

A Comprehensive Review of Natural Polymer with Crosslinker Methodologies

Sejal S. Adsul*, Piyush R. Joshi, Suryakant A. Jadhav, Dr. Laxmikant M. Purane, Dr. Vivekkumar K. Redasani

YSPM's Yashoda Technical Campus, Faculty of Pharmacy, Wadhe, Satara.

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ABSTRACT:

Natural polymers have gained significant attention due to their biocompatibility, biodegradability, and renewable nature. This review aims to explore the diverse aspects of natural polymers, focusing on their definition, characteristics, sources, extraction methods, properties, and applications. Furthermore, the role of crosslinkers in enhancing the performance of natural polymers is examined, with an overview of various types of crosslinkers, their mechanisms, and their influence on polymer properties. The methodologies for crosslinking natural polymers are also discussed in detail, categorizing them into chemical, physical, and biological methods. The synthesis and modification of natural polymers through crosslinking enhance their mechanical strength, thermal stability, and other functional properties, making them suitable for a wide range of applications in biomedical, environmental, and industrial fields.

Key words: Natural polymer, crosslinker, Extraction, Methodologies, Alginate

I. INTRODUCTION

Both the renewable nature and biodegradability of natural polymers, which are one of the important members of functional materials used especially in drug delivery and tissue engineering applications, make their building blocks potential substitutes for petrochemical-based polymers[1]. The most important features of natural polymers, which can be used as drug delivery systems as well as tissue engineering materials, are being biocompatible with the human body[2]. In tissue engineering applications, natural polymers are preferred since they provide more suitable environments for cells, confirm cell adhesion, and provide better cell protecting events[3]. There are many different natural polymers obtained from different sources such as bio utility, chitosan, alginate, and pollutant[4]. Polyphenols also contain many antioxidants active

substances with numerous biological activities and are an important class of secondary plant metabolites obtained from plant sources[5]. This chapter examines the protective incision depending on in vitro and in silico tests conducted with these biopolymers, and also investigates the body's potential benefits and drawbacks. Moreover, the development of natural polymers plays a critical role in revealing the physiological, bioactive, barrier, and antioxidant properties of polyphenols and their potential uses[6].

In modern days, quantitative approaches exist in all human life fields and this is supported by many different methods, from information processing to sap flowing in plant cells, due to what the plant is[7]. The many and diverse aspects of plant water relationships range in many areas, from forestry to military, agriculture, industry, and health sciences, multidisciplinary of many basic science branches. The necessity of the safety of the researches made on these subjects has for some time highlighted. These plants, which are the source of life, must be protected and kept alive with all their assets by ensuring that these relationships maintain their sustainability. The most basic needs are to adapt to quickly changing climates and to develop suitable characteristics. Natural polymers are compounds used in a wide range of applications and obtained entirely from nature and their structures consist of simple repeat units called polymers[8].

NATURAL POLYMER

Defination: A polymer is essentially synthesized by joining small molecules or substances into a single giant molecule through a chemical process. These small molecules used in polymer synthesis are called monomers. Natural polymers are substances obtained naturally. They occur in various forms and play crucial roles in living organisms[9].

Characteristic of natural polymer :

Biocompatibility: Natural polymers are generally biocompatible. Because they are

Intrinsic Because they come from natural sources, they are less likely to cause negative immunological reactions.

Biodegradability: The body breaks them down spontaneously.

Non-toxic Degradation: Their breakdown produces harmless byproducts. They imitate the extracellular matrix

(ECM), which promotes cell adhesion and proliferation.

Chemical Versatility: They can be modified to have desired properties and are versatile.

Minimal Inflammation: Usually, they result in very little inflammation.

Regenerative Properties: A few support the repair and regeneration of tissue. Their capacity to attract water makes them hydrophilic, which promotes cell survival.

Surface Features: They facilitate cell attachment and protein adsorption.

Regulatory Approval: Their safe usage in medical applications dates back a long way [10].

Structural Components: In living organisms, natural polymers are part of the structure. Examples include:

Proteins and polypeptides: proteins are malleable, capable of being catalysts for enzymes. Hemoglobin, found in the blood, is a transporter of oxygen.

Collagen: is present in the connective tissues, which gives skin elasticity. Cellulose: It forms the finest cotton fiber and supports plant architecture, due to its abundance in plants.

Formation: Most natural polymers are formed by condensation polymerization, where water is produced as a byproduct.

Condensation polymerization: A chemical reaction in which monomers combine to make a polymer by simultaneously releasing molecules such as water, alcohol and hydrogen chloride is called condensation polymerization. The reactions between monomers with two function groups, such as hydroxyl (OH) and carboxyl (COOH) or amino (NH₂), are generally involved in this process. The polymerization takes place step by step, and each step will result in the loss of a single molecule resulting in formation of long chain polymers. Is called condensation polymerization [11].

Examples:

Natural rubber obtained from rubber trees.

Chitin is found in exoskeleton of insects

Nucleic acids DNA and RNA are essential for genetic information.

Carbohydrates are found in cellulose and starch.

Lignans: Here in the cell wall of a plant.

Versatility: polymers have a wide range of properties and functions, making them indispensable in life processes Sources of natural polymer

Plants: yield a range of naturally occurring polymers from plant substances. For instance, take into account:

Cellulose makes up the primary component of a plant's cell wall.

Starch : a type of carbohydrate utilized for storage, is commonly present in grains, legumes, and tubers. Pectin, which is present in fruits, contributes to the thick, jelly-like texture of jams and jellies.

Animals:

Gelatin: Obtained from collagen in animal by-products

Chitin and Chitosan: Found in the exoskeletons of crustaceans and insects.

Collagen: A major protein in connective tissues.

Marine Sources:

Alginate is Derived from brown seaweeds, it is used in wound dressings and drug delivery.

Carrageenan: Extracted from red seaweeds, it acts as a thickening agent in food and pharmaceuticals [12].

Extraction Methods:

Extraction of gelatin from animals: For the manufacture of gelatin, collagen derived from animals is used. It is called the extraction of gelatin from animal materials such as skin, bone and connective tissue which are natural polymers. These animal tissues contain collagen, which is a protein called gelatin. The extraction process involves a number of steps, which are usually followed by the following:

1. Preparation of raw materials: skins, bones and connective tissues are collected from slaughterhouses or meat processing facilities. A thorough cleaning is required to remove any pollutants or impurities from these raw materials.

2. Pre-Treatment: The collagen is subsequently broken down into soluble form by treating the gathered raw materials. It is usually necessary to soak them in an acid or alkaline solution for the removal of collagen matrix and extraction of non

collagenous proteins and minerals. It is commonly used to do this by using an alkali solution, e.g. lime water or acid solutions like dilute hydrochloric acid.

3. Extraction: In order to extract the collagen following a prior treatment, the raw materials are heated in water. This process breaks the collagen molecules to smaller pieces, which are dissolved by water. Next, the mixture is filtered to remove any remaining bits of solid matter, leaving behind a solution with high levels of collagen.

4. Clarification: The solution of collagen extract may be explained again in order to remove any remaining traces of contaminants and insoluble substances. Filters and centrifugation are among the ways to achieve this .

5. Concentration: extra water is removed by evaporation or another method after the collagen solution has been reconstituted. This results in a thicker solution with a higher concentration of collagen.

6. Gel formation: A gellike substance is formed as a result of gelation when the concentrated collagen solution is cooled. After drying, the residual water in this gel is removed and it turns into gelatin.

7. Processing: To obtain the required particle size or form (such as powder, sheets, or granules), the dried gelatine may go through additional processing procedures like milling or grinding[13].

Two main processes:

Acid process (type A):

The process of obtaining gelatin from animal collagen through acid is referred to as acid treatment. Gelatin is a naturally occurring material produced primarily from the collagen found in the bones, skin, and connective tissues of animals. In this process, collagen molecules are broken down to produce gelatin, which is extensively used in the food, pharmaceutical, and cosmetics sectors.

New policies are being introduced by the company to enhance both employee satisfaction and productivity. The initial step in preparing raw materials involves thoroughly cleaning animal skins or bones to eliminate impurities such as fat, blood, and other proteins.

2. Pretreatment with acid: Cleaned materials are immersed in weak acid solutions like hydrochloric acid, sulphuric acid, or citric acid for several hours to days. This process aids in weakening the cell structure and partly breaking down collagen, leading to increased solubility and easier elimination.

3. Removal of excess acid from the material will be done through washing, followed by hot water extraction post acid treatment. To obtain the highest gelatin yield and quality, it is vital to meticulously monitor the temperature and duration of the extraction process. Extraction occurs between temperatures of 40 to 60 degrees Celsius.

4. Filtration and clarification are used to eliminate insoluble residues from the extracted solution, which contains gelatin and other soluble components. To enhance purity, additional clarification methods like centrifugation or activated carbon can be utilized.

5. Other purification techniques, such as ion exchange chromatography, can be utilized to remove any remaining impurities.

The candidate needs a minimum of five years of experience in the industry. **Drying and grinding:** The concentrated gelatin must undergo drying methods such as air drying, drum drying, or freeze drying. Once dry, the product is grinded to the necessary particle size and then packaged[14].

Alkaline Process (Type B Gelatin):

Another method of producing gelatin from animal collagen, in particular from the hides and bones of animals, is the alkaline process, also known as Type B gelatin extraction. Unlike the acid process (Type A gelatin), which uses acid treatments, the alkaline process involves treating the raw materials with a basic (alkaline) solution. For collagen sources which are more difficult to remove, such as hides of bovine animals, this process is especially efficient.

1. Preparation of raw materials: To remove any extraneous material such as fat, blood or non-collagen proteins, the animal hides and bones shall be thoroughly cleaned.

2. Alkaline treatment: For an extended period, often several weeks to a few months, cleaned raw materials are soaked in dilute alkaline solutions such as lime calcium hydroxide. This step, called liming, is helpful to increase the strength of collagen fibers, degrades not collagenous proteins and increases gelatin extraction efficiency. It is normal to maintain a pH of 11 or 13 in the solution.

3. Neutralization and washing: The materials are washed to remove the lime when alkaline treatment is performed. In order to avoid any residual lime affecting subsequent steps and quality of the gelatin, washing shall be essential.

4. Extraction: Hot water extraction is then carried out on the treated materials. At progressively increasing temperatures of about 50 C to 90 C,

extraction is carried out in a number of steps. The gelatin is solubilized and collected in an aqueous solution after that step.

5. Filter and clarification: To remove any insoluble residues, the gelatin solution is filtered. In order to improve purity and clarity, clarification steps such as centrifugation or the use of activated carbon may be used.

6. Concentration and purification: Under reduced pressure, the clarified solution is concentrated by evaporation. Further impurities removal and improvement of the quality of gelatin can be achieved using other purification techniques, such as ion exchange chromatography.

7. Drying and Milling: The concentrated gelatin is dried using methods such as air drying, drum drying or freezing drying. After drying, the gelatin is ground to a desired particle size and packaged for use[15].

Extraction of Chitin and Chitosan:

Chitin

A tough material found in the exoskeletons of arthropods.

Chitin is a derivative of glucose that forms a long-chain polymer of N-acetylglucosamine. It is structurally similar to Cellulose, making it crucial in arthropod exoskeletons and fungal cell walls. Chitin, coming after cellulose, ranks as the second largest natural biopolymer on Earth[16].

Method of evaluation:

Chemical extraction involves treating crustacean shells with acid and alkali to eliminate calcium carbonate and proteins. This technique is effective, yet it produces chemical waste.

Extraction with enzymes: Utilizes proteolytic enzymes to eliminate proteins, providing a greener option. Nevertheless, it is generally pricier and less efficient than chemical techniques.

Biological extraction: Uses microorganisms for the elimination of unchitin components. This method is environmentally friendly and can be cost effective, but requires longer processing times and careful monitoring of microbial activity[17].

Extraction of Chitin

The process of extracting chitin from natural sources usually involves three key stages: removing minerals, separating proteins, and adding color.

1. The process involves removing inorganic minerals, such as calcium carbonate, from the raw

materials, known as demineralization. Usually, this procedure is conducted using a weak acid solution like hydrochloric acid.

Method:

The crustacean shells undergo grinding and treatment with hydrochloric acid at room temperature for multiple hours.

In order to remove acid and dissolved minerals, the mixture shall be washed with water.

2 Deproteinization: Proteins binding to chitin are removed by this procedure. The alkaline solution is usually sodium hydroxide, or NaOH.

Procedure: at higher temperatures, the demineralized material is treated with a dilute NaOH solution. This process breaks down and solubilizes the proteins, which are washed away.

3. Decolorization: removal of pigments and other color impurities is performed by this optional step.

Procedure: Solvents or oxidizing agents such as potassium permanganate or hydrogen peroxide can be used to treat the material[18].

Chitosan

The deacetylated derivative of chitin is Chitosan. It is produced by a solution of an alkaline substance like sodium hydroxide, which removes alkyl groups from the chitin. The transformation gives Chitosan unique chemical characteristics, such as solubility in acidic solutions, which makes it more flexible for a variety of uses[19].

Extraction of Chitosan

To remove acetyl groups from chitin polymer, the extraction of chitosan requires a series of chemicals and enzymes.

Source Material: Usually the exoskeletons of crustaceans such as shrimp and crabs or fungal cell walls are derived from them.

Deproteinization: To remove proteins, the material is treated with a high alkali, eg sodium hydroxides.

Demineralization: minerals are removed, in particular calcium carbonate, by acid treatment such as hydrochloric acid.

Deacetylation: In order to remove acetyl groups and convert them into chitosan, the chitin is then treated with concentrated alkali frequently sodium hydroxide at high temperature.

Enzymatic Method:

Enzyme treatment: In milder conditions than in chemical methods, certain enzymes such as chitin deacetylases are used for the removal of Acetyl Groups from Chitin. This method is more

environmentally friendly, but it is currently more expensive and less widely used in the industrial sector.

Purification: In order to remove residual chemicals and enzymes, the resulting chitosan must be thoroughly washed. For various applications, it is soaked and crushed to the required particle size[20].

Applications

There are a variety of uses for chitin and chitosan:
Biomedical: It is used for wound dressing, drug delivery system and tissue engineering scaffolds.
Agricultural purposes include using it for seed coating, soil conditioners, and biopesticides in farming.

Food industry: Designed to preserve food products, food additives, and packaging materials.

Water treatment:

Flocculants for wastewater purification in water treatment[21].

Other Natural Polymers:

Cellulose Extraction:

Alkaline treatment of plant materials.

1. Preparation Collect, clean, dry, and grind plant material
2. Delignification Treat with sodium hydroxide (NaOH) to remove lignin and hemicellulose Wash and optionally bleach the material
3. Isolation Filter to separate the cellulose fibers Dry the isolated cellulose
4. Crosslinking Select an appropriate crosslinker Dilute cellulose with a crosslinker at regulated temperatures, pH. Wash, neutralize, dry and treat crosslinking cellulose[22].

Pectin Extraction:

From fruit peels using acid extraction.

Here's a concise version of the pectin extraction and crosslinking process

1. Preparation:

- Collect, clean, dry, and grind plant material (e.g., citrus peels).

2. Extraction:

- Treat with hot dilute acid (e.g., citric acid) to extract pectin.
- Filter to separate the liquid extract.
- add alcohol to precipitate pectin (e.g., ethanol).
- precipitated pectin separate dry and wash

3. Crosslinking:

- Dissolve extracted pectin in water.
- Add a crosslinker (e.g., calcium chloride for calcium crosslinking).
- Allow the pectin to form a gel or film.
- Wash, neutralize, and dry the crosslinked pectin.

4. Characterization:

- Test for gel strength, thermal stability, and solubility.
- Analyze structure using microscopy and spectroscopy. These extraction methods yield natural polymers that can be further purified and modified for various applications in medicine, food, and materials [23].

Properties of natural polymer

Natural polymers are well-tolerated by living tissues, making them suitable for medical applications. When exposed to biological systems, they show minimal adverse reactions.

Biodegradability: Over time, a number of naturally occurring polymers become harmless components. The eco friendly nature of them contributes to the sustainability.

Structural Components: Natural polymers serve as structural element.

Cellulose is abundant providing strength and rigidity.

Collagen which contributes to elasticity.

Chitin found in an insect's exoskeleton.

Formation: Natural polymers are often formed through condensation polymerization, producing water as a by-product.

Proteins, nucleic acids, DNARNAs, and carbohydrates are examples.

Versatility: The properties of natural polymers are diverse, which make them necessary for life processes[24].

Application of natural polymer

Biomedical Applications:

Tissue engineering: regeneration of damaged tissue scaffold material is used .

Drug delivery: natural polymer have capability of encapsulating and releasing drugs gradually.

Wound healing: Collagen based dressing promotes wound closure.

Food and Packaging:

Edible Films: Natural polymer create biodegradable material eg. starch, chitosan. for administration of drugs and dietary supplements gelatine capsule are used

Textiles and Clothing:

Cotton: It is a natural polymer used in textiles derived from cellulose fibres.

Silk: It's strong and light because it's made from silkworms.

Agriculture:

Starch Based Biodegradable Mulches: reduce plastic waste in agriculture.

Chitosan Based Pesticides: environmentally friendly alternatives.

Environmental Applications:

Water treatment: Chitosan is removing heavy metals and pollutants from water. Biodegradable plastics: plastic pollution is reduced by natural polymers.

Cosmetics and Personal Care:

Hydrogels: The basis for skin care products is naturally polymer.

Alginate Masks: For facial masks and cosmetic treatments[25].

CROSSLINKERS

Definition:

A crosslinker is a molecule that forms covalent bonds between polymer chains or biomolecules, which creates a network structure[26].

Types of crosslinker :

Polyfunctional Molecules: These molecules are make bonds with other molecules because they include numerous functional groups.

Reactive Groups: Amine (-NH₂), carboxyl (-COOH), hydroxyl (-OH), and thiol (-SH) groups are examples of common reactive groups.

Chemical Nature: crosslinkers can be either organic or inorganic molecules[27].

Applications of crosslinker

Chemistry of Polymers: In polymer chemistry, crosslinkers are widely used to increase a polymer's mechanical strength, thermal stability, chemical resistance. In electronics, construction, automotive and aeronautics, applications for crosslinked polymers are found[28].

Sealants and adhesives: The addition of crosslinkers enhances the strength and durability of these products. Crosslinking adhesives are particularly used to challenging applications in electronics, building and vehicle industries because they offer better resistance to heat, moisture and exposure to chemicals[29].

Paints and Coatings: Crosslinkers are essential for the manufacture of paints and coatings. They form a three-dimensional network inside the polymer matrix, which increase coating adherence, scratch resistance, and chemical resistance. Crosslinked

coatings are used by the architectural, aerospace, marine and automotive sectors[30].

Vulcanization of Rubber: In order to produce rubber products their elasticity, strength, and durability, Sulphur crosslinks between polymer chains are generated during the vulcanization process, which is where crosslinkers are used. Gaskets, hoses, tyres, and other commercial and industrial products are used with rubber which has been vulcanised[31].

Uses in Biomedical Sciences: Medical devices and biomaterials are developed using crosslinkers. They are used to control the properties of crosslinking polymers, including mechanical strength, degradation rate and biocompatibility, in hydrogels, scaffolds and drug delivery systems. Wound healing, tissue engineering and control of medicinal products are applications for crosslinked biomaterials[32].

The Textile Sector: In textile finishing procedures, crosslinkers are used to give materials dimensional stability, wrinkle resistance, and crease resistance. Because of their increased washing speed and durability, crosslinked fabrics are ideal for home textiles, industrial uses and clothing[33].

Paper and packaging: Crosslinkers are added to paper coating and packaging materials, in order to improve their strength, water resistance or printability. The packaging products are more durable and have a longer shelf life when they are made with crosslaminated paper and packing materials due to their higher tear resistance, flexibilities and barriers[34].

Membranes Crosslinked: Membranes for a variety of separation procedures, contain gas separation, ultrafiltration, and reverse osmosis, are made with crosslinkers. Because of their better mechanical strength, stability and selectivity, crosslinking membranes are useful for industrial separation, medicinal products and water treatment[35].

Properties of crosslinker :

Reactivity: When it comes to the functional groups found in polymer chains, crosslinkers usually show strong reactivity. They form covalent bonds with polymer chains through chemical processes LIKE addition, cooling or polymerization[36].

Functional Groups: Crosslinkers have a many functional groups that to interface with polymer chains for the creation of crosslinks. examples of

common functional groups are epoxides, isocyanates, aldehydes, amines, and silanes[37].

Molecular weight: The molecular weight of the crosslinker may differ significantly depending on the specific use and. The use of more molecular weight crosslinkers is often the result of improved and more robust networks[38].

Solubility: The quantity of solubleness of the crosslinker in different solvents is one of the most important factors affect on the compatibility of the crosslinker with the polymer matrix. Some crosslinkers are compatible with specific polymer systems or soluble in water, but others are soluble in organic solvents[39].

Thermal stability: Crosslinkers should be sufficiently stable to cope with processing conditions, e.g. higher temperatures in the polymerization or drying phases. The crosslinking reaction will proceed effectively without the crosslinker degrading if thermal stability is maintained[40].

Stability in chemistry: crosslinkers must maintained under a variety of chemical conditions to preserve the connection between polymer networks. They resist to deterioration or chemical reactions that may compromise the chemical or mechanical properties[41].

Crosslink density: Crosslink density, which is determined by the concentration of crosslinker molecules and the degree of crosslink, influences the ultimate properties of the crosslink material. Higher stiffness, strength and deformation resistance are generally found in materials with a higher crosslink density[42].

Curing Rate: The rate at which crosslinkers cure affects how long a crosslinked material takes to process and how quickly it acquires the desired qualities[43].

Biocompatibility: Crosslinkers used in biomedical applications must biocompatible to avoid negative reactions when come in contact with biological tissues or fluids. Biocompatibility crosslinkers are crucial for the development of implants, medication delivery systems and medical devices[44].

Methodologies for crosslinking natural polymer

Chemical Crosslinking:

Chemical crosslinking involving forming of covalent bonds between polymer chains. It results in a stable three-dimensional network.

Examples

Vulcanisation: Sulphur crosslinking rubber, which increases its mechanical properties and durability.

Curing: Thermosetting resins (e.g., epoxy) crosslink during curing, leading to rigid materials.

Influence on Properties

Increased rigidity

Enhanced thermal stability

Improved chemical resistance[45].

Physical Crosslinking:

Physical crosslinking is based on noncovalent interactions between polymer chains:.

Types:

Ionic/Electrostatic Interaction: Oppositely charged segments associate.

Hydrogen Bonding: Hydrogen atoms form bridge

Crystallization/Stereo-complex: Ordered structures stabilize the network.

Hydrophobic Interactions: Hydrophobic segments cluster.

LCST/UCST Induced Hydrogel Formation

Ultrasonication Mediated Sol-to-Gel Transition:

Influence on Properties:

Reversible behaviour

Responsive materials

Biological Crosslinking:

In biology, crosslinking involves linking proteins or other biomolecules.

Protein Crosslinking:

Crosslinkers (bifunctional) attach to specific functional groups on proteins.

Used to study protein-protein interactions and biological processes[46].

Applications:

Tissue Engineering: Scaffold materials.

Drug Delivery: Controlled release.

Wound Healing: Collagen-based dressings.

Food and Packaging: Edible films.

Textiles: Cotton and silk.

Environmental: Water treatment.

Cosmetics: Hydrogels and alginate masks[47].

Crosslinking mechanism

Disulfide Bond Formation: In an oxidative environment, proteins with cysteine residues can form disulfide bonds (-S-S-), which can lead to crosslinking. As demonstrated by the crosslinking of collagen in connective tissue and the synthesis of keratin in hair, the production of disulfide bonds contributes to the stability and structure of proteins[48].

The process of transglutaminase-mediated crosslinking involves the enzymatic creation of covalent connections between the γ -amino group of lysine residues in proteins and the γ -carboxamide group of glutamine residues. The stability and structural integrity of many protein based enzymatic matrices such as meat products or baked dough is the result of this crosslinking process[49].

Enzymatic crosslinking of polysaccharides, such as chitosan, alginate and cellulose, may be catalysed by a number of enzymes including tyrosinase, laccase or peroxidase through oxidative coupling processes. An enzymatic crosslinking improves the strength, stability and biocompatibility of hydrogels and materials derived from polysaccharides[50].

Hydrogen bonding: Hydrogen bonds between polar groups of functions, i.e. hydroxyl(OH) or amine NH₂, can lead to the development of structural crosslinks within natural polymer systems. Due to hydrogen bonding, natural polymer matrices, such as starch and gelatine gel, are cohesive and have mechanical properties. Influence on natural polymer[51].

Thermal properties: The crosslinking increases the thermal stability and heat resistance of polymers by limiting polymer chain mobility and inhibiting molecular motion at high temperature. Crosslinked polymers usually show lower thermal expansion and higher breakdown temperatures compared to their uncrosslinking counterparts[52].

Chemical resistance: Crosslinking increases the chemical and solvent resistance of polymers by making reactive groups more difficult to access in a polymer matrix. As a barrier, the crosslink prevents chemicals from penetrating and ensures that polymers are not degraded chemically or inflamed[53].

Dimensional Stability: Crosslinking enhances the dimensional stability and shape retention of polymers by limiting their susceptibility to deformation, shrinkage or swelling under mechanical or environmental stresses. Water absorption and thermal expansion coefficients are reduced by crosslinking polymers, resulting in little dimensional changes over time[54].

Elasticity and Flexibility: Crosslinking affects the elasticity and flexibility of polymers by changing the structure of the network and the mobility of the polymer chains. Depending on the level of crosslinking, polymers can act in a variety of ways from rubbery to glassy. This affects applications

such as gels, thermoplastic elastomers and elastomeric[55].

Processing properties: Crosslinking influences rheological characteristics and polymer processing behaviour during production processes such as extrusion, shaping or casting. Crosslinked polymers may display increased viscosity, reduced melt flow or a variety of melting conditions when compared to uncrosslinked polymers that require change in processing parameters[56].

Biocompatibility: Crosslinking may affect the biological reactions and biocompatibility of a polymer in biomedical applications. Compared to uncrosslinking polymers, well designed crosslinked polymers can exhibit better biocompatibility, reduced immunogenicity, enhanced tissue integration and are capable of being used for drug delivery systems, tissue engineering scaffolds or surgical implants[57].

Some natural polymer with crosslinkers

Alginate: Alginate is a polysaccharide extracted from brown seaweed. Crosslinking agents such as calcium ions or polyvalent cations can be used to form crosslinked alginate hydrogels through ionic interactions. Crosslinked alginate hydrogels exhibit improved mechanical properties, stability, and control over drug release kinetics, making them suitable for biomedical applications such as drug delivery, tissue engineering, and wound healing.

Collagen: Collagen is a protein-based polymer found in connective tissues such as skin, bone, and cartilage. Crosslinking agents such as glutaraldehyde or ribose can be used to stabilize collagen matrices and enhance their mechanical properties and stability. Crosslinked collagen scaffolds are widely used in tissue engineering, regenerative medicine, and cosmetic surgery.

Starch: Starch is a polysaccharide derived from plant sources such as corn, wheat, or potatoes. Crosslinking agents such as phosphorus oxychloride or epichlorohydrin can be used to modify the properties of starch-based materials, such as films, coatings, or adhesives. Crosslinked starch exhibits improved water resistance, mechanical strength, and thermal stability compared to native starch.

Silk Fibroin: Silk fibroin is a protein-based polymer derived from silkworm cocoons. Crosslinking agents such as methanol or glutaraldehyde can be used to stabilize silk fibroin hydrogels and films for applications in tissue engineering, drug delivery, and wound healing. Crosslinked silk fibroin exhibits improved

mechanical properties, stability, and biocompatibility compared to uncrosslinked silk fibroin[58].

II. CONCLUSION :

Natural polymers present a sustainable alternative to synthetic polymers, with their inherent biocompatibility and eco-friendly characteristics. The comprehensive understanding of their sources, extraction methods, and intrinsic properties is crucial for their effective utilization. Crosslinking plays a pivotal role in improving the functional properties of natural polymers, with different types of crosslinkers and mechanisms offering various enhancements. Chemical, physical, and biological crosslinking methods provide versatile approaches to tailor the properties of natural polymers to meet specific application requirements. Future research and development in this field are expected to focus on optimizing crosslinking techniques and expanding the application scope of natural polymers, thus contributing to advancements in materials science and environmental sustainability.

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