. Conversely, adapting biomass to PVA, when G was applied, resulted in a threefold increase in the PVA breakdown rate, albeit with a fivefold prolonged lag phase. However, the extended breakdown duration, surpassing the retention time of wastewater during activation, negated the positive effect. The addition of PH to the blends did not show a favourable impact. The incorporation of S led to a shorter lag phase, and the degradation rate increased by approximately 1.5 times. The combination of LI and S significantly accelerated blend degradation, but the drawback was an incomplete breakdown of the substrate, lowering the final biodegradation percentage. As a compromise, a blend of PVA/G PH S was identified, with a breakdown time half that of pure PVA and mechanically more convenient films.

Haque *et al.* [35] created a biodegradable composite plastic film by combining cotton gin trash (CGT), a promising lignocellulose resource, with poly(vinyl alcohol) (PVA). The composite film maintained a 50:50 CGT/PVA ratio, utilizing both coarse and fine CGT powder particles. The study investigated the impact of particle size on various properties such as morphology, crystallinity, tensile strength, optical transmittance, thermal stability, and biodegradability. The scanning electron microscope (SEM) image revealed a uniform distribution of CGT in the PVA matrix, especially with the fine powders (~5.7 μm). The incorporation of CGT improved tensile strength, biodegradability, and thermal stability, and provided complete UV protection. Although the flexibility of the composite film decreased, the tensile strength increased by 10% and 20% with the coarse and fine CGT powders, respectively, compared to the pure PVA film. Considering the estimated fabrication cost in the study, findings suggest that CGT has significant

potential as a cost-effective reinforcement material for PVA in the production of biodegradable plastic.

Song *et al.* [36] enhanced the toughness of poly(vinyl alcohol)-cryogens (PVA-CGs) by adjusting three key parameters: PVA concentration (7.5%–12.5%), freezing–thawing cycles (1–5 FTCs), and the inclusion of 0%–10% glycerol as a cryoprotectant. This research explored the impact of shear stress-induced destruction (SSID) on mechanical strength, achieved by inducing rapid erosion through high frictional force. The tolerance to SSID (Tol-SSID) demonstrated varying sensitivities and trends based on the fabrication parameters. The assessed Tol-SSID displayed consistent and inconsistent correlations with tensile strength and swelling, respectively. The evaluation of Tol-SSID provides valuable insights into the practical mechanical strength of PVA-CGs against intense friction, simulating extreme shear stress in a bioreactor. A PVA-CG with a 10% PVA concentration and two FTCs showed Tol-SSID and tensile strength of 88.3% and 0.59 kPa, respectively. Additionally, 5% glycerol was added to maintain bacterial respiration activity for immobilized nitrifiers, resulting in a survival rate of 88.6% and an oxygen consumption rate of 0.097 mg- $\text{O}_2/\text{g-VSS}\cdot\text{min}$. In continuous nitrification mode using the optimized PVA-CG for 10 days, an ammonia removal rate of 0.2173 kg-N/ $\text{m}^3\cdot\text{d}$ was achieved, representing an improvement compared to cases without glycerol addition (0.1426 and 0.1472 kg-N/ $\text{m}^3\cdot\text{d}$ for PVA-CGs in two and three FTCs, respectively).

Pan, Y. *et al.* [37] studied wastewater containing poly(vinyl alcohol) (PVA) can have a dissolved organic carbon concentration of up to 10,000 mg/L, leading to significant chemical oxygen demand (COD) issues, especially in industries like textiles and chemicals. To address this, we propose a two-stage treatment method involving Fenton pre-oxidation and Ca-induced coagulation to reduce PVA and COD levels. Optimal concentrations of FeSO_4 and CaCl_2 per gram of PVA were found to be 0.8 g/g- PVA and 4.0 g/g-PVA, respectively—considerably lower than reported in other treatments. Successful oxidation broke down the long chains of PVA molecules, partially converting hydroxyl (OH) groups to carboxyl (COOH) groups. In the coagulation stage, Ca^{2+} is effectively bound to the pre-oxidized PVA products, forming insoluble compounds. Applying this two-stage process to wastewater with initial COD and PVA concentrations of 20,450 and 10,000 mg/L, respectively, resulted in the removal of up to 81.3% COD and 96.0% PVA. Additionally, the sludge residue demonstrated a capacity to adsorb Sb (III) from the

wastewater, achieving an adsorption capacity of 16.0 mg/g. This study offers valuable insights into an economical and efficient approach for treating high-concentration PVA- PVA-containing wastewater.

Lan *et al.*[38] created active biodegradable packaging films using a combination of polyvinyl alcohol (PVA), chitosan (CS), and d-Limonene (DL). The study systematically investigated the impact of varying DL content levels (0%, 2.5%, 5%, 7.5%, and 10% w/w) on the structural, mechanical, biodegradable, and antimicrobial properties of PVA/CS films. Fourier transforms infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) revealed the favorable compatibility between DL and PVA/CS, as well as a more uniform continuous, flat, and smooth surface. The incorporation of DL significantly enhanced the antibacterial, mechanical, and barrier properties of PVA/CS films, contributing to their substantial biodegradability. However, excessive DL loading was found to weaken the hydrogen bonds between polymer chains, negatively impacting the physical performance of the film. Notably, the PVA/CS/DL-5% film exhibited the highest water contact angle and transmittance value. Moreover, it effectively preserved packaged mango fruits over a 10-day storage period at $20 \pm 2^\circ\text{C}$, as evidenced by assessments of fruit weight loss, decay rate, firmness, titratable acidity, soluble solids, and ascorbic acid. In conclusion, DL/PVA/CS composite films show promise as environmentally friendly packaging materials for food preservation.

Bian *et al.* [39] investigated that bacteria capable of degrading polyvinyl alcohol (PVA) were identified through screening sludge samples, where PVA served as the sole carbon source. A new bacterial strain, identified as *Bacillus 9iacin*, was isolated based on partial 16S rDNA nucleotide sequencing and morphological analysis. The PVA-degrading enzyme (PVAase) from *Bacillus 9iacin* was then immobilized as cross-linked enzyme aggregates (CLEAs) through a process involving ammonium sulfate precipitation followed by glutaraldehyde cross-linking. The impacts of precipitation and cross-linking on PVAase-CLEAs activity were studied and characterized. Precipitation with 70% ammonium sulfate and a 1.5% glutaraldehyde cross-linking reaction over 1 hour resulted in approximately 90% activity recovery for PVAase-CLEAs, indicating the potential for extended use without additional purification steps. Immobilization did not significantly alter the optimal pH and temperature values of the PVAase. The PVAase-CLEAs exhibited a

spherical morphology and demonstrated improved efficiency in degrading PVA compared to the free PVAase in solution. Additionally, the PVAase-CLEAs displayed outstanding thermal stability, pH stability, and storage stability when compared to the free PVAase. After four usage cycles, the PVAase-CLEAs retained approximately 75% of their initial activity, suggesting their potential applicability for PVA degradation in industrial settings.

Biodegradable plastics (BP)

BP has emerged as a viable alternative to traditional plastics [[40], [41], [42], [43], [44], [45]]. This research employed the solvent casting method to create ternary plastics using varying proportions of octenyl succinic anhydride (OSA) esterified potato starch, gliadin, and polyvinyl alcohol (PVA), with subsequent characterization of their structural, physicochemical, and degradable attributes. The findings indicated that the composite plastic exhibited higher elastic modulus (EM), water resistance, and degradability compared to pure PVA. Optimal compatibility was achieved when the ratio of OSA potato starch to gliadin was 1:1, and PVA replacement was at 25%. Notably, with PVA constituting 75% of the total plastic composition, the composite plastics displayed larger values for T_m , ΔH_c , and ΔH_m compared to pure PVA plastics. This implies that the addition of OSA potato starch and gliadin enhances the biodegradability of PVA plastics, making them effective as food packaging materials with improved properties.

Authors [46] examined the impact of PVA molecular weight on the biodegradable properties of PVA/starch blends by blending PVAs of different molecular weights with varying compositions of cross-linked starch (CLS). A PVA exhibiting superior biodegradability was identified from the PVA/starch blends with higher biodegradability. Subsequently, this selected PVA was blended with acid-modified starch (AMS) to systematically investigate the effects of starch modification on the biodegradable characteristics of the PVA/starch blends. Higher molecular weight PVA demonstrated greater biodegradability across all PVA/starch blends. The biodegradability of PVA/modified-starch blends increased with higher modified starch contents, with PVA blended with 1N AMS showing superior biodegradability. Bio-reaction kinetics experiments indicated the decomposition tendencies of the PVA/starch blends under ambient conditions. According to the first-order reaction kinetic model, it is estimated that PVABF- 17/starch blends with

20% and 40% CLS would take approximately 16.20 years and 12.47 years, respectively, to degrade by 70%. In contrast, the specimen meets the biodegradable material criteria of the Environmental Protection Administration (EPA) of Taiwan. Overall, PVA/AMS specimens exhibit better decomposition potential than PVA/CLS specimens [[43], [47]].

Conclusion

Eco-friendly plastic materials become an interesting area due to their safety in industries such as packaging materials for the food industry, and applications in the medical and agricultural fields. Novel biodegradable packages based on the percentage of biodegradability of materials in different conditions and atmosphere attention. The produced biodegradable composite exhibits excellent tensile strength, outstanding thermal stability, pH stability, storage stability and environmentally friendly materials, making them effective barriers against moisture and oxygen gas.

Prospects. The processes of development of biodegradable polymers are still in progress and to

be simple with special recycle and cost-effective. Also, many processes of development of biodegradable composites are expected soon as these new biodegradable polymers may possess effective and important properties such as excellent tensile strength, outstanding thermal stability, and environmentally friendly materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Биологиялық ыдырайтын полимерлерге шолу: синтезі, модификациясы және қолданылуы

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ТҮЙІНДЕМЕ

Биологиялық ыдырайтын полимерлер бұл дамып келе жатқан жаңа сала. Кең ауқымды қасиеттерінің арқасында синтетикалық және табиғи полимерлі материалдар күнделікті өмірде маңызды және барлық жерде қолданылады. Крахмал, целлюлоза, лигнин, хитозан, мақта қабығы (CTS) және мақта тазартатын машинадан шығатын қоқыс (CGT) сияқты түрленген табиғи полимерлік материалдар жақсы қасиеттерге ие. Поливинил спирті (ПВА), биологиялық ыдырайтын пластиктер, биологиялық ыдырайтын көбіктер синтетикалық биологиялық ыдырайтын полимерлі материалдар. Биопластика - бұл әртүрлі микроорганизмдердің

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	арқасында шағын молекулаларға (мысалы, H ₂ O, CO ₂ және CH ₄) дейін ыдырайтын полимерлердің бір түрі. Биопластика қалдықтарды ерітеді, ал биологиялық ыдырайтындығының арқасында белгілі бір жағдайларда қызметінің соңына дейін пайдалануға болатын жаңа қасиет. Биопластиктер өз жұмыстарын орындағаннан кейін заттарды кәдеге жаратудың арзан әдістерін қажет ететін қолданбалар үшін қолданылуы керек (мысалы, азық-түлік орауыштары, ауыл шаруашылығы немесе медициналық бұйымдар).
	Түйін сөздер: Биологиялық ыдырайтын полимерлер, крахмал, биологиялық ыдырайтын пластмассалар, биологиялық ыдырайтын көбіктер.
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Обзор биоразлагаемых полимеров: синтез, модификация и применение

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Поступила: 8 января 2024 Рецензирование: 1 февраля 2024 Принята в печать: 13 февраля 2024	Аннотация Биоразлагаемые полимеры представляют собой развивающуюся область. Благодаря своим разнообразным свойствам как синтетические, так и природные полимерные материалы играют жизненно важную и повсеместную роль в повседневной жизни. Модифицированные природные полимерные материалы, такие как крахмал, целлюлоза, лигнин, хитозан, оболочка хлопкового семени (CTS) и мусор хлопкоочистительной машины (CGT), обладают улучшенными свойствами. Поливиниловый спирт (PVC), биоразлагаемые пластмассы, биоразлагаемые пены - синтетические биоразлагаемые полимерные материалы. Биопластики — это разновидность полимеров, которые могут разлагаться различными микроорганизмами до небольших молекул (например, H ₂ O, CO ₂ и CH ₄). Замечено, что биопластики растворяют отходы, а биоразлагаемость — это всего лишь новое свойство, которое можно использовать в конце его срока службы в определенных условиях. Их следует использовать для применений, требующих дешевых методов утилизации предметов после того, как они выполнили свою работу (например, для упаковки пищевых продуктов, продуктов сельского хозяйства или медицинских товаров).
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