#### **REVIEW PAPER**



# A comprehensive review on recent advances in preparation, physicochemical characterization, and bioengineering applications of biopolymers

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#### **Abstract**

Biopolymers are mainly the polymers which are created or obtained from living creatures such as plants and bacteria rather than petroleum, which has traditionally been the source of polymers. Biopolymers are chain-like molecules composed of repeated chemical blocks derived from renewable resources that may decay in the environment. The usage of biomaterials is becoming more popular as a means of reducing the use of non-renewable resources and reducing environmental pollution produced by synthetic materials. Biopolymers' biodegradability and non-toxic nature help to maintain our environment clean and safe. This study discusses how to improve the mechanical and physical characteristics of biopolymers, particularly in the realm of bioengineering. The paper begins with a fundamental introduction and progresses to a detailed examination of synthesis and a unique investigation of several recent focused biopolymers with mechanical, physical, and biological characterization. Biopolymers' unique non-toxicity, biodegradability, biocompatibility, and eco-friendly features are boosting their applications, especially in bioengineering fields, including agriculture, pharmaceuticals, biomedical, ecological, industrial, aqua treatment, and food packaging, among others, at the end of this paper. The purpose of this paper is to provide an overview of the relevance of biopolymers in smart and novel bioengineering applications.

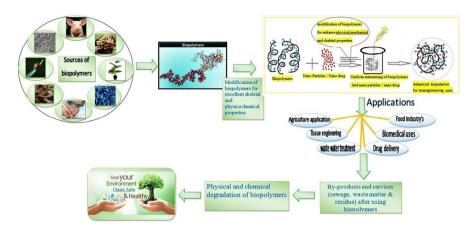
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# **Graphical abstract**



The Graphical abstract represents the biological sources and applications of biopolymers. Plants, bacteria, animals, agriculture wastes, and fossils are all biological sources for biopolymers, which are chemically manufactured from biological monomer units, including sugars, amino acids, natural fats and oils, and nucleotides. Biopolymer modification (chemical or physical) is recognized as a crucial technique for modifying physical and chemical characteristics, resulting in novel materials with improved capabilities and allowing them to be explored to their full potential in many fields of application such as tissue engineering, drug delivery, agriculture, biomedical, food industries, and industrial applications.

 $\textbf{Keywords} \ \ Biopolymers \cdot Biocompatibility \cdot Biodegradation \cdot Bioengineering \cdot Pharmaceuticals \cdot Eco-friendly$ 

#### **Abbreviations**

PA Polyamide

PVC Polyvinylchloride PP Polypropylene PE Polyethylene

PMMA Poly(methyl methacrylate)

PGA Poly(glycolic acid)
PLA Poly(lactic acid)
PCL Polycaprolactone
PHB Polyhydroxy butyrate
PPF Polypropylene fumigates

PDS Polydioxanone DS Degree of substation

DDSA Dodecenyl succinic anhydride

CDs Cyclodextrins

PPV Poly(p-phenylenevinylene) POB Poly-3-hydroxybutyrate



EPS Extracellular polymeric substances

ALE Alginate-like exopolymer

TC Cholesterol
AI Apolipoprotein
HDL Lipoprotein density
DDA Degree of deacetylation
DA Degree of acetylation

DOX Doxorubicin HAp Hydroxyapatite CS Chitosan

RSM Response surface method TPS Thermoplastic starch

UDP-GLC Uridine diphosphate glucose

NC Nanocellulose KGM Konjac glucomannan

KSAP KGM-based superabsorbent polymer

AA Acrylic acid
UV Ultraviolet
PU Polyurethane
KL Kraft lignin
WG Wheat gluten

HPLC High-performance liquid chromatography

GSE Grapefruit seed extract HNT Halloysite nanotube

ST Starch Glycerol

PLGA Poly(lactide-co-glycolic acid)

NPs Nanoparticles

RROP Radical ring opening polymerization

MDO 2-Methylene-1,3-dioxepane ROP Ring-opening polymerization

PLLA Poly(L-lactide)
PDLA Poly(D-lactide)
PDLLA Poly(DL-lactide)
3D Three dimension
DMSO Dimethyl sulfoxide
DCs Dendritic cells

NMR Nuclear magnetic resonance

XRD X-ray diffraction

SEM Scanning electron microscope
TEM Transmission electron microscopy

FTIR Fourier transform infrared
ATR Attenuated total reflection
CMC Carboxymethyl cellulose
CNF Cellulose nanofibrils
BC Bacterial cellulose



PAC Polyaluminum-chloride COD Chemical oxygen demand

SS Suspended solids

PA Polyamide

PEGDA Poly(ethylene glycol) diacrylate
MCC Microcrystalline cellulose
BNC Bacterial nanocellulose
LDPE Low-density polyethylene
EAA Poly(ethyleneco-acrylic acid)
HPMC Hydroxy propyl methyl cellulose

CAB Cellulose acetate butyrate
PHAs Polyhydroxyalkanoates
PVAP Poly(vinyl alcohol phosphate)

TPP Tripolyphosphate GSH Glutathione

PEG Poly(ethylene oxide)
CaP Calcium phosphate
SC Supercapacitor

PHA Polyhydroxyalkanoates

MO Methyl orange
GG Guar Gum
XG Xanthan Gum
CN Cellulose nitrate
MC Methyl cellulose

AgNPs Silver oxide nanoparticles

5-FU 5-Fluorouracil

#### Introduction

Monomers are simple building blocks. A polymer is a substance made up of a large number of molecules with a high molecular mass. A polymer is created by the repeating unit of a monomer chain, which can occur naturally (natural polymer) or be created artificially (manmade polymer or synthetically derived polymer). Biopolymers are natural polymers found in living organisms. A biopolymer is a long chain molecule made up of monomeric components that are covalently bound together to produce a biodegradable molecule. Plants, trees, microbes, and other natural sources are the primary sources of biopolymers. Synthetic polymers are simpler and more arbitrary than biopolymers, which are complex molecules with well-defined three-dimensional structures [1]. Renewable resources are used to create a wide range of biopolymeric materials with various physical and chemical characteristics. Nature contains lignin, starch, cellulose, hemicelluloses, and a variety of other biopolymers [2]. Biopolymer's future demands on manufacturers for novel materials are enormous. However, because the materials are being given expressly for sustainable development, their cost-effectiveness must improve. The qualities of these polymers should be used in applications that



utilize novel materials, and products should be produced based on those features. They are beginning to appear as a result of this for being more responsible in caring for the planet we live in. New biodegradable polymers with good skeletal and mechanical characteristics have been the focus of recent study. Biopolymers originating from natural organisms have been manufactured in enormous quantities. The biodegradability of biopolymers has been linked to the presence of certain microorganisms and enzymes with distinct degradable characteristics [3]. The biodegradability of biopolymers is facile, because the biopolymers are bearing the oxygen and nitrogen atom in their skeletal backbone. Biopolymer is converted to  $CO_2$ , water, biomass, humid water, and other natural components during biodegradation. Biodegradable polymers offer a wide range of applications in bioengineering, including tissue engineering, drug delivery systems, and wound dressing, among others [4]. Biopolymers have a distinctive helical structure, stiffness, charge-free chains, and a strong resistance to salt and cold; thus, they thicken and stabilize better under harsh pool conditions [5].

# General conversion of monomer to polymer

Monomers are small molecules, most of which are organic, that may combine with other monomers to produce larger molecules, known as polymers. Every monomer molecule has the ability to make chemical connections with at least two other monomers. Polymers are a type of synthetic material made up of several smaller pieces known as monomers. Polymers are chains of monomeric units with an undetermined number of them. Polymerization is a chemical reaction in which a large number of monomer molecules combine to produce a polymer (Fig. 1). A polymerization can yield macromolecules with a linear or branching structure. They can also take the form of a three-dimensional complicated network. The basic approach for converting monomer to polymer is shown in the diagram depicted below.

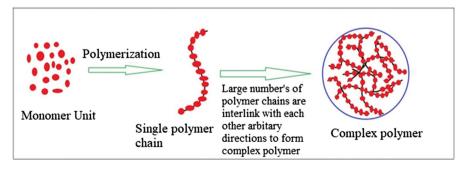


Fig. 1 Polymerization of monomer to polymer



# **Biopolymer and classification of biopolymers**

Biopolymers are naturally occurring polymer found in living organisms such as plants, animals, microbes and other natural sources. Biopolymers are basically classified according to their origins, into two groups, i.e., natural and synthetic biopolymer and classified in Fig. 2.

#### **Natural biopolymer**

Natural biopolymer is a biopolymer that formed organically from living organisms. Proteins and polysaccharides are biopolymers that fall under the category of natural biopolymers [6].

#### **Protein**

Proteins are big, complex molecules that serve a number of important functions in the human body. Proteins are made up of hundreds or thousands of smaller components known as amino acids that are linked in lengthy chains. They perform the majority of the work in cells and are essential for the construction, function, and control of the body's tissues and organs. A protein is made up of 20 distinct types of amino acids that may be combined in different ways. Plant proteins, such as those

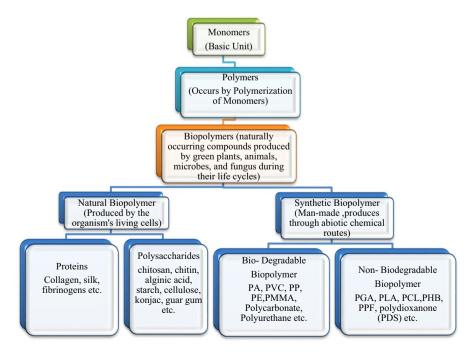


Fig. 2 Classification of biopolymers



found in foods like wheat, corn, and soybeans, are more immunogenic than animal proteins. Plant proteins have a low molecular weight and a large net negative charge, which makes them ideal for effective medication delivery. Proteins are hydrophilic in nature because they include polar amino acids, which attract cells sympathetically. Natural biopolymers such as collagen, silk, and fibrinogens are accessible; commercially available collagens are utilized as injections for skin sensitization and antibody responses, as well as immunological uses [7]. Proteins' main structure is made up of peptide bonds and disulfide bonds. A peptide bond is produced when the carboxyl group of one molecule combines with the amino group of the other molecule, releasing a molecule of water in the process ( $H_2O$ ). This is a condensation process (also known as a dehydration synthesis reaction) that happens between amino acids. The mechanism of a peptide bond is seen in the diagram below (Fig. 3).

# Polysaccharide

Polysaccharides are lengthy chains of monosaccharides connected by glycosidic linkages that our bodies normally employ for energy or to aid cellular structure. Chitosan, chitin, alginic acid, starch, cellulose, konjac, and gums (guar gum, gum Arabic, gum karaya, etc.) are examples of naturally occurring polysaccharides. Chitosan is a natural polysaccharide with a wide range of uses in medication administration and tissue engineering. In the food business, alginic acid is used extensively in food

Peptide Bond

Fig. 3 Peptide bond formation in protein biomolecules



processing and manufacturing. Starch is a typical natural polysaccharide that is used as a coating and adhesive because it is water-insoluble [8].

# Synthetic biopolymer

Synthetic biopolymers are polymers that have been modified from natural polymers or chemically produced from synthetic monomers such that they can degrade naturally without leaving residues that are hazardous to living things and the ecosystem. Synthetic biopolymers have received a lot of interest in recent years due to their significant advantages over natural polymers in terms of stability and flexibility to fit a wide range of applications. Synthetic biopolymers, on the other hand, are preferred over synthetic polymers due to their biodegradable qualities and environmental safety. Synthetic biopolymer synthesis may now be tuned to match specific applications thanks to breakthroughs in new molecular designing tools and polymer chemistry. Because of some of its unique qualities, including as stability, controlled release, no immunogenicity, and removal from the body, synthetic biopolymers have found one of their most important uses in the medical industry, which matches their application in human bodies. In comparison with ceramic and metal particles, synthetic biopolymers are easier to produce in many shapes and sizes. They are used in industry and have cheap production costs, and they play a vital part in our daily lives. Enzymes and live cells generally carry out biopolymer synthesis to the target biopolymer molecules [9]. Synthetic biopolymers are generally classified into two categories, i.e., non-biodegradable biopolymers and degradable biopolymers.

# Non-biodegradable biopolymer

Non-biodegradable polymers are those that are resistant to environmental breakdown and hence end up in the form of garbage. Non-biodegradable biopolymers are resistant to the environment and are often used in non-biomedical applications. Some common examples are PA, PVC, PP, PE, PMMA, polycarbonate, PU, etc. [10].

# Biodegradable biopolymer

Biodegradable polymers are those that breakdown when exposed to the elements. Biopolymer's biodegradability makes it a viable alternative for replacing petrochemical-based packaging materials. Synthetically biodegradable polymers are made in a controlled environment and have consistent skeletal and mechanical characteristics, such as rigidity and accomplished modulus. When compared to biological scaffolds, they are less expensive to make and promote contact with endothelial cells [11]. Artificially generated biodegradable synthetic polymers serve an important role in tissue engineering and other biological fields. The decomposition of synthetic polymers is accomplished by simple hydrolysis [12]. PGA, PLA, PCL, PHB, PPF, PDS, etc., which are the synthetically biodegradable polymers have been used in medicine and pharmaceuticals process. The hydrophilicity of PGA is extensively greater



than that of PLA, leading to higher crystallinity; thus, it was used as evolutionary of entire initially synthetic adsorbable structure [13].

# Properties of biopolymers

Biopolymers are a type of polymer made from biological resources. Because of their abundance, high tolerance, high thermal stability, non-toxicity, antibacterial activity, antifungal activity, biocompatibility, biodegradability, and other unique qualities such as strong adsorption capacities and ease of functionalization, they have been studied for a variety of applications in the industrial, biomedical, pharmaceutical, drug-delivery, tissue engineering, medications, tablets, adhesives, paper, food, cotton, and rayon sectors, including sorption [5].

# Synthesis methods of biopolymers

Synthetic biopolymers are biopolymers that have been artificially modified by a biotic chemical process. Biopolymer synthesis may be accomplished using a variety of methods and techniques. Some typical biopolymer synthesis techniques for producing well-generated structural and mechanical characteristics of biopolymer are listed below

- Esterification of biopolymers
- Dehydration of biopolymers
- Polycondensation of biopolymers
- Hydrolysis of biopolymers
- Granulation of biopolymers etc.

### **Esterification of biopolymer**

Esterification is a chemical process that occurs during the ester's synthesis. Esterification is a chemical reaction that produces an ester (RCOOR) and water by combining alcohol (ROH) with an organic acid (RCOOH). Through an esterification reaction between a carboxylic acid and an alcohol, this chemical reaction produces at least one ester product. The esterification of following biopolymer starch, cellulose, and hemicelluloses is given below.

#### Esterification of cellulose

Esterification of cellulose occurs either in throughout polymeric chain or occurs at outer cellulose thread to design cellulose ester. When enormous amounts of cellulose are generated by a homogeneous or heterogeneous process, the surface is altered. Cellulose nitrate (CN) is the most widely used inorganic cellulose ester, with huge volumes generated in industry. It's commonly found in plastics, coatings,



explosives, and propellants, among other things. In heterogeneous equilibrium, the esterification of cellulose nitrate is carried out by cellulose and a combination of nitric acid and sulfuric acid with a degree of substitution (1.8–2.8). The heterogeneous direct reaction between cellulose and sulfuric acid is known as CS esterification. Synthetic CS is formed through the displacement of an ether or ester group in cellulose [14].

#### Esterification of starch

As an esterification reagent, acetic acid and acetic anhydride are used to make starch acetate. The pH, time interval, and the presence of a catalytic agent all influence the incorporation of acetyl groups into starch molecules. For low (0.01–0.2), medium (0.2–1.5), and high (1.5–3) acetyl starch, the degree of substation (DS) ranges from 0.01 to 0.2. The alkenyl succinic anhydride DDSA is a unique alkenyl succinic anhydride. The esterification of DDSA starch in an aqueous solution produces a water-resistant product that is widely utilized in the film and paper industries [15].

#### **Esterification of hemicellulose**

Hemicellulose is a polymer present in plant dell cells and cell walls. Hemicelluloses, a biopolymer used to make films and hydrogels, has been employed in biomedical applications such as medication delivery and tissue engineering. Chemical synthesis of hemicellulose yields furfural, xylitol, ethanol, and lactic acid. The eco-friend-liness, low hydrophobicity, higher electrochemical and thermal balance, and faster reaction rate of biomaterials such as cationic hemicelluloses, carboxymethyl hemicelluloses, lauroylated hemicelluloses, and acylated hemicelluloses are the homogenous upgradation of hemicellulose. The esterification of xylan-rich hemicelluloses with maleic anhydride in the presence of a catalyst, LiOH, in an ionic liquid medium under homogeneous conditions with a degree of substation (DS) of (0.095–0.75) has a wide range of applications in agriculture, food, waste water treatment, and pharmaceutical industries [16].

#### **Dehydration of biopolymers**

Trehalose's exceptional performance as a cryo- and dehydroprotectant of fluctuating systems is the dehydration of biopolymer. Cyclodextrins (CDs) have been employed as a dehydrating agent to increase the mechanical potentiality of proteins using the dehydration technique. Chemical conjugation between enzymes and CD derivatives in aqueous medium leads in enhanced thermal stability of the enzymes due to supramolecular superior reciprocal action on the enzyme surface. The bimolecular of biopolymer is well protected by dehydration of the biopolymer [17]. Glass transition features are seen in the biopolymer polysaccharide. The glass transition affects the thermal characteristics of native dehydrate biopolymers in a significant way [18]. The pace of dehydration is slowed by the evaporation of free water. Water diffusion occurs in the liquid phase, the vapor phase, or both phases during the dehydration



of biopolymers. The shrinking of the film during the dehydration process causes a change in the structure of the polymer film. Adhesives, coatings, food industry, and drug delivery in the pharmaceuticals sectors have all leveraged the kinetics of dehydration of diverse biopolymers [19].

# Polycondensation of biopolymers

Polycondensation is the process of combining different monomers to generate polymers. The process is frequently accompanied by the release of a variety of lowmolecular-weight subsidiary products (water, alcohol, and salt). The polycondensation synthesis of biopolymers provides a flexible toll procedure for biopolymer modification. Polycondensation of diols and diesters of H-phosphonic acid, phosphoric dihalides, or phosphoric acid can be used to make phosphorus-containing polymers. In poly-condensation synthesis techniques, dihydroxy(oligolactide) and ethyl dichlorophosphate react in solution to create bulk polilactofate [20]. In acidic settings, polycondensation of water-soluble melamine/formaldehyde results in a gel with a large spherical cavity. Melamine polycondensation and melamine replacement with formaldehyde can also be utilized to generate more flexible foam and fiber resins. In addition, monodisperse melamine/formaldehyde microspheres may be made using the polycondensation method [21]. During the Knoevenagel polycondensation synthesis, where the backbone double bond substitution occurs, where the modified PPV containing cyano groups has a higher electropolymerizing activity [22].

#### Hydrolysis of biopolymer

The non-toxic properties of biopolymeric synthetic polymers are attributable to the fact that they do not need the formation of hydrocarbons or carbon dioxides; their breakdown produces water. The ultimate outcome is carbon dioxide, which is damaging to human biology and globalization. Azotobacter maintains a critical role in the creation of the synthetic biopolymer Poly-3-hydroxybutyrate (POB) through hydrolytic modification. In the presence of phosphate buffer, the hydrolysis of POB synthetic biopolymer forms a film at 70 °C. The temperature, incubation medium, chemical content of the biopolymer, and molecular weight all influence the hydrolytic breakdown of POB. The hydrolysis of PBA occurs at the surface area during the hydrolytic synthesis [23]. The biopolymer cellulose has a strong intermolecular arrangement in its structural backbone, which gives it significant strength and resilience to hydrolysis, whereas hemicellulose is random and amorphous in nature, with little cohesiveness. Dehydration followed by hydrolysis reaction at critical water condition was used to initiate thermal cleavage at one end of the cellulose biopolymeric chain. The bond brake occurs during the hydrolysis of cellulose at temperatures of 200-350 °C in the presence or absence of a catalyst in a nitrogenic environment. Lignin and hemicellulose are biopolymers that may be generated through hydrolysis, which involves the breakdown of bonds around -critical water. In an aqueous atmospheric solution, enzymatic hydrolysis of the cellulose biopolymer



produces xylitol and furfural. In addition, hydrolysis is important in the destruction of lignin because the reaction medium is encouraged by the high ion product of water [24].

# **Granulation of biopolymer**

The biopolymer's granular production method has become speculative and uncertain. The bio granulation of biopolymers dominates the prospective applicability, which includes greater toxicity tolerance, treatment of high-loaded carbon/nutrient load pollutants, high-grade settleability, and increased biomass with holding, among other things [25]. Granulation produces EPS, which include proteins, lipids, humic acids, polysaccharides, and nucleic acids that keep microorganisms together. For full granulation of biopolymer, a long time period of roughly 308 days is required, which accelerates through two phases, phase-1 and phase-2. Phase 1 takes day 0 ~ 182–220 for low granular mechanism, whereas phase 2 takes pale after 182–220 days for steady granular mechanism. Granulation under local microbial composition improves the stability of ALE, which aids in subsequent qualitative research for industrial use [26].

# Physical properties and geographical orientation of recent studied biopolymers

## Chitosan (CS)

Rouget, who discovered chitosan in 1859, discovered it when chitin was heated in an alkaline medium. However, Hoppe-name Seyler's was first used in 1894 [27]. CS is an a linear amino polysaccharide biopolymer derived naturally from shrimp and crab exoskeletons. Hoppe-alkaline Seyler's deacetylation of chitin to produce chitosan. CS is a heterogeneous polymer with a well-defined chemical structure that consists of 1–4 connected 2-acetamido-2-deoxy- $\beta$ -D-glucopyranose and 2-amino-2-deoxy- $\beta$ -D-glucopyranose. The structure and processing of chitosan is given in Fig. 4.

CS's biocompatibility and degradability make it useful in biomedical applications such as wound healing and tissue engineering. CS's unique structural and antibacterial qualities make it suitable for use in film or membrane fabrication as well as medication administration. Chitosan is water insoluble but soluble in acidic media. In the presence of a nucleophilic amino group, Chitosan has three reactive groups that cause a nucleophilic substitution process. CS's potential actions, such as disinfection, non-toxicity, antibacterial, and antimicrobial qualities, make it a good fit for biopesticides and the food industries as cited in Fig. 5 [28]. When human serum albumin is exposed to peroxyl radicals, CS has a similar potency to vitamin C in that it prevents the formation of carbonyl and hydroperoxide groups. Because CS has a low molecular weight, it limits neutrophil activation and serum albumin oxidation, which reduces oxidative stress. The availability of high molecular weight chitosan



Fig. 4 Deacetylation of chitin forms chitosan

will lower cholesterol (TC) and apolipoprotein (AI) levels while increasing lipoprotein density (HDL) [29].

With increasing antimicrobial action, the degree of deacetylation (DDA) of CS rises. CS is a biomolecule with a DDA of 70 percent or less, whereas water-soluble chitosan has a DDA of 50 percent or less. Protonation is facilitated by the amino group (R-NH<sub>2</sub>) rather than the acetamido group (R-NH-C(O)-CH<sub>3</sub>) at the C<sub>2</sub> position of chitosan, which has a higher DDA value. When the protonation half-life period occurs, chitosan delivers a positive charge, resulting in a reduction in pH when the protonated group attaches to its cytoskeletal molecular body [30]. CS is a polysaccharide-rich in bonding hydrogen that degrades before reaching the glass transition. CS solution is used to make films, gels, fibers, and sponges as a result of this phenomenon. The dissociation potential of CS in acidic solution will be demonstrated by its polyelectrolyte charters and polycationic nature (pKa). The value of pKa at zero charge of chitosan varies from 6.46 to 7.32, depending on the degree of acetylation (DA) [31]. CS, which is found in mango and also in guava, inhibits the growth of bulk bacteria, resulting in a decrease in weight and respiration rate [32]. CS-based hydrogels are used for sensory detection. Hydrogel is a biocompatible biopolymer with a high fluid absorbability property that may be utilized to make a base biosensor. A CS-based hydrogel was used to detect certain target chemicals electrochemically. Furthermore, because to their difficult cell-matrix



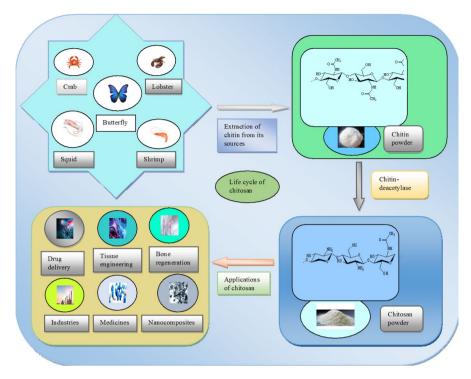


Fig. 5 Life cycle of chitosan biopolymer

interaction, chitosan-based nanofibers play a significant role in drug delivery and tissue engineering, as evidenced by the formation of doxorubicin (DOX)-incorporated hydroxyapatite (HAp)-chitosan (CS) nanocomposite induced on osteosarcoma cells [33]. Life cycle of other biopolymers is depicted in Figs. 6, 7, and 8.

CS derivatives are used in the textile industry for antimicrobial finishing of bioactive textiles and in the paper industry to increase paper weight strength [34]. Because the green biopolymer CS contains antibacterial agents, it limits surface contamination of meat and fish. According to recent study, the antibacterial capabilities of CS film against L-monocytogenes make roast beef suitable for food consumption [35]. CS's biocidal qualities have been employed to prevent the growth of spoilage microorganisms, making it useful for food preservation and food safety [36].

#### Gelatin

Gelatin is a macromolecular protein biopolymer that is formed by the perfect hydrolysis of collagen. When compared to other naturally occurring biopolymers, it exhibits non-toxicity, a thermally reversible sol–gel transition, high mechanical strength, high water solubility, and greater elastic characteristics [37]. Amino acids are linked together through peptide linkage in the biopolymer gelatin's structural makeup. The chemical structure of gelatin is depicted in Fig. 9.



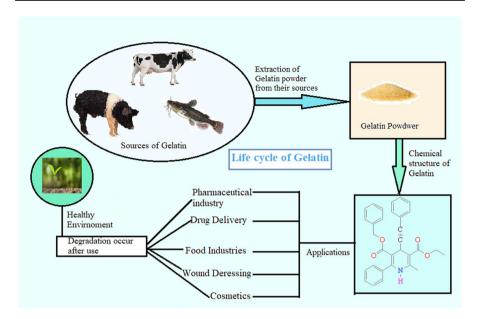


Fig. 6 Life cycle of gelatin biopolymer

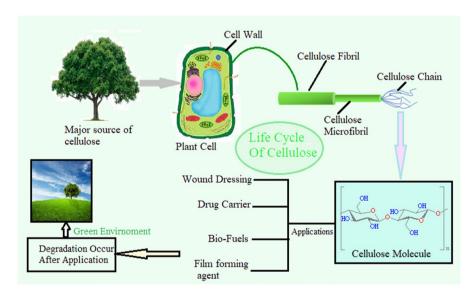


Fig. 7 Life cycle of cellulose

Gelatin is odorless and tasteless, and it is insoluble in acetone, chloroform, ether, ethanol (95%), and methanol, but it is soluble in acids, alkalis, and glycerin. Gelatin biopolymer molecules are soft and swell due to their high absorption and water binding capability. After full dissolution, the mixture of hot water and gelatin is



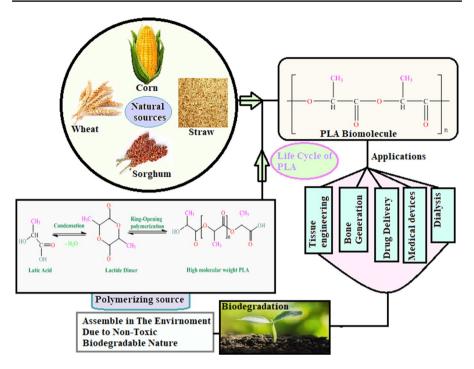


Fig. 8 Life cycle of PLA

Fig. 9 Chemical structure of gelatin

cooled to form a jelly structure. In the presence of functional groups, gelatin biopolymers' particular properties to water produce hydrogels (OH, NH<sub>2</sub>, COOH). The hydrolytic reaction produces two forms of gelatins (A&B), which are generated by



acidic hydrolysis of pig skin and basic hydrolysis of bones, with positive and negative properties for animal skins, respectively. At particular pH levels, the presence of charge on the gelatin body affects biocompatibility [38, 39]. Recent study has shown that gelatin produced from the kumakuma (Brachyplatystoma filamentosum) species is suitable for response surface technique (RSM) [40]. Also, gelatin biopolymer extraction from the lamina of lizard fish. In a conventional laboratory process, the Zhou and Regenstein method will detect the percentage of yield concentration of gelatin biopolymer, whereas the Biuret method using bovine serum albumin would detect the concentration of protein in the extract solution [41]. Bovine and porcine gelatin biopolymer are the most common sources for gelatin extraction and manufacture. Chitosan is utilized in vitamin encapsulation, plasma replacements, capsule and tablet binder, and other biomedical science applications. The special qualities of gelatin form gelation are employed in food sectors for chewing, gelling, sanitary food packaging, and dairy product manufacture. It is also used to make film coatings, printer ink, and colored sheets [42]. Biomimetically preparing gelatin and HAp composites under coprecipitation results in well-organized pore architectures with significant tissue scaffolding potential. Biopolymer gelatins have a higher propensity for hydrophilicity and gas barrier, making them suitable for tissue engineering applications. However, their lower skeletal strength makes them unsuitable for usage in packing materials [43].

#### Starch (ST)

ST is a natural biopolymer obtained from plant photosynthesis, by using carbon dioxide and water as a basic supplement, providing energy to human beings. Entire structural biodegradability, less price and suitable renewable properties of starch have been used for developing of viable bio-based polymeric compounds. ST-based biopolymeric materials has been successfully used for conservation of petrochemical resources and decrease the harmful biological impact on atmosphere. Ecofriendly and biodegradable polymeric behavior of starch molecules is used for developing novel bioplastic polymeric materials. The modification of thermoplastic starch (TPS) with different di-isocyanate derivatives will enhance the modulus and tensile strength and hydrophobic nature of TPS promotes a bosting plasticizer [44]. ST molecules have complex helical structure made up of D-glucose units, bonded by  $\alpha$ -D (1–4) glucosidic linkage form linear polymeric backbone chain (amylase) and  $\alpha$ -D(1–4) linkage with  $\alpha$ -D (1–6) linkage glucosidic backbone chain form branched (amylopectin) represented in Fig. 10 [44, 45].

The biomolecule starch plays an essential part of the human food hierarchy system. Tacca leontopetaloides is a Polynesian arrowroot starch that is related to corn starch and belongs to the Dioscoreaceae family. Tacca starch contains 77.5% amylopectin and 22.5 percent amylase. This ST is a perennial herb with a tuberous rhizome that serves as a biocompatible processing substitute. Recent research has shown that incorporating glycerol into tacca starch results in the development of ecofriendly biodegradable polymers with poor specific resistance capabilities [46].



Fig. 10 Basic chemical structure of starch biopolymer

The blend of ST-based polymer became poor, because of their immiscible nature in biofield. So, ST-based biopolymer is needed to be modified chemically for enhancing the supermolecular mechanical properties and extensional environmental uses. The hydroxyl modification and graft copolymerization are the versatile method for chemical modification of ST through by which its properties get change. Biocompatibility uses of starch-g-polymer occur through graft copolymerization. Also, starch-g-PCL and starch-g-PLA that are the graft co-polymer have been used as direct thermoplastics and compatibilizer and are clearly biodegradable and reveal supermechanical supports [47].

ST is the prevalent carbohydrate stored in many plants like potato, tapioca, cornstarch, wheat etc. The biopolymer starch has semicrystalline morphology with distinctive degree of crystallinity. Amylose and amylopectin are the two leading ingredients of starch bio- molecules with linear linkage. ST without accumulative is biodegradable and non-toxic and performs excellent biocompatibility. ST is a most common present biomolecule which is capable of switching synthetic polymer. The biomolecule starch was discovered as an applicable agent for the polyester fiber assembly. Spinning technology has been used for modification of fiber based starch molecules. Wet spinning technology was liable to eject the contents of aqueous starch dispersion and glycerol in a methanol/glycerol coagulation bath to accomplished starch fibers. According to the study, the melted thermoplastic ST eject through a spinneret to produce filaments for fabrications. Fiber spinning is carried out by using distinct plasticizer and used melt spinning technology. Recent research has been proved that the assembly of ST filaments, by using mixture of ST, water, plasticizers and other alternative supplement through electrospinning technology [48]. ST-based modified substances have low water accomplished attribution and week mechanical support, as analyze to synthetic polymer due to their high hydrophilicity and water binding capacity. It has been found that the film made by mixture of urea plasticizer and corn starch is resulting, enhance of mechanical strength of



starch by increasing the urea plasticizer concentration within that film [49]. Phloroglucinol, also known as 1,3,5-trihydroxybenzene, is a phenolic compound that is antagonistic to marine brown seaweeds (phaeophyceae). In the perinuclear region of microbes, acetyl-malonate is used in the biosynthesis of phloroglucinol. Phloroglucinol monomeric units bind together to form the backbone of over 700 secondary metabolites. Antiplasmodic, antibacterial, antiviral, antimalarial, antioxidant, antidepressant, and anticarcinogenic properties have been demonstrated for phloroglucinol and its derivatives. The encapsulation of soluble starch provides significant protection to phloroglucinol, extending its control release potential [50].

#### Cellulose

Cellulose is a molecule made up of hundreds, if not thousands, of carbon, hydrogen, and oxygen atoms. Cellulose is the main substance in plant cell walls, which helps plants stay stiff and upright. Although cellulose cannot be metabolized by humans, it is essential in the diet as a source of fiber. Anselme Payene was the first to discover cellulose. Due to their biocompatibility and ecological livable, cellulose and its derivatives are attracting increasing immersion and are thought to have big implications. It is critical nowadays to keep packaged food from spoiling. Particularly in the current COVID-19 pandemic situation, where industries, workers, and transportation are completely shut down, certain premeditated strategies to prevent food waste and degradation are required. As a result, the material used in food packaging can help to keep food from spoiling. Cellulose is a low-cost element with high mechanical strength and a high demand in the global market, particularly in the food and textile industries [51, 52]. The chemical structure of cellulose and its intramolecular hydrogen bonding is given in Fig. 11.

Cellulose is polymerized by organisms other than plants. Bacteria are also able to generate the polysaccharide. Acetobacter xylinum has been the most extensively studied bacterial cellulose synthesis. The physiochemical influence of bacteria-produced cellulose is assumed to be used to aid in flocculation or to preserve specific environments, such as aerobic environment or allowing connection to plants. Bacterial cellulose is assembled similarly to plant cellulose, with

Fig. 11 Structure of cellulose



polysaccharide chains forming microfibrils and microfibril bundles forming ribbons. Bacterial cellulose, unlike plant-based cellulose, is highly pure and does not require separation from lignin during processing. In addition, bacterial cellulose has excellent moisture absorption properties to plant cellulose; plant cellulose has a water holding capacity value of 60%, whereas bacterial cellulose can hold water up to 1000% of the cellulose specimen. Bacterial cellulose's superior water weight permits the polymer to have high crystallinity while remaining seamless and malleable, increasing its viability for therapeutic diagnostics such as building elements of artificial abdominal organs and blood vessels. In plants, cellulose syntheses is a challenging of enzymes that encompasses the entire cell membrane; in bacteria, it covered the whole cell wall. Uridine diphosphate glucose (UDP-GLC) is an essential cofactor in the synthesis of cellulose including both plants and bacteria. The cellulose synthase comprehensive takes the glucose monomers from UDP-GLC, carries it all over the cell membrane or cell wall, and attaches it to the incipient extracellular cellulose backbone chain [53–56].

The production of nanocellulose microfibers from cellulose biopolymer occurs through the use of acid hydrolysis methods and analytical techniques, which result in a high surface area and homogeneous communication with the polymeric resins. The microfiber nanocellulose (NC) was created by polymerizing micro limpid cellulose with a routine method that did not require the use of any harmful chemicals such as sulfuric acid or hydrochloric acid. The bionanocomposite film based on agar-nanocellulose, which is totally biocompatible and biodegradable, has a significant potential for use in biodegradable packaged foods or bio sensing applications [57].

Due to their adequate mechanical and physical properties, cellulose and its variants have sparked significant interest as biocompatible polymers for advancements in the biomedical field. By taking advantage of its hierarchical structure, cellulose innately develops functionality, flexibility, and high specific strength. It is also low in density, low in cost, and biodegradable. Cellulosic materials allow for the fine-tuning of permeability and interdependences, both of which are beneficial for biological and biomedical applications. Conventionally, cellulosic resources have been used in companies to develop paper and textiles, but in recent decades, cellulosic ingredients have been used for a wide range of applications, including tissue engineering applications [58]. Because of their cytocompatibility, good biocompatibility, biodegradability, and minimal side effects, cellulosic materials in particular hold great potential as cost-effective forwardlooking materials for biomedical applications. Cellulosic components can also be conveniently developed to produce high-quality substances due to their chemical features and functions. Mechanisms are shown conventional disease surveillance but also medic-care relies heavily on cellulosic natural resins. Meantime, many emerging application regions, such as tissue engineering, wound healing, enzymatic manipulation, and drug carriers, are being investigated. The results of extensive examination on cellulose from numerous sources and the preparation of cellulose derivatives, as well as their applications as innovative medical and biological ingredients in the fields of tissue regeneration, antiseptics, and drug delivery etc. health related resources.



Fig. 12 The fundamental biochemical structure of cellulose derivatives can be mono-, di-, or tri-substituted depending on -R group

**Table 1** There are a variety of -R groups that are capable of occurring in molecules of cellulose derivatives

Functional groups (R)
H, C <sub>2</sub> H <sub>3</sub> O
H, SO <sub>3</sub> H
$H, NO_2$
H, CH <sub>2</sub> CO <sub>2</sub> H
H, CH <sub>2</sub> CH <sub>3</sub>
$H, CH_3$

#### Derivatives of cellulose

Cellulose derivatives are a feasible alternative to pure cellulose because of their greater dissolving capabilities. Ethanolic or aqueous hydrolysis may also convert them to cellulose, which can then be used to make paper. Cellulose esters (cellulose acetate), ethers (carboxymethyl cellulose, methyl cellulose, and ethyl cellulose), cellulose sulfate, and CN are the most well-known cellulose derivatives, although others exist (Fig. 12, Table 1). Various cellulose derivatives have been produced and used in biomedical sectors to increase the value or broaden the adaptability of cellulose. The functionalization pattern throughout the polymer chain affects the characteristics of cellulose derivatives in addition to the type and degree of substitution. Because of cellulose's low solubility in organic solvents and its bulky and stiff main chain, it is difficult to synthesize certain cellulose derivatives regio-selectively. On the cellulose chain, the hydroxyl group is the most reactive and may be targeted for reaction. It is difficult to take advantage of the modest reactivity variations between the 2-, 3-, and 6-OH groups because cellulose hydroxyl groups are generally weak nucleophiles. Excipients, filtration membranes, wound dressings, bioadhesives, and drug delivery systems are just some of the many uses of cellulose derivatives in the cosmetic and pharmaceutical industries.

**Cellulose sulfate** Cellulose sulfate has unique biological characteristics and is a semi-synthesized cellulose derivative with a simple chain structure. It is an ester of cellulose that may be generated using heterogeneous, homogeneous, or quasi-



homogeneous sulfation processes. Water solubility and antibacterial capabilities at high concentrations are two benefits of cellulose sulfate over virgin cellulose. For heterogeneous sulfation of cellulose,  $H_2SO_4$  and propanol are the most often employed reactants In order to synthesize cellulose sulfate using  $SO_3$ -complexes as a reactant,  $N_2O_4/DMF$  was employed, which has equal distribution, strong solubility, and minimal chain degradation. Cellulose acetate is a chemical that might be used to synthesize cellulose sulfate because of its high solubility in reactants and ease of purification [59].

Cellulose sulfate has well-defined structure and absence of polymer chain branching, cellulose sulfate is ideal for quality control and study into the relationship between structure and activity. Cellulose sulfate has been discovered to have a stronger anticoagulant activity than heparin in their experimental settings, and in vivo investigations have shown that the anticoagulation activity of this compound was accomplished by speeding the inhabitation of antithrombin III on coagulation components in plasma.

Recent study has found that the microencapsulation benefits from cellulose sulfate generated in a homogenous process because of its high viscosity, strong water solubility, and consistent sulfate group distribution. Novel research shows was discovered that the chitosan-cellulose sulfate system might be utilized to carry drugs directly to the colon, where they would be destroyed by bacteria present in the colon, rather than the bloodstream. A study has demonstrated that cellulosic sulfate may be useful in the control of cell activity. As a result, it is a potential material for cell immobilization/encapsulation, which protects cells from the external environment and provides a milieu for cell promotion, and controls cell survival, proliferation, and the release of therapeutic compounds.

**Cellulose nitrate** Cellulose nitrate (CN) is a polynitrate ester that is derived from cellulose. Its structure typically contains 2.2-2.8 nitrate groups for per glucose unit. A powerful nitrating agent is used to nitrate cellulose derived from wood pulp or cotton linters (e.g., nitric acid). The electrophilic assault of  $NO_2^+$  ions on the OH moieties of cellulose replaces the hydroxyl groups with nitrate esters during the nitration process.

The use of commercial lateral flow assay (LFA) kits, which are based on antibodies or nucleic acids immobilized on a CN membrane, makes it possible to identify particular biomolecules within the materials that are being examined. This makes it possible to provide an accessible platform for prenatal testing, testing for oncogene mutations, the diagnosis of infectious disorders, and the identification of microorganisms. NC/PCL membranes are utilized in bioengineering for the detection of Zika virus and enzyme-linked immunosorbent assays, among other applications (ELISA) [60].

**Methyl cellulose** Methyl cellulose (MC) is a major cellulose ether. MC is the simplest alkyl ether that may be made in an alkaline media using a methylating agent, such as methyl chloride or dimethyl sulfate. No matter how much you substitute for the water in an organic solvent, you'll still be able to dissolve methyl cellulose.



For example, MC dissolves in water when the degree of substitution is between 1.4 and 2.0, and it is typically soluble in water and several organic solvents when this degree is between 2.4 and 2.8.

During the hydrogelation process, silver oxide nanoparticles (AgNPs) were synthesized in situ from Ag+ions using a silver acetate precursor salt (CH<sub>3</sub>COOAg). Both the burn wounds and the skin regeneration were improved by the use of hybrid materials that were successfully evaluated. Post-surgery tissue adhesion is minimized thanks to the polymeric blend's lubricant coatings, such as those seen on the CMC/PEG/MC composites.

It is also beneficial for medication delivery systems because of its role as an emulsifying agent. For biological applications such as tissue engineering, wound healing, and pharmaceutical formulations, methyl cellulose is most often utilized [61].

Carboxymethyl cellulose Carboxymethyl cellulose (CMC), one of the most significant cellulose ethers, is made by treating raw cellulose with sodium hydroxide, extracting the alkali cellulose, and reacting it with monochloroacetic acid or sodium monochloroacetate in an alcohol medium.

The biomedical field can benefit from the application of CMC as a viscosityincreasing agent, rheological control agent, binder, stabilizer, and film forming, especially in drug delivery and tissue engineering systems. Many biological uses of CMC and NaCMC have been investigated because of their excellent gelation ability and pH-sensitive swelling capabilities, notably the development of smart stimuli responsive hydrogels for controlled drug administration. This new study shows how to make hydrogels with redox and pH-responsive behavior, better mechanical characteristics and swellability by cross-linking CMC/quaternized chitosan (HACC) hydrogels. 5-Fluorouracil (5-FU), a broad-spectrum anticancer drug, was included into the composite hydrogels. Under physiological settings (pH 7.4), the model drug's release was maintained, but it was accelerated in an acidic or reducing environment. Because of its cheap cost, biodegradability, biocompatibility, non-toxicity, and minor immunogenicity, CMC has been extensively employed in tissue engineering applications. Biomimetic CMC/dopamine tissue adhesive hydrogels were inspired by mussel sticky proteins. Due to the interfacial interactions between the catechol moieties of the hydrogel and the biomolecules on the wet tissue surface, the materials had a six-fold increased wet tissue adhesion force over a commercial suture agent (fibrin glue). Furthermore, the gels showed excellent biodegradation and biocompatibility.

As a result of recent reports that CMC has the capacity to promote bone growth, several investigations have been undertaken on its bone tissue engineering applications. Using calcium phosphate (CaP)-loaded NaCMC nonwoven sheets made by immersing protonated CMC alternately in calcium chloride and sodium phosphate solution, researchers looked at how well they might stimulate osteoblast development and bone repair in vivo. Even after lengthy storage at room temperature, CMC provides a good support for protein and enzyme immobilization [62].



# Konjac glucomannan (KGM)

Konjac glucomannan (KGM) is the key ingredient of konjac tubers, which are a longstanding Araceae plant. Konjac glucomannan has been shown in biomedical studies to improve health by limiting cholesterol in the blood and striving to improve carbohydrate metabolic activity, bowel movement, and colonic ecosystems. KGM is a staple ingredient that is commonly used to thicken and bind gravies, curries, sauces, animal fat, and livestock. In an alkaline medium or when coupled with certain other hydrocolloids like as xanthan gum or k-carrageenan, KGM can form hydro gel. These gels are essential building blocks in a variety of food implementations, including jelly, noodles, tofu, and snacks. Collagen and KGM have been used to transport drugs in living organisms. The combined emulsion effect of collagen and konjac glucomannan can improve collagen dissolution in aqueous. The physical properties of collagen, KGM, polyphenols, and ginsenoside Rb1 with polyphenols and ginsenoside Rb1 may influence the ability to control release of drug. Furthermore, the appearance of these polymers in the complex can aid in the bioactivity and storage of polyphenols and ginsenoside [63].

KGM is a naturally existing substance polysaccharide retrieved from the tubers of Amorphophallus konjac. It is a copolymer made up of of  $\beta$ -(1,4)-linked D-glucose and D-mannose residues in a molar ratio of 1:1.6 with a lower degree of acetyl moieties at the C-6 position (1 in 17 residues, approximately). The structural representation of KGM is given in Fig. 13.

Because of the appearance of very active primary hydroxyl (CH<sub>2</sub>OH) functional groups at the C-6 position of KGM, a variety of chemical treatment, including graft polymerization, are conceivable. KGM is extensively used in pharmaceutical and food applications due to its high viscosity, extremely good water retention capabilities, gelling potency, non-toxicity, biocompatibility and biodegradability. Recently, a KGM-based superabsorbent polymer (KSAP) was created by grafting acrylic acid (AA) onto a KGM template and irradiating it with 60Co-g at room temperature. FTIR spectroscopy and SEM imaging data analysis were used to characterize KSAP. The transplant of AA onto KGM was revealed by the large effect in bands in the FTIR spectra of KSAP, KGM, and AA. XRD patterns revealed that crystalline structure in KSAP was lower than in native KGM. SEM images revealed a rough surface in the case of KGM and a micro porosity in the case of KSAP. The relatively

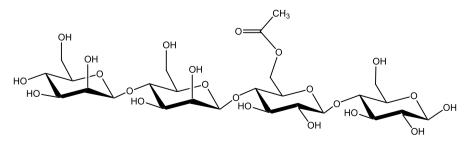


Fig. 13 Structure of Konjac glucomannan (KGM)



hydrophilic nature of KSAP resulted in greater velocity and abilities for water absorption. Graft copolymers compiled with an amount of radiation of 5.0 kGy and a monomer to KGM ratio of 5 could accumulate 625 times their dry weight in water. Ions, especially multivalent positively charged ions, considerably lowered KSAP's water permeability power [64]. In comparison with many other thermoreversible gels, KGM forms a thermally balance gel after the addition of an alkaline agglomeration, and the gelation of KGM is aided by heating. Gelation happen as a consequence of the arrangement of a network structure of crossing zones that are thought to be established by hydrogen bonding. The green pharmaceutical characteristics of KGM that contribute for its behavior in nanotechnology based drug delivery mechanism include its elevated concentrations of mannose, which effectually enables the communication of KGM with biotic surfaces that really are extremely lucrative in mannose synapses, such as M-cells enveloping Peyer's fragments and phagocytosis. Ionic gelatinization of chitosan with TPP (chitosan/TPP ratio values of 3/1 and 6/1) yielded chitosan nanoparticles [65, 66]. By solubilizing phosphorylated KGM in the nanoparticle rescinding medium, it was possible to incorporate it onto the nanoparticle configuration. Intra-molecular hydrogen bonds, as well as electrostatic interactions among oppositely charged groups in phosphorylated KGM derivative and free – NH<sub>3</sub><sup>+</sup> in chitosan, are responsible for the heterotypic relationship in this co-gelled system. As the chitosan/konjac glucomannan ratio changes from 6/6 to 6/24, the nanoparticles' hydrodynamic diameter decreases from 800 to 400 nm. Regardless of the CS/KGM ratio, the zeta potential of these nanoparticles was close to the expected neutral value, ranging from -0.4 to -2.3 mV for about the same content. This has been explained as a result of the plant polysaccharide shielding the chitosan charges. The addition of KGM fiber to a diet may enhance metabolic functional capacity in humans, and rats with low levels of KGM have lower plasma cholesterol. KGM can also be fabricated into films or formed into blend film for coating and packaging implementations, and KGM gels have considerable potential applications in a controlled release matrix [67, 68].

#### Lignin

Lignin is the second most prevalent biomaterial in plant species after cellulose and is a fundamental natural biopolymer found in the cell walls of woody materials. This is one of the basic components with a high potential for use in the production of bio fuels, and it can be used as an operational polymer in the synthesis of bio-based polymer blends [69].

Lignin is among the most common natural polymer found in plants. Lignin, the second most prevalent renewable bio-resource after cellulose, is regarded as a solid waste in a variety of industrial processes. Attempts to valorize lignin have been posted in a large number of articles and reports in recent years. The significant characteristics of lignin, such as its abundance, inexpensive, and biodegradability, increasing carbon content, aromaticity, and reinforcing abilities, make it an excellent candidate as a potential component for bio-composites. Over 50 million tons of lignin are produced as a by-product of bio refineries each year, with 98 percent of it



being burned to generate energy. Only 2% of the lignin has been used for other purposes, primarily as dispersants, adhesives, and fillers. Commercial lignin consists primarily of lignosulfonates from sulfite pulp mills (approximately 1 mill. ton/year) and less than 100,000 tons/year of Kraft lignin (KL) [70].

Depending on the application, lignin can be used as a factor in biocomposites with or without modification. Acetylated KL was used to optimize its affinity with PLA. The incarnation of Kraft lignin, on the other hand, diminished the tensile ultimate strength of the PLA with rising lignin loadings of 10% and 20%. Additionally, when acetylated lignin was combined with a thermoplastic, the tensile strength was increased. Lignin can be integrated directly into a polymeric matrix without reconfiguration, such as a UV-light stabilizer, antioxidant, flame retardant, plasticizer, and flow enhancer, to reduce the cost of manufacture, plastic, and potentially enhance mechanical characteristics. Lignin can also be used as a coupling agent in bio composites made from natural fibers. Lignin can act as a cross-linking agent between hydrophilic fibers and hydrophobic matrix polymers, thereby reinforcing the fiber matrix interface. Lignin therapies of hemp and flax fibers have been shown to improve the compatibility of the fibers with the thermoset matrix, thereby enhancing the mechanical strength of the biocomposites. When compression-molded PLA-cotton composites were treated with lignin, the tensile properties improved. Lignins are formed through the polymerization of cinnamyl alcohols (monolignols), the structure of which varies depending on the plant type Coniferous wood lignin is almost entirely composed of coniferyl alcohol (G-units), with minor amounts of coumaryl alcohol (H-units) present. The latter, on the other hand, is a major component of condensing wood lignin. In wood fibers, however, both coniferyl alcohol and sinapyl alcohol (S-units) are used as building blocks, and all three alcohols are used as lignin precursors in monocotyledonous tissue [71, 72]. The chemical structure of lignin is given in Fig. 14.

Coniferous wood lignin is almost entirely made up of coniferyl alcohol (G-units), with only trace amounts of coumaryl alcohol (H-units). In contrast, the latter is a crucial constituent of condensing wood lignin. Coniferyl alcohol and sinapyl alcohol (S-units) are both used as fundamental building blocks in wood fibers, and all three alcohols are lignin blueprints in monocotyledonous tissue [72].

The polyurethane (PU) reaction is used to stabilize the soil for building engineering, in which two types of solution were implanted deep into the earth before tunneling and then the soil was exhumed after the reaction was completed. This strategy is beneficial when removing a large amount of soil with an excavator because it relieves the risk of collapse. However, the eliminated soil that has been cross-linked by synthetic polymers is not biodegradable. To address the aforementioned issue, an attempt was made to use lignin polyol to stabilize sand. The quantity of lignin polyol used is less than 5% of the total sand, and a crystallized sand block can be obtained. It has also attempted to develop PU composite encapsulated fertilizers that can be kept in the soil for a longer period of time by releasing slowly [73].

The Mannich reaction was used to make a low-cost, environmentally friendly, and magnetic lignin-based nano-adsorbent. Phosphate was effectively removed from solution via adsorption. Furthermore, the nutrients in magnetic adsorbent nanoparticles, such as recycled phosphate and chelated iron, can be reused as a multielement



$$CH_2OH$$
 $C=O$ 
 $CH_2OH$ 
 $CH_2OH$ 

Fig. 14 Structure of lignin biopolymer

fertilizer. The release behaviors revealed that the Fe and phosphorus release rates from M/ALFeP increased steadily over time, reaching 69.1% and 67.2 percent after 30 days in neutral soil, respectively. Batch experiments on cycle adsorption revealed that M/ALFe has good recyclability and reusability, lowering costs and avoiding soil pollution. As a result, a method for making lignin-based high-value-added nanomaterials in wastewater treatment has been developed, and phosphate-laden nanoparticles as Nano fertilizers show promise in sustainable agriculture [74]. A number of bio-based composites based on starch, lignin and cellulose were fabricated from an ionic liquid, 1-allyl-3-methylimidazolium chloride and coagulated in a system without solvent. The study found that the mechanical strength of the biocomposites was evidently depending on the contents of lignin, starch and cellulose, resulting from the mutual supplement among different components. High gas barrier ability and great thermal stability were clearly observed in the biocomposites. Holocellulose and acid insoluble lignin of Pecan nutshell fiber were utilized as reinforcements of PLA-based bioplastics. Because of its radical scavenging activity, lignin can act as a stabilizer in protein-lignin bioplastics. Thermal molding was used to incorporate KL and WG into materials. During material mixing, the results suggested that KL has a radical phagocytic action toward thiyl radicals.

The good connection of WG and KL was confirmed by size isolation HPLC. To improve the physical and functional properties of the bioplastics, different concentrations of alkali lignin and lignosulfonates were added to enzymatically modified



Fig. 16 Structure of agarose

soy protein. Alkaline lignin and lignosulfonates showed typical radical scouting activity when compared to commercial butylated hydroxytoluene, suggesting that they could be used in active packaging. The blends with alkaline lignin had a strong UV-blocking ability due to the color of the lignin. Thermal stability and tensile stability of the lignin-added films were significantly improved when compared to the control films without lignin [75].

#### Agar

Agar is a polysaccharide mixture made composed of agarose and agaropectin with carrageenan-like functional characteristics. It is largely derived from red algal cell walls. They are recovered in the same way as carrageenans are: with hot water. Agars are employed as emulsion and suspension stabilizers and gelling agents, similar to carrageenans. Agar is utilized in the food sector for around 90% of its output; the rest is used to create capsules for clinical use and as a medium for bioreactors for cell and tissue development. Agar contains a few bioactive characteristics and modulates UV light absorption [76, 77].

These are members of the Rhodophyceae family of red seaweeds. Agarose, which is responsible for gelling, makes up the majority of agar. Its structural unit is made up of (1–4) linked 3,6-anhydro-a-L-galactose and (1–3) connected b-D-galactose units that alternate. The structures of agar and agarose are given in Figs. 15 and 16.

It is among the natural polymers with the strongest mechanical properties. Microbial growth has little effect on the gel since agar is not enzymatically degradable by



most bacterial species. As a result, it will remain stable, and microbial deterioration will be low. Its high crystallinity guarantees a high level of strength and stiffness. The food-grade agar used in this investigation was made by Urban Platter in Mumbai, India. Gelation hysteresis is a unique feature of agar biopolymer. As a result, the temperatures at which it melts and gels varies significantly. The temperature at which agar begins to dissolve in water is roughly 85 °C, while the actual temperature varies depending on the agar source. When the temperature goes below 30–40 °C, the viscosity of an agar solution increases, and it forms a stiff unyielding gel. By combining agar with soil in the form of a heated solution and enabling it to gel within the porous medium of the soil sample, this feature of agar was used to generate homogeneous soil specimens [78, 79].

The biopolymer agar has lately been investigated for soil erosion management and improved hydraulic conductivity. Among biopolymers, agar has the maximum mechanical strength. Within the soil mass, it can create a three-dimensional gel network, forming a thick film and covering the soil particles. Furthermore, the agar biopolymer's complicated structure assures that it is less biodegradable. It has a long history of safe food consumption, which supports its environmental friendliness [80].

Seaweed-based nanoparticles were utilized to construct and test the effect of using seaweed nanoparticles filler in agar-based biopolymer composite on improving physical water vapor barrier, mechanical, and biodegradable qualities, according to recent research. When agar-based biopolymer is reinforced with seaweed nanoparticles, the characteristics of the biopolymer alter, although there are no visible changes in the water vapor transfer rate (WVTR). The mechanical strength of the agar-based biopolymer was increased by increasing the concentration of seaweed nanoparticles, indicating that the agar-based biopolymer composite incorporating seaweed nanoparticles could be used in food industrial applications such as food packaging to replace petrochemical-based plastics [81].

Proteins (beans, seaweeds like agar–agar, and seeds), starches (pectins and gums), and certain other plant tissues are employed to stabilize emulsions in longer-lasting suspensions. Dressings, frozen desserts, jellies, mousses, pickles, puddings, salad dressings, sauces, and yoghurt are all common uses for stabilizers [82].

Agar is the most often used microorganism growth medium. Because of the ease with which agar may be moved (dry, dissolved, and gelled), it is widely used in modern laboratories. When fed with adequate nutrients, solid agar plates can promote microbial growth or be used for antibiotic selection. Agar medium is vital for the study of microorganisms and molecular biology, and it is frequently employed in pathogen cultivation and detection from contaminated food and water [83]. Agar is also commonly employed in biomolecular separation and purification due to its porous 3D architecture. Agar is a basic medium that is commonly used in gel electrophoresis, gel bead chromatography, and size exclusion chromatography. Aside from being used as a solid growth medium, agar has been manufactured in various forms (e.g., microspheres and films) to encapsulate molecules for continuous drug administration or to immobilize proteins for tissue engineering. Because of agar's gelation capability, it is most commonly utilized as a hydrogel. To provide long-term medication administration, agar hydrogels were modified by including additional



Fig. 17 Chemical backbone structure of PVA

Fig. 18 Synthesis of PVA

biopolymers to build an interpenetrating network. This agar hydrogel network topology can increase the mechanical properties of drug delivery devices while also extending the drug release profile. Agar hydrogels with high porosity have demonstrated encouraging outcomes in tissue engineering for promoting cell adhesion and proliferation [84, 85].

## Poly(vinyl alcohol)

Herrman and Haehnel developed poly(vinyl alcohol) (PVA) in 1928, which is an odorless and tasteless transparent white or cream-colored granular powder. PVA is a non-toxic, semicrystalline, biocompatible, and biodegradable polymer that is soluble in water. Textile sizing, paper coating, flexible water-soluble packaging films, controlled drug administration systems, dialysis membrane, wound dressing, and artificial skin are just a few of the uses. Due to its remarkable qualities, such as strong oxygen and aroma barrier capabilities, high tensile strength and flexibility, and great film building, emulsifying, and adhesive properties, it has a broad range of applications. The fully hydrolyzed and partially hydrolyzed grades of PVA have melting points of 230 °C and 180–190 °C, respectively. It may pyrolyze at high temperatures and has a decomposition temperature of around 200 °C [86, 87]. The chemical backbone structure of PVA is given below (Fig. 17).

PVA is a thermoplastic biopolymer made from the hydrolysis of the polyvinyl acetate precursor. The following is the PVA synthesis (Fig. 18):



The activity of biological microbes degrades it. Because of its increased crystal-linity, it is extremely soluble in water. Many polymer end goods, such as liquors, surgical threads, and food packaging, are made with PVA. It is a polymer that is strong, ductile, and extremely flexible. PVA is a biodegradable and non-toxic polymer that is used in food packaging. Contact lenses, heart surgery, medication administration, and wound dressing are just a few examples of biomedical uses [88, 89].

Other polymers, such as food additives like citric acid, succinic acid, and tartaric acid, could be blended with the biopolymer PVA. In the packaging industry, PVA blended with poly(3-hydroxybutyrate) (PHB) can be used. PVA/CS films have mechanical, water vapor barrier, and antibacterial qualities that make them suitable for use in food packaging. For food packaging applications, PVA has been investigated active packaging with grapefruit seed extract (GSE) and PVA. Active films from apple pomace and PVA for antibacterial activities during food packaging applications have been discovered in recent hybrid study [90, 91].

Halloysite nanotube (HNT) is a non-toxic material used largely for medicine delivery in medical applications and food packaging. As a result, HNTs were used in this study as natural reinforcement for a feasible poly(vinyl alchol)/starch/glycerol/Halloysite nanotube, (PVA/ST/GL/HNT) nanocomposite film to enhance its water resistance and water contact angle, as well as its mechanical and thermal behavior, serving as a novel application for food packaging in the industries [92].

Although PVA hydrogels have been the most extensively studied biomaterials for articular cartilage replacement due to their biocompatibility, permeability, load-bearing characteristics, and ease of preparation, it has been discovered that they lack the surface lubrication and biomechanical strength that natural cartilage requires. The use of doxorubicin-encapsulated hydroxyapatite-polyvinyl alcohol (DOX-HAp-PVA) nanocomposite for osteosarcoma-affected bone tissue healing has been demonstrated in the recent study [93, 94]. In recent years, PVA or its extracts hydrogel microparticles and NPs have been reported for a variety of drug carriers, including PVA NPs encapsulated by poly(lactide-co-glycolic acid) (PLGA) microparticles and paclitaxel-loaded PVA-g-PLGA NPs for the treatment of restenosis, as well as DNA nanocarriers obtained by a modified solvent displacement method. Since the late 1990s, PVA in the form of hydrogel NPs has been employed for protein/peptide medication delivery [95]. The novelty production of a homogeneous microstructured HAp/PVAP nanocomposite might have applications in bone implantation [96].

# Polycaprolactone (PCL)

PCL is a biodegradable semicrystalline aliphatic polyester with a melting point of approximately 60 degrees Celsius and a glass transition temperature of around 60 degrees Celsius. In physiological settings (such as the human body), PCL is destroyed by hydrolysis of its ester bonds, and as a result, it has attracted a lot of interest for usage as an embedded biomaterial [97]. The structure of PCL and its monomer unit is given in Fig. 19.

It has been proved that the first synthesis of PCL by thermal treatment of ε-caprolactone. Despite several studies focusing on the radical ring opening



Fig. 19 Chemical structure of A PCL and B PCL monomer unit

polymerization (RROP) of 2-methylene-1,3-dioxepane (MDO) under various conditions and the condensation of 6-hydroxycaproic acid, PCL is still primarily synthesized by ionic and metal catalyzed ring-opening polymerization (ROP) of the cyclic monomer  $\varepsilon$ -caprolactone [98], which is given in Fig. 20.

PCL's physical, thermal, and mechanical qualities are largely determined by its molecular weight and degree of crystallinity, which also influence its capacity to breakdown under physiological circumstances (through hydrolysis of its ester bonds). PCL is extremely hydrophobic, semicrystalline, highly soluble at ambient temperature, and easy to process due to its low melting temperature and excellent mix compatibility, prompting researchers to investigate new uses, mostly in the biomedical industry [99]. Because it is versatile for multiple manufacturing techniques, poly(caprolactone) (PCL) has been an exceptional polymer for use as a biomaterial in scaffolding for use in tissue engineering as well as bioabsorbable sutures, wound dressings, and adhesion boundaries among synthetic biodegradable polymers. Scaffolding techniques can be characterized as soft or hard tissue applications in the context of tissue engineering and regeneration. Selection of material and fabrication

Fig. 20 Different synthesis methods of PCL biopolymer



process should be examined due to the variations in soft and hard tissues and their needs. Recent research on the usage of PCL-based scaffolds in tissue engineering applications are discussed in the next section [100]. The details of applications, origin of various biopolymers have been discussed in tabular form later (Table 2).

# Polylactic acid (PLA, Polylactide)

PLA, a leading contender, is a thermoplastic, high-strength, high-modulus polymer that may be manufactured from yearly renewable resources to generate a variety of components for application in industrial packaging or biocompatible/bioabsorbable medical devices. It can be easily processed into molded pieces, film, or fibers using ordinary plastic processing equipment [116]. PLA is one of the most promising biopolymers as a bioabsorbable polymer since the monomers may be made from non-toxic renewable feedstock and because it is a naturally occurring organic acid. PLA has stereoisomers such as poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLA). Lactic acid (2-hydroxypropionic acid, LA), a PLA component unit, occurs as two enantiomers, L- and D-lactic acid [117]. PLA biopolymer has chiral chemical structure containing asymmetric helical orientation, which given in Fig. 21.

Lactic acid is produced by fermenting sugars derived from renewable sources such as sugarcane or maize starch. As a result, PLA is a more environmentally friendly substance with greater properties for usage in the human body (non-toxicity). PLA is the first commercial polymer made from renewable resources that are harvested once a year [118].

Poly(lactic acid) is made through a polycondensation process that starts with lactic acid. L-lactide polymerization gives PLLA, whereas D-lactide polymerization yields PDLA. Except for stereochemistry, PLLA and PDLA exhibit identical characteristics. PLA may also be made with different proportions of L and D lactide. After the polymerization process, the un-reacted monomer must be removed by washing with ethanol, since the remaining monomer in the polymeric matrix might function as a plasticizer, lowering the mechanical strength and thermal stability of PLA [119]. The PLA synthesis reaction is depicted in the diagram below (Fig. 22).

PLA/CS-based copolymers have a higher material potency and a longer time to degrade. In vivo tests show that PLA strength is sufficient for 8–12 weeks after implantation. PLA may be useful for internal bone fixation, according to these data. PLA has also been shown to retain a high level of infertility, which aids in infection prevention. To promote cell proliferation, orthopedic implantables made of PLA can be injected with osteogenic or anabolic bioactive. Biodegradable fixation devices can help prevent osteopenia from occurring as a result of stress shielding caused by metallic implants. PLA produced with a L-LA/D-LA ratio of 85/15 was effectively employed to make screws and fixing plates for fracture fixation. The findings demonstrated that the plates may be used to mend fractures without the requirement for extra support [120–122].

PLA has the potential to play a substantial role in tissue regeneration. PLA scaffolds may carry bioactive medicines that aid wound healing, similar to drug delivery systems targeting carcinomas. Drug-loaded PLA scaffolds, on the other hand, may



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-	Chitosan	Sources: crustacean shells, such as lobsters, crabs, and shrimp, as well as fish scales and a variety of other creatures (insects and fungi)	Biomedical applications, bioplastics, nanocomposites, textile industries, packaging of food, fuel cell, Wastewater treatment,	[101]
7	Gelatin	Sources: Pig (porcine skins) and cow bones or beef hides, malian skins, biovin hides fishes, salmon, catfish, squid, bigeye snapper, cuttlefish, lizardfish, etc.	Food industry, crime scenes, fingerprints, gelling agent, cosmetics (bath salts, shampoos, sunscreens, body lotions, hair spray and facial cream), medical industry, pharmaceutical industry, medicine, wine and beer, controlled drug delivery, wound dressing, etc.	[102]
8	Starch	Sources: Maize, wheat, rice, potatoes, banana, cassava, etc.	Food industry (baked foods, confectioneries, pastas, soups and sauces, and mayonnaises), medicine, textile, paper, fine chemicals, petroleum engineering, agriculture, and construction engineering, physical and chemical modifications, drug delivery applications, pharmaceuticals industries, etc.	[103]
4	Cellulose	Sources: Agro-waste, domestic-waste, wood, plant, paper, bamboo, sugar beet, banana rachis, potato tubers, cotton, fique, kapok, agave, jute, kenaf, flax, hemp, vine, sisal, coconut, grass, wheat, rice and barley, etc.	Bio-fuels, consumables, film-forming agent, thickener, blocker, sustained-release agent, blending agent and suspending agent, wound dressing, drug carrier, pharmaceutical applications, food, drug delivery, coating of solid dosage, scaffolding, biomedical implants such as cardiovascular implants, Bone and connective tissue repair, etc.	[104]
<b>5</b> 0	KGM	Source: roots of the elephant yam, bulb of the konjac plant	Improve metabolic control, lowering plasma cholesterol in rats, formation of films and blend membranes, coating and packaging, controlled release matrix, food additives, thermoreversible gels	[89]
9	Lignin	Sources: agricultural residues, hemp, cotton, woody biomass, and energy crops, jute, wood pulp, etc.	Pharmaceutical industries, wound dressing, wound healing, medicine, photocatalyst, drug delivery, controlling disease, immune booster, electrospinning, water treatment, power sources, electrochemical energy materials, synthesis of polymers, dyes, adhesives and fertilizers 3-D printing- plastic composite, etc.	[105]



Table 2	Table 2 (continued)			
SI. No	Sl. No Biopolymers	Origin: Sources/synthesis	Applications	Refs.
7	Agar	Sources: Found in the cell walls of certain species of red algae such as Gracilaria and Gelidium	Antibiotic selection, culture and detection of pathogens from contaminated food and water, bimolecular separation and purification, gel electrophoresis, gel bead chromatography, drug release, tissue engineering, drug delivery, vaginal capsules, bacteriological culture, food industries,	[106]
∞	PVA	Synthesis: Obtained by the polymerization of vinyl acetate monomers followed by partial hydrolysis	Textile, paper industry, and food packaging industry, gene therapy	[107, 108]
6	PCL	Synthesis: Using a catalyst such as stannous octanoate, PCL is made via ring-opening polymerization of &-caprolactone	Plastics, weather resistance, drug delivery, tissue engineering, additives, food industry, textile industry, chemical factory, steel manufacturing, automobile industries, paper industries, etc.	[109]
10	PLA	Source: wheat, straw, corn, and sorghum etc. Synthesis: ring opening polymerization of lactate	Tissue engineering, bone re generation, implants, industries, drug delivery, food industry, medical devices, dialysis, plastics, 3- D printing, etc.	[110]
11	Gallen Gum	Source: It naturally occurs on water lilies, secreted by the microorganism <i>Sphingomonas elodea</i> , Synthesis: synthesis chemically by fermenting sugar with a certain bacterium strain	Thickener, binder, and stabilizer in different food applications, stabilizes the water-based gels, such as desserts and drinking jellies, yogurt and sour cream in vegan items, bone repair and cartilaginous tissue regeneration	[111]
12	Pullulan	Source: Produced aerobically by growing a yeast like fungus  Aureobasidium pullulans	Food industry (coating or packaging material of dried foods, including nuts, noodles, confectionaries, vegetables and meat), binder for (tobacco, seed coatings and plant fertilizers), adhesives, pharmaceutical industry (tablets, pills, granules), flocculating agent, rayon industries, paper industries, printing and writing, photographic, lithographic and electronic applications, etc.	[112]
13	Dextran	Synthesis: synthesized by the action of the bacterium <i>Leuconostoc</i> mesenteroides	Anticoagulant, treatment against shocks, surgery, trauma, burn, drug, etc	[113]



Jable 2	lable 2 (continued)			
Sl. No	Biopolymers	SI. No Biopolymers Origin: Sources/synthesis	Applications	Refs.
41	Curdlan	Source: Produced by bacteria, such as Alcaligenes spp., Agrobac-terium spp., Paenibacillus spp., Rhizobium spp., Saccharomyces cerevisiae, Candida spp., and fungal sources like Aureobasidium pullulan, Poria cocos, etc. Synthesis: Biosynthesis of curdlan from glucose (uridine diphosphate (UDP)-glucose pyrophosphorylase)	Food (pasta, canned meat) and Dairy products, Therapeutic products, Adjuvant, Antioxidant and anti-inflammation agent, Protection against hyperglycemia, immunomodulation, anti-allergic activity, etc	[114]
15	Scleroglucan	Scleroglucan Sources: Produced by various filamentous fungi especially of the genus Sclerotium, belonging to the phylum basidiomycota. Industrially it obtained from, S. rolfsii and Sclerotium glucanicum, Schizophyllum commune, Botrytis cinerea, and Epicoccum nigrum	Oil industry for thickening, discharge of drilling mud's and enhanced oil recovery, construction engineering, adhesives, water colors, printing inks and liquid animal feed composition, thickener in paintings, stabilizer in fire drencher foams and in pesticides used in agriculture, food industry (stabilization of dressings and ice creams), cosmetics, creams and protective lotions, pharmaceutical products, drug delivery, antitumor, antiviral and antimicrobial compound, immune-stimulator, etc	[115]



Fig. 21 Chiral structure of PLA biopolymer

Fig. 22 Synthetic route of PLA biopolymer

be limited owing to unanticipated changes in the scaffold's and/or pharmaceuticals' characteristics during the synthesis method. The PLA/PEG-based porous matrix films for the delivery of gentamicin sulfate or metronidazole for wound dressing treatment have been described in recent studies [123]. PLA-based drug delivery systems have showed potential in cancer therapy therapeutic methods. PLA scaffolds offer a particularly desirable property for drug delivery systems: long-term drug release, thanks to their adjustable breakdown rate. In cervical cancer mice models and in vitro studies, PLA stereo complexes demonstrated drug transport potential. Improved tumor cell absorption of anti-tumor drugs is aided by sustained doxorubicin release. As a consequence, as compared to non-loaded drug performance, tumor cell activity was reduced using the drug delivery mechanism. Doxorubicinloaded stereocomplex micelles also showed increased tumor prevention rates [124]. Modern technical breakthroughs have broadened the scope of critical care equipment uses. In response to the COVID-19 outbreak, 3D printing has been used to manufacture ventilators that can handle many patients. Novel studies described a 3D-printed circuit splitter that allowed two patients to be ventilated using a single ventilator [125, 126].

#### Gellan gum

Gellan gum is a water-soluble negatively charged polysaccharide generated by Pseudomonas elodea. It is generally made up of a tetrasaccharide, which is made up of two D-glucose residues and one each of D-glucuronic acid and L-rhamnose residues. One of the most costly hydrocolloids is gellan gum in the market [127].

Gellan is a linear anionic heteropolysaccharide with a straight chain made up of 1.5:1:1 molecular ratios of the building ingredients d-glucose, l-rhamnose, and



d-glucuronic acid. The chain is made up of a tetrasaccharide repeat unit that is joined together by  $\beta$ -(14)-linked glucose, glucuronic acid, glucose, and rhamnose in  $\alpha$ -(13) linkage given in Fig. 23. The natural product is partly esterified, with a C2-linked 1-glycerate and roughly 50% C6-linked acetate substituents in the (13)-linked glucose residue. Two acyl substituents—acetate and glycerate—are present in its natural or high-acyl form. Both residues are found on the same glucose residue, with one glycerate and one acetate for every two repeating units on average. After heating and cooling, the molecule is anticipated to acquire a two-or triple helical form, according to X-ray diffraction investigations [128].

Gellan gum is a non-cytotoxic substance that may be injected into tissues. It has been employed as an eye medication delivery vehicle in humans in vivo [13]. Gellan is a gelling agent that is widely used. It may, however, be utilized to make structured liquids that are very effective suspending agents. These structured liquids are gelling systems that were sheared during or after the gel formation [129]. In comparison with other polysaccharide hydrogels (carrageenan, alginate, and agar), gellan gum hydrogel is less pH dependent. As a result, gellan gum is widely employed in the medical and food industries. Despite the fact that gellan gum hydrogel has good gelation and mechanical properties, there are few reports of gellan gum hydrogel 3D printing [130]. Ionically cross-linking gelation through trivalent aluminum cations and covalent cross-linking have been used to create a new type of glipizide-loaded acetylated gellan gum hydrogel networking beads in recent study (using glutaraldehyde). Spherically shaped trivalent aluminum cation-induced gellan gum beads were shrunk with distinctive wrinkles on the filament surface after treatment with glutaraldehyde for drug delivery techniques [131]. Despite having unique features that make it ideal for producing wound healing dressings, gellan gum remains an underutilized polysaccharide. Gellan is also endotoxin-free when purchased commercially and has been found to be a viable material for tissue engineering. Gellan gum has also been studied for use in the administration of antimicrobial medications to wounds and as a non-toxic tissue engineering scaffold. As a result, gellan gum has the potential to be used as a multipurpose dressing that can be used as an in situ gelling liquid or a hydrogel sheet. Despite the fact that gellan gum is an appealing wound healing source material, there are limited published data on its effectiveness in vivo [132, 133].

Fig. 23 Chemical structure of Gellan Gum



#### **Pullulan**

Pullulan is a microbial polymer generated in the extracellular matrix of Aureobasidium pullulans, a polymorphic fungus. It is a linear homopolysaccharide made up of repeated units of maltotriose and maltotetraose linked by  $\alpha$ -(1,6) and  $\alpha$ -(1,4) linkages. Although pullulan's chemical composition is mostly made up of repeating maltotriose units, maltotetraose repeating units can make up to 7% of the overall length. Regular changes in the  $\alpha$ -(1, 6) and  $\alpha$ -(1, 4) bond geometry result in important features including structural flexibility and high solubility [134, 135].

Pullulan is a non-hygroscopic polymer that is soluble in water but not in organic solvents [except DMSO]. It is also esculent, non-toxic, and non-carcinogenic, with a decreased viscosity in aqueous solutions. Pullulan's repeated linking pattern [ $\alpha$ -(1,6) and  $\alpha$ -(1,4)] gives thermal stability up to 250 degrees Celsius. It possesses a number of distinguishing characteristics, including fiber formation, adhesiveness, and biodegradable film formation. As a result, pullulan is used as a blood plasma replacement, as well as a culinary, beauty products, and medicinal ingredient [136, 137]. The chemical structure of pullulan is given in Fig. 24.

Pullulan solutions aid in the maintenance of normal colloid-osmotic pressure in the blood and tissues, as well as the extension of plasma supply. It functions as a plasma extender, providing the required therapeutic impact while avoiding unwanted side effects. Pullulan, when mixed to antigens or viruses as a carrier, makes it easier to inject antigens or viruses into animals, resulting in antibodies or antiviral vaccinations. Pullulan gels can be used to purify enzymes chromatographically or as a support for enzyme immobilizations [138]. Pullulan bioconjugates can be deployed to target tumors and deliver genes or drugs. Pullulan-containing hydrogels can help with wound healing, function as molecular chaperones, and minimize phototoxicity.

**Fig. 24** Chemical structure of pullulan, bears  $\alpha$ -(1, 4) linkage and  $\alpha$ -(1, 6) linkage



Pullulan and its derivatives, like other polysaccharides, can be utilized to improve the biocompatibility of different nanoparticles as well as their colloidal stability [139, 140].

When compared to direct application on the food surface, the benefit of integrating antimicrobials into pullulan films is the control and gradual release of the compounds over time. There are three benefits to employing pullulan packaging films as an antibacterial delivery technique for meat and poultry products. When antimicrobials are included into pullulan films and coatings, less antimicrobial is required to inhibit microorganisms on food surfaces. Furthermore, antimicrobial-containing pullulan films exhibited long-term inhibitory efficacy and allowed for regulated antimicrobial component transfer from the film to the food product [141].

#### Dextran

Dextran is a hydrophilic polysaccharide made up of D-glucopyranose with  $\alpha$ -1,6 linkage shown in Fig. 25. Dextran is made from sucrose and maltodextrins, respectively, using dextransucrase and dextrinase enzymes. Dextran may be broken down using dextranase, which can be found in mammalian tissue [142]. Dextran is a non-toxic, biocompatible polysaccharide extensively utilized in pharmaceutical and biological applications [143]. Dextran has been extensively employed in organ transplantation to minimize inflammatory responses, circulatory thrombosis, and ischemia reperfusion damage as a reactive oxygen species scavenger and excess platelet activation reduction. Dextran can be utilized as a blood supplement in emergency situations, according to reports. Dextran has also been utilized as a coating on substrates to increase their biocompatibility [144, 145]. The chemical structure of dextran is given in Fig. 25.

Dextran appears to have antithrombotic effects as well as the ability to build scaffolds that prevent protein and cell adhesion. Dextran-based scaffolds have been examined for use as coatings for brain implants because of this. Dextran has been used as a biomaterial in several biomedical research because it is biocompatible, biodegradable, and accessible in a variety of molecular weights, as well as being easily derivatized [146].

Fig. 25 Chemical structure of dextran



In the field of tissue engineering, a novel conductive interpenetrating polymer network (IPN), preparations of hydrogel composed of polyaniline-grafted gelatin, carboxymethyl CH, and oxidized promotes, conductive hydrogels have gained considerable attention, combining conductivity properties with the ability to form a three-dimensional network. Cell attachment, proliferation, and differentiation can all be aided by these hydrogels. The amino groups of modified gelatin were connected with carboxymethyl CH using oxidized dextran as a cross-linker in that study [147].

Dextran-modified liposomes have been studied for a range of biological applications, including improved thrombolysis, vascular targeting, and the formation of pH-sensitive liposomes. Liposomes were enhanced using a pH-sensitive dextran derivative containing 3-methylglutarylated residues as an efficient antigen-delivery method. They were able to successfully transfer antigen into the cytoplasm of dendritic cells (DCs). The formulation increased the induction of antigen-specific humoral and cellular immune responses in mice when given subcutaneously. Also, Human endothelial cells were targeted using liposomes modified with functionalized dextran [155]. The details of chemical modifications of some specific biopolymers along with modified skeletal structures have been given in tabular form discussed later in Table 3.

#### Curdlan

Curdlan is a bacterial polysaccharide produced by Alcaligenes faecalis fermentation, and its linear structure is made up completely of  $1,3-\beta$  glucosidic links found throughout nature shown in Fig. 26. Curdlan has lately gotten a lot of interest because of its remarkable gelling qualities, which include the capacity to form either a thermo-reversible or thermo-irreversible gel and powerful physiological functions including anti-tumor and anti-HIV activity [156].

Alkali-soluble curdlan biopolymer, microbial nutrition, and acid-producing alkaliphilic bacteria were combined together and injected into Berea Sandstone cores [157]. Due to their intrinsic biological activity and capacity to form polymeric matrices, sulfated curdlan has medicinal uses as an antiviral and anticancer drug [158]. The anticancer effects of MGlu-curdlan-modified liposomes were greater than those of dextran derivative-modified liposomes. Furthermore, even in the absence of a traditional lipid adjuvant (MPLA), MGlu-curdlan-modified liposomes generated robust antitumor immunity, that may be due to MGlu-strong curdlan's adjuvant function and MGlu-curdlan-modified liposomes' excellent intracellular delivery capability [159, 160].

## Scleroglucan

Scleroglucan is a neutral polymer generated by aerobic fermentation by the fungus Sclerotium rolfsii. Scleroglucan is a branched neutral homopolysaccharide composed of a linear (1–3)-linked  $\beta$ -D-glucan main chain with (1–6)-linked  $\beta$ -D-glucopyranosyl groups connected to every third residue. Scleroglucan produces by



Table 3 Recent chemical modification of some specific biopolymers with specific reagents and their modified structures

SI No	Biopolymer	Modifying agent	Modified biopolymer	Refs
1	Starch—CH	O CH —CH2CI	CH Starch—O—OH, CHCH2—O—Stand	[148]
2	Starch — OH	Cl Cl NaOH	O Starch — O PO — Starch O'N a	[148]
4	HO OH OH OH OH	0		[149]
	Cellulose	Malei c anhydride		
5	HO NH <sub>2</sub> Chitosan	Lacto bio nic aci d HOOC - N <sub>3</sub>	10 10 01 01 01 01 01 01 01 01 01 01 01 0	[150]
6	HO NH <sub>2</sub> Chito san	нs-сн <sub>2</sub> -соон carbodiimide	H 0 H N 0 H N	[151]
7	$\operatorname{Gelatin}-\operatorname{NH}_2$		Gelatin—N	[152]
8	Gelatin — NH <sub>2</sub>		Gelatin H OH	[153]
9	Dextran	N ₄BH.CN and Hexamethylene diamine	NO COLUMN NE	[154]

Fig. 26 Structure of biopolymer curdlan

the fungus that forms linear rod-like triple helices that are kept together by intermolecular hydrogen bonds [161]. The chemical structure of scleroglucan is represented in Fig. 27.



Fig. 27 Structure of scleroglucan

Scleroglucan has a variety of industrial uses, but it was first utilized in the oil sector for thickening, discharge of drilling muds, and increased oil recovery, where it outperformed xanthan and other polymers in terms of efficiency and durability. In building engineering, scleroglucan and other pseudoplastic biopolymers are used. Adhesives, water colors, printing inks, and liquid animal feed formulation are among the other industrial applications. Scleroglucan would be ideal for the stability of sauces and ice creams in the food business. However, food safety law in Europe and the USA has yet to authorize scleroglucan [115].

# **Characterization of biopolymers**

The capacity to correctly assess and validate the structures and purity of biopolymers is provided through characterization. When novel materials are being synthesized, a competitor product is being analyzed, or a product's performance has to be enhanced, biopolymer characterization is critical. The molecular weight distribution, molecular structure, shape of biopolymers, thermal characteristics, mechanical properties, and any additions are all part of polymer characterization. Microscopy methods, FTIR spectroscopy, NMR spectroscopy, and XRD are all covered in the physicochemical characterization section. Physical characterizations of biopolymer membranes and films, such as swelling, degradation/erosion degree, and Porosity measurements, are then explained. Finally, the primary biological characterizations, such as cytotoxicity and antimicrobial research, are presented.

### Physicochemical characterization

#### Nuclear magnetic resonance (NMR)

For the determination of polymer structures and the presence of functional groups in polymer chains, NMR is the most sensitive and powerful enabling technology. NMR



spectroscopy provides information on the number of magnetically different atoms of the type being researched and is a frequent technique for determining the structure of a chemical as well as material purity. The sample weight is less than a milligram, and the substance might be solid or liquid, pure or mixed. In fact, when used in conjunction with IR spectroscopy, it generally provides enough information to establish the chemical structure [162, 163].

NMR can be a useful tool for biopolymers. Recent research using 23Na<sup>+</sup> NMR measurements has been conducted, and they have proven to be significant in the investigation of anionic biopolymers as blood flow sensors [164]. The use of NMR to analyze the antibiotic lipopeptide daptomycin in 1,2-dihexanoyl-sn-glycero-3-phosphocholine micelles was reported in the recent study [165]. Solid-state NMR is useful for studying the structure and dynamics of insoluble and non-crystalline biopolymers, and it's also useful for probing membrane protein structure and dynamics in natural lipid membranes, despite its low sensitivity and poor resolution. Additionally, some approaches, such as magic angle spinning in solid-state NMR spectroscopy to characterize the structural dynamics of biopolymers at atomic resolution, can be employed to optimize the research [166, 167].

#### **XRD**

The XRD method is used to determine if a material is crystalline or amorphous. It will specify how cementation materials will be quantified. The atomic arrangement, crystallite size, and defects of crystalline materials may all be investigated via XRD analysis. An X-ray source of Cu Ka radiation (11/4 1.5406 Å) is used for the XRD examination. It will use the Brag Brentano approach to evaluate and identify unknown crystalline substances [168, 169]. Because each solid substance has its own X-ray diffraction pattern, this approach may be used to determine the phases and components present. The XRD approach involves concentrating an X-ray beam at an initial angle of  $2\theta$  on the biopolymer membrane or film and then reading the intensity of the diffracted ray using specialized detectors. Following the reading, the incident ray's angle  $2\theta$  is changed for a fresh reading up to a final  $2\theta$  value Bragg's law governs the diffracted beam by crystalline phases (Eq. 1)

$$\lambda = 2d (\sin \theta) \tag{1}$$

where 'd' is the crystalline phase separation between atomic planes, ' $\lambda$ ' is the incident radiation wavelength, and ' $\theta$ ' is the angle of incidence with respect to the evaluated plane. A copper radiation source (Cu K $\alpha$ ) with a 2 scan range from 5 to 70 degrees (0.20 degrees/min–0.30 degrees/min scanning speed) is often utilized for biopolymer film examination [170, 171].

#### SEM

Scanning electron microscope (SEM) is an acronym for scanning electron microscopy. The SEM is a microscope that creates images by using electrons rather than light. The sample picture is created when an electron beam interacts with the atom



sample, creating various signals that are collected by detectors. Because biopolymers are non-conductive, SEM examination requires the sputtering of a thin coating of metal [172].

The SEM method is utilized for surface and fracture investigation in biopolymer films and membranes, allowing for the determination of sample structure and morphology features. The surface of biopolymer films and membranes is generally smooth and uniform, especially when created using the casting process [173]. Depending on the film preparation technique and/or biopolymer mixing, a porous structure can be observed by SEM on the surface and fracture analysis in some circumstances. SEM may be employed as an essential tool to validate the structure of the sample on silk fibroin/gelatin multilayered films, according to a recent study. This approach is important because it offers three-dimensional images of the eye's interior, which aids knowledge of component components' surface morphology [174, 175].

#### **TEM**

When an electron beam is conducted through a testing material sample, transmission electron microscopy (TEM) pictures are acquired from electron interactions with resources. Because of the 3-D effect, TEM pictures offer more detailed views of the surface. In compared to SEM photos, the images acquired through TEM analysis provide a more enlarged perspective of the material TEM gives a more comprehensive surface morphology to understand the behavior of the contacts before and after the interactions due to the magnification and 3-D analysis capabilities. The thickness of the outer surface of the testing material may also be determined using TEM images [176, 177].

Microstructural investigation of biopolymer films and membranes not visible by SEM, such as microporous structures generated in a modified film production process, can be done with the TEM method [178]. In biopolymer composites, TEM is also utilized to investigate nanoreinforcement dispersion [179].

#### **FTIR**

Infrared spectrometry is for investigating how matter interacts with light radiation, especially infrared radiation in the electromagnetic spectrum. Chemical substances and materials can be identified and characterized using infrared spectroscopy. In biopolymers, FTIR may be utilized to investigate the different functional groups and interactions. Hydrogen bonding, amide linkage, and other interactions may be easily spotted by studying the spectra [180]. Attenuated total reflection (ATR) sampling device-based Fourier transform infrared (ATR-FTIR) spectroscopy is one of the methodologies being studied. It needs minimum sample preparation, allows for simultaneous estimation in both lab and field settings, and is simple to use. Variable-temperature Fourier transform infrared (FTIR) absorption spectroscopy was used to explore the thermotropic phase behavior of a group of recently created self-forming synthetic biopolymers [181]. The FTIR method has been extensively utilized to investigate the physical and mechanical



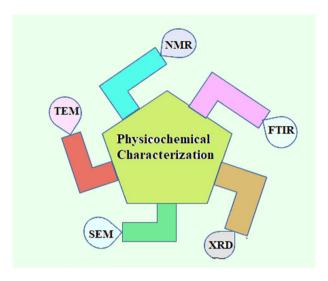


Fig. 28 Physicochemical characterization of biopolymers

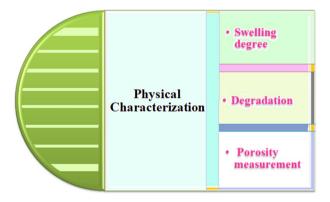


Fig. 29 Physical characterization of biopolymers

characteristics of biopolymers in a number of research. The ATR spectral intensity changes of immature and mature cotton fibers were studied using two-dimensional (2D) correlation mapping [182]. The interactions between several biopolymers in its composite materials may also be verified via FTIR measurement [183]. The vibrational ranges of biopolymers were used to identify the specific functional group of the biopolymers, such as ketones, R-CO-R, which absorb at 1730–1740 cm<sup>-1</sup>. R-COOH carboxylic acids have two distinct bands at 1700 cm<sup>-1</sup> and about 3500 cm<sup>-1</sup> that correspond to the C=O and O-H stretching vibrations of the carboxyl group, -COOH. Carboxylic salts or metal carboxylates absorb at 1550–1610 cm<sup>-1</sup>, while saturated/aromatic carboxylic acids absorb at 1680–1690 cm<sup>-1</sup> [184]. Although different characterizations of biopolymers can be presented pictorically as in Figs. 28, 29, 30.



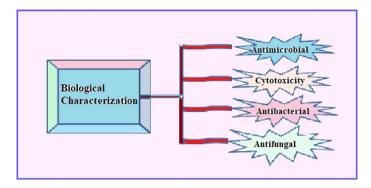


Fig. 30 Biological characterization of biopolymers

### Physical characterizations

#### Swelling degree

Polymer swelling is a mass transfer process caused by fluid diffusion into the substance. The tendency of polymeric systems to absorb the solution of interest, quantified in mass or volume is termed as swelling degree. Polymer swelling capacity is determined by the nature of the polymer, the solvent/polymer interaction, and the polymer structure, and it is a quality that has a direct impact on its use. Because of their natural source and hydrophilicity, most biopolymers are more vulnerable to the action of water (swelling characteristic) [185].

Swelling degree studies typically include measuring the sample's initial mass and the mass after 't' time in contact with the solution of interest. The swelling degree is expressed as a percentage in Eq. (2):

Swelling Degree (%) = 
$$\frac{W_t - W_0}{W_0} \times 100\%$$
 (2)

 $W_0$  is the initial sample mass and  $W_t$  is the sample mass after 't' time.

The swelling degree of biopolymers is a useful parameter for determining material behavior after application. Low swelling qualities are required for food packaging applications, since they provide better barrier features [186]. Swelling behavior is an important feature in rehydration and exudates absorption for wound-healing applications. For the optimum wound-healing environment, enough moisture must be given to prevent dehydration, bacterial development, and infection [187, 188].

#### Degradation

The focus of biopolymer degradability research is on unwanted behavior or property loss upon application. The word 'degradability' relates to the capability of a polymer to deteriorate during or shortly after application. Photodegradation, mechanical degradation, thermal degradation, and chemical degradation are all examples of biopolymer degradation. Photodegradation is the degradation of polymer chains



caused by ultraviolet (UV) light and radiation; mechanical degradation is the effect of mechanical forces on polymer stability; thermal degradation is the degradation of the polymer caused by temperature changes; and chemical degradation is the degradation of the polymer caused by hydrolysis, enzymatic degradation, or pH change [189].

Sample mass loss and mechanical property loss are the most typical criteria used to assess biopolymer degradation. Degradation degree by sample mass is calculated by Eq. (3)

$$Degradation(\%) = \frac{W_i - W_t}{W_i} \times 100\%$$
 (3)

where  $W_i$  and  $W_t$  are the dry weight of the sample with respect to time 't.'

The degradation degree is computed by measuring the mass or mechanical characteristics of a sample in a simulated application environment (simulating chemical composition, pH, and temperature). Microscopy (in general, SEM method) may also be used to see biopolymer erosion since deterioration destroys the biopolymer structure. For a wide range of applications, determining the degree of degradation/erosion of biopolymer membranes and films is critical. Degradation can be a goal attribute depending on the application, for as in biodegradable bags and skin tissue engineering [190–192].

### Porosity measurements

Porosity measurement is a physical characterization method for determining the capacity of polymer film membranes to absorb water. The procedure entails A little piece of uniformly sized pre-weighed polymer films was submerged in the solution like alcohol. The film fragments are removed after a few minutes, and the ultimate weight is calculated.

The porosity of the polymeric film membrane can be calculated by using mathematical formula is given below in Eq. 4

Porosity 
$$(P) = (W_2 - W_1)/(\rho V_1)$$
 (4)

where  $W_1$  and  $W_2$  are the weight of the film before and after immersing in the alcohol solution, respectively.  $V_1$  is the volume of the solution taken before the immersing the film and  $\rho$  is the density of the solution.

#### **Biological characterization**

#### Cytotoxicity

Nowadays, most tests are carried out in vitro, in accordance with international recommendations to reduce in vivo testing. To evaluate the effect induced by the biomaterial's exposure to the cells, the first three biocompatibility tests can be done using cell cultures, either primary or cell lines. The cytotoxicity test, which is done



on all biomaterials, employs BALB/c 3T3 mouse fibroblasts or normal human epidermal keratinocytes as the cytotoxicity endpoint and neutral red uptake as the cytotoxicity endpoint. Other vital dyes, such as 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) or 3-(4,5-dimethyl-2-thiazolyl)-5-(3-carboximetoxiphenyl)-2-(4-sulfophenyl)-2H-tetrazolium bromide (MTT), might be used [193]. The toxicological endpoint linked with substances that have the inherent capacity to produce skin sensitivity is known as sensitization. An overreaction of the adaptive immune system causes this negative consequence. Sensitization was induced on the initial touch with allergy symptoms, and subsequent interaction resulted in sensitization [194, 195].

## **Antimicrobial activity**

In terms of antimicrobial activity, the biostatic or biocide microbiological characteristics of films in solid or liquid media may be determined. The procedure used will be determined by the qualities of the film as well as the microorganism to be utilized. The Clinical and Laboratory Standards Institute standards for macrodilution and microdilution in broth might be used to test antimicrobial activity. Employing bigger volumes and, as a result, more samples, macrodilution is used. In both situations, the microorganism was put in varied quantities to the tubes (macrodilution) or 96 microplate wells (microdilution), and the films were added in proportion. There were both positive and negative controls. Using pure medium as a control, the final concentration was determined as the minimum concentration that resulted in no observable bacterium development after 24 h of incubation at 37 °C, depending on the studied microorganism. The biostatic level was evaluated by plating a 100 L solution from the test tubes onto agar plates without obvious bacteria growth and incubated for further 24 h at 37 °C. The films are regarded biostatic if there is growth, but they are also considered biocides if there is no growth [196, 197].

## **Applications of biopolymers**

#### Water treatment

Novel approaches for water purification have been developed by researchers. Water recycling solutions that include green water treatment are also being researched. Due to the remarkable qualities of biopolymers, using natural polymers in membrane synthesis, manufacturing, and production to create entirely biodegradable membrane materials becomes perfect and appealing [198]. The adsorption—desorption process has recently been utilized to remove chlorophenoxyacetic acid herbicides from water using orange peel-activated carbon. As a result, chlorophenoxyacetic acid herbicides were considerably absorbed from water by this bio-sourced activated carbon. Membranes may be adjusted using these biopolymers. Because of their abundance of polysaccharides, cellulose polymers have been widely used in water applications [199]. Membranes made from carboxymethyl cellulose (CMC), cellulose nanofibrils (CNF), and bacterial cellulose (BC) modified cellulose with



various functions. As a result, the azo and anthraquinone dyes were effectively removed from wastewater using these modified membranes [200].

The electrospun cellulose acetate nanofibrous membrane may filter out chromium, metal ions, and hazardous organic compounds in addition to microorganisms. For the removal of lead from contaminated water, magnetic nanoparticles immobilized on cellulose acetate nanofibrous membranes were created [201]. The densely interconnected porous cellulose acetate nanofibers membrane with homogenous distribution over the polymer bodies has been discovered to have a unique use in water filtering. The cellulose acetate nanofibrous membrane has an average fiber diameter of 30–110 nm. As a result, the electrospun cellulose acetate membrane contains homogeneous, continuous, smooth, and interconnected porous nanosized fibers, which are mostly used to filter microorganisms in water [202].

Biopolymer-based flocculants have the promise to be scaled up for commercial use. A triangle assessment model was designed to evaluate the effectiveness of biopolymer-based flocculants in wastewater treatment in terms of economic sustainability [203]. Chemical flocculants such as polyaluminum chloride (PAC) were utilized in the removal of chemical oxygen demand (COD), suspended solids (SS), and aluminum (Al<sup>3+</sup>) from unclean water during water treatment. CS composite flocculants produced utilizing a mixture of CS, polyaluminum chloride, and silicate were shown to be more effective in eliminating contaminants than standard flocculants [204]. Tanfloc, a natural polymer derived from Black acacia, was compared to the commercial synthetic polymers Flopam and Zetag for flocculation of microalgae, Nannochloropsis oculata, and Chlorella vulgaris. Both commercial and biopolymers effectively treated both fresh and marine water, showing that Tanfloc, a natural polymer, can be used as a promising polymer due to its cheap cost and environmentally benign properties [205].

#### Tissue engineering applications

Chitosan has a number of intriguing features, including the ability to form a gel, increased adsorption capacity, superior biodegradability, exceptionally high biocompatibility, and non-cytotoxicity, as well as enhanced biological qualities including antifungal, antibacterial, and antitumor activity. Because of its strong cell adhesion, cell survival, cell interaction, and neurite outgrowth, the hydrogel form of chitosan is most commonly utilized in tissue engineering. Long-term stability, elasticity, self-assembly, and biological activity are all characteristics of elastin, a structural protein. Elastin is a protein that provides elasticity to organs and tissues. It is found in organs, particularly elastic ligaments, blood vessels, skin, and the lungs, where elasticity is important. Where the elastic effect in parts of our body, such as skin and blood vessels, is visible, the insertion of elastin inside biomaterials is extremely important. As a result, it is more commonly employed for soft tissue regeneration [206, 207].

In the recent decade, interest in DNA- and RNA-based scaffolds has grown at an exponential rate. DNA-derived polymers can build nanostructures or tridimensional networks among hybridized DNA or RNA chains, in addition to serving as



cross-linkers between copolymers, as in DNA-acrylamide hydrogels. When certain sequences were recognized by the enzymatic complex, DNA-based hydrogels were used to regulate the mechanical characteristics of the materials. Hydrogels based on DNA-polyamide (DNA-PA) have improved cellular behavior and may be used for tissue cultivation in live organisms. The convergence of poly(ethylene glycol) diacrylate (PEGDA)/DNA hybrid hydrogels for a cell-free system using a physically cross-linked DNA network-based cell fishing technique has been described in recent works. As a consequence, bone marrow mesenchymal stem cells were efficiently captured via 3D enveloping and enzyme-triggered release [208, 209].

## **Drug delivery**

The qualities of biopolymers and their derivatives were superior in terms of functionality, water solubility, non-toxicity, biodegradability, and biocompatibility. Furthermore, by releasing drugs in a regulated manner, these biopolymers can lessen medication toxicity. Collagen is the most prevalent protein in the animal kingdom, consisting of a glycine–proline–hydroxyproline repeating unit in a triple helix shape. It has been used in drug delivery applications as microparticles, coatings, and films due to its good biocompatibility [210].

The most ubiquitous biopolymer, cellulose, has outstanding mechanical and biological features such as biocompatibility, low cytotoxicity and biodegradability. Microcrystalline cellulose (MCC), cellulose nanomaterials (CNC and CNF), and bacterial nanocellulose (BNC) are examples of materials with different aspect ratios that are good prospects for drug delivery systems [211]. Chitosan-drug conjugation is among the most effective drug delivery methods. Various molecular weights of chitosan were utilized for conjugation formation, and the cleaving condition might be pH or GSH (glutathione) sensitive depending on the drug type. For any sensitive protein or gene delivery, chitosan hydrogel production is another option [212].

#### Agriculture applications

A variety of natural biopolymers incorporating pesticide active groups have been commercialized in order to generate suitable controlled release combinations for fungicides and herbicides. When coupled with one or more fungicides, the gum biopolymers have a specific use in the defense of seeds against fungal pathogens [213].

Chitin and CS are naturally occurring chemicals that have the potential to manage plant diseases in agriculture. They were shown to have antifungal, antiviral, antibacterial, and antiparasitic properties. They have also been used to chelate nutrients and minerals to prevent diseases from gaining access to them, as well as to boost plant defense [214].

A degradable agricultural mulching film made from a starch-polyvinyl alcohol film containing up to 40% starch, urea, ammonia, and varying amounts of low-density polyethylene (LDPE) and poly(ethyleneco-acrylic acid) (EAA) might be covered with a thin layer of water-resistant biopolymer [215].



The biopolymeric coating offers various advantages, including the ability to extend the active ingredient's action. Because it releases the appropriate quantity of active agent over a longer period of time, biopolymer coating permits significantly smaller amounts of effective component to be employed than traditional pesticides [216].

To allow an initial burst of 2,4-D followed by a regulated bioactive release, the non-toxic and biodegradable matrices of cellulose derivatives ethylcellulose/hydroxy propyl methyl cellulose (HPMC), cellulose acetate butyrate butyryle (CAB)/HPMC, and pure CAB were utilized in microparticles. This method enabled for high herbicide effectiveness to be achieved early on and to be maintained for a long time [217].

### Food packaging

polyhydroxyalkanoates (PHAs) are now one of the most abilities of different to fossil-derived polymers in the Bioeconomy, with the greatest potential to replace polyolefins in packaging applications, due to their biocompatibility and physical qualities,. Although cellulose acetate's gas and moisture barrier qualities are not ideal for food packaging, it is ideal for items that require a lot of moisture since it allows for breathing and avoids fogging [218, 219]. According to recent study, PE and PP packaging foils coated with CS and polyphenol colloidal formulations have a lot of promise as active (antioxidant and antibacterial) packaging in the food business [220].

## Application of biopolymer for energy

Biopolymers are used to study polymer electrolytes. Membranes holding ions dissolved in polymer serve as polymer electrolytes. Ionic conduction requires the presence of electron donor atoms, such as N, O, or S, in the polymer. The dissolved salt cations have just a weak interaction with these atoms. Conductivity in polymer electrolytes is influenced by both cations and anions. Biopolymers Only two of the compound's atoms, O and N, have a lone pair of electrons. Since chitosan's backbone comprises hydroxyl, ether (C–O–C) and amine functional groups, it may be designed to address the needs of a particular application. The presence of polar functional groups in their structure explains their water-attracting abilities [221].

Dissolving CS in acetic acid produces a membrane layer with extremely low room temperature conductivity ( $-10^{-10}$  to  $10^{-9}$  S cm<sup>-1</sup>). It may, however, function as a matrix for ionic conduction because of its strong film-forming capacity and ability to solvate numerous inorganic salts. Adding lithium salt or ammonium salt to chitosan for proton conduction improves the conductivity at room temperature. An very high conductivity ( $2.42\pm0.01$ )× $10^5$  (S cm<sup>-1</sup>) was achieved using the phthaloylation combination of 70% phthaloyl chitosan–30%NH<sub>4</sub>SCN (S cm<sup>-1</sup>) [222].

Glucose molecules with three hydroxyl functional groups are bonded to form the polymer cellulose. It is defined as the average number of substituted hydroxyl groups per glucose in the specified form of methyl cellulose. Because of the presence of lone pair electrons on the oxygen atoms in methyl cellulose, these atoms



may function as complexation sites and interact with salt cations in a weak way. An electrolyte based on methylcellulose exhibits ionic conductivity when composed of 63.75 weight percent methylcellulose, 21.25 weight percent NH<sub>4</sub>NO<sub>3</sub>, and 15 weight percent PEG, as well as 75 weight percent methylcellulose, 25 weight percent NH<sub>4</sub>NO<sub>3</sub> –  $1.1 \times 10^{-4}$ , and  $2.10 \times 10^{-5}$  (S cm<sup>-1</sup>), respectively [223].

Recently, it has been shown that polymer electrolyte membranes are very efficient and dense in energy. By using biopolymer in polymer electrolyte fuel cells (Fig. 31), less CO<sub>2</sub> is released into the atmosphere, which benefits the environment.

Solid gellan gum (GG) polymer electrolyte for energy use has been shown in recent study. Solid gel electrolyte synthesis based on carbohydrate polymer (Phytagel/GG) was established in this work. As a dye-sensitive solar cell material, this substance might be used (DSSC) [224].

In chemistry, physics, materials, and microelectronics, biopolymers are employed in FETs. Material applications expand beyond sophisticated biological devices to electrical/electronic materials, making them unique for electronic switches, storage devices, gates, biosensors, and biologic transistors. Due to their vast surface area, excellent electrical conductivity, and porous nanostructures, biopolymers are being employed to produce Supercapacitor (SC) (more ion adsorption and active sites for the charge transfer reactions). Biopolymer dielectrics boost supercapacitor efficiency. Due to their cheap cost and photolytic ecofriendliness, biopolymers are employed in LED, PV, and photodetector systems [225].

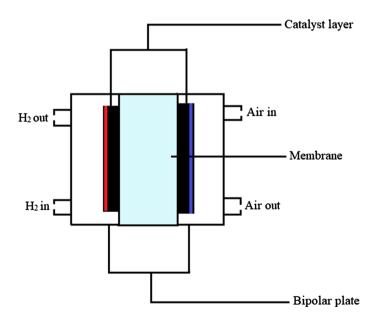


Fig. 31 Diagram showing polymer electrolyte membrane fuel cell



### **Environmental application**

Biopolymers are viable alternatives to non-renewable goods because of their biodegradability, environmentally benign production methods, and broad variety of uses. Since synthetic polymers have harmed our ecosystem, it is clear that any attempt to get materials from renewable sources that degrade rapidly in the environment is critical if we are to repair the damage done by their indiscriminate use and avoid further deterioration. Biopolymers such as lipids, polysaccharides, and proteins, which have been examined as renewable raw resources and are viewed as a replacement to plastic non-biodegradable and based on petroleum, have been increasingly in demand in recent decades [226].

The thermoplastic nature of biopolymers means that they have many of the same qualities as petroleum-based plastics. Unlike synthetic materials, biodegradation by bacteria, fungus, and algae yields products such as CO<sub>2</sub>, water, and compost. Polyhydroxyalkanoates (PHA), a biopolymer generated by microorganisms, has physical qualities comparable to petroleum-based plastics (e.g., are rigid, brittle or flexible) [227].

Polyaniline-based titanium dioxide nanocomposite (PANIs/TiO<sub>2</sub> NCs) has been shown to have been blended by hydrothermal and low-temperature thermal treatment processes in recent study. Photocatalytic activity for the liquid-phase breakdown of methyl orange (MO) was shown to be greater in the PANIS/TiO<sub>2</sub> NCs when irradiated with both UV and visible light. An improved sol–gel photocatalytic activity was used to make the hierarchical 3-D flowerlike TiO<sub>2</sub>/PANIs NCs, which were effective in degrading organic contaminants when exposed to visible light. Under visible-light irradiation, Pei et al. created a synergetic effect of ZnO/PANIs NCs by chemisorption and a cold plasma treatment approach [228].

To enhance soil properties, biopolymers may be useful because of their biodegradability, which has no detrimental impact on the environment. Also, unlike MICP, biopolymer treatment may be utilized to enhance soil with a finer particle size distribution. Biopolymers also have an advantage over MICP since they do not need to be injected with nutrients before they can be utilized to enhance the ground. Research has shown that biopolymers like Guar Gum (GG), Xanthan Gum (XG), CS, and Beta 1,3/1,6 Glucan (BG) can significantly enhance the engineering qualities of soil [229].

## **Advanced biomedical applications**

Biopolymers have a wide range of medical applications, including occlusion, suturing, covering, fixing, isolation, adhesion, cellular proliferation, controlled drug delivery, contact inhibition, and tissue guiding. As a result of their outstanding pliability and consistent knot toughness, poly-(L-lactic acid), poly-(glycolic acid), and copolymers of these two substances are commonly used as sutures. Poly(ortho ester) and poly-hydroxy groups are often used in medication delivery. In order to create artificial blood arteries, polyurethanes must have properties like pliability, hardness,



and resistance to wear and tear [230, 231]. The administration of drug delivery, the creation of hydrogels, and tissue engineering all benefit from the use of polyesteramides. These include surgical masks, gloves, surgical gowns, towels, sanitary napkins and diapers as well as surgical headgear, panties shielded and antimicrobial textiles for surgical curtains and surgical curtains as well as wipes. In surgical gowns, bio-based PET may be used in lieu of cotton, polyester, and PE [232]. Due to the adaptability of polylactic acid, it may be used to create a wide variety of items, including but not limited to hats, gowns, and masks. For its remarkable absorption properties, thermoplastic starch is an essential ingredient in the manufacture of diapers for young children. Alginate fibers, catgut, collagen, chitosan, and superabsorbent polymer are just a few of the biomaterials often used in medical and hygienic applications [233].

## Challenges and future perspectives

In this review, we discussed the potential use of biopolymeric materials in bioengineering applications, which has been expanded by evaluating their physical, mechanical, degradability, biocompatibility, etc. qualities, the most promising province technologies for the synthesis of smart biopolymers, and the varied green uses in bioengineering.

The most pressing issues for humanity in the future will be energy and resources, food, health, transportation and infrastructure, and communication. Biopolymers will be crucial in overcoming these issues. Polymers will be the material of the next century, and their manufacture will provide global access to the best solutions. Synthetic biopolymers have long been used in medicine. Synthetic polymers are used to make medical devices and artificial organs. Future pharmacy may also use synthetic polymers. Polymer science can conserve energy and boost renewables. In the future, fossil fuels will not meet global energy needs. Fuel cells are intended to help achieve the aim. Fuel cells may replace batteries and ICE generators. Next, research will be commercialized. Fuel cells will be a worldwide commodity. Modifying biopolymer and nanofiller characteristics may increase their use in electrical components.

Biopolymers are expected to rise in value as new solid adaptations are developed and the cost of manufacturing these bio-plastics continues to decrease. Bio-plastics may replace conventional plastics in a variety of applications, such as food packaging, plastic plates, mugs, cutlery, and storage packs, and so assist to reduce the impact on the environment.

Electrical industries have increasingly accepted plastics for plugs, sockets, wire and cable insulation, and housing electrical and electronic equipment. Major polymer-targeting sectors include ceramics, stem cell biology and regenerative medicine, packaging, food retorting, automotive, aerospace, and electronics.

According to research, smart packaging may improve the accuracy of predicting the expiration date and time of packaged food and materials. Further study on biopolymer and filler nanoparticles will provide nutritious packaged food and increased shelf life for both food and packaging.



In the future, new biopolymer-based materials with regulated functions will be developed, allowing for a wider range of biomedical applications. Bioengineering, biochemistry, and molecular biology advancements in recent years have contributed to enhancing the biological performance of biopolymer-based formulations and new application areas.

Cellulose is a sustainable biomedical material that has encouraged researchers to develop innovative cellulose-based products. Cellulosic materials have good physical and biological characteristics, biocompatibility, biodegradability, and low cytotoxicity, making them ideal for tissue engineering scaffolds, wound and burn dressings, medical implants, and drug delivery systems. Surface and/or bulk changes of cellulose allow for novel functional materials. Modification alters materials' physicochemical characteristics, particularly at the nanoscale. Future studies should examine how foreign molecule inclusion affects nanocellulose's cytotoxicity and biocompatibility. The use of organic—inorganic bionanocomposite for vaccine administration is a relatively new phenomenon, and the area has yet to witness substantial advancements. Calcium phosphate, iron oxide, and layered double hydroxides are some of the nanoparticles that might be useful in these applications.

This is an exciting new field of study that capitalizes on the synergistic assembly of biopolymers and nanosized solids derived from natural or synthetic organic and inorganic compounds.

#### **Conclusion**

Over the last few decades, there has been a progressive development in industry interest in biopolymers and biopolymer-based green goods. Biopolymers are renewable, non-toxic, environmentally friendly, biodegradable, lightweight, easy to manufacture and have a high skeletal behavior that improves mechanical strength and stiffness and can be customized to meet a variety of performance needs. Many factors influence the qualities of hybrid biopolymer-based materials, including chemical composition, specific temperature, environmental effect, particle size, and surface area. The comprehensive study showed that biopolymers are acceptable with tissue engineering, drug control, agricultural, pharmaceutical, biomedical, bioengineering, and food sectors, as well as that they have a wide range of uses. Further research on biopolymer-based products has the potential to replace conventional harmful non-biodegradable materials in the near future. When these bioproducts grow more durable and function better, there is the potential for the establishment of new markets. Continuous research into performance and life-cycle evaluation is required to determine the biopolymers' usefulness.

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