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Natural Polymers as Pharmaceutical Excipients: A Review of Their Applications and Benefits

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Abstract: The use of natural polymers as pharmaceutical excipients has gained significant attention due to their biocompatibility, biodegradability, and availability from renewable sources. These polymers, including cellulose derivatives, starch, chitosan, alginate, and gums, play crucial roles in drug formulation and delivery. They function as binders, disintegrants, controlled-release agents, film formers, and stabilizers, enhancing the physical and chemical properties of pharmaceutical products. Their unique properties, such as mucoadhesion, gel formation, and bioactivity, contribute to improved drug bioavailability and therapeutic efficacy. Additionally, natural polymers offer advantages in terms of safety and reduced side effects compared to synthetic counterparts. Advances in extraction, modification, and characterization techniques have expanded the applications of these polymers in novel drug delivery systems, such as hydrogels, nanoparticles, and transdermal patches. The ongoing research in this field focuses on overcoming challenges related to variability, stability, and scalability to fully harness the potential of natural polymers in pharmaceutical formulations.

Keywords: Natural polymers, Drug formulation, Resin, Gel, Agar, Gums, Cellulose, Chitosan, Pharmaceuticals

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Introduction

Poly implies "many," and meros means "parts or subunits of high molecular mass" in Greek. Both of these expressions are the source of the word "polymer." Every molecule is made up of an enormous number of individual structural components connected by hydrogen bonds to form predictable structures. Through joining together, a huge number of fragile molecules, known as monomers, polymers-- giant molecules with a high molecular weight-- are created. Polymerization is the process via which monomers join to produce polymers. A process

of chemistry referred to as polymerization happens whenever multiple substances come together, regardless of the presence of heat, water, or any other solvents, to form an extremely dense molecule (Upreti and Srivastava, 2003). The resultant substance is recognized as a polymer, and the raw material used to create polymers is known as a single monomer.

The pharmaceutical sector relies heavily on natural polymers, especially for drug delivery systems. These are macromolecules, including proteins, carbs, and muscle fibers, made up of repetitive structural units bound together by covalent connections. Natural polymers are better for drug delivery applications than synthetic polymers because of their biodegradability and biocompatibility. With the goal of achieving gradual and tissue-specific release, they are employed as excipients and in the creation of innovative drug delivery systems. Polysaccharide-based biomaterials and hydroxypropyl methyl-cellulose (HPMC) are two instances of natural polymers utilized in the pharmaceutical sector. The advantages of natural polymers have been the subject of research, particularly about their ability to transfer medicinal substances to the intended tissue. Natural polymers are used in pharmaceutical drug delivery systems, as covered in a few review articles and research papers showcasing their abilities and bright future in this industry

Source of natural polymer

It is possible to extract natural polymers from a variety of sources and they are widely distributed in nature. Polysaccharides can be produced through recombinant DNA techniques and are abundant in nature. They can be obtained from a variety of sources, including microbes, plants, animals, and algae (e.g., xanthan gum, pectin, guar gum, mannan). Many different tasks are carried out by these polymers, which are derived from biological systems. Known for their negative carbon footprint and renewability, they are frequently based on water. In the manufacturing of food products, paper goods, textiles, nutraceuticals, functional foods, and the biomedical field, among other industries, natural polymers are employed. Plant polysaccharides vary greatly in their structural makeup, and these differences are associated with different plant species as well as the specific plant parts that they originate from, including leaves, seeds, roots, and tubers. The intricacy and diversity of polysaccharides can be explained by two unique structural features: firstly, monosaccharides can be linked in α- or β-configurations; and secondly, because branched side-chains are present.

Merits of natural polymer

(A) Biodegradable: Biodegradable polymers that occur naturally come from biological or renewable sources, including plants, animals, microorganisms, and the ocean. These are a unique class of polymers that decompose naturally into water, biomass, inorganic salts, CO_2, N_2, and other by-products after serving their intended purpose through bacterial processes. Natural biodegradable polymers comprise proteins, other biopolymers sourced from renewable resources, and polysaccharides such as cellulose and starch. Because of their mechanical resistance, biocompatibility, and bio absorbability, these polymers are used in a wide range of industries, including packaging, agriculture, medicine, and biomedical applications.

(B) Economic: Natural polymers show promise for a range of applications due to their numerous economic benefits. Because they are abundant, renewable, and have a low carbon footprint, they may lower production costs and promote sustainable development. Natural polymers have demonstrated their economic potential by being used in food packaging, textiles, and biomedical applications, among other areas. Examples of these applications include cellulose and chitin. Natural biopolymers are particularly appealing in comparison to synthetic polymers because of their readily available nature and inexpensive cost of production. Because of these qualities, natural polymers are a good option for a variety

of industries and help to create a more environmentally friendly future. They also align with the principles of sustainable development.

(C) Biocompatibility: They can be used in a variety of biomedical applications because the human body typically tolerates them well.

(D) Renewability: The sustainable and environmentally friendly nature of natural polymers stems from their sourcing of renewable resources.

(E) Easy Availability: They are produced in numerous nations since they are used in numerous industries.

(F) Safe and devoid of side effects: They are from a natural source and hence, safe and without side effect.

Demerits of natural polymer

(i) Contamination of microbes: One major concern is the possibility of microbial contamination of natural polymers. The environment and different industries can be impacted by the degradation of natural and synthetic polymers by microorganisms. Studies on the occurrence, dispersion, and microbial degradation of polymers show the promise of biodegradable plastics and the necessity for sustainable methods. Although there is currently little proof that dominant plastic polymers break down under microbes, natural polymers like proteins and polysaccharides are being explored as potential sources of edible and biodegradable packaging materials. Understanding the effects of microbial contamination of natural polymers and creating long-term solutions require research on this topic.

(ii) Variation between batches: Manufacturing synthetic materials is a regulated process with set quantities of components, whereas the environment and different physical conditions affect the synthesis of natural polymers

Owing to variations in the assortment of materials from nature throughout past times, in alongside variability in place of residence, species, and season the proportion of the chemical elements in any material might differ

(iii) Sluggish procedure: The environment and numerous other factors influence the production rate, making it unchangeable. So logical the rate at which polymers are produced is slow.

(iv) Contamination with heavy metals: The use of herbal excipients is frequently linked to the possibility of heavy metal contamination

Cellulose:

Cellulose (Fig. 1) was discovered in 1838 by the French scientist Anselme Payen. After removing it from plant detritus, he determined its chemical formula. Forming a long chain of a few dozen to over a hundred thousand ranging from (1→4) coupled D-glucose units, rayon is a chemical polysaccharide with the formula $C_6H_{10}O_5$ (Gallert and Winter, 2005). It is chiral in nature tasteless, odourless, and does not dissolve in liquids and most organic solvents. Cellulose is also biodegradable and weighs 1.5 g/cm^3. Wood, which contains 40–50% cellulose, and cotton, which has 90% cellulose, are common sources of it (Shirwaikar *et al.*, 2008; Jani *et al.*, 2009).

In addition to being used as a dietary fiber supplement and in the production of paper and paper products, cellulose is also utilized in the production of building materials, clothing, and renewable energy products (Piotrowski and Carus, 2011).

Hemicellulose:

A heterogeneous polymer, hemicellulose is composed of multiple sugars, specifically C5 and C6 sugars such as galactose, xylose, mannose, and arabinose (Fig. 2). It can also be observed that Hemicellulose from various sources also includes pentoses like arabinose as well as hexoses like fructose, mannose, and galactose. In some instances xylans like glucuronoxylan, arabinoxylan and xyloglucan can also be observed. The majority of D-pentose sugars and, on rare occasions, trace amounts of L-sugars are found in hemicelluloses. Hemicelluloses exhibit

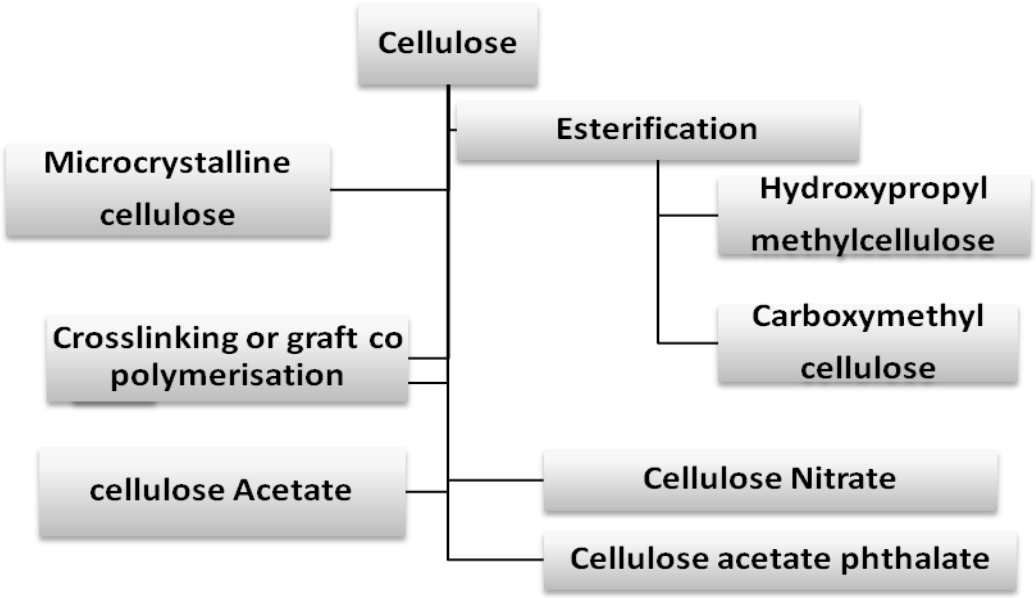

Fig. 1: Chemical Modification of cellulose.

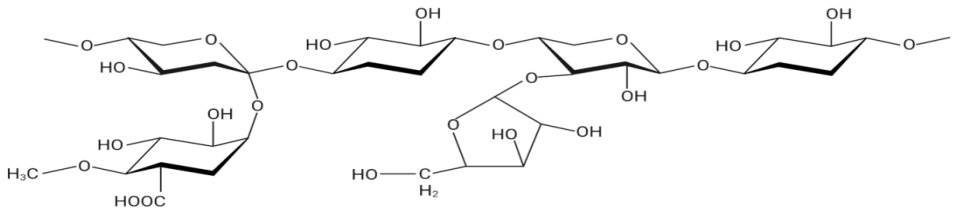

Fig. 2: Structure of Hemicellulose

characteristics such as shorter chains, branching, and a tendency to crystallize in contrast to cellulose. They are chemically unrelated to cellulose (Upreti and Srivastava, 2003; Gallert and Winter, 2005).

Glucomannan:

One source of Fiber found in food, a substance known as is the root of the ginger shrub (Upreti and Srivastava, 2003; Gallert and Winter, 2005). Beta-D-glucose and beta-D-mannose are joined by acetyl groups in a beta1-4 polysaccharide chain with a molar ratio of 1:1.6 to form glucomannan (Fig. 3). With an average molecular weight of one million Daltons, this dietary fiber is among the most viscous substances known to science. It is capable of taking in as much as half its own weight in liquids (Jani *et al.*, 2009). By suppressing hunger and delaying intestinal absorption because of its higher viscosity, glucomannan may enhance glycaemic parameters (Jani *et al.*, 2009). Hydrophilic cylinders and particles for regulated DNA release were formed using glucomannan (Nishiyama *et al.*, 2002). Trisodium Tri Meta phosphate and glucomannan cross-linked to create hydrogel structures that, depending on the crosslinking density and

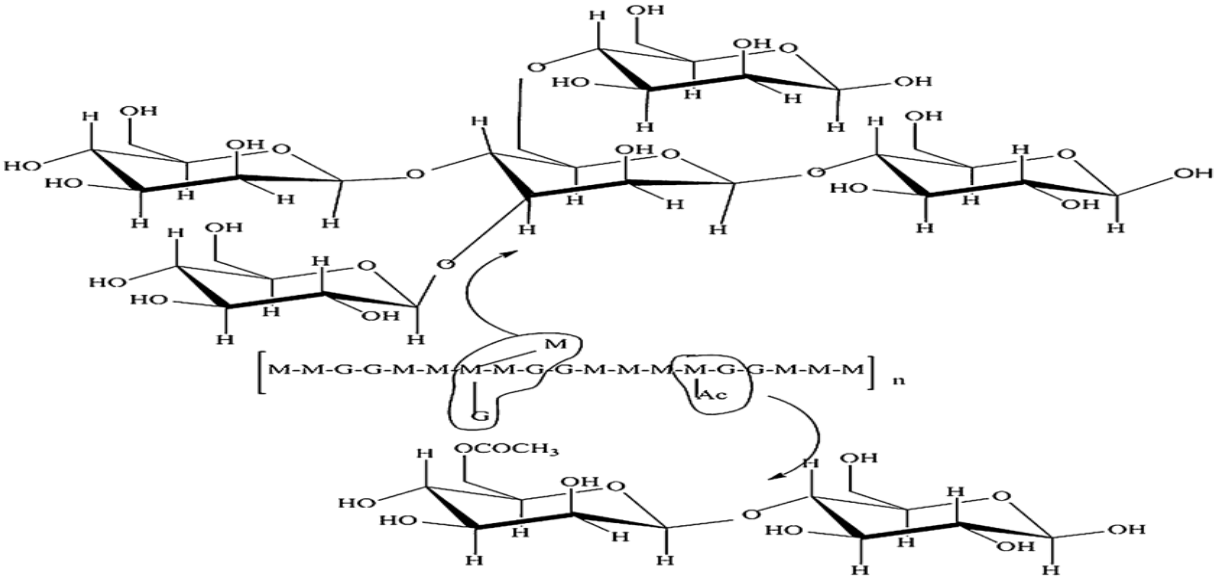

Fig. 3: Structural Properties of Glucomannan.

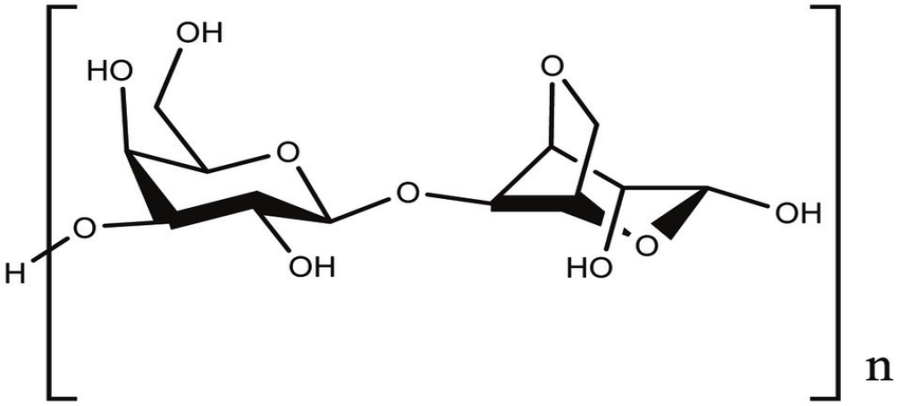

Fig. 4: Structural properties of Agar.

enzymatic breakdown, could prolong hydrocortisone release (Piotrowski and Carus, 2011).

Agar:

Agar, sometimes known as agar-agar, is a jelly-like material made of polysaccharides that are extracted from the cell walls of several red algae species, particularly "ogonori" (Gracilaria) and "tengusa" (Gelidiaceae)(Gallert and Winter, 2005). The two polysaccharides that make up agar are agarose and agaropectin, with agarose accounting for roughly 70% of the combination and agaropectin for about 30% (Upreti and Srivastava, 2003) Repetitive units of agarobiose, a disaccharide consisti ng of D-galactose and 3,6-anhydro-L-galactopyranose, make up agarose, a linear polymer (Jani *et al.*, 2009)

When used at equal quantities, its exceptional gelling activity in an aqueous environment enables it to generate gels that are stronger and more resistant than those of any other gel forming chemical. Among its many uses are as a laxative, bacterial culture medium, pill disintegrants, surgical lubricant, gelling agent in suppositories, and suspending agent. Furthermore, it is employed in tissue culture

research, microbiology, candy making, and jelly preparation.

Starch:

The connotations of the Germanic origin of the word "starch" are "strong, stiff, strengthen, stiffen. A polymeric carbohydrate known as starch or amylum is made up of many glucose units connected by glycosidic linkages. Actually, the idea has two aspects to it – (i) polymers: amylopectin, which is highly branched and contains both α-1,4 and α-1,6 connected D-glucose monomers, and (ii) amylose, which is a non-branching helical polymer made up of α-1, 4 linked D-glucose monomers (Upreti and Srivastava, 2003). The majority of green plants synthesize this polymer in order to store energy. It is the most common carb encountered in diets for human beings worldwide and may be found in significant quantities in common foods including wheat, potatoes, corn (maize), rice, and cassava (manioc). There are several starches that are approved for use in medicine. Among them are potatoes (*Solanum tuberosum*), rice (*Oryza sativa*), wheat (*Triticum aestivum*), and maize (*Zea mays*) (Jani *et al.*, 2009).

Modified starch:

The process of altering the physical, enzymatic, or chemical characteristics of native starch results in modified starch, also known as starch derivatives (Gallert and Winter, 2005). To make it, potato starch was broken down enzymatically, then the product was filtered, washed with ethanol, and precipitated (retro gradated). Modified starches are utilized in almost all starch applications, including as a disintegrant in medicines, a binder in coated paper, and a thickening, stabilizing, or emulsifying agent in food items (Jani *et al.*, 2009).

A plethora of additional applications also make use of them (Upreti and Srivastava, 2003). The material has several benefits, such as being simple to prepare tablets, having the capacity to integrate large percentages of pharmaceuticals with various physicochemical features, and having the possibility to have a steady release rate (zero-order) for a long time. substances with various physicochemical characteristics. Retro-graded pregelatinized starch tablets can have their release rates adjusted to meet specific requirements by varying various factors, such as tablet geometry, compaction force, and the inclusion of extra excipients (Jani *et al.*, 2009).

Native starch:

The amylopectin and amylose concentration of native starch is linked to its semi-crystalline or partly crystalline form, which is characterized by various levels of crystallinity. The unmodified starch's crystallinity is determined by the polymer's amylose and amylopectin, which comprise the starch grain. Amylose constitutes the amorphous portion of native starch, whereas amylopectin mostly represents the crystalline domain, which is defined by organized, closely spaced parallel glucan chains (Gallert and Winter, 2005). Because of its significant swelling and quick enzymatic breakdown, which causes many medicines to release too quickly, it might not be appropriate for use in controlled release drug delivery systems (Upreti and Srivastava, 2003). Protease inhibitors can be added to the aqueous phase of the cross-linking process to preserve the natural or amino-protected aprotinin. Aprotinin-containing microcapsules have been shown to protect bovine serum albumin *in vitro* (Jani *et al.*, 2009)

Pectin:

The natural polymer pectin is a hetero-polysaccharide (Fig. 5) and structural acid that is found in the cell walls of terrestrial plants as well as the main and middle lamella (Upreti and Srivastava, 2003; Gallert and Winter, 2005). The primary component of pectin is a linear polysaccharide with an average molecular weight of between 50,000 and 1,80,000 made up of α-1,4-linked D galacturonic acid residues broken up by 1,2-linked L-rhamnose residues. Each molecule can have several hundred to a thousand building blocks (Jani *et al.*, 2009).

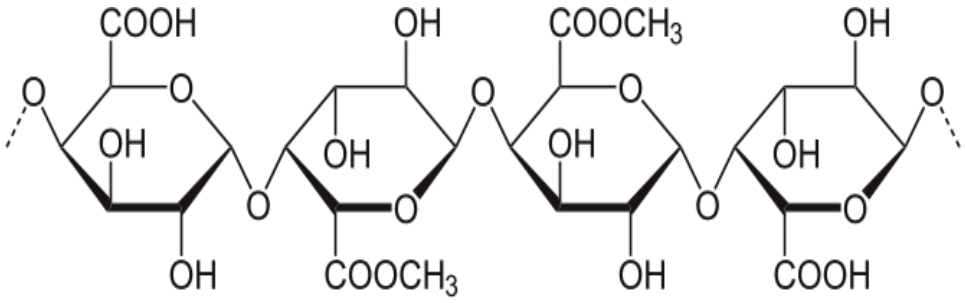

Fig. 5: Structural features of Pectin

The capacity of pectin to create a gel-like consistency in aqueous solutions with calcium ions or in a mixture of a certain quantity of acid and sugar is a significant characteristic. Furthermore, biogenic toxins, xenobiotics, anabolic steroids, metabolites, and physiologically hazardous substances that can build up in the body can all be absorbed and eliminated by pectin. The extent to which galacturonic acid units within the pectin structure have undergone esterification has a significant impact on the physicochemical aspects of pectin, including its solubility and gelling and film-forming capabilities. The extent of the process of ester of the pectin structure is impacted by a number of variables which include the origin of the plant source employed for pectin mining, storage, isolation, purification, and other associated aspects of processing and harvesting (Nishiyama *et al.*, 2002; Shirwaikar *et al.*, 2008). The understanding of the chemical composition, biological activity, and physiochemical characteristics of pectin has yielded several notable improvements. Pectin's effective use in a variety of delivery methods paves the door for its further advancement.

Inulin:

In 1804 German scientist Valentin Rose discovered inulin. Boiling-water extraction of *Inula helenium* roots yielded "a peculiar substance" (Upreti and Srivastava, 2003; Gallert and Winter, 2005). It is a polysaccharide derived from *Taraxacum officinale* (Compositae) stems and *Inula helenium* (Compositae) bulbs of dehlia. The chicory plant stems (*Cichonium intybus*) or burdock roots (*Saussurea lappa*) are members of the Compositae family (Jani *et al.*, 2009). A complex combination of fructose polymers makes up inulin. It is composed of a repeating fructosyl component and chain-terminating glucosyl components (Shirwaikar *et al.*, 2008). They are joined by links of ranging from 2,1. A typical inulin's degree of polymerization, also referred to as DP, might be anywhere via 2 and 60. Highly efficient inulin is what's left behind after the production process eliminates the fractions with DP values under ten (Piotrowski and Carus, 2011; Nishiyama *et al.*, 2002). The tiny image research studies investigating the impact of inulin on health have revealed that it causes gastrointestinal side effects like bloating and flatulence, possesses little impact upon levels of triglycerides or the development of fatty liver, may help prevent travelers' diarrhea, and may help adolescents absorb more calcium (Ebringerova *et al.*, 2005).

Rosin:

The crystalline form of resin known as rosin, frequently called Greek pitched or colophony (Latin: pixgraeca), is derived by pines and specific

other plants, usually conifers. It is made by burning pure resin in order to evaporate all of its volatile terpene elements (Upreti and Srivastava, 2003; Gallert and Winter, 2005). The primary component of rosin is abietic acid, which when combined with caustic alkalis yields rosin soaps, also known as rosinates or pinates. Biopolymers like rosin and its derivatives are being employed more often in uses in medicine. Investigations on microencapsulation, film-forming and coating qualities, and matrix substances in pellets for controllable and prolonged release have been conducted in the pharmaceutical domain (Upreti and Srivastava, 2003). It has been suggested that the fumes emitted throughout riveting are the cause of occupational asthma. Bronchial epithelium desquamation is another sign (Jani *et al.*, 2009).

Gum Arabic:

Gum arabic, additionally referred to as gum acacia, gum sudani, Senegal gum. It is a naturally generated gum that was first made from the hardened sap of two types of Acacia trees, *Senegalia senega* and *Vachellia seyal* (Gallert and Winter, 2005). But "gum arabic" really refers to a plant source that is not specifically mentioned. Polysaccharides and glycoproteins, predominantly arabinose and galactose polymers, compose the intricate mix known as gum Arabic (Upreti and Srivastava, 2003) As a safe thickener, emulsifier, and stabilizer, gum arabic is a rich source of dietary fiber. It is also widely used in the food and pharmaceutical sectors. Numerous *in vitro* and *in vivo* studies have unambiguously demonstrated an array of health advantages of gum Arabic (Jani *et al.*, 2009). Gum Arabic has been effectively employed as an encapsulating material for the matrix of the enzyme endoglucanase. (Shirwaikar *et al.*, 2008). To create the one-piece osmotic tablet method, gum Arabic was utilized as an ionic stabilizing and expanding agent. (Nishiyama *et al.*, 2002)

Gum Tragacanth:

Gums are recognized as pathological materials that result from plant damage or adverse environmental factors (such drought) breaking down cell walls, a process known as extracellular formation or gummosis. There are two main categories of GT in terms of structure: flake, or harmony, and ribbon, or the highest grades. Iranian tragacanth ribbons are graded into five categories upon collection, and flakes are offered in seven grades (Jani *et al.*, 2009). The research indicates that the physicochemical characteristics and compositional changes of GT are contingent upon its origins, which are distinct *Astragalus* species (Nishiyama *et al.*, 2002). While *Astragalus microcephalus* is currently thought to be the main source of GT, *Astragalus gummifer* was historically the main source (Piotrowski and Carus, 2011). GT is known to consist of two primary fractions: tragacanthin and bassorin. The varying ratios of these two fractions contribute to the various physico-chemical and rheological characteristics of GT (Vickie and Elizabeth. 2007).

Karaya Gum:

The *Sterculia urens* tree is the source of gum karaya. The acid polysaccharide gum karaya is a compound made up of galactose, the rhamnose, and galacturonic acid, which comes from sugar (Gallert and Winter, 2005). In order to create directly compressed matrices, karaya gum was utilized to serve as a release-controlling agent. Using a dissolved machinery (basket technique) at various agitation speeds, caffeinated and ibuprofen sodium, which have independent dissolution rates in aqueous medium, were chosen for gum erosion, hydration, and drug release investigations (Upreti and Srivastava, 2003). It was demonstrated that karaya gum-prepared waterproof tablets for buccal distribution had better adhesive qualities than guar gum and could provide zero-order drug release; nevertheless, concentrations higher than 50% w/w could be necessary to produce an appropriate sustained release (Jani *et al.*, 2009).

Locust Bean Gum:

The leguminous plant *Ceratonia siliqua* Linn

(Leguminosae), which is indigenous to the Western geographic area, is the foundation of plantain gum, which originates from the scions of the carob tree. In 2016, Portugal, Italy, Spain, and Morocco contributed to over 75% of global output (Gallert and Winter, 2005). Powdered locust bean gum can range in colour from white to yellow-white. It is mostly made up of high molecular weight hydrocolloidal polysaccharides, also known as galactomannan chemically, which are formed of lactose and the sugar mannose units joined by glycosidic connections (Upreti and Srivastava, 2003). The primary component of locust bean gum is neutral that exhibited comparable drug release characteristics to scleroglucan and guar gum for several model pharmaceuticals (Jani *et al.*, 2009). In a different research, Mini matrix devices consisting of locust bean gum might provide prolonged release of diclofenac sodium (Shirwaikar *et al.*, 2008). Commercially available tablet galacto-mannan polymer consisting of 1,4-linked Dmanno-pyranosyl units where a D-galacto-pyranosyl unit is replaced on C6 every fourth or fifth chain unit. Since locust bean gum is a neutral polymer, pH variations between 3 and 11 have minimal effect on its solubility or viscosity (Nishiyama *et al.*, 2002).

Aloe gel:

The layer of connective structure that harbors the mucilaginous gel is found inside the inner portion of the leaves of *Aloe vera* (Gallert and Winter, 2005). The acetone deposit was immediately crushed in the matrix structures using diclofenac sodium as a model medication following the extraction of the *A. vera* gel from the leaves and a filtering process. Direct compressible matrix tablets made from the mucilage demonstrated excellent dilatation and prolonged release of the model medication (Upreti and Srivastava, 2003). *Aloe vera* gel coverings have an enormous effect on the hardness, color, general look, and weight loss (which is directly correlated with fruit size). Plant extracts containing *Aloe vera* has antimicrobial properties that either destroy or inhibit the growth and proliferation of microorganisms, such as bacteria, fungus, and viruses (Shirwaikar *et al.*, 2008). Furthermore, significant medicinal uses include the additive of dehydrated *A. vera* gel powder used in long-acting pharmacological dosage forms. (Nishiyama *et al.*, 2002).

Alginate:

Brown seaweed is the primary driver of alginate, a kind of linear polymer that degrades in water. It is generated up of 1-4 connected segments of -L-glucuronic and Mannuronic acid (Upreti and Srivastava, 2003; Gallert and Winter, 2005). Tablets encapsulating alginate are utilized as a therapeutic route of administration for the intestines. Additionally, alginate is used as encapsulating materials for medication distribution to mucosal tissue under control. Furthermore, it is employed in the manufacturing of sticky systems for delivering medications.

Polymers are essential for the delivery of drugs. Accordingly, choosing the right polymer is crucial for the production of pharmaceuticals. However, while choosing polymers regarding its toxicity, medication compatibility, and degradation pattern, caution must be exercised. Based on this analysis, it can be concluded that natural polymers can serve as a suitable replacement for synthetic polymers and can even mitigate many of the latter's adverse effects.

Conclusion

Natural polymers have emerged as versatile and valuable excipients in pharmaceutical formulations, providing a range of functional benefits. Their biocompatibility, biodegradability, and non-toxic nature make them ideal candidates for various applications. Key uses of natural polymers in pharmaceuticals include acting as binders, fillers, disintegrants, and controlled-release agents in tablet formulations. They enhance drug stability, improve bioavailability, and offer protection against environmental factors. Additionally, natural polymers play a crucial role in developing novel drug delivery

systems, such as hydrogels, nanoparticles, and microspheres, which enable targeted and sustained release of therapeutics. The ongoing research and advancements in the modification and characterization of natural polymers continue to expand their potential, promising innovative and effective solutions for pharmaceutical applications

Natural biodegradable polymers have gained significant attention in recent decades due to their applications in environmental protection and health maintenance. This review concludes that incorporating drugs into natural polymers allows for the creation of dosage forms that provide prolonged drug release in various shapes and sizes. Polymers are crucial in drug delivery, making the choice of polymer essential in drug manufacturing. However, it is important to consider the polymer's toxicity, drug compatibility, and degradation pattern. This review suggests that natural polymers can be excellent substitutes for synthetic polymers, potentially reducing many of the side effects associated with synthetic alternatives.

Ethical Statement

This is a review article hence no Ethical Statement needed.

Author Contributions

BP: Conceptualization, Resources, Original Writing; *SS*: Data curation, Writing-Review & Edit, *DD*: Writing-Review & Edit, Supervision; *PD*: Original Writing, Data curation. All authors have read and agreed to the published version of the manuscript.

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Conflict of Interest

The authors declare no conflicts of interest.

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