# Polymeric Materials from Renewable Resources

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## Abstract

The growing worldwide interest in renewable polymers may be attributed to both worries about the environment and the limited availability of petroleum. There are three types of polymers that fall under the category of renewable: natural polymers, synthetic polymers made from bioderived monomers, and microbial fermentation polymers. While certain natural polymers are used extensively in the production of consumer goods, others are mostly ignored. The processes of isolating, purifying, chemically modifying, and physically modifying natural polymers all need to be improved. A synthetic polymer made from bio-based lactic acid is called poly(lactic acid). It can be worked with in the same manner as other thermoplastics, but the exorbitant cost of the material prohibits its widespread use. Increased interest in researching and developing biodegradable polymeric materials may be attributed to the recent appearance of the first commercially available biodegradable polymeric materials on store shelves. Even in potentially fruitful applications like as packaging and mulch films, the majority of currently used polymers are not being replaced because of either poor performance or expensive costs. Rarely are either petroleum or renewable polymers used in isolation. The processes of blending and compositing increase productivity. Composites made from renewable materials came before polymers. The mechanical characteristics of polymers may be improved by fibers. Because of the availability of renewable raw ingredients, cellulose fiber-reinforced polymers are making a comeback. The majority of plant parts are made of cellulose. The majority of naturally occurring polymers are functional when combined with hydrophilic cellulose. Filler reinforcement is very necessary for renewable polymers to have in order for them to have reduced softening temperatures and moduli. One of the benefits is that the hydrophilic compatibility of the mineral filler with the majority of natural polymers. Natural polymers that are hydrophilic and water-soluble The fact that it is soluble in water hastens the process of disintegration, but its sensitivity to moisture restricts its use. Blends of natural and renewable polymers as well as multilayer constructions may result in improved characteristics. Blends have the potential to provide low-cost goods with superior performance. The value of renewable polymers is being increased via the use of inventive blends and composites.

## Introduction

During the last two decades, there has been a significant uptick in interest in polymers that are derived from renewable resources due to increasing awareness of the limited nature of the world's petroleum reserves. Additionally, this helps farmers make additional money. Polymers derived from renewable resources can be broken down into three primary categories: natural polymers, which include starch, protein, and cellulose; synthetic polymers from bioderived monomers, which include poly(lactic acid) (PLA); and polymers derived from microbial fermentation, which include polyhydroxybutyrate. Natural polymers include polymers such as polyhydroxybutyrate.

The study of natural polymers and the use of their products date back many millennia. Artifacts composed of everyday materials including skin, bone, silk, and paper have been found in museums all around the globe. Some of these artifacts date back thousands of years. The natural environments that natural polymers call home are home to a diverse array of uses for these materials. Polysaccharides serve as components of membranes as well as a means of intracellular communication. Proteins serve both as building blocks and as catalysts. Lipids serve as energy storage. There is a broad range of polymers that may be found in nature. These polymers can be processed into a large number of different things, including fibers, adhesives, coatings, gels, foams, films, thermoplastics, and thermoset resins. The broad availability of low-cost petroleum and the biochemical inertness of goods based on petroleum wreaked havoc on the natural polymer sector and caused it to collapse. It took almost half a century, but people are now starting to understand the benefit of producing goods that are less harmful to the environment. During the course of the last decade, considerable shifts in these age-old materials have been brought about by the environmental problem as well as the continuously rising cost of oil.

There is a vast range of naturally occurring polymers that may be derived from environmentally friendly sources and used in a number of different material applications (Scholz & Gross, 2000). Starch, cellulose, and rubber are just a few examples of the materials that are often included into today's industrial processes; yet, there are a great deal of other materials that are still mostly underutilized. In certain instances, the classification of natural polymers is possible via the use of the physical features of the polymers. Although the chemical classification system separates cellulose fibers and starch granules into separate groups, both of these substances are regarded to be polysaccharides. The table (1) contains examples of natural polymers.

**Table (1): List of Natural Polymers (Kaplan, 1998)**

Polysaccharides
- from plant/algal: starch, cellulose, pectin, konjac, alginate, caragreenan, gums
- from animal: hyluronic acid,
- from fungal: pulluan, elsinan, scleroglucan
- from bacterial: chitin, chitosan, levan, xanthan, polygalactosamine, curdlan, gellan, dextran

Protein
soy, zein, wheat gluten, casein, serum, albumin, collagen/gelatine
silks, resilin, polylysine, adhesives, polyamino acids, poly($\gamma$-glutamic acid), elastin, polyarginyl-polyaspartic acid

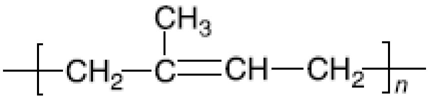
Lipids/Surfactants
acetoglycerides, waxes, surfactants, emulsan

Speciality Polymers
lignin, shellac, natural rubber

## 1- Natural Rubber

Natural rubber is one of the most well-known and mature types of materials, and it has seen a significant amount of use in today's culture. After its usefulness had been recognized as early as the beginning of the seventeenth century, widespread production of rubber did not begin until the early years of the nineteenth century. There are two main cell types that are able to participate in the production of rubber in plants. These cell types are called latex-vessel-specific cells and parenchyma cells. The most prevalent mode of transportation is latex boats. Several research facilities have investigated the potential of introducing genes for the production of rubber into the genomes of different species of animals.

The chemical structure of polyisoprene is seen in Figure (1); all such latexes have a milky white appearance. Coagulation techniques allow for the recovery of natural rubber. Its molecular weight is 3 x $10^6$ g/mole and its glass transition temperature is at -70°C. Large cis-polymerizations, characteristic of rubber, are concentrated in the molecular core. The amount of these condensations is the most significant determinant of the molecular weight and molecular weight distribution of rubber, and it varies greatly across various types of rubber.



$$-\left[ CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2 \right]_n-$$

**Figure (1): The chemical structure of natural rubber.**

Olefinic double bonds at every fifth carbon atom make natural rubber very reactive. Thus, natural rubber is high-molecular. Due to high unsaturation and tight double bonds, they are susceptible to free radicals and oxidation. The molecule may undergo hydrogenation, addition, and substitution. Chlorinating rubber to 65 weight percent completely chlorinates its double bonds, rendering it inert. Natural rubber is insoluble in aromatic, aliphatic, and chlorinated solvents due to its large molecular weight.

Additives include carbon black fillers, antioxidants, plasticizers, colors, and vulcanizing chemicals improve the chemical and physical qualities of natural rubber, which would otherwise be unusable. Vulcanized rubber is not biodegradable, however biodegradable literature seldom mentions natural rubber-based goods. Natural rubber is one of the earliest natural materials utilized.

Acylation, peroxide, permanganate, alkaline, and silane may increase the compatibility of natural fiber and rubber matrix, according to various scientific studies. Silane and permanganate have been used to change the surfaces of natural fibers. During silanization, a silane coupling agent interacts with fiber hydroxyl groups, reducing the quantity of cellulose hydroxyl groups at the fiber-matrix interface (Masowski et al., 2019). Permanganate reduces natural fibers' water attraction and promotes their compatibility with polymer matrices. Hemp fiber composites and natural rubber have been little studied for silane and permanganate effects (Manaila et al., 2015).

## 2- Starch

The majority of higher plants produce the carbohydrate known as starch in order to store energy. Granules ranging in size from 2 to 100 μm are how it is stored within the cell. The size of these granules can change (Whistler et al., 1984). Sugars can be found in corn, rice, wheat, and tubers like potato and tapioca; starches, on the other hand, are refined forms of these sugars and can be bought in most grocery shops.

The starch's properties depend on the components' molecular make-up and structure, which vary greatly across plants and species. Due to their molecular and structural variations, the components vary. The starch granule is a heterogeneous material because it has linear (amylose) and branching (amylopectin) chemical structures and amorphous and crystalline components. These properties form the starch granule (Vamadevan & Bertoft, 2015). Starch's amylose-to-amylopectin ratio depends on its origin, age, and processing.

Plants store excess carbohydrates mostly as starch. It's a polysaccharide with anhydroglucose units connected by $\propto -D(1 \rightarrow 4)$ glucosidic linkages. Although starch's precise microstructures are still being clarified, it has been shown that starch is a heterogeneous substance consisting of two microstructures (amylose and amylopectin) at the extremities of the chain structure spectrum. To put it simply, amylose is a linear structure made up of α-1,4-connected glucose units, whereas amylopectin is a highly branching structure made up of short α-1,4 chains joined together by α-1,6 bonds. Amylose and amylopectin are depicted in their structural form in Figure (2).

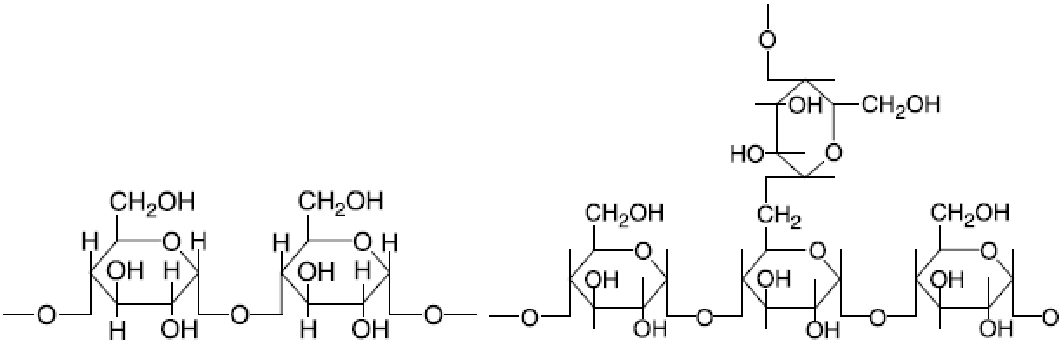


**Figure (2): The structures of amylose (left) and amylopectin (right).**

The linear polymer amylose functions similarly to other artificial polymers. It is 10 times larger than the majority of synthetic polymers and has a molecular weight of around $10^6$. The source of the starch and the method of extraction are what define this range. Amylopectin, however, is a branching polymer. It has a substantially greater molecular weight than amylose. The polymer chains are less mobile and unable to properly orient due to their huge size and branching form, which prevents significant amounts of hydrogen bonding.

Semicrystalline starches have 20–45% crystallinity. Amylose and amylopectin branching points form amorphous patches. Small branching strands of amylopectin give granular starch its crystalline form. Crystallines are 5 nm double helices. In crystalline sections, amylopectin segments follow the large helix. Starch's amylose-to-amylopectin ratio depends on its origin and the extraction procedure. Starch granules contain trace lipids and proteins.

In Figure (3), we see the WAXS patterns of cornstarch with varying amounts of amylose and amylopectin. Both waxy and maize starches exhibit the classic A-type diffraction pattern, with sharp peaks at 2θ between 13° and 21° and an unresolved big doublet in between. In both G50 and G80, the greatest diffraction peak occurs at about 2θ = 16°, with smaller peaks appearing at 18°, 20°, and 22°. Around 2θ= 4°, an extra peak appears. The later spectra seem quite similar to the typical B-type. Since amylopectin in starch granules is widely believed to be responsible for the crystalline structure (as seen in Figure (3)), it is not surprising that amylopectin-rich starches have a larger crystalline area than amylose-rich starches.

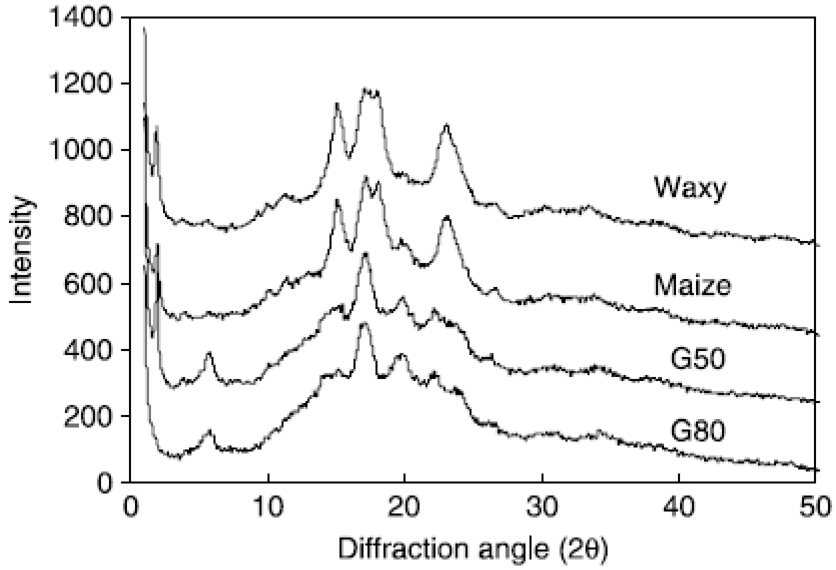


**Figure (3): WAXS patterns of cornstarch with different amylose/amylopectin content.**

Granules that are round and angular in shape come from the floury and horny endosperms, which are found in starch (Chen et al., 2006). Instead of membranes, starch granules are made up of tightly packed chain ends, giving them the appearance of the bottom of a broom when the straws have been squashed together. Starch granules that have not been damaged may mature and absorb some water when exposed to cold water.

The phenomenon known as phase transition refers to a broad variety of chemical and physical activities that take place during the production process. It is one of the distinctive characteristics of products that are based on starch. Several of these processes, such as crystallization, breakdown, melting, and swelling of the starch, are examples of what may potentially take place (Vamadevan & Bertoft, 2015). A well-known order-to-disorder phase transition occurs in the presence of water when starch granules are roasted while the molecule of water is present. This transition takes happen in the presence of water. This transformation takes happen while the molecule is still present. When the starch is subjected to an amount of water sufficient to bring about this change, which is referred to as "gelatinization," the starch effectively becomes water-soluble. This process is known as "gelatinization." The process in question is referred to as "gelatinization" (Vamadevan & Bertoft, 2015). Although it is often believed that the crystalline structure of the starch granules are destroyed during the gelatinization process, this interpretation is not totally true. The popular knowledge is that this destruction occurs. Granular expansion, native crystalline melting, loss of birefringence, and starch solubilization are all irreversible processes that need to be completed in order to make insoluble starch. Granular expansion is the first of these processes, while native crystalline melting is the last. The procedure starts out with granular expansion as the initial phase. Changes in the quantifiable properties of starch granules, such as changes in viscosity, heat absorption, crystallinity, and size variation, can be used to identify starch gelatinization as it takes place. For example, changes in viscosity can be used to measure how well the starch granules are absorbing heat (Xie et al., 2008; Xue et al., 2008).

Shear circumstances need less water to gelatinize starch than shearless conditions (Vamadevan & Bertoft, 2015). Shear stress helps the body absorb environmental starch. Starch-based goods must be converted before extruding, frying, or otherwise processing them. Gelatinization is often done by extruding a substance under high pressure, shear, and minimal water. This gelatinizes the mixture.

In point of fact, the basic components of starch cannot be readily transferred to any use that is not connected to the food industry. A variety of modified starches, such as starch graft copolymers, glycosides, cationic starch, and oxidized starch, have been manufactured specifically for use in sectors other than the food industry. These industries include: These modified starches may be discovered in a wide range of different items (Wurzburg, 2000). The use of starch that has been oxidized with sodium hypochlorite, for instance, is favoured over the utilization of native starches in the sectors of papermaking and textile manufacturing. This is as a result of the stunningly pure white color of the oxidized starch, the ease with which it may be gelatinized, and the great degree to which it can be dissolved in water. When compared to native starches, cationic starch is advantageous for usage in applications involving paper manufacturing and the textile industry since it carries a charge in the direction of the positive direction. This is due to the fact that cationic starch is more effective in these applications than other types of starch because it is attracted to the fibers' rejection of the negative charges. Utilizing superabsorbent polymers, which are produced by grafting acrylonitrile onto starch, can be beneficial to a wide variety of fields, including but not limited to personal hygiene, cosmetics, and even agricultural operations. This is because superabsorbent polymers are able to retain large amounts of liquid without breaking down or leaking.

In recent years, the technique of reactive extrusion has been used for the goal of altering starches in order to get a desired result (Xie et al., 2006). It has been proven that reactive extrusion is a practical and effective way for modifying starches and generating end products that can be utilized in a larger number of applications. The success of this method was demonstrated by the fact that it was able to achieve both of these goals. If the extruder being used is simultaneously functioning as a chemical reactor, then even high-viscosity polymers may be dealt with without the need for any additional solvents. A high degree of operational flexibility is possessed by the system, and one of the variables that contributes to this flexibility is the possibility for repeated injections. Other aspects that contribute to this flexibility include the controlled residence time (distribution), and the degree of mixing. The temperatures during the procedure may vary anywhere from 70 to 500 degrees Celsius, and the pressure can be anywhere from 0 to 500 atmospheres (0 to 50 MPa).

3- Protein

Proteins, one of the three most important macromolecules in living systems, are very simple to extract from their natural environments. For decades, scientists have tried to decipher how proteins organize themselves supramolecularly in tissues and organs and how they create primary, secondary, and higher-order structures that are crucial to their biological function.

Proteins are built from something called "fundamental components," which are more often referred to as amino acids. These amino acids can be neutral, such as glycine, or basic, such as lysine, or acidic, such as aspartic acid, depending on the quantity of extra acid groups that are present inside them. Glycine is an example of an amino acid that is acidic. They may also have alcohol or thio functional groups, each of which serves as a chemical "handle" that synthetic, inorganic, and organic chemists can use to modify the proteins that contain them or the amino acids that make up those proteins. These modifications can be made to the proteins that contain them or to the amino acids that make up those proteins. Amide bonds, also known as the links that exist between amino acids, are seen in figure 4.

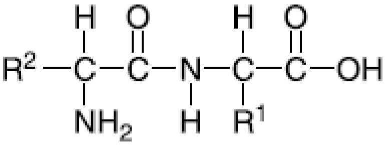


**Figure (4): Structure of the amide bond linking amino acids.**

Proteins are organized into four distinct layers: Primary structure is the order of amino acids throughout the polypeptide chain. Polypeptides, or proteins, are long chains of amino acids held together by peptide bonds. The term "secondary structure" describes the polypeptide chains in their stretched or helical-coiled shape; A protein's tertiary structure is its three-dimensional folding of polypeptide chains into a globular structure, whereas a protein's quaternary structure is its three-dimensional spatial organization of polypeptide subunits. Multiple interactions and linkages, including steric strain, van der Waals contacts, electrostatic interactions, hydrogen bonding, hydrophobic interactions, and disulfide cross-links, are known to play a role in the creation of secondary, tertiary, and quaternary structures (Cheftel & Cuq, 1985).

Through either their peptide bonds or their amino acid side chains, proteins are able to participate in interactions with water that are classified as hydrophilic. The thermodynamic state of proteins is one of a vast variety of parameters that determine whether or not they are soluble in water. The process of solubilization involves dispersing the protein molecules throughout the solvent in order to increase the amount of interaction that may take place between the protein and the solvent. The solubility of proteins is extremely sensitive to shifts in pH, ionic strength, temperature, and the kind of solvent that is used (Cheftel & Cuq, 1985). The process of a protein undergoing a change in conformation (secondary, tertiary, or quaternary) without the concomitant breaking of primary structural peptide bonds is referred to as "denaturation," and the name "denaturation" refers to the process. The process of denaturation is a complicated one that leads to the production of new conformations, the majority of which are merely temporary in nature. If a denaturing agent is able to quickly damage the connections or linkages that serve to stabilize the secondary, tertiary, or quaternary structure of a protein, then it will be simple to denature the protein. There are many different types of physical denaturation agents. Some of these agents' employ heat or cold, whilst others use mechanical treatment, hydrostatic pressure, irradiation, interfaces, and so on. Chemical denaturation agents fall into distinct group (acids and alkalis, metals, organic solvents, etc.).

Soybean protein is the most accessible and refined plant-based protein option. Biotechnology allows for the modification of all four levels of soy protein structure, increasing the protein's potential as a biomaterial and in food applications (Utsumi, 1992). Most beans, but soybeans, in particular, have a protein level of around 40%. Crushing soybeans (for oil extraction) and processing protein components are two of the most important steps in turning soybeans into protein ingredients for use in food and industrial goods. Soybean proteins are typically water-soluble, globular, and reactive. The amino acid composition, with its high proportion of polar and hydrophilic amino acids, gives plant proteins exceptional water solubility. Amino acids include several reactive groups, including carboxylic, primary and secondary amine, aliphatic and aromatic hydroxyl, and sulfhydryl.

Similar to starch, materials based on proteins are significantly more difficult to process than typical polymers, particularly when it comes to the use of thermal extrusion. The complex and irreversible changes in the physicochemical interactions of protein molecules, such as unfolding and disulfide-disulfide interactions, make it difficult to conduct an analysis of the melt rheology of biopolymers. Plasticizers are frequently included into protein-based polymers in order to reduce shine and improve workability. Methods that may be used with goods that are based on proteins are now being created in a variety of different ways, some of which are more conventional than others. It is necessary to have a deeper understanding of the physical and chemical changes that underlie the various processes in order to achieve additional improvements in the materials that are produced via these methods.

Soy protein plastics were first studied in the 1940s. Back then, soy protein was mostly employed as a filler or extender in petroleum-based polymers to bring down their prices. Because of its remarkable adhesive characteristics, soy protein is mostly used in the industrial coating of paper. The creation of biodegradable polymers made from soy protein has been the focus of recent studies. The findings of the experiments prove that soy protein (either alone or combined with starch) may be molded into plastic objects including disposable containers, cutlery, toys, and sporting goods. Films made of soy protein can be extrusion-blown or cast. Films made from soy protein have been found to be effective oxygen barriers and UV blockers, making them a desirable packaging material. Soy protein may be converted into foam materials with the right processing. Soy protein-based polymers provide distinct and desirable qualities, such as biodegradability, flammability, and electrostatic neutrality.

4- Cellulose

Cotton, hemp, jute, ramie, kenaf, silk, feathers, and down are all examples of natural fibers derived from plants. Wool, silk, spider silk, feathers, and down are all examples of natural fibers derived from animals (such as asbestos, and inorganic whiskers). Natural plant and wood fibers, which are rich in cellulose, are the most common kind of biodegradable fibers. Despite cellulose being the most accessible and renewable polymeric resource, only a fraction of available supplies is put to use. Cellulose is the primary component of plant cell walls and is found in all plant species. Wood, cotton fiber, and cotton linters are the most common plant-based materials used to produce cellulose for industrial applications.

Cellulose does not arise in nature as an individual molecule but rather as assemblies of individual cellulose chain-forming fibers. Cellulose does not occur in nature as an isolated molecule. This is because cellulose is produced as a series of individual molecules, which, at

the place where it is being biosynthesized, go through a process of spinning in a hierarchical sequence. In a typical scenario, approximately 36 separate cellulose molecules come together to form larger units called elementary fibrils (protofibrils). These elementary fibrils then pack into even larger units that are referred to as microfibrils, and finally, these microfibrils are assembled into the well-known cellulose fibers. However, the circumstances under which biosynthesis takes place may cause celluloses derived from various sources to pack in a variety of distinct configurations. The processes of biopolymerization, crystallization, and spinning all take place simultaneously in a rosette-shaped plasma membrane complex with a diameter of 30 nm. This complex is controlled by certain enzyme terminal complexes that function as biological spinnerets. Crystallization during the process of cellulose synthesis occurs very closely after polymerization of the cellulose chains by the terminal complexes. This is due to the fact that all of the cellulose chains in a single microfibril must be extended by the complex at the same pace (Habibi, Lucia & Rojas, 2010).
Cellulose is a homoglucan made up of $(1-4)-\beta-D-$glucopyranosyl units linked together in linear chains (see Figure (5)). The strong molecular side-by-side association is common in natural plant cellulose, notably in trees and other woody sections of plants, because of cellulose's inherent linearity. Both amorphous and crystalline forms of cellulose exist. Solvents and chemical reagents readily penetrate the amorphous areas. However, cellulose is often insoluble and extremely crystalline due to the strength of the glucosidic linkages that hold it together.

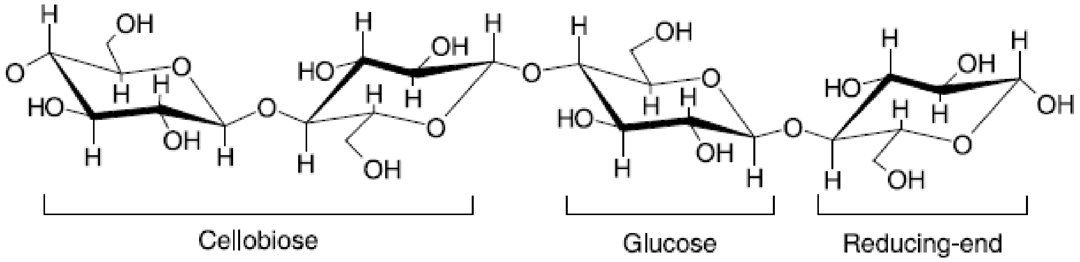


**Figure (5): The chemical structure of cellulose.**

Rope, canvas, and kenaf sacking are only a few examples of the historic uses of cellulose. Cellulose, however, will not melt at high temperatures because of its crystalline structure. Thermal processing of cellulose cannot be as straightforward as that of more typical polymeric materials. The thermoplasticity of a compound can be enhanced by undergoing chemical processes on its free hydroxyl group, such as etherification or esterification. Cellulose acetate, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyalkyl cellulose, carboxymethyl cellulose, fatty acid esters of cellulose, and many more are all commercially available cellulose derivatives (Blackburn, 2005). For aqueous processing, scientists have created a wide range of solvent solutions (Cai et al., 2006). In the real world, cellulose has been included as a reinforcing component in several polymer composites, particularly eco-friendly composites.

5- Chitin and Chitosan

Chitin, after cellulose, is the second most common natural polymer. Many insects and crustaceans rely on chitin as their primary structural carbohydrate. Crustaceans from the sea, including crabs and shrimp, are the best candidates for obtaining chitin because of how simple it is to extract the substance from them. Many different types of life use chitin as a structural component. It is a component of fungal cell walls, where it helps provide structural integrity. Chitin biosynthesis is a very ancient cellular function that has persisted from the earliest times of life on Earth (Parrisher, 1989).

However, some of the glucopyranose residues in chitin are in the deacetylated state as 2-amino-2-deoxy-b-D-glucopyranose. After being deacetylated to a level of 50%, chitin is known as chitosan and is soluble in weak acids. The building seen in Figure (6) is typical.

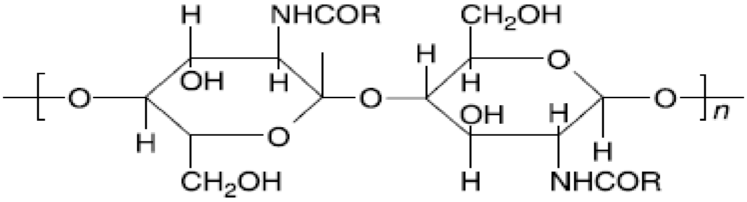


**Figure (6): Representative structure of chitin.**

The amid group in chitin is often hydrolyzed under alkaline conditions to produce chitosan. The presence of a main aliphatic amine is reflected in chitosan's chemical structure, which else resembles that of cellulose. Chitosan has a molecular weight of 0.1–4 x$10^6$. Chitosan forms several ester and amide products upon reaction with carbonyl compounds (i.e., acylation with acid anhydrides). Because of its cationic polyelectrolyte qualities, bioactivity, biocompatibility, water-thickening ability, and selective chelation capabilities, chitosan has many practical applications. The versatility of chitosan is further demonstrated by the ease with which it may be processed into a wide variety of other forms, including fibers, films, coatings, beads, powders, and solutions (Hudson, 1998).

# Synthetic polymers from bioderived monomers

Creating synthetic polymers from bioderived monomers is a promising new avenue for harnessing renewable resources for the manufacture of biodegradable polymers. Poly(lactic acid) (PLA) is a potential polymer for this purpose since it can be easily biodegraded and is produced from agricultural byproducts. Obtainable from the fermentation of maize, sugar cane, or sugar beat, lactide is a cyclic dimer produced by controlled depolymerization of lactic acid. Even though PLA has been around for a while, it is currently at the forefront of the burgeoning biodegradable plastics industry because of advances in manufacturing that have made it more cost-effective to produce monomers from agricultural feedstocks.

1- Poly(lactic acid)

Polylactic acid (PLA) is an aliphatic polyester similar to polyglycolic acid and polymandelic acid (Casalini, Rossi, Castrovinci & Perale, 2019). As a commercially viable material, PLA is appealing because of its high strength, transparency in films, biodegradability, and accessibility. It is also possible to produce PLA by biotechnological methods using sustainable inputs. Corn has the benefit of producing the requisite high-purity lactic acid, however many other sources of biomass can also be employed. Synthesis of PLA from lactic acid can occur by either a direct polycondensation process or ring-opening polymerization of a lactide monomer. The result of ring-opening polymerization has a larger molecular weight, which is a benefit of the method.

Figure (7) depicts the chemical structure of lactic acid, the primary component of PLA. Because lactic acid monomers are chiral, the stereochemistry of PLA is intricate. The characteristics of PLA are affected by the stereoisomeric L/D ratio of the lactate units. Poly(D, L-lactic acid), also known as poly(mesolactic acid), is a racemic polymer made by reacting equal parts of D- and L-lactic acid.

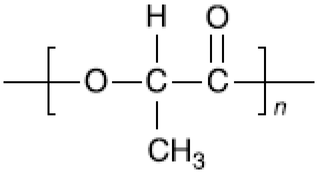


**Figure (7): Basic structure of PLA.**

The glass transition and melt temperatures for PLA homopolymers are around 60°C and 180°C, respectively. Common methods of working with thermoplastics, such as extrusion and injection molding, are well suited to processing PLA. It is important to keep PLA away from moisture and heat. Hydrolysis, lactide reformation, oxidative main-chain scission, and inter- or intramolecular transesterification processes all contribute to PLA's thermal breakdown at temperatures of 200°C (Garlotta, 2001). Plasticizers may be utilized for films and to increase toughness, and mineral fillers have been utilized as nucleation sites for injection products (Bleach et al., 2002). Medical implant materials and drug delivery systems have benefited from the use of PLA. Many people are interested in thermoformed goods and biaxially oriented films made from biodegradable polymers at the moment.

2- Propanediol

Glycerol is an aerobically fermentable substrate for a wide variety of bacteria. Feculent anaerobic bacteria may then use the glycerol to produce propanediol, ethanol, butanediol, acetic, and lactic acids. Propanediol (PDO) stands out among fermentation byproducts because it may be employed as a monomer in the creation of polymers such as polyesters, polyethers, and polyurethanes (Deckwer, 1995).

The usage of vegetable propanediol increases the amount of moisture that is available and does not provoke any irritation. As a result, it is perfect for use in goods that care for the skin and hair, as well as deodorants, scents, and other cosmetic and personal care items. It is also possible to use it in the capacity as a component in a variety of other sorts of components, such as a carrier for active chemicals, botanical extracts, or scents. In addition to these functions, vegetable propanediol may also be used to increase viscosity, act as a plasticizer, and contribute to the enhancement of preservative activity. Propanediol, a vegetable-based solvent, is capable of dissolving even the most insoluble of the raw ingredients, such as ferulic acid.

# Polymers from microbial fermentation

As an essential element of their metabolic processes, a wide range of microbes manufacture a unique class of polyesters for use as internal carbon and energy storage (Suriyamongkol et al., 2007). The chemical compound poly(β -hydroxybutyrate) (PHB) was first referenced in the scientific literature in 1901, and in 1925, researchers began conducting in-depth investigations on it. After then, over the following 30 years, research into PHB inclusion bodies was conducted mostly out of curiosity. The energy crisis of the 1970s spurred the quest for natural alternatives to synthetic plastics, which accelerated the development and widespread use of PHB.

1- Polyhydroxyalkanoates

It is shown in Figure 8 how polyhydroxyalkanoates are typically structured (PHAs). Poly(-hydroxybutyrate) is the simplest PHA (PHB). These biopolyesters are found as submicrometer inclusions inside the cell and are analogous to starch, the reserve material in plants. In the meanwhile, genetic engineers are cloning promising genes although commercial progress thus far has relied on fermentation technology.

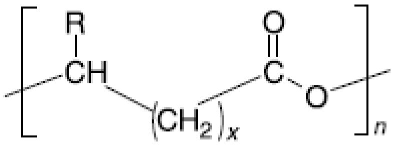


**Figure (8): Generic structure of PHAs.**

Bacteria that are often cultured on agricultural raw materials are responsible for the natural production of polyhydroxyalkanoate polymers. They may be processed into a number of useful products, and the fact that they are biodegradable and made of natural materials gives them many advantages, in particular for use in applications such as agriculture and packaging for one-time use (Bugnicourt, Cinelli, Lazzeri & Alvarez, 2014).

2- Copolymers of the PHA Family

PHB in its purest form is fragile and breaks easily. spherulites, which are massive crystals, are mostly responsible for PHB's brittleness. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a copolymer of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) that has attracted attention because it is less crystalline, more ductile, simpler to shape, and harder than PHB (Suriyamongkol et al., 2007). Full biodegradability and optical activity are only two of the fascinating qualities added to poly(b-hydroxyvalerate) (PHV) copolymers by their biosynthetic origin. Since PHBVs and polypropylene share a similar morphology, several studies have found that their mechanical qualities are comparable. According to reports, the tensile strength was 45 MPa, and the elongation was around 10%. At temperatures much below its melting point, PHB is prone to thermal deterioration. When performing a thermal procedure, precise temperature regulation is essential. PHB and PHBVs have a broad variety of potential uses because of their unique characteristics. Use as a biodegradable substitute for nonbiodegradable materials is one of the easiest ways PHBVs may be put to use. Its ability to prevent gases from escaping might make it useful in food packing. Controlled release and surgical swabs are two of PHBVs' more niche uses (Hocking & Marchessault, 1994).

# Conclusion

Around the turn of the 2000, environmental and economic concerns encouraged the development of novel polymers from renewable resources. The former is connected to the global goal of constructing ecologically friendly processes, while the latter is related to a continued concern over fluctuating fuel prices, which have largely affected emerging economies. Renewable resources are the key sources of polymeric materials for the 21st century.

Over the past many decades, major efforts have led to an apparently universal recognition that renewable resources alone cannot meet the Paris accord's and COP26's ambitious environmental commitments. To avoid deforestation and competition with the food sector, the renewable resource must be carefully selected. Additionally, renewable origins should be combined with green methods, whose carbon effect should be continuously monitored. The post-use polymer business's environmental impacts must also be addressed, and the circular economy concept is new to this field. The scenario is broad and requires activity from all stakeholders—research and development, enterprises, governments, and customers.

The practicality of large-scale polymer manufacture from renewable resources is now hampered by inexpensive, well-established fossil-based equivalent processes, but increasing petroleum prices and climate change mandates are expected to change this.

# References

[1] Blackburn RS. 2005. Biodegradable and Sustainable Fibres. Cambridge, UK: Woodhead Publishing.

[2] Blanshard JMV. 1987. Starch granule structure and function: a physicochemical approach. In: Galliard T, editor. Starch: Properties and Potential. New York: John Wiley & Sons. p. 16.

[3] Bleach CN, Nazhat NS, Tanner EK, Kelloma¨ki M, Torma¨la¨ P. 2002. Effect of filler content on mechanical and dynamic mechanical properties of particular biphasic calcium phosphate polylactide composites. Biomaterials 23:1579–1585.

[4] Cai J, Liu Y, Zhang L. 2006. Dilute solution properties of cellulose in LiOH/urea aqueous system. J Polym Sci: Part B Polym Phys 44:3093–3101.

[5] Casalini, T., Rossi, F., Castrovinci, A., & Perale, G. (2019). A perspective on polylactic acid-based polymers use for nanoparticles synthesis and applications. Frontiers in bioengineering and biotechnology, 7, 259.

[6] Cheftel CJ, Cuq JL. 1985. Amino acids, peptides, and proteins. In: Fennema RO, editor. Food Chemistry, 2nd ed. New York: Marcel Dekker. p. 254–265.

[7] Chen P, Yu L, Chen L, Li X. 2006. Morphologies and microstructure of cornstarch with different amylose/amylopectin content. Starch 58:611–615.

[8] Chen P, Yu L, Kealy T, Chen L, Li L. 2007. Phase transition of cornstarch under shearless and shear stress conditions. Carbohydr Polym 68:495–501.

[9] Deckwer WD. 1995. FEMS Microbiology Review 16:143–149.

[10] Donovan J. 1979. Phase transitions of the starch–water system. Biopolymers 18:263–275.

[11] Garlotta DA. 2001. Literature review of poly(lactic acid), J Polym Environ 9(2):63–84. Gross RA, Scholz C. 2001. Biopolymers from Polysaccharides and Agroproteins. Washington DC: American Chemical Society.

[12] Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: chemistry, self-assembly, and applications. Chemical reviews, 110(6), 3479-3500.

[13] Hocking JP, Marchessault HR. 1994. Biopolyesters. In: Griffin G, editor. Chemistry and Technology of Biodegradable Polymers. London: Chapman & Hall. p. 48–96.

[14] Hudson MS. 1998. Polysaccharides: chitin and chitosan: chemistry and technology of their use as structure materials. In: Kaplan DL, editor. Biopolymers from Renewable Resources. Berlin: Springer-Verlag. p. 97–118.

[15] Kaplan DL. 1998. Biopolymers from Renewable Resources. Berlin: Springer-Verlag.

[16] Manaila E, Stelescu MD, Doroftei F (2015) Polymeric composites based on natural rubber and hemp fibers. Iran Polym J 24:135–148.

[17] Masłowski M, Miedzianowska J, Strzelec K (2019) Silanized cereal straw as a novel, functional filler of natural rubber biocomposites. Cellulose, 26, 1025–1040.

[18] Moonart, U., & Utara, S. (2019). Effect of surface treatments and filler loading on the properties of hemp fiber/natural rubber composites. Cellulose, 26(12), 7271-7295.

[19] Parrisher E. 1989. The Chitin Source Book. New York: Wiley Interscience.

[20] Scholz C, Gross AR. 2000. Polymer from Renewable Resources: Biopolyesters and Biocatalysis. ACS Symposium Series 764. Washington DC: American Chemical Society.

[21] Suriyamongkol P, Weselake R, Narine S, Moloney M, Shah S. 2007. Biotechnol Adv 25:148–175.

[22] Utsumi S. 1992. Plant food protein engineering. In: Kinsella JE, editor. Advances in Food and Nutrition Research, vol 36. London: Academic Press.

[23] Vamadevan, V., & Bertoft, E. (2015). Structure-function relationships of starch components. Starch-Stärke, 67(1-2), 55-68.

[24] Whistler LR, Bemiller NJ, Paschall FE. 1984. Starch: Chemistry and Technology, 2nd ed. New York: Academic Press. p. 1–9; 153–242.

[25] Wurzburg OB. 2000. Modified Starches: Properties and Uses. Boca Raton, FL: CRC Press.

[26] Xie F, Yu L, Chen L, Li L. 2008. A new study of starch gelatinization under shear stress using dynamic mechanical analysis. Carbohydr Polym 72(2):229–234.

[27] Xie F, Yu L, Liu H, Chen L. 2006. Starch modification using reactive extrusion. Starch 548:131–139.

[28] Xue T, Yu L, Xie F, Chen L, Li L. 2008. Rheological properties and phase transition of starch under shear stress. Food Hydrocolloids 22(6):973–978.

[29] Bugnicourt, E., Cinelli, P., Lazzeri, A., & Alvarez, V. A. (2014). Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging.