

Recent Advances in Edible Polymer Based Hydrogels as a Sustainable Alternative to Conventional Polymers

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ABSTRACT: The over increasing demand of eco-friendly materials to counter various problems, such as environmental issues, economics, sustainability, biodegradability, and biocompatibility, open up new fields of research highly focusing on nature-based products. Edible polymer based materials mainly consisting of polysaccharides, proteins, and lipids could be a prospective contender to handle such problems. Hydrogels based on edible polymer offer many valuable properties compared to their synthetic counterparts. Edible polymers can contribute to the reduction of environmental contamination, advance recyclability, provide sustainability, and thereby increase its applicability along with providing environmentally benign products. This review is highly emphasizing on toward the development of hydrogels from edible polymer, their classification, properties, chemical modification, and their potential applications. The application of edible polymer hydrogels covers many areas including the food industry, agricultural applications, drug delivery to tissue engineering in the biomedical field and provide more safe and attractive products in the pharmaceutical, agricultural, and environmental fields, etc.

KEYWORDS: *edible polymers, hydrogel, cross-linking, food packaging, biomedical*

1. INTRODUCTION

The increasing concerns over the use of low-quality products particularly in the biomedical, pharmaceutical, and food industries leads one to look for new alternatives with high-quality, biodegradable, sustainable, and biocompatible products. Edible polymers which are generally regarded as safe (GRAS) by the Food and Drug Administration become an alternate candidate and has being under much discussion due to its beneficial properties.^{1,2} Edible polymers are mainly polysaccharides (hydrocolloids, polypeptide, and lipids etc., (Figure 1) which can be easily consumed by lower animals and human beings without showing any harmful effect on health. The very important reasons for exploring edible polymers are

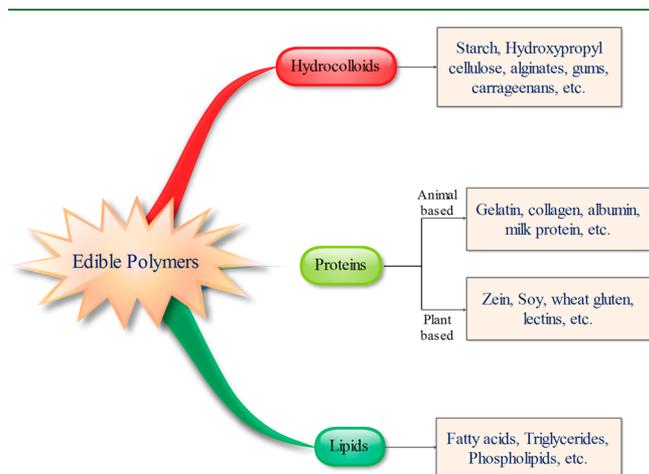


Figure 1. Different categories of natural edible polymers and examples.

the introduction of new safe, high-quality, and suitable food grade products in functional food industries, like edible coatings, which protect the loss of nutrients, food packaging material, and in the pharmaceuticals fields for drug delivery systems.³ Edible polymers have received incredible attention toward food applications in current times as a substitute for synthetic plastic due to its beneficial characteristic, as it can be consumed like the food itself. Another important property of an edible polymer is biodegradability.⁴ Environmental contamination and its consequences is another major issue facing everyone on the earth. The use of nonbiodegradable products for various applications in day to day use like food packaging and wrapping results in a large amount of pollution, which can be reduced by the use of biodegradable and edible polymer-based materials. The various edible polymers include hydrocolloids (starch, carrageenans, cellulose, pectins, alginates, etc.), proteins (gelatin, zein, wheat gluten, etc.) and lipids, with the protein-based edible polymers as the most attractive ones.^{5,6} Currently, edible polymers have gained considerable attention toward an edible packaging material as an alternative to the synthetic films. Natural polymers or the polymers derived from natural sources, like food protein, are of great interest due to their biodegradability and environmental compatibility. Besides food packaging, others applications includes drug delivery, cancer diagnostics, and treatment using nanomedicine and other biomedical fields.⁷

The concept of a hydrogel is very old and has being under consideration for centuries, but its practical importance has

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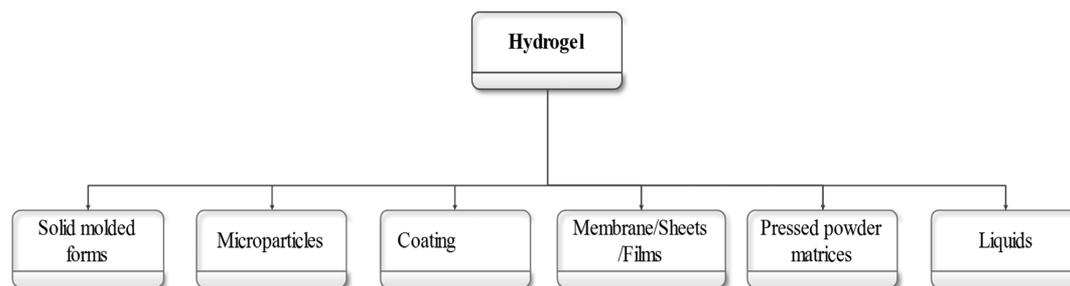


Figure 2. Different physical forms of hydrogels.

been increasing day by day. Although, during its initial phase much of the attention has been paid toward synthetic polymeric materials and has brought dramatic development in different areas, it now has become a major part of research in polymer chemistry. However, with the passage of time researchers have diverted the direction of hydrogels toward nature-based materials due to their overwhelming properties. Natural polymer-based hydrogels have witnessed tremendous progress as a novel alternative in the recent years due to various environmental, health, and ecological issues faced by the excessive usage of plastic materials. In this review, we have focused and analyzed the development of hydrogels from a nature based-edible polymer, their properties, and applications in different areas predominantly in the food industry and in agricultural materials.

1.1. Hydrogels. Hydrogels are three dimensionally cross-linked macromolecular network structures formed from both synthetic and natural hydrophilic polymers that can swell, absorb, and retain a significant quantity of water without dissolving in it. The hydrogels' swelling properties and resistance to dissolution depends on the hydrophilic functionality and extent of cross-linking present in the structure.⁸ The water absorption by the hydrogels arises due to the hydrophilic functionality in the polymer and the resistant to dissolution was provided by the cross-linking among the polymer network. Water also plays an important role in shaping some of the peculiar characteristic of hydrogels.⁹ Many materials, both naturally occurring and synthetic, follow the description of hydrogels. However, new ideas and approaches are being introduced by researchers to design hydrogels with significantly enhanced mechanical properties, biocompatibility, superporous nature and grafted hydrogels, hybrid hydrogels, and genetically engineered triblock copolymers with high stability and fast response time imitating hydrogels with a smart future.^{10,11}

1.2. Classification of Hydrogels. The classification and types of hydrogels are broad and can be classified on a different basis like, its origin (natural and synthetic), its compositions (homopolymeric, copolymeric, and multipolymeric interpenetrating hydrogels, etc.), their configuration (crystalline, semi-crystalline, and amorphous), and the interaction among polymer network (permanent/chemical gel and reversible/physical gel), besides these some other categories are also possible.^{12,13} Hydrogels derived from only one type of monomeric species are known as homopolymeric hydrogels; however, when the hydrogel is comprised of two or more different types of monomeric units it is known as a copolymeric hydrogel. In copolymeric hydrogels, the monomeric units can be arranged in various fashions like random, alternating, or in block, along the chain of polymer

network.^{14,15} The interaction between the polymer networks in the hydrogel is the origin of another category. When the interaction between networks are covalently cross-linked, a chemical or permanent gel was obtained. Molecular entanglements and/or other types of secondary forces like hydrogen bonding, hydrophobic and ionic interaction gave a reversible or physical type of hydrogel.^{8,16} Hydrogels may exist in different physical forms. Figure 2 show different forms of hydrogels that can be designed.¹⁷

2. METHODS FOR PREPARATION OF HYDROGEL

Cross-linking of polymer chain is the main principle behind hydrogel preparation. This can be done by either using external cross-linking agent, chemical modification, or by exposure to high energy radiation.¹⁸ Various preparatory techniques employed by different researchers or scientists for the preparation of hydrogels can be broadly classified into two categories, i.e., physical and chemical cross-linking techniques. Chemical techniques involves the formation of new covalent bonds between polymer chains in the hydrogel, while physical interactions exist between polymer chains in physically cross-linked hydrogel.¹⁹ Figure 3 represents a schematic diagram

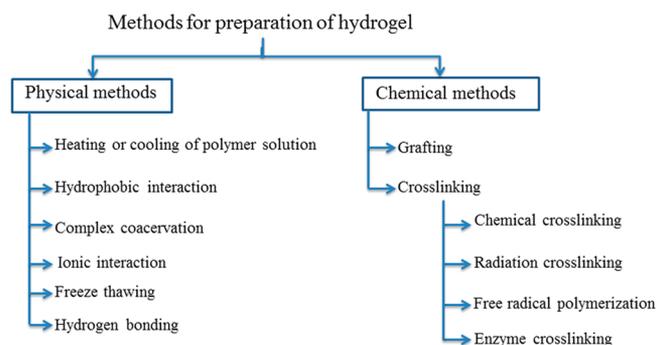


Figure 3. Different methods for preparation of hydrogel.

showing different methods employed for the preparation hydrogel. Both physical and chemical techniques have their own benefit and drawbacks associated with them.

2.1. Physical Cross-Linking Methods. Physical cross-linking involves various physical interactions among polymer chains like ionic interaction, hydrophobic interaction, stereocomplex formation, hydrogen bonding, and protein–polysaccharide interaction resulting in hydrogel formation.⁸ Physical cross-linking techniques in hydrogel chemistry are being evolved as an important tool in current years due to the absence of external cross-linker. The absence of cross-linker in edible polymer-based hydrogel maintains their low toxicity and biocompatibility property, thus upholding the benefits of their

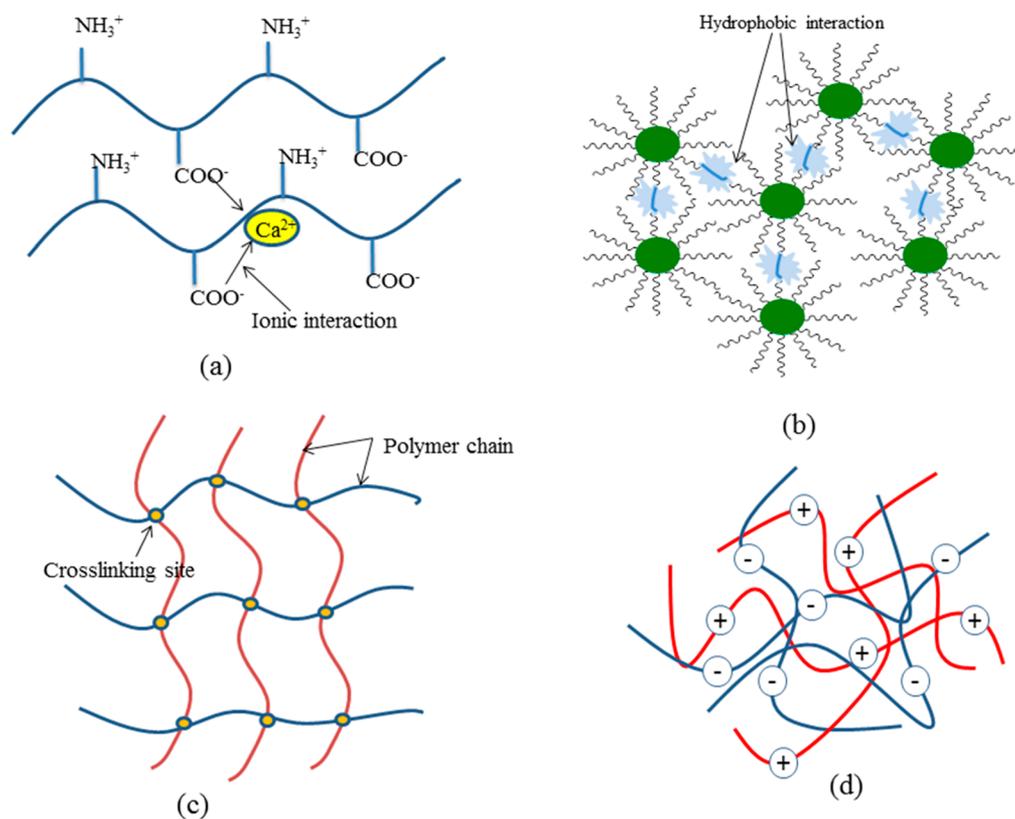


Figure 4. Graphical representations of different types of physical cross-linking in hydrogels: (a) ionic interaction, (b) hydrophobic interaction, (c) cross-linking junction by cooling, and (d) complex coacervate.

usage. Physical cross-linking provides reversible hydrogel and there are structural imperfect or inhomogeneties may occur due to free chain ends. There are few methods reported in the literature that describe in detail how to achieve physically cross-linked hydrogels.

2.1.1. Ionic-Cross-Linking or Ionic-Interaction. Ionic polysaccharide like sodium alginate can be cross-linked by the addition of counterions (like calcium ions). The hydrogel can be cross-linked under mild conditions, at physiological pH and ambient temperature (Figure 4a). However, there is a major disadvantage: the gelation rate is hard to control, with nonuniformity in the structure. Kuo et al. prepared ionically cross-linked alginate hydrogel using calcium carbonate (CaCO_3), calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), and calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) along with D-glucono- δ -lactone.²⁰ The gelation rate became higher at low concentration of alginate and increases with increasing concentration of counterions and temperature.²¹ Slow gelation gives more mechanically stronger gels with uniform structure.

2.1.2. Hydrophobic Interaction. Polymers containing hydrophobic domains can cross-link in aqueous atmosphere via reverse thermal gelation also well-known as “sol–gel” chemistry. Hydrophobic interaction takes place in amphiphilic polymer solution at elevated temperature. Such polymers are soluble in aqueous medium at low temperature; however, as the temperature increases, hydrophobic domains start aggregating to minimize the contact with water molecule.¹⁹ These cause the solvent entropy in the solution to maximize. The larger hydrophobic segment contributes more toward solvent entropy, driving more hydrophobic interaction and lowering the gelation temperature (Figure 4b).

2.1.3. Thermoreversible Gelation. Polysaccharides like carrageenan or gelatin suffer physical cross-linking upon cooling forming a hydrogel. The gel formation results due to helix formation, helices association, and forming junction zones (Figure 4c).²² Carrageenans above their transition temperature exist as random coil, which turns to rigid helical rods upon cooling.²³ In the presence of salt ions (Na^+ , K^+ etc.) due to repulsion of sulfonic group (SO_3^-), stable gels form in aggregates.²⁴

2.1.4. Complex Coacervation. The mixing of polycationic and polyanionic polymer leads to formation of complex coacervate gel. The principle behind this technique implies the idea of opposite charged polymers aggregate together forming complex highly depending on the pH and concentration of the solution (Figure 4d). Highly stretchable hydrogel based on hyaluronic acid and chitosan via complex coacervation was reported by Lalevee et al.²⁵ The mechanical properties of hydrogel changes from fragile (at pH close to pK_a of chitosan, amine groups) to stretchable and strong (at pH close to pK_a of hyaluronic acid, carboxylic groups). Similarly, proteins below its isoelectric point exists as positively charged and associates with anionic polysaccharides forming coacervate complex hydrogels.²⁶

2.1.5. Hydrogen Bonding. Hydrogen bonded hydrogel can be obtained by lowering the pH of polymer solution containing carboxyl groups. Takigami et al. reported carboxymethyl cellulose (CMC) based hydrogel by dispersing in 0.1 M HCl solution.²⁷ In acidic solution, sodium ions were replaced by hydrogen promoting hydrogen bonding and consequently a decrease in the solubility of CMC, forming an elastic hydrogel. Polyacrylic and polymethacrylic acid forms a hydrogel with polyethylene glycol at low pH, owing to the hydrogen bonding

interaction between the acidic group ($-\text{COOH}$) of acrylate and the hydroxyl groups ($-\text{OH}$) of PEG.²⁸

2.1.6. Freeze Thawing. The freeze thaw technique has been considered as one of the promising techniques for hydrogel development, especially for polysaccharides based gels due to their well-documented biocompatibility and nontoxicity.²⁹ Freeze thawing usually involves freezing of polymer solution at relatively low temperature (-20 to -80 °C) followed by melting at room temperature. The final property of the hydrogel can be modulated by monitoring the pH, freezing duration, temperature, rate of thawing, and number of thawing cycles. Cryogelation of xanthan gum was reported by Giannouli et al.³⁰ Freeze thawing of solution forced xanthan gum chains to align, associated by conversion of water to ice crystal, which remains as such resulting cryogel network. Mechanical strength of the gels can be increased by subjecting the gels to additional freeze thaw cycle or by decreasing the temperature (to -80 °C).

2.2. Chemical Cross-Linking Methods. Despite the fact that physically cross-linked hydrogels enjoy the advantage of developing gels without any cross-linking agents or chemical modification, they have certain limitations also. The mechanical strength of hydrogels is the main concern, which is related to many other properties directly. In contrast, chemically cross-linked hydrogels are mechanically strong, resist dilution of hydrogel matrix, and prevent diffusion of hydrogel. Chemical cross-linking involves chemical modification of polymer chains or use of additional cross-linking agent and other foreign tools to bond the two polymer chains. Different chemical cross-linking techniques were reported in the literature, and out of these two main or important chemical techniques will be discussed here in the sections [Grafting](#) and [Cross-Linking](#).

2.2.1. Grafting. The grafting technique usually involves the polymerization or addition of a monomer on the backbone of a preformed polymer, like polysaccharides. The activation of polymer chains is done via the action of chemical reagents or by treatment with high-energy radiation. Thus, the grafting of functional monomer on activated polymer chains results in branching followed by cross-linking. The chemical modification of edible polymers via grafting constitutes one of the most important methods to advance their properties and widen the range of its application. Starch grafted with hydrophilic monomers like acrylic acid, acrylamide, and acrylonitrile have been utilized and explored as a superabsorbent hydrogel.^{31–33} Such hydrophilic monomer grafted polysaccharide exhibit higher water absorption capacity.³⁴ The grafting technique was further categorized into chemical grafting and radiation grafting, depending on the source of activation. Chemical grafting uses chemical initiators (like potassium persulfate, benzoyl peroxide, etc.) for the activation of polymer chains, while radiation grafting involves high energy radiation (like γ -radiation) as a source of initiators.^{35,36} Few examples of chemical grafting and irradiation grafting on the polysaccharide backbone were discussed here. Djordjevic et al. exhaustively investigated grafting of acrylic acid on potato starch in the presence of various initiators (benzoyl peroxide, potassium persulfate and azobis(isobutyronitrile)).³⁵ Potassium persulfate was found to be the most effective initiator in terms of grafting yield, percentage, and efficiency, while the highest amount of monomer was found in benzoyl peroxide initiated grafted samples of hydrolyzed potato starch. Biodegradable superabsorbent polymer based on starch was prepared via graft copolymerization of acrylamide/itaconic acid onto casa starch

were reported by Lanthong and co-workers, using ammonium persulfate and *N,N,N',N'*-tetramethylethylenediamine as initiator and *N,N'*-methylenebis(acrylamide) as cross-linking agent.³⁷ The highest grafting percentage and maximum water absorption were shown at a polymer to monomer ratio of 1:2. In the irradiation technique, high-energy radiation was used to generate a free radical followed by polymerization via free radical polymerization. Sorour et al. reported an irradiation technique involving microwave and ultraviolet for hydrogel preparation from acrylamide grafted polysaccharide blend containing starch, chitosan, and alginate.³⁸ Potassium persulfate was used as initiator and methylenebis(acrylamide) as cross-linker. Maximum percentage grafting (% G) and percentage grafting efficiency (% GE) was 148% and 67% for microwave irradiated graft and 208% and 80%, respectively. The swelling ratio was affected by pH, having a maximum swelling at pH 9. Sadeghi et al. investigated the effect environment parameters (like pH and salinity) on the swelling capacity of vinylic monomers (such as acrylic acid, acrylamide, and methacrylic acid) grafted kappa carrageenan based superabsorbent hydrogel.³⁹ The swelling degree exhibits pH sensitivity and the maximum water absorption was recorded at pH 8. The charge screening effect became responsible for lower swelling in a highly basic and saline medium. Therefore, such a hydrogel with a pH responsive swelling–deswelling performance can act as an appropriate biomaterial to design new drug delivery systems.

2.2.2. Cross-Linking. The use of a chemical cross-linker, such as glutaraldehyde, epichlorohydrin, glyoxal, PEG, in situ generated cross-linker etc., in hydrogel formation has been practiced with both synthetic as well as natural polymers.^{40–42} This type of cross-linking involves the insertion of a new molecule with reactive functionality between the polymeric chains. However, such a type of cross-linker (like glutaraldehyde) increases the toxicity of hydrogel, limiting their applicability. Therefore, to counter such problems, in situ generated novel biocompatible cross-linker using polysaccharide as a base material was found to be a better substituent for chemical cross-linker to prepare biocompatible hydrogels particularly in biomedical, agriculture, and food related applications. Periodate oxidation of polysaccharide to generate dialdehyde groups has been reported as a safe and efficient biocompatible cross-linker.^{43–45} The degree of cross-linking can be controlled by monitoring the extent of oxidation. Jayakrishnan et al. have thoroughly investigated the usage of such oxidized polysaccharide (alginate, hyaluronic acid, chitosan, chondroitin-6-sulfate, etc.) as in situ generated cross-linker in biodegradable and biocompatible hydrogel preparation.^{43,46,47} Other types of chemical cross-linking include radiation cross-linking, enzyme cross-linking, and free radical polymerization, etc. Enzyme catalyzed cross-linking reaction is another emerging approach regarding in situ hydrogel formation and can act as innovative alternative for conventional cross-linking methods. Microbial transglutaminases enzyme, which catalyzes the formation of amide linkage between primary amine groups and the carboxamide group, has been extensively studied in hydrogel preparation.^{48,49} The enzyme cross-linking method became a useful tool for cross-linking of natural polysaccharide that cannot tolerate harsh chemical conditions.⁵⁰ Chen et al. investigated the catalytic ability of enzyme microbial transglutaminase and mushroom tyrosinase to form gels from gelatin and chitosan solutions.⁵¹ Both enzymes revealed gel formation; however, tyrosinase only

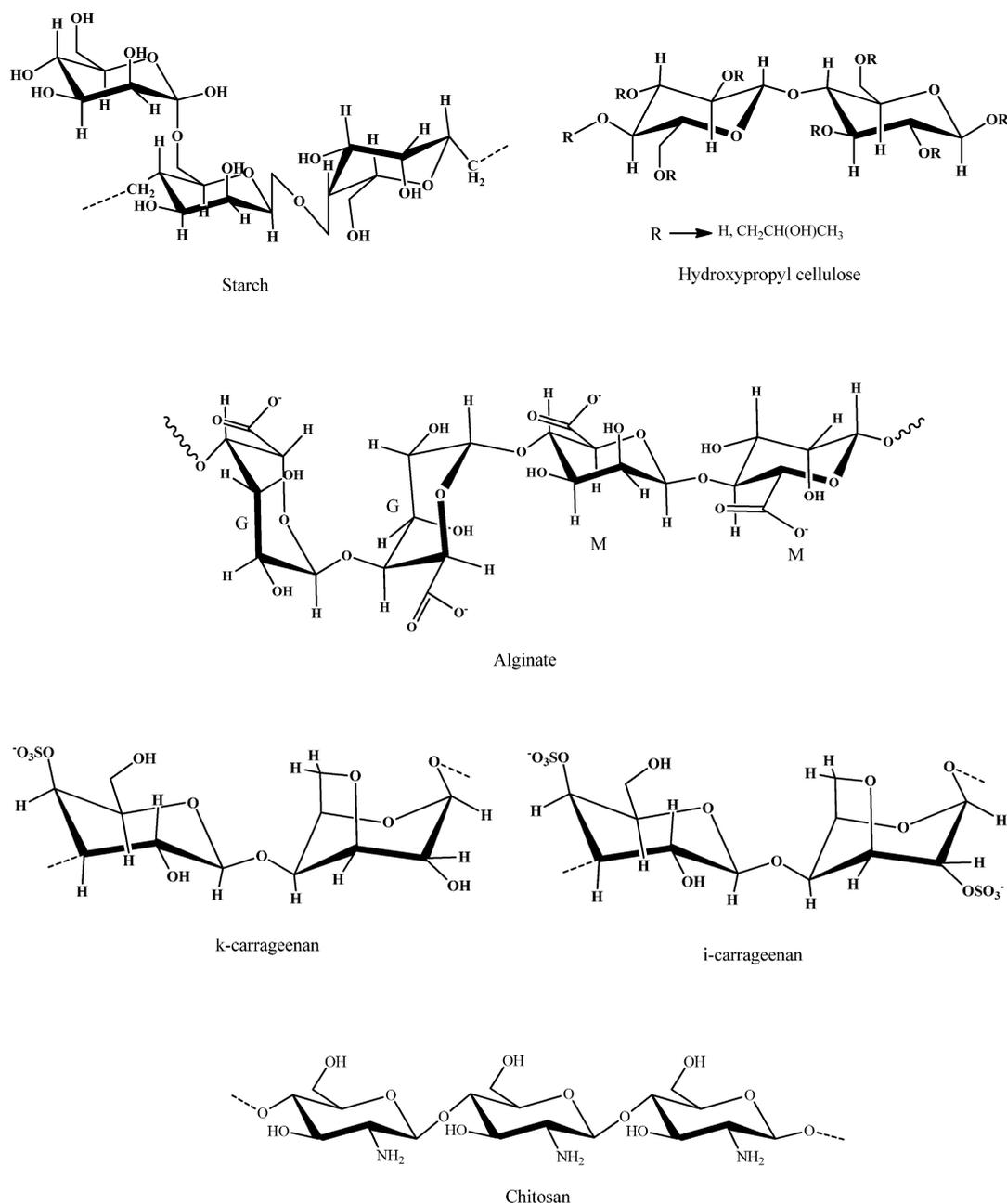


Figure 5. Representative structures of some polysaccharides.

forms gel in the presence of chitosan. Transglutaminase catalyzed gelatin-chitosan gels do not show a thermal reversible transition, and the tyrosinase catalyzed gels are weaker, which were strengthened by cooling below the gelatin gelling point. Addition of chitosan to transglutaminase catalyzed hydrogel adjusts the mechanical properties. Thus, such a hydrogel may act as a potential scaffold for tissue engineering.

3. EDIBLE POLYMERS BASED HYDROGELS

Both synthetic as well as natural polymers can be used for hydrogels preparation. However, most of the synthetic hydrogels are considered as nonbiodegradable and sometimes stimulate inflammation and toxicity from chemicals traces.⁵² Although, synthetic polymers possess precise chemical structure which become suitable to design hydrogels at the molecular level. Natural polymers also show improved

properties when forming hydrogels as compared to synthetic polymers.⁵³ Thus, natural polymers can act as an alternative source to traditional synthetic polymers with good biodegradability and biocompatibility properties along with less waste and pollution; however, the mechanical properties of edible polymers is a subject of concern although it can be improved by using suitable biocrosslinker or plasticizer.^{54–56} The properties associated with the hydrogels are highly influenced by the nature of the polymers. Linear polysaccharide having a stiff and rigid nature with proteins forms membrane, sheets, and coatings, while flexible and globular polysaccharides form film-type hydrogels.⁵⁷ To date, numerous types of edible natural polymer-based hydrogels have been synthesized and utilized for different applications like coating, drug delivery, packaging, etc. The subsequent section concisely describes different types of edible polymer based hydrogels.

3.1. Different Categories of Edible Polymers. Polysaccharides, proteins, and lipids are used as the main sources of edible polymers (Figure 1). Sometimes the blends of two or more type of polymers were used to yield composite types hydrogels, having advanced and smart properties paralleled to individual polymers. Thus, the following four categories of edible polymers are under consideration: polysaccharides, proteins, lipids, and blended or composite edible polymers.

3.1.1. Polysaccharides Based Hydrogel. Polysaccharide based hydrogels have got some excellent properties due to their versatile functionalities and biocompatibility, thus attracted plentiful interest as biomaterials particularly in medical applications, drug delivery, electronic domains, tissue engineering, wound dressing, implants, semipermeable membranes and bioengineering, etc.^{58,59} Many polysaccharides were accessible commercially for use in the food and nonfood industries as thickening, stabilizer, and encapsulating agents, crystallization inhibitors, and gelling agents.⁶⁰ Polysaccharides as edible polymer include starch, alginates, carrageenans, pectin, xanthan gum, and cellulose derivatives, etc.^{61,62}

Starch is the most abundant storage polysaccharide in plant products, acting as the main food reserve containing a bulk of nutrients and an energy source.⁶³ Starch mainly consists of two different kinds of molecules, the major is amylopectin (normally 70–80%) and the minor portion is amylose (20–30%). Amylose is normally a linear (1 → 4)-linked α -D-glucan but sometimes branched to a small extent, whereas the amylopectin part is a multiple branched macromolecules (95% α -(1 → 4) and 5% α -(1 → 6) linkages)⁶⁴ (Figure 5). It has been reported that the amylose part was responsible for the film type hydrogel forming capacity of starch.⁶⁵ The starch based edible polymer possesses some physical characteristic similar to plastic in many ways like tasteless, odorless, biologically absorbable, nontoxic, semipermeable to carbon dioxide, colorless, and oxygen resistant. Starch based hydrogels show better biocompatibility, nontoxicity, and biodegradability and thereby find immense application in biomedical, food packaging, drug delivery, tissue engineering, agricultural uses, personal care, and food preservatives, etc.^{66–68} Szepes et al. prepared a starch based hydrogel for drug delivery containing theophylline (respiratory diseases drug) applying isostatic ultra high pressure (IUHP).⁶⁹ Treatment of aqueous solution of potato and maize starch with IUHP generates highly viscous gels followed by a structural change in the maize starch. The structural and morphological change display noteworthy influence on the dissolution process of drug. Potato starch hydrogel also promotes faster drug dissolution as compared to aqueous theophylline suspension, while the maize starch gel shows sustained drug release behavior. Corn starch-based membranes display sufficient strength, water holding capacity, and better biocompatibility with L929 fibroblast cells and mice splenocytes.⁷⁰ Biofouling and nonspecific protein absorption remains a leading problem mainly in biomedical applications. Wang et al. prepared ionic starch-based hydrogels with different charges on the polymer backbone via etherification reactions to incorporate both ionic solvation groups and hydrogen bonding into one molecule.⁷¹ Three different charged derivatives of starch, cationic starch (C-starch), an anionic starch (A-starch), and zwitterionic starch (Z-starch) and their hydrogel was prepared through chemical cross-linking. The hydrogels show good protein resistance, which depends on the ionic strength of the medium. The protein resistance follows the order, Z-starch > A-starch > C-starch.

Zwitterionic starch hydrogel highly resisted protein absorption at all ionic strengths; however, cationic starch hydrogel shows low protein resistance.⁷² However, in its original form, starch has many limitations, like loss of viscosity, retrogradation characteristics, thickening upon storage and cooking, and absence of certain functional groups.⁷³ Thus, starch has been modified to overcome such limitations. Acrylates modified starch-based hydrogels have been reported to have numerous advanced features comprising of desirable kinetic behavior, pH sensitivity, fascinating swelling characteristics, better degradability, super absorbent properties, etc.^{74–77} Zhang et al. synthesized superabsorbent hydrogel by acrylic acid grafted onto corn starch through free-radical polymerization using *N,N*-methylenebis(acrylamide) as a cross-linker and ammonium persulfate as an initiator.⁷⁸ Sodium dodecyl sulfate and *p*-octyl poly(ethylene glycol) phenyl ether were used as pore forming agents. The hydrogel demonstrates 90% swelling within 10 min, having a maximum equilibrium water absorbency of 417 g/g, when the weight ratio of acrylic acid and starch is 5:1. Similarly, nanosuperabsorbent based on copolymerized acrylamide and acrylic acid grafted on starch in the presence of montmorillonite using ⁶⁰Co γ -ray irradiation was reported by another researcher.⁷⁹ The maximum water absorbency of the absorbent was found to be 1200 g/g, which can improve the water retention capacity of soil. Such a type of superabsorbent can be beneficial in agricultural applications.

Carrageenans are natural marine-based seaweed (Rhodophyceae) derived polysaccharide, mainly composed of D-galactose and 3,6-anhydro-D-galactose sugar units with sulfate as the main substituents along with some methyl ethers (Figure 5). The major applications of carrageenans are in the food industries, especially in dairy products. The effectiveness of carrageenans in the food industry is mainly due to its thickening, gelling, and stabilizing properties.⁸⁰ Based on the number and position of sulfate groups (SO₃⁻), carrageenans are conventionally divided into six basic forms: kappa (κ), lambda (λ), iota (ι), mu (μ), nu (ν), and theta (θ). Out of the six the most common types are kappa, lambda, and iota.⁸¹ Iota and kappa types of carrageenans suffer coil–helix conformational transition upon cooling under suitable salt conditions leading to gelation and developing thermotropic and ionotropic gels.⁸² The gelation can further be improved by using suitable salt ions (Ca and K). Iota carrageenans form soft elastic gels in both hot and cold waters, while kappa type carrageenan dissolve only upon heating forming strong gels that tend to be firm and brittle.^{83,84} Santo et al. developed kappa carrageenan based hydrogel beads as a sustained delivery system for the re-establishment of angiogenesis.⁸⁵ They have incorporated platelet derived growth factor (PDGF, as the angiogenic factor), into the hydrogel and tried to study some of the processing parameters and their influence on the final hydrogel properties. Their study revealed that kappa carrageenan based hydrogel beads can act as an efficient encapsulation agent as well as displays a better controlled release profile similar to that required for the development of a fully functional vascular network. Kappa carrageenan has been modified by means of various processes like addition of pore forming agents,^{86,87} nanoparticles,⁸⁸ and natural cross-linkers⁸⁹ to adjust its physical and chemical properties by increasing its applicability in various biomedical fields and food packaging areas.^{88,90} Meena et al. developed agar and kappa carrageenan based hydrogels using genipin as a natural cross-linker.⁹¹ The cross-linked hydrogels exhibit remarkable stability with the pH

ranging 1–12 and in Ringer's solution as well as thermal stability and swelling ability. Such a kind of hydrogel can be used for pH specific and food related applications. Temperature, ionic strength, and pH play a very important role in drug delivery. Rasool et al. reported a vinyltriethoxysilane cross-linked hydrogel of kappa carrageenan and acrylic acid for insulin delivery.⁹² The hydrogel exhibit maximum swelling at a low monomeric ratio (1:7, carrageenan–acrylic acid); additionally, the behavior of these hydrogels under different pH, ionic strength, and temperature conditions were reported.

Alginate is a natural anionic copolymer polysaccharide found in brown seaweeds, having excellent biocompatibility and biodegradability. Alginate consists of (1 → 4) linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) arranged in a nonregular blockwise fashion between M and G units (Figure 5).⁹³ Alginate possesses a unique binding property to various metal ions (di and trivalent ions) in water leading to the formation of a tough and rigid well-ordered hydrogel.⁹⁴ This unique property acted as the foundation for the biological and industrial applications of alginates. The binding strength mainly depends on the nature of metal cation, and the alkaline earth metal ions obey the following increasing order $\text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$, while the first row transition metal ions follow: $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} \gg \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$.⁹⁵ The alkaline earth cation forms ionic bonds, whereas the transition metal ions form strong coordination-covalent bonds. Alginate based hydrogels found immense applications as matrix for delivery and protection of sensitive nutraceutical compounds⁹⁶ and biomedical fields like wound healing, cartilage repair, bone regeneration, drug delivery, tissue engineering, etc.^{97–100} Alginate based 3D hydrogels were successfully developed as an in vitro coculture model platform for the toxicity screening of new drugs.¹⁰¹ This type of 3D coculture platforms can be used to evaluate drug dose concentration as well as it can provide a scalable and flexible method to test multiple-cell types in a hybrid setting within cell culture plates. Calcium-alginate based hydrogel as an electrically controlled release system for both anionic and cationic drugs and the effect of different parameters, like cross-linking ratio, model drugs, and electric field strength were evaluated by Paradee et al.¹⁰² Cationic drug show a lower diffusion coefficient as compared to the anionic drug, and also the drug delivery is precisely controlled by the applied electric field potential and electrode polarity.

Cellulose, the most abundant and important renewable resource, considered as nearly inexhaustible source of raw material, will become the leading chemical resource in the future due to environmentally benign and biocompatible products.¹⁰³ Cellulose is mainly composed of α-D-glucopyranose units linked by (1 → 4) glycosidic bonds, with a degree of polymerization of around 10000 and 15000 glucopyranose units in wood and native cotton cellulose, respectively.^{104–106} Cellulose and cellulose derivatives are exploited to its full potential under different fields to make their full usages. Only four water-soluble cellulose derivatives have been used as edible polymers: carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxypropyl cellulose (HPC), and hydroxypropyl methylcellulose (HPMC).¹ Thus, cellulose based hydrogel can be designed by proper cross-linking of aqueous solution of such cellulose ethers. These forms of cellulose derivatives find wide application in food industries as thickeners and emulsifying agents, cosmetics and pharmaceutical industry, due to their low cost and nontoxicity.¹⁰⁷ Such

hydrophilic derivatives form reversible hydrogels, which possess specific properties, such as better swelling behavior, thermogelation, gel point, and sensitivity to external stimuli.¹⁰⁸ Cellulose derivatives exhibit a thermogelation property, i.e., they exhibit a unique property of reversible gel formation when heated and return to its solid state when cooled down. Addition of salts lowers the gelation temperature due to dehydration.¹⁰⁹ Cellulose based hydrogels have potential application in the food industry as a packaging material, stabilizer, and gelling and thickening agents.^{103,110} These types of hydrogel also exhibit good skin tolerability, high water content, biocompatibility, biodegradability, and bioadhesiveness, making it similar to living tissue and find applications in dermal and transdermal drug delivery systems. CMC-based hydrogel doped with Al^{3+} holds integrated capability of self-healing, photoluminescence, and stretchability, with the healing efficiency reaching up to 95.04%.¹¹¹ Microwave radiation incorporated silver nanoparticle into CMC-poly-(vinyl alcohol) hydrogel exhibit excellent antibacterial activity against urinary tract infection pathogens (*E. coli*, *P. aeruginosa*, *Klebsiella pneumonia*, *Proteus vulgaris*, *Proteus mirabilis*, *S. aureus*).¹¹² Hydrogel formation by HPMC in water was evaluated using ¹H NMR, via measuring the ¹H spin–lattice (T_1) and spin–spin relaxation (T_2) times for water protons from an equilibrated HPMC/water mixture by varying the polymer concentration.¹¹³ Both T_1 and T_2 found to be decreased with increasing HPMC concentration, due to increase in number of hydrogen bonding interaction in the polymer chains.

Chitosan is another important polysaccharide known for its inherent antibacterial property, nontoxicity, biodegradability and the second most abundant after cellulose.¹¹⁴ Chitosan is produced from chitin a structural element in the exoskeleton of crustaceans via deacetylation¹¹⁵ (Figure 5). Structurally it consists of β-(1 → 4) linked D-glucosamine and N-acetyl-D-glucosamine units. Chitosan possess a cationic amino group and can easily complex with other negatively charged or anionic molecules forming hydrogels. Chitosan hydrogels have being prepared in many forms and shape as per the required applications including gels, films, microparticles, microspheres, fibers, beads and composites, etc.^{116,117} In each cases they are stabilized via cross-linking; either physically or chemically. However, the physical gels are short lived and can be only used for short-term applications. In order to increase the strength of the hydrogel, other chemical moieties have being used as cross-linker. Zang et al. prepared chitosan based hydrogel having a multiresponsive and self-healing property via Schiff base formation with a dibenzaldehyde terminated telechelic poly-(ethylene glycol).¹¹⁸ Glycolic and phloretic acid grafted chitosan hydrogel was prepared using horseradish and hydrogen peroxide as a cross-linking agent for cartilage tissue engineering application.¹¹⁹ The hydrogel displays good biocompatibility with chondrocyte culturing. As packaging material, chitosan based hydrogels shown excellent capability to protect food quality and therefore can be used to improve food safety and shelf life.¹²⁰

Similarly, others edible polysaccharides like pectin, agar, natural gums (guar gum, arabic gum, xanthan gum etc.) have also being used for hydrogel preparation and their applicability has been tried for various applications in different fields.^{121–123}

3.1.2. Protein or Polypeptide Based Hydrogels. Proteins are biological macromolecules consisting of amino acids as fundamental units bonded together via peptide bonds (Figure

6). Proteins commonly exist in two forms, fibrous and globular. Fibrous proteins are water insoluble and present as the main

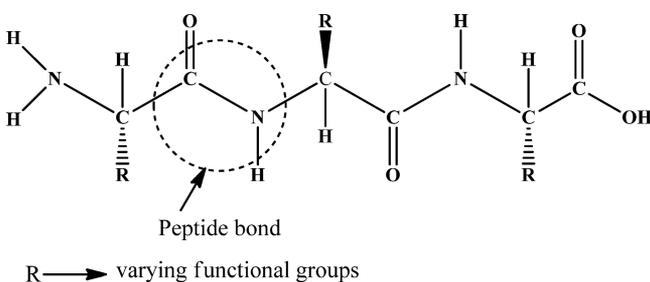


Figure 6. Backbone structure of polypeptide.

structural materials of animal tissues, while the globular proteins are water-soluble and act as functional material in living systems. The physical and chemical properties of proteins are highly dependent on the relative amount of amino acid component and their placement along the polymer chain. Hydrogen bonding plays an important role in maintaining the structure of fibrous proteins, while a combination of hydrogen, hydrophobic, ionic, and covalent interactions are responsible in the case of globular proteins.^{124,125} Different types of proteins as edible polymers have been used for hydrogel preparation, which includes gelatin, whey protein, corn zein, casein, soy protein, wheat gluten, etc.

Gelatin is a nonimmunogenic biodegradable polymer obtained by the partial hydrolysis of collagen and widely applied in the food industry and biomedical field (Figure 7).^{96,126} Gelatin has a long history in the food industry as a food ingredient (such as gelling and foaming agents) and other nonfood applications mainly due to its low immunogenicity level and low cytotoxicity.^{127–129} Gelatin has exhibited the ability of self-gel formation through triple helicalization of chains;¹³⁰ however, chemical modification remains an important tool to obtain gelatin based hydrogels with high structural integrity and reproducible performance of the gels.¹³¹ Gelatin solution also possesses a low temperature (20–30 °C) gelation capability forming a hydrogel upon cooling. These hydrogels attain a unique thermo reversible character resulting from the breakage of nonspecific bonds (like hydrogen bonding and hydrophobic and electrostatic interactions) among the polymer chains upon heating.¹³² Gelatin based hydrogels have good flexibility, reversibility, and transparency; however, its mechanical and thermal stability are rather low, which can be enhanced through chemical modification for long-term food packaging applications.^{133–136}

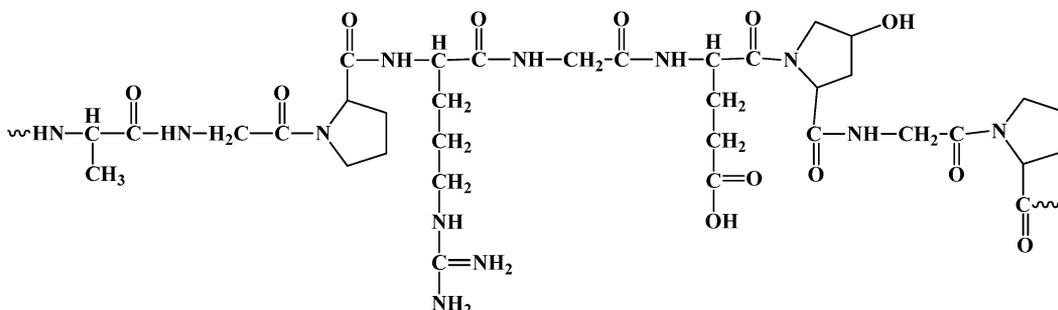


Figure 7. Chemical structure of gelatin.

Whey proteins are the main byproducts of cheese manufacture, also known as the serum protein having high nutritional value and biocompatibility and thus have been widely used in food products. The main components of whey proteins are α -lactalbumin, β -lactoglobulin, and bovine serum albumin. It has been also known for its ability to form gels, emulsion, and gelled emulsion.¹³⁷ Whey protein hydrogel exhibit good pH sensitive swelling capability particularly when the pH is above its isoelectric point.¹³⁸ Whey protein-based hydrogels are found to be brittle thus limiting its industrial applications; therefore, low molecular weight substances like glycerol were used as a plasticizer to achieve flexibility.¹³⁹ The viscoelastic properties of whey protein gels are highly influenced by temperature and its protein contents.¹⁴⁰ Marta et al. prepared whey protein gels via cold gelation processes induced by metal ions (Ca^{2+} , Mg^{2+} , and Fe^{2+}), having a different microstructural and rheological properties.¹⁴¹ The gels exhibit high storage moduli having a stability of 41 days at 7 °C when the gels were aerated with Ca^{2+} and Fe^{2+} ; however, there is a decrease in the bubble size that was observed in Mg^{2+} aerated gels. Such types of gels could be used for the supplementation of such microelements (Mg^{2+} and Fe^{2+}) for the human body. Whey protein-based microgels attained favorable attention due to their heat sensitivity. Upon heating, the whey protein microgel particle forms via involvement of some interaction among polymer chains like electrostatic, hydrophobic, and cross-linking between disulfide bridges rather than a single layer.¹⁴² Such a particle shows appreciable resistance to coalescence and thus can act as a promising candidate for food and innovative pharmaceutical applications.

Zein is a low cost major storage protein found in corn endosperm, classified as α , β , γ and δ depending on their solubility, with α -zein being the most abundant one accounting 75–80% of the total zeins.¹⁴³ α -Zein is insoluble in water due to its hydrophobic amino acid composition (>50%), mainly aliphatic amino acids (leucine, alanine, and proline), and demonstrates the tendency to aggregate. Zein has been used as greaseproof coatings, microspheres in drug delivery, biodegradable films, and plastics and have also antioxidative properties, etc.¹⁴⁴ Zeins also act as bioactive molecule, α -zein producing angiotensin-converting enzyme inhibitors, when hydrolyzed with thermolysin enzyme.¹⁴⁵ Zhong et al. investigated zein as a nanoscale matrix structure to encapsulate lysozyme as antimicrobials and their release profile.¹⁴⁶ Such a type of system may act as a low cost food grade antimicrobial delivery system suitable for using a long shelf life food component like beverages. Because of its insolubility, zeins maintain their structure stabilities in such conditions for a long time. Although zein usually cannot form a

hydrogel with high water retention capability due to its major hydrophobicity character, chemical modification can act as a means to alter their properties and increase their applicability as biomaterials.¹⁴⁷ Wheat gluten is a strongly elastin protein insoluble in water. It has attracted great attention due to their large scale availability and share many similarity with zein protein. Gluten consists of two classes of polypeptides “gliadin and glutenin” mainly differing in their tendency to form intermolecular disulfide bonds.¹⁴⁸ The complexity of gluten and lack of proper knowledge on their structure restrict the use of gluten in various fields. Gluten shows too high viscosity comprising 1.7 g of water per 1 g of protein in its hydrated form, and also the elasticity becomes too high (typically 1 kPa).¹⁴⁹ The porous membrane based on fibers obtained from wheat gluten was prepared and investigated for urea release in agricultural applications.¹⁵⁰ The membrane exhibit good thermal stability up to 117 °C with an equilibrium reached at around 300 min having 98% of the total urea released.

Soy protein is a globular protein obtained as a byproduct while extracting soybean oil. It is composed of glycine (11S globulin) and β -conglycinin (7S globulin), with glycine accounting for around 52% protein content, while β -conglycinin contributes 35% to protein content.¹⁵¹ Soy proteins are known for its foaming and gelling abilities leading to porous hydrogel formation which have a high swelling capacity. The foaming capability and emulsifying performance of glycine is lower than β -conglucinin, due to its dense network structure stabilized by disulfide bond.¹⁵² Soy protein-based hydrogels have found immense applications in various fields like nutrient delivery, superabsorbent material, tissue engineering, controlled release of agricultural products, etc.^{153–155} The understanding and familiarity of different factors responsible in hydrogels formation are important in selection and designing the material for appropriate applications. Various interactions involved in soy based hydrogels includes electrostatic interaction and hydrogen and disulfide bonds.¹⁵⁶ There are a few methods which are frequently reported in the literature for preparing soy based hydrogels including cold gelation, thermal treatment, and enzymatic and chemical cross-linking having their own advantages one over the others.^{157–159} Thermal and cold gelation treated hydrogels are generally mechanically weak and displays fast degradation, which can be improved by enzymatic and chemical cross-linking methods.¹⁶⁰ Chemically cross-linked hydrogels possess good stability and mechanical strength; however, its applicability was restricted due to the toxicity of a cross-linker. Chien et al. prepared hydrogel using mechanical force with varying percentage of soy protein (15, 18, and 20%) in water without using chemical modifiers.¹⁶¹ This method gives the advantages of direct usage of in vivo hydrogel. It was demonstrated that the concentration of soy protein has a direct influence on the swelling, rheological, mechanical, and release profile of the encapsulated ingredient. A higher concentration of protein increases the strength of the hydrogel and thereby lowered the amount of encapsulated ingredient. Also the hydrogel shows good biocompatibility and thus can act as a promising biomaterial, especially for wound healing applications. In another interesting report, a hydrogel based on soy protein prepared via cross-linking using a Maillard type cross-linking agent (glutaraldehyde) in the presence and absence of salt solution.¹⁵⁹ The swelling degree does not appear to be dependent on the microstructural properties; however, the salt does have a direct ionic contribution toward swelling of hydrogel. Enzyme catalyzed

(transglutaminase, TGase) gelation of soy proteins is an interesting area of research. TGase catalyzes an acyl transfer reaction between carboxamide groups of peptide-bound glutamine residues (acyl donors) and a variety of primary amines (acyl acceptors), including the ϵ -amino group of lysine residues in certain proteins.^{162,163} Enzyme catalyzed soy protein isolate (SPI) based hydrogel were prepared by Song et al. with tunable gelation time and mechanical strength. Microbial transglutaminase (MTGase) effectively catalyzes the cross-linking of soy protein isolate in aqueous medium. The activation energy for a 4.0 wt % SPI system at pH 8.0 and 0.008 wt % MTGase was found to be 125.4 ± 19.2 kJ/mol. The resulted hydrogel was reported to exhibit controlled release behavior and could be a potential device in a controlled delivery system.¹⁶²

Albumins were also reported to have a wide range of application as edible coatings and packaging materials due to its biodegradability and good biocompatibility.^{164–166} In a very interesting article by Ma et al. it has being reported that glutaraldehyde cross-linked bovine serum albumin (BSA) and human serum albumin (HSA) establishes autofluorescence hydrogel (green and red fluorescence) without using any additional fluorescent labels, which will become highly helpful in biosensing and tissue engineering.¹⁶⁷ Disulfide-cross-linked albumin hydrogels shows normal swelling profile in water in the presence of denaturants like urea and guanidinium; however, the hydrogels exhibit normal erosion behavior in the absence of denaturants.¹⁶⁸

3.1.3. Lipids Based Hydrogels. Lipids are group of chemically heterogeneous substances, insoluble in water but soluble in nonpolar solvents.¹⁶⁹ Lipid compounds exploited as edible polymers consist of acetylated monoglycerides, surfactants, and natural wax. The primary applications of lipids were reported as edible protective coatings and films acting as efficient barriers for water transfer to control moisture loss in food packaging. The efficiency of the coating to control moisture loss was found to be reliant on the structure, chemical arrangement, nature of lipid, and hydrophobicity level. Among lipids, paraffin wax and beeswax as a model of edible lipids displays lowest water vapor permeability value because of their highly hydrophobic nature (Figure 8).¹⁷⁰ The mechanical properties were enhanced or improved by combination with other polysaccharides or chemical modification. Acetylated

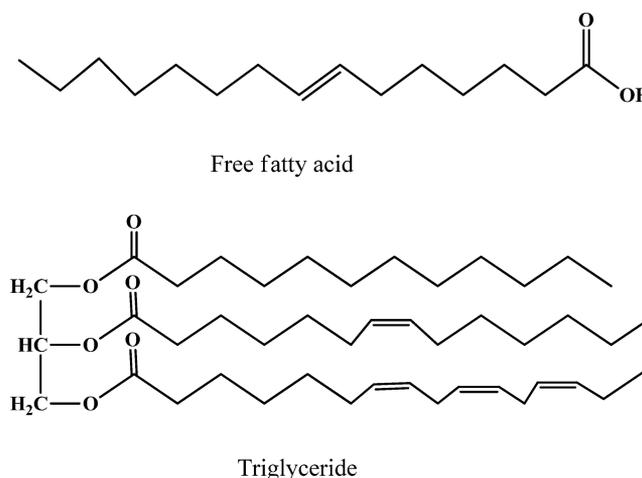


Figure 8. General backbone structures of lipids.

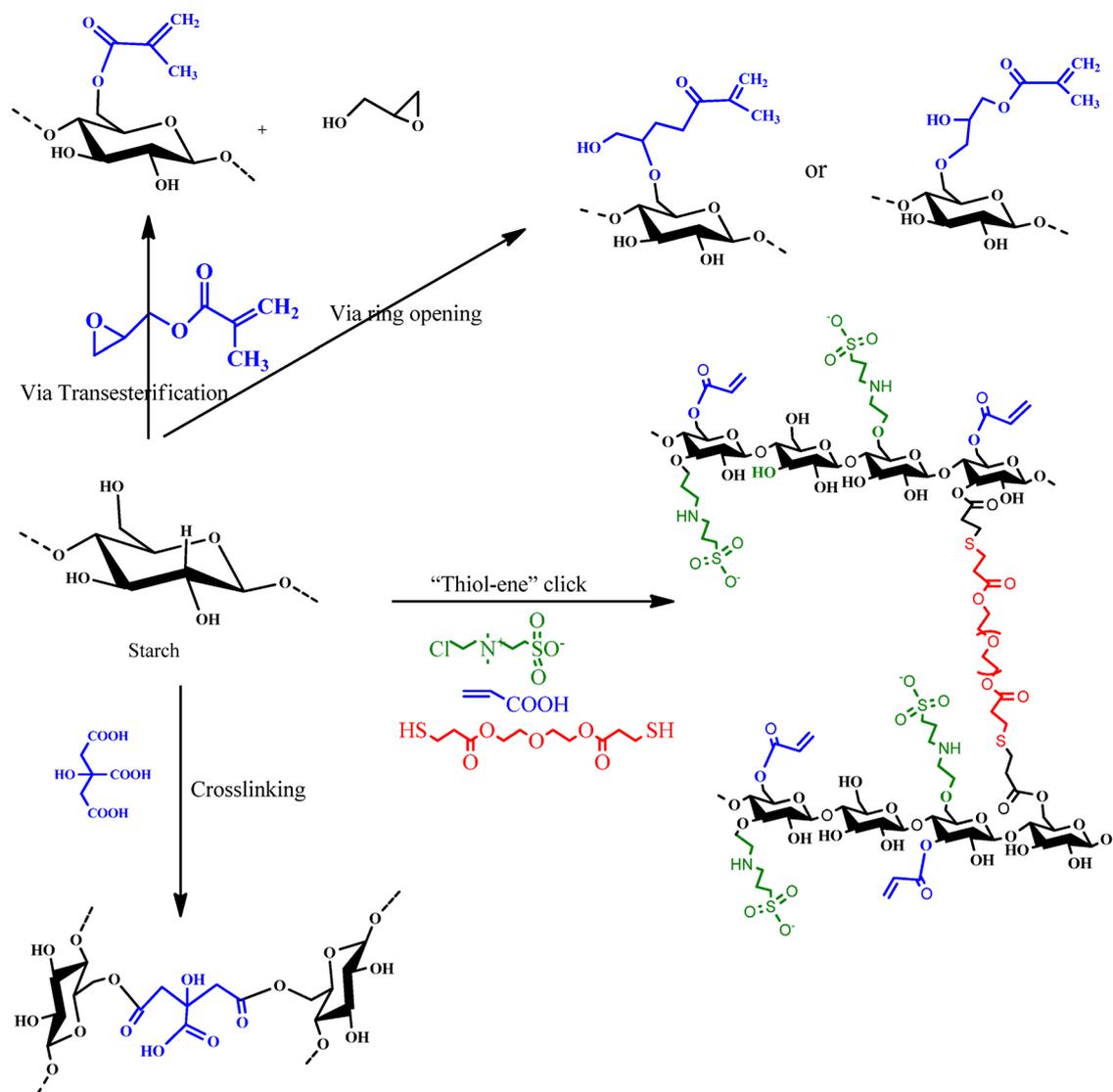


Figure 9. Preparation of chemically modified starch based hydrogels.

monoglyceride shows the distinctive property of solidifying from the molten state into a flexible, wax like solid. The flexibility depends on the degree of acetylation, product with a low degree of acetylation loss their flexibility gradually with time.¹⁷¹ Acetylated glycerol monostearate displayed a stretchability up to 800% of its original length, which the most lipids appeared to have only 102% of its original length.¹⁷² In a drug delivery system, lipids are known to promote oral absorption of drugs. Solid lipid nanoparticles (PEG fatty acid esters and glyceryl monostearate) based hydrogels as potential carriers for oral transmucosal delivery of Risperidone (antipsychotic drug) were evaluated by Silva et al.¹⁷³ The nanoparticles retain their colloidal range after hydrogel formation for a month, which thereafter shows a slight increase in the particle size. The release mechanism was found to be pH sensitive, with a Fickian diffusional process followed by erosion. Such a type of system could act as a suitable carrier for oral transmucosal delivery. Fatty acids have found tremendous applications in personal care and cosmetics industries. Some fatty acids undergo gelation only in the presence of other di/oligomeric amines. The gelation property of stearic acid and eicosanoic acid in water in the presence of various oligomeric amines were

investigated by Basit et al.¹⁷⁴ The primary interaction between the two components involved ionic interaction between carboxylate and ammonium ions, followed by continuous hydrogen bonded network structure forming gel. Hydrophobic interaction also played important role in packing of fatty acids. Such a system proved as a good medium for the synthesis of nanoparticle, giving a gel-nanoparticle composite.

3.2. Chemically Modified Edible Polymer Based Hydrogels. Biopolymers show abundant potential and have plentiful valuable properties, but still there are numerous drawbacks associated with it. Thus, to utilize their full potentials, scientific researchers were focused on the chemical modification of such biopolymers to reduce the drawbacks and increase their performance under various conditions. Chemical modification generally referred to a process involving formation of a chemical bond between to components (biopolymer and new reagent) to form a new product. The chemical modification of biopolymer occur due to the susceptibility of hydroxyl groups to multifunctional compounds, examples of chemical modification reported on biopolymers include electrophilic and nucleophilic substitution reactions, oxidation, reduction, acylation, esterification, sulpho-

Table 1. Edible Polymers Based Hydrogels

polymers	chemical modifiers	key aspects	applications	refs
Polysaccharide Based Hydrogels				
Corn starch	Acrylic acid or methyl methacrylate	Highly pH sensitive	Biomedical application as polymerized cements	410
Starch	Polyvinyl alcohol (PVA), Turmeric	Sufficient mechanical strength for dressing	Wound dressing/antibacterial	411
Starch	Acrylic acid and 2-hydroxy ethyl methacrylate	Reversible pH responsive at pH 2 and 8.	Controlled delivery	412
Corn starch	Acrylamide and acrylic acid	Most desirable kinetic behavior	Drug delivery system	74
Carboxymethyl cellulose	Starch	Higher water uptake in high electrolyte concentration	Superabsorbent	413
Gellan gum	Retrograded starch	High strength, elasticity, adhesiveness	Mucoadhesive drug delivery system	414
Chitosan	PVA, gelatin	Good coagulation effect	Wound dressing	415
Chitosan	Polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP)	Fast healing property, antibacterial activity	Scar prevention wound healing	416
Sodium alginate	PVP, acrylic acid, gelatin	Efficient and eco-friendly absorbent	Removal of heavy metal ions	417
Sodium alginate	Poly(<i>N</i> -isopropylacrylamide)	Noncytotoxic and stimulates cell proliferation	Cell delivery in tissue engineering	418
Sodium alginate	G ₁ RGDASSP peptide, nanofiber mesh	Sustained delivery of rhBMP-2 for functional regeneration of bone	Repair of bone injuries	366
Carboxymethyl cellulose	Acrylic acid	Fickian diffusion at low pH (pH = 1) and nonfickian diffusion at normal pH (pH = 7)	Site specific delivery system	419
Hydroxypropyl methylcellulose	Pluronic, anti HIV activity of mini-CD4M48U1	Efficient barrier against HIV diffusion through macaque cervicovaginal mucus	Topical microbicide	420
κ -carrageenan	Acrylic acid- <i>co</i> -2-acrylamido-2-methylpropanesulfonic acid	pH sensitive on-off behavior	Drug delivery system	187
κ -carrageenan	<i>N</i> -isopropylacrylamide	Chloride ion-induced phase transition	Biomedical application	421
Guar gum	<i>N</i> -isopropylacrylamide	Thermo responsive release behavior	Drug delivery system	422
Pectin	<i>N,N</i> -methylenebis(acrylamide)	Deliver drug to intestine without losing in the stomach	Oral drug delivery system	423
Gum arabic	Acrylic acid and acrylamide	On-off switching behavior in different solvent	Controlled delivery if bioactive agents	424
κ -carrageenan and sodium alginate	Polyacrylamide	Antisalt superabsorbent	-	425
Sodium alginate and κ -carrageenan	Ca ²⁺ and K ⁺	Support the cell viability as well as proliferation	Cell delivery in regenerative medicine and tissue engineering	426
Chitosan, κ -carrageenan and carboxymethyl cellulose	Sodium chloride	Sensitive to ambient pH	Controlled release system	427
Proteins Based Hydrogels				
Gelatin	β -cyclodextrin, oxidized dextrin	Drug loaded hydrogel showed enhanced cancer cell inhibition	Controlled and targeted drug delivery	428
Gelatin	PEG, ethylenediaminetetraacetic dianhydride, glutaraldehyde	Swelling/degradative kinetics modified	Bioresorbable cell/drug carrier matrix	429
Gelatin	PEG, nitrobenzyl moieties	Light triggered cell delivery	3D culturing platform for capture and release of cell	430
Gelatin	Lysine diisocyanate ethyl ester	Tailorable elastic properties	Regeneration of damaged soft tissue and temporal replacement	431
Whey protein	Diethylene glycol, ethylene glycol, glycerol	The hydrogel allowed the attachment and growth of cutaneous cells	Substrate for in vitro cell culture	432
Soy protein	Polyethylenimine	Selective adsorption of copper from waste products	Waste water treatment	433
Soy protein	PEG	-	Wound dressing	434
Zein protein	Acrylic acid, acrylamide	Good copper ion chelation capacity	Heavy metal ion chelators	435
Casein protein	Polyacrylamide	Highly stretchable and notch-insensitive	Biomedical application and tissue engineering	436
Casein protein	Genipin	Genipin act as cross-linker for casein	Protein drug delivery	437
Lipids Based Hydrogels				
Stearic acid or eicosanoic acid	Di or oligomeric amines	Three dimensional ordering in one direction in gel state	Template for the synthesis of nanoparticles	174
Fish oil (containing omega-3 fatty acid)	Carbopol 971	Long-term stability	Topical delivery	438
Myverol saturated monoglycerides	Palmitic and stearic acid	Reduce total saturated fat contents	Food applications	439

nation, oxidative cleavage reaction, click chemistry, cross-linking, grafting, and quaternization etc.^{175,176} (Figure 9). Chemical modification can alter the character of the biopolymer. Most of the biopolymer is insoluble in water and other organic solvents. Chemical modification changes the

solubility of such biopolymer. For example, charged biopolymer (such as quaternized chitosan) exhibit excellent solubility in water. Table 1 contains a list of edible polymer based hydrogels, chemical modifiers used, its properties, and applications.

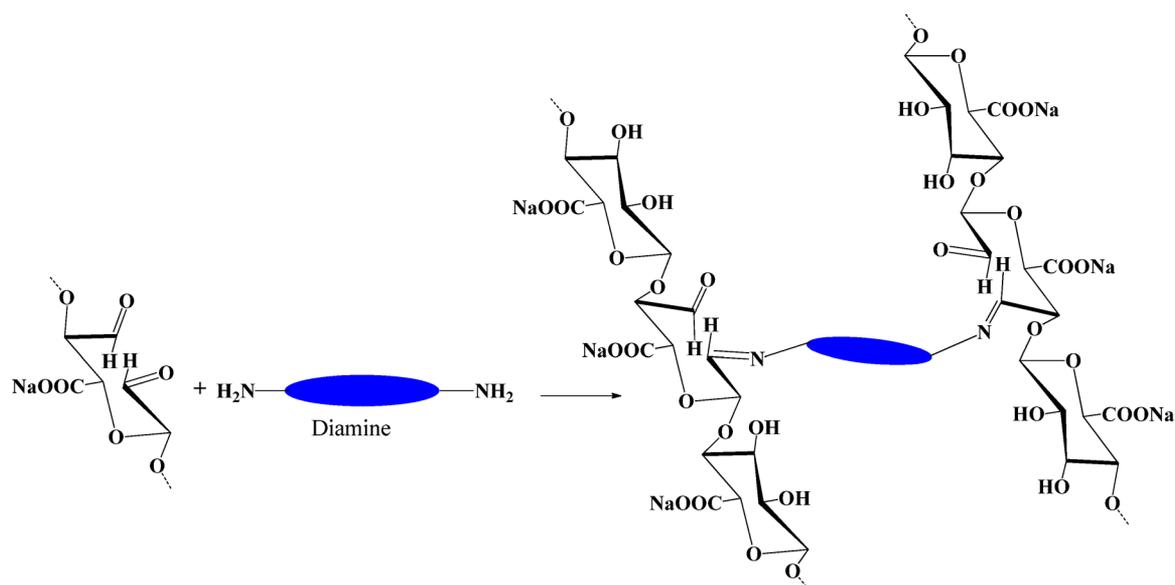


Figure 10. Cross-linking pattern of oxidized alginate with diamine.

Chemically modified starch based hydrogels, particularly polyacrylamide grafted starch have been reported with advanced properties.⁷⁴ Polyacrylamide due to its biocompatibility and availability have found as the most investigated chemical modifier. These types of hydrogels found various applications such as super absorbents, wound dressing, drug delivery, agricultural applications, and tissue engineering, etc.^{177–179} Adriano et al. reported glycidyl methacrylate (GMA) modified starch based cross-linked hydrogel for a targeted delivery system.¹⁸⁰ The swelling behavior of this hydrogel was not affected by the change in pH and temperature of the surrounding liquid. Zwitterionic starch-based “clickable” hydrogel was prepared using an acylated-modified sulfobetaine (SB-ST-A) derivative of starch and dithiol-functionalized poly(ethylene glycol) (PEG-SH) via a “copper and light free” Michael-type “thiol–ene” addition reaction for 3D cell encapsulation (Figure 9).¹⁸¹ Sulfobetaine derived starch (SB-TA) and PEG incorporation in the hydrogel protected it from nontarget protein absorption to act as “blank platform”. The stiffness of hydrogel was reported to be close to native tissue, having a gelling time less than 7 min under normal physiological conditions. The resistance to nonspecific protein absorption and cell adhesion was attributed to antifouling properties of SBTA and PEG moieties. The hydrogels exhibit complete *in vitro* degradability within 21 days. The encapsulated A549 cells in the hydrogel maintained high viability and proliferated in number as well morphological extension started after 2 days culture, attributing to the high vitality and hydrolysis of ester bonds.

Citric acid has been used as a cross-linking agent in polysaccharide chemistry to prepare superabsorbent hydrogels. Such hydrogels had shown improved tensile strength, decreased solubility of starch in water, and increased thermal stability.¹⁸² Cross-linking reaction between starch and citric acid take place without the use of any toxic catalyst via a cyclic anhydride intermediate formation.¹⁸³ Starch based hydrogels with controlled hydrophilicity were obtained by modifying starch with polyester and cross-linked with citric acid.¹⁸⁴ This hydrogels type of hydrogels could be a potential device for drug delivery, coating, and biomaterials.

Chemical modification of carrageenan and its hydrogel were prepared with excellent pH responsiveness and antisalt properties. Carrageenan based hydrogels possess low sensitivity toward salt solution, which could be attributed to the antisalt property of sulfate groups.¹⁸⁵ Poly(*N*-vinyl-2-pyrrolidone) grafted using γ -irradiated on kappa and iota carrageenan exhibit enhanced stimuli responsive swelling and mechanical strength. The swelling property increased by about hundred times to its dry weight.¹⁸⁶ Copolymerization of kappa carrageenan with acrylic and 2-acrylamido-2-methylpropane-sulfonic acid results a biodegradable hydrogel with potential applications.¹⁸⁷ Acrylate grafted κ -carrageenan based super-absorbent hydrogel (activation energy of the reaction is 2.93 kJ/mol) reveals high water retention capacity with maximum water absorbency of 79 g/g.¹⁸⁸ Alginates also have enough capability of hydrogel formation, although the alginates hydrogel cross-linked ionically loss more than 60% of their original mechanical strength within 15 h of exposure to physiological buffers.¹⁸⁹ Therefore, covalent cross-linking could be used as an alternative to retain the hydrogel mechanical strength. Poly(ethylene glycol) diamines cross-linked alginate hydrogels displayed a controllable mechanical property, controlled by the molecular weight and weight fraction of PEG.¹⁹⁰ Lee et al. investigated the effect of cross-linker type (lysine, dihydrazide, and poly(ethylene glycol)-diamine) and cross-linking density on the swelling and mechanical properties of alginates hydrogel.¹⁹¹ The mechanical properties were found to be mainly controlled by the cross-linking density but are also shown slight dependency on the cross-linker type. Introduction of hydrophilic molecule in the hydrogel balance the loss of hydrophilic character of the polysaccharide during the cross-linking reaction. Periodate oxidation involving rupture of C–C at C-2 and C-3 to introduce two aldehyde groups in the alginate followed by cross-linking is another chemical modification reported by many researchers for hydrogel preparation.^{192–194} Aldehyde group react with amine forming the well-known Schiff base complex. Schiff base reaction has been explored enormously in polysaccharide chemistry (Figure 10). Adipic dihydrazide cross-linked oxidized alginate and κ -carrageenan based hydro-

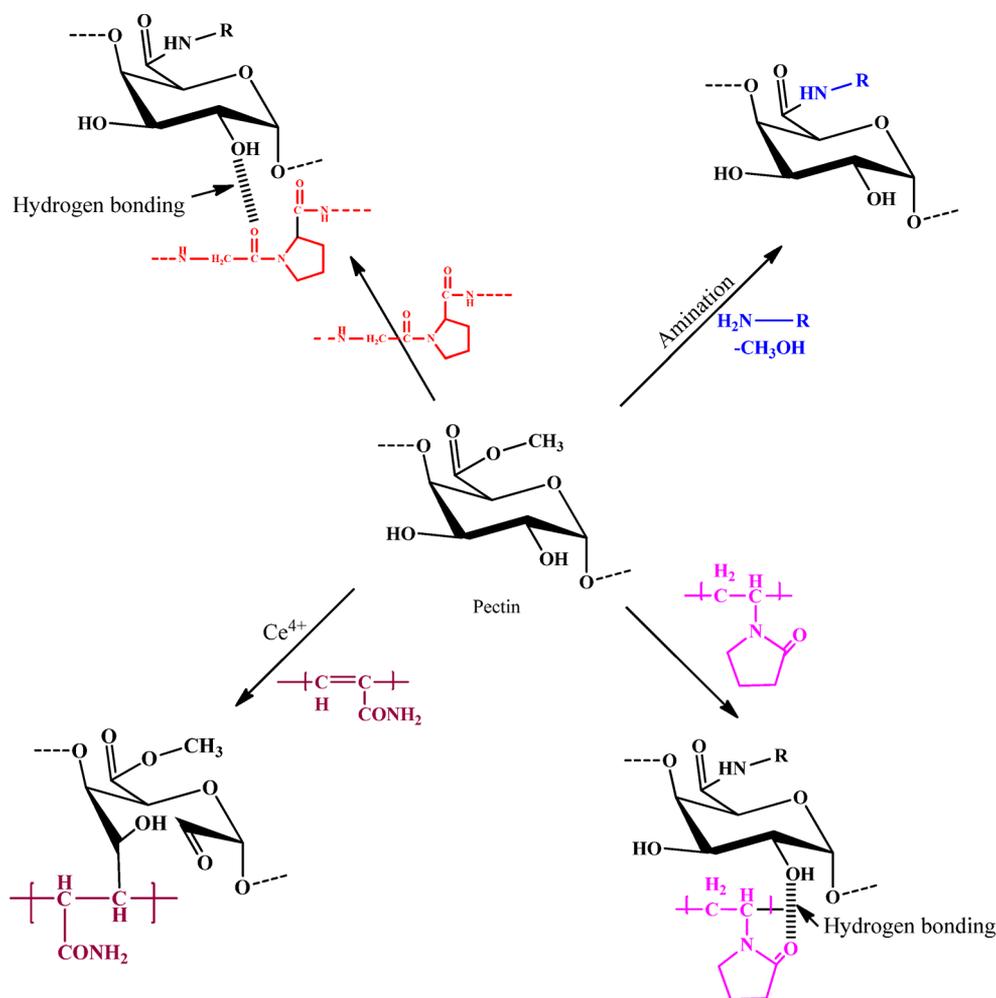


Figure 11. Chemically modified pectin based hydrogel.

gel was reported by Pascalau et al.¹⁹⁵ The hydrogel has shown good mechanical characteristic; however, it has become more susceptible to water during swelling, resulting in the disintegration of the gel.

Oxidation also increases the biodegradation rate of alginate hydrogel, although the rate of biodegradation is faster in vitro than in vivo, which becomes helpful in regenerative medicine. Oxidized alginate and its modification with methacrylate were done to obtain a photo-cross-linkable hydrogel having controllable physical and cell adhesive properties.¹⁹⁶ Different properties of hydrogels like swelling behavior, storage modulus, and degradation profile can be controlled by varying the degree of oxidation level. The methacrylate modified hydrogel displayed cyto-compatibility when cultured with mesenchymal stem cells (a human bone marrow derived cell). Such type of hydrogel could find application in tissue engineering and other biomedical fields.

Pectin a heterogeneous polysaccharide mainly prepared from apple pomace and citrus peel is modified with acrylamide via grafting followed by cross-linking with glutaraldehyde.¹⁹⁷ The acryl modified pectin hydrogel shown better gelation and film forming property as compared to parent polymer. The swelling behavior and drug release mechanism were found to be pH dependent. Poly(*N*-isopropylacrylamide) grafted pectin was studied as a potential device for colon targeted delivery of theophylline (Figure 11).¹⁹⁸ The gels were prepared by using

ceric ammonium nitrate as initiator and *N,N'*-methylenebis-(acrylamide) as cross-linker. The hydrogel showed maximum drug release at pH 7.4 and minimum at pH 5.5, without thermosensitive behavior. Mishra et al. thoroughly investigated pectin/gelatin, pectin/polyvinylpyrrolidone (PVP), and pectin/PVP/glycine based hydrogels as wound dressings and other delivery systems.^{199–201} The association of different components in the hydrogel are because of the strong intermolecular interaction or hydrogen bonding between different components proved by a FTIR study. Tensile strength and elongation break increases with gelatin content in the hydrogel up to a certain point, and thereafter it decreases. Pectin/gelatin based hydrogel were found to be cytocompatible with B16 melanoma cells. Addition of glycine helps in the healing process, thus such hydrogels can act as good wound healing material.

Dextran based biocompatible self-healing hydrogel was reported using click chemistry reactions. Wei et al. reported a cytocompatible hydrogel based on fulvene modified dextran (as dienes) and dichloromaleic acid modified PEG (as dienophiles) using Diels–Alder reaction under physiological conditions.²⁰² Diels–Alder based reversible linkages permit the hydrogel to restructure dynamically and self-heal under mechanical disruption. Increase in the molar ratio of the two components accelerates the gelation processes. Thiol–Michael addition reaction, another click chemistry reaction

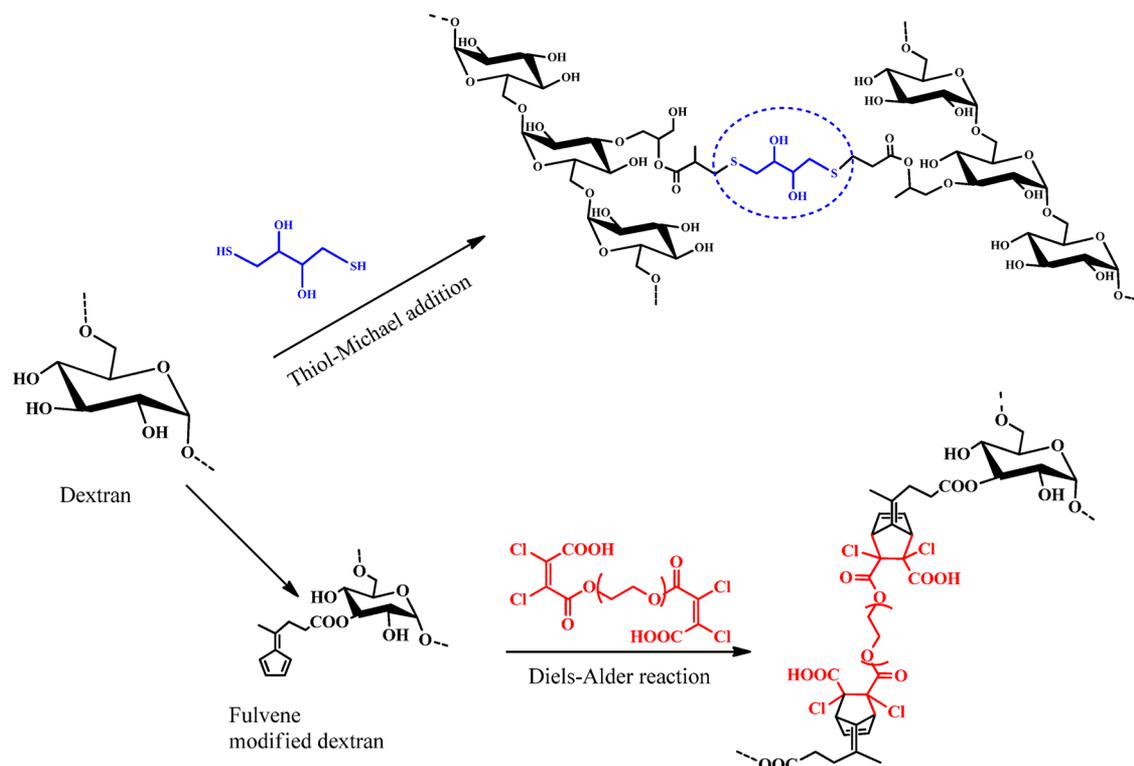


Figure 12. Chemically modified dextran based hydrogel.

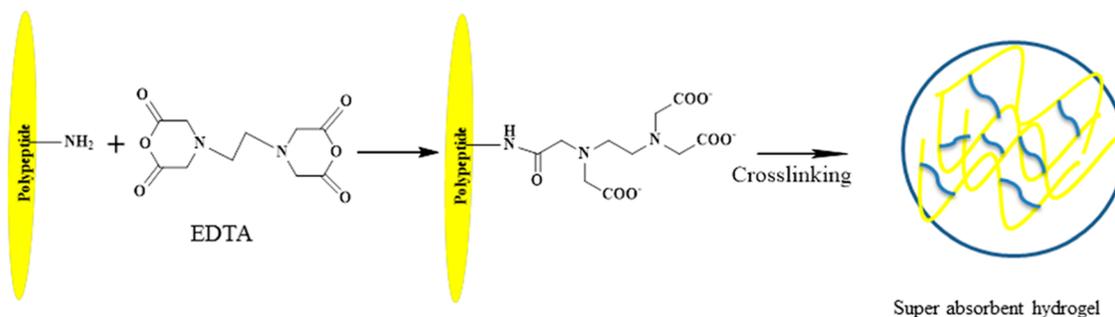


Figure 13. Polypeptide modified super absorbent hydrogel.

with high regioselectivity has been reported by Liu et al. aimed at in situ hydrogel formation for 3D cell encapsulation (Figure 12).²⁰³ In this process, dextran was initially modified by glycidyl methacrylate. The modified dextran was then cross-linked with dithiothreitol via thiol–Michael click reaction under physiological condition. System pH (7.0–7.8) has shown a very advanced effect on the different features such as swelling degree, gelation, morphology, and mechanical properties of the gel and can be used to control. The cell encapsulation ability of the hydrogel shown high viability of bone marrow mesenchymal cells as well as maintains their differentiation potential and fibroblast cells. Thus, such hydrogel could find enough potential in biomedical fields.

Similarly, proteins and polypeptides were also chemically modified to enhance its properties and applications, although as compared to polysaccharide there are only few reports available regarding the chemical modification of polypeptides. The most studied polypeptides include soy protein, fish, and collagen based proteins. Pegylation (attachment of polyethylene glycol to protein chain) of protein started in the late 1970s by Frank Davis to protect protein from destruction

as delivery systems.²⁰⁴ This also improves the pharmacokinetic and pharmacodynamics of polypeptide preparations. Polyethylene glycol has also been used as a cross-linker in protein centered system due to their low toxicity. Chemical modification of proteins has been used to produce biotherapeutics, with extended circulatory half-life and to produce protein conjugates.²⁰⁵ One limitation of protein based hydrogels is that they do not swell to their original volume once they are dried due to increased protein–protein interaction via hydrogen bonding, hydrophobic and electrostatic interaction. These types of drawbacks can be overcome by applying appropriate chemical modification in the protein side chains. Soy protein isolate (SPI) chemically modified with ethylenediaminetetraacetic dianhydride (EDTA) followed by cross-linking with glutaraldehyde resulted into a gel that absorb more than 105 g of water per gram of dry hydrogel.²⁰⁶ EDTA introduction in the protein results in the addition of a large number of hydrophilic carboxyl groups. This causes extensive unfolding of protein, resulting in polyanionic character with abundant sites available for water binding and hydration. Theoretically, three carboxyl groups can be introduced with

the modification of one amino group (Figure 13). Genipin cross-linked SPI based hydrogels showed improved mechanical property and also the biodegradability of the hydrogel can be controlled from 14 to 33 days.²⁰⁷ This sort of hydrogel might find potential application in food packaging. Song et al. reported that genipin cross-linked SPI hydrogels could act as site-specific drug delivery device in the intestine.²⁰⁸ The use of naturally occurring cross-linking agent (like genipin) could reduce the toxicity level of the hydrogel. The initial gelation time was detected to decline with increasing the amount of genipin, while the gel strength increases. Liu et al. prepared and investigated glutaraldehyde and *N,N'*-methylenebis-(acrylamide) cross-linked poly(acrylic acid) (PAA) modified soy protein based hydrogel for bovine serum albumin (BSA) release in different buffers.²⁰⁹ The BSA release was found to be strongly pH dependent having a Fickian diffusion pattern at pH below pK_a value of PAA and non-Fickian type at pH above the pK_a of PAA acid. The BSA release was found to be decreasing with increasing the amount of soy protein and cross-linking agent in the system.

Gelatin was also modified through various chemical reactions to tune its properties as per the required applications. Addition of another ionic polysaccharide to gelatin solution acts as cogelators and enhances its rheological property. The interaction between the charged gelatin and cogelators polysaccharide ions leads to the compatibility and stability of the system forming polyelectrolyte complexes. Addition of an anionic polysaccharide (κ -carrageenan) to gelation solution not only accelerates the gelation processes but also increases the viscoelastic parameters of the hydrogel.²¹⁰ The complex formation results due to the electrostatic interaction between the positive charge in gelatin and the negative charged sulfate group of carrageenan. There is also a drastic change observed in the supramolecular structure of hydrogel. Photodegradable gelatin-based hydrogel was prepared using azide modified gelatin and dibenzocyclooctyl-terminated photocleavable tetra arm-PEG.²¹¹ The hydrogels were designed in 30 min through the click cross-linking reaction. Methacrylate modified gelatin-based hydrogel and its structural and rheological properties were studied by Bulcke et al.²¹² Hydrogel was prepared using modified gelatin with methacrylate and subsequently cross-linked by radical polymerization via photoinitiation. The rheological properties of the hydrogel could be controlled by monitoring the degree of substitution, concentration of polymer and initiator, or by UV irradiation conditions. The gelation time can also be controlled by changing the concentration of photoinitiator. These type of hydrogels also exhibited high storage modulus and low degradation rate.²¹³

Chemical modification of fish protein (FP) and its resultant hydrogel has been investigated for a nonfood application as superabsorbent. Modification of FP with ethylenediaminetetraacetic dianhydride (EDTAD) introduces a large number of hydrophilic groups into the protein network.^{214,215} Proteins were then cross-linked through a sulfhydryl-disulfide interchange reaction between the endogenous sulfhydryl groups ($-SH$) and disulfide bonds ($-S-S-$) to produce an insoluble superabsorbent hydrogel. The swelling capacity depended on the pH and ionic strength of the medium, having a water absorption capacity of 540 g/g of dry gel, when 76% of FP was modified with EDTAD. It has been reported that the addition of nonprotein polymer (like CMC, PVA, PEG, or guar gum) at a concentration of 2.5% in the 80% EDTA modified fish protein hydrogel strangely decreased the absorption uptake

capacity of the gel.²¹⁶ This effect could attribute to the thermodynamic incompatibility of these polymers with the fish protein consequently affecting the degree of relaxation of the cross-linked polypeptide network.

3.3. Hybrid or Mixed Polymer Hydrogels. Various industries have been using hydrogels formulated from consumable polysaccharides. However, the hydrogels containing single polymer arrangements are not sufficient to fulfill the required properties and performance. Therefore, in order to enhance various properties, mixed polysaccharides based hydrogels have been under consideration. The new hybrid polysaccharide hydrogels can be expected to show better structural and functionality resemblance with the living tissue, synergistic effect, better stability and biodegradability, accompanied with new functionality for enhanced performance.⁵²

Carboxymethyl chitosan (CMC) and sodium alginate-based hybrid hydrogel was prepared by oxidizing sodium alginate (OSA) to introduce dialdehyde groups followed by cross-linking with the amino group of carboxymethyl chitosan.²¹⁷ The minimum gelation time was found around 6.3 s with the addition of 8 mL of OSA. The degree of swelling also decreases with increasing the amount of OSA, indicating a higher degree of cross-linking. In another report, biocompatible CMC and OSA-based self-healing injectable hydrogel were developed as a carrier of neural stem cells.²¹⁸ Under physiological conditions, these hydrogels had shown the ability to self-heal. Also the stiffness of the hydrogel becomes similar to the natural brain tissues which support the proliferation of loaded neural stem cells inside the 3D hydrogel. As a consequence, this kind of hybrid polysaccharide-based hydrogels will open the doors for hydrogels in neural stem cell applications.

Dextran and gelatin were modified via oxidation and amination, respectively, by Pan et al. to provide a fast forming gel material without the application of an external cross-linking agent.²¹⁹ Dextran was modified with periodate to dextran dialdehyde and gelatin with ethylenediamine. The hydrogel was evaluated for its potential in cartilage tissue engineering application using synovium derived mesenchymal cell accompanying TGF- β 3 (growth factor) injected subcutaneously in the dorsa of athymic nude mice. The final observation did not find any inflammatory reaction followed by higher production of glycosaminoglycans and huge cell accommodation with newly formed cartilage. Therefore, such nontoxic, biocompatible hydrogel can be useful in the various applications, where synthetic polymer based hydrogels becomes limited due to toxicity issues. Similarly, oxidized alginate and gelatin-based cross-linked adhesive hydrogels were reported by Yuan et al.²²⁰ Gelling time, bond strength, and swelling behavior of the hydrogel were found to be dependent on the aldehyde groups present in the oxidized alginate and amino groups in gelatin. Adhesive strength of the gel become equal to commercially available adhesive fibrin glue at an aldehyde content of 75.24% and amino content of 0.61 mmol/g.

A ternary polysaccharide system-based biocompatible hydrogel consisting of Pullulan, dextran, and fucoidan was appraised as an innovative biomaterial designed for Endothelial Progenitor Cell (EPC) culture by Thebaud et al.²²¹ Sodium trimetaphosphate was used as a cross-linker, obtaining a transparent, homogeneous gel with water content higher than 90%. The EPCs used were comprised of CD34+ derived from cord blood and two sorts of CD133+ from human bone marrow (30-days old and 4-days young). The EPCs adhered to

Table 2. Method of Preparation, Crosslinker, and Tensile Strength of Some Edible Polymer Based Films Hydrogels

polymer	method of preparation	plasticizer/cross-linking agent	tensile strength (MPa)	elongation (%)	ref
Agar	Casting	Glycerol	19.8–35.3	14.33–26.67	440
Agar	Casting	Glycerol	42.11 ± 3.27	6.51	441
Cassava starch	Casting	Glycerol	35.17 ± 4.60	2.64	441
Normal rice starch	Casting	Glycerol	28.85 ± 3.53	2.07	441
Waxy rice starch	Casting	Glycerol	8.51 ± 3.12	0.72	441
Pea starch	Casting	Polyols and monosaccharides	3.4–44.9	4.2–93.7	442,443
Mango kernel starch	Casting	Glycerol and sorbitol	1.90–26.41	3.82–37.06	444
Methylcellulose	Casting	Malic acid and Sorbitol	29.2–34.6	24–32	445
Gelatin	Solvent evaporation	Glycerol and sorbitol	24.88	107.48	446
Gelatin	Chemical cross-linking	1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide	0.196 ± 17	-	447
Amaranth	Emulsification process	Glycerol	2.6	148	448
Konjac Glucomannan	Casting	Glycerol, Sorbitol	35–55	10–80	449
Alginate & pectin	Casting	Glycerol	39.7–61.5	1.8–20	450
Zein	Rolled using pasta roller	Oleic and Linoleic acid	2.0–9.4	5.9–46.9	451
Zein	Casting	Pluronic F127	9.2–29.1	16–92	452
Zein	Casting	Glycerol	17.67	4	453
Zein	Casting	Tributyl citrate	3.25–17.80	1.96–4.53	454
Whey protein (WP)-hydroxypropylmethylcellulose (HPMC)	Casting	Glycerol	3.9–61	16–112	455
WP-okra polysaccharide	Casting	Glycerol	1.1–8.4	10–90	456
WP-methyl cellulose	Casting	Glycerol	15.88	~45	457
WP-HPMC	Casting	Glycerol	14.92	~35	457
WP-starch	Casting	Glycerol	0.66	~35	457

this hydrogel in 4 and 24 h after seeding in serum free conditions. Therefore, such a kind of hydrogel could act as a potential candidate for some novel applications.

4. PROPERTIES OF EDIBLE POLYMERS BASED HYDROGELS

Once the hydrogel has being formed, the important properties which the hydrogel should possess or one has to evaluate which define its applicability are swelling rate, mechanical properties, and toxicity level or its biocompatibility. A very important characteristic feature of hydrogels is that it can control the swelling state in response to environmental variations such as temperature, pH, ionic concentration, and ionic species, and also to external stimuli like electric potentials, UV light, pressure and magnetic fields.^{222,223} These features in turn assist dynamic control over the expansion and contraction of the hydrogels generating stimuli responsive smart materials. Keeping this properties in attention scientists are trying to mimic the biological functions of human organs (muscles, tissue, permeable membrane, cartilage, etc.) using smart hydrogels. Examples include magnetic responsive actuators, electro driven artificial muscles, temperature controlled shape memory hydrogels, and the very common delivery systems. The degree of flexibility of these hydrogels is also reported to be very similar to natural tissue. Swelling processes are governed first by binding water molecule at the hydrophilic sites followed by entrapment in the hydrogel network. During swelling, the hydrogel contains three forms of water molecules.²²⁴ The first one is a free water molecule which is physically trapped in the polymer matrix and can be easily removed by the temperature effect, while the second form was bonded directly with the polymer through a strong hydrogen bond acting as part of the gel and cannot remove

easily. Some water molecule exhibit properties between the first two and called a semibonded molecule.⁹

For food packaging and biomedical application, mechanical properties of hydrogels are very important. Sometimes packaging material is commercially used below room temperature; therefore, it is essential to assess the mechanical function or performance under such conditions.²²⁵ From the biomedical view of point, the areas where mechanical property of hydrogel play an important role are wound dressing material, tissue engineering, drug delivery, ligament and tendon repair, and cartilage replacement materials.²²⁶ During drug delivery the hydrogel should maintain its physical texture for the predetermined period of time. Mechanical properties of hydrogel can be adjusted by controlling the degree of cross-linking. Higher cross-linking gave a stronger hydrogel, but the % elongation capacity decreases resulted in more brittle structure. Table 2 reports the mechanical properties of some edible polymers based hydrogels.

Biocompatibility is another important characteristic of edible polymer based hydrogels, particularly for pharmaceuticals and biomedical and food related applications. Biocompatibility is the ability of a material to perform its anticipated function with an appropriate host response.²²⁷ Thus, the hydrogel must pass the in vivo toxicity tests to be used for a particular application. Most of the edible polymer based hydrogels however found to be biocompatible and nontoxic.²²⁸ Therefore, such types of hydrogels find immense application in the pharmaceutical and biomedical fields.

5. APPLICATIONS OF EDIBLE POLYMER BASED HYDROGELS

The level at which hydrogels have been under investigation in different fields reflect its potential as smart materials for future

applications. Though, it is not mandatory for a new invention or development to be only a high-tech device deprived of any of-sight ambitions. This is very well reflected by hydrogel development. Hydrogels have gained their position in every aspect of industrial revolution, whether it is in the food industry or pharmaceutical industry and other fields. Two very significant areas where edible polymer-based hydrogels were enormously studied and find their practical applications are food based industries and pharmaceutical industries. The other application includes agriculture and cosmetics industries, bioelectronics devices, personal care products, and so forth.

5.1. Food Packaging. The main objective of food packaging is to maintain food quality and safety from the stage of manufacture to product utilized by the customer. The total global population as estimated by the Food and Agricultural Organization of the United Nations (FAO) will reach to 9.15 billion by 2050, which is directly linked to an increase in total world food production by about 70%.²²⁹ Food storage and protection is an integral part of food production. The packaging should prevent or reduce food spoilage and product damage as well as eliminate the threat of adulteration and deliver the food in a hygienic way. Different properties that a good packaging material should possess are listed in Figure 14. Presently, plastic materials represent the main source of



Figure 14. Properties which determines the quality of good packaging materials.

packaging as well as for storing, processing, preserving, transporting, and protection. Plastic materials achieved enough success in packaging fields due to a mixture of properties like good flexibility, mechanical strength, stability, lightness, and impermeability. However, the main challenge with plastic product remains with the disposal of huge masses of nonbiodegradable product, which act as the main source of pollution in the environment. Thus, the development of long-term food storage and packaging materials having high chemical durability, nontoxic, biodegradable, and eco-friendly property becomes a matter of necessity. To meet the rising demand of biodegradable and recyclable packaging materials to provide safer and better quality food, new technologies to develop novel food grade packaging materials have continued to be developed. Thus, in this case, edible polymer or nature based polymers could improve many challenges related to conventional plastic product in the food industry. Some natural

products have been reported to exhibit various beneficial properties like moisture loss prevention, reduce lipid oxidation, color retention, improve flavor attributes, and enhance microbial stability of foods.²³⁰ Today the use of natural renewable and biodegradable product in food packaging is growing at a faster rate.²³¹ It includes polysaccharide such as starch, cellulose derivatives, natural gums, etc., polypeptides like gelatin, zein, whey protein, etc. and lipids either alone or in blend forms.^{232–234} The important factors that a good packaging material depends are barrier properties, oxygen transmission rate, water vapor, and carbon dioxide transmission rate, chemical resistance, and mechanical strength.²³⁵ Polysaccharide exhibit good barrier properties; however, their moisture resistance is low. Whereas proteins have good mechanical strength and lipids provides low water vapor permeability. The another advantage of edible polymer as packaging materials are it can also act as a food component with required properties as high barrier and mechanical competences, physicochemical, biochemical, microbial stability, low cost, nontoxic, and nonpolluting.^{236–238} Edible polymers can use in the form of either films, gels, and as coatings. Various techniques applied for films formation includes casting, spraying, wrapping, foaming, and brushing, etc.²³⁹ Polysaccharides like starch, pectins, cellulose ethers, carrageenan, and alginate were used for films formation which imparts compactness, adhesiveness, hardness, and thickening quality, while the lipid films could produce anaerobic conditions.²⁴⁰ The starch based films were physically similar to plastic in many orders like colorless, tasteless, odorless, biologically absorbable, resistant to oxygen, and semipermeable to carbon dioxide.^{241–243} Addition of lipids to starch based films improves water vapor barriers because of its hydrophobicity, while cellulosic fibers and chitosan shows tremendous improvement of strength and gas permeation.^{244,245} The addition of food additives like antimicrobials, antioxidants, flavors, fortified nutrients, and colorants to edible films or coatings improves its functionality and applicability.^{246,247} Pranoto et al. reported that addition of garlic oil (0.4% v/v) to alginate-based edible films improves its antimicrobial potential and other properties.²⁴⁸ Alginate based coating and films imparts better moisture retention, reduction in shrinkage, retard oxidation, improve product texture, color, juiciness, and odor in muscle food packaging.²⁴⁹ Alginate and gellan based films in the presence of various additives were explored for its potential in coating of high moisture containing fresh cut fruits.²⁵⁰ Alginate films exhibit higher water vapor permeability (WVP) than gellan film; however, addition of sunflower oil decreased WVP of gellan films. Starch-alginate based composite films with stearic acid and tocopherol having different composition was evaluated for its effect on moisture loss and lipid oxidation of precooked beef patties.²⁵¹ Stearic acid incorporation displays better moisture loss control, whereas tocopherol have better control on lipid oxidation. Thus, it has been suggested that tocopherol treatment of edible polymer films can act as excellent antioxidant carrier. Song et al. evaluated the effect of antioxidant incorporated (vitamin C and tea polyphenols) sodium alginate based coating on quality and shelf life of refrigerated bream (*Megalobrama amblycephala*).²⁵² The results concluded that alginate based coating maintains better quality, reduce bacterial growth, retard water loss, enhance sensory values, and reduce the degree of chemical spoilage. Carrageenans are water-soluble sulfated seaweeds derived polysaccharide, exhibiting

high film forming potential and tensile strength (22–32 MPa), which is higher than polyethylene films (13–28 MPa).²⁵³ It has also exploited as coating and films in various areas of food industry like coating on fresh and frozen meat, fish, and poultry to stop superficial dehydration, granulation coated powders, soft capsule particularly nongelatin capsule and sausage casings.^{254–256} Carrageenans films were also reported as encapsulating agent of polar aroma compounds and their steady release with time.²⁵⁷ Chitosan is another edible polysaccharide having abundance next to cellulose and exhibit strong antimicrobial and antifungal activity.²⁵⁸ Chitosan based films has being effectively used as packaging tools and encapsulating materials for bioactive ingredients in the preservation of food quality.^{259–261} In a recent report, Remya et al. demonstrated chitosan films containing ginger oil (*Zingiber officinale*) improved the antimicrobial property and acted successfully in keeping the quality of chilled stored barracuda fish for 21 days.²⁶² Besides this type of packaging system, today's researchers were motivated further toward a novel intelligent or active packaging system which would interact with the materials inside or the surrounding environment. Such systems are characterized by their ability to monitor the condition of packaged food or the outside environment.^{243,263–267} This includes gas detectors, time–temperature indicators, and ripening or freshness indicators, etc.²⁶⁸ Further, the advancement of nanotechnology and engagement of nanomaterials has started at a faster rate and bionanocomposites are going to play a very important role in future for establishing a more consumer friendly, economical, and environment caring packaging materials.²⁶⁹

5.2. Agriculture Applications. In agricultural fields, the use of synthetic polymer based superabsorbent has raised serious concerns regarding environmental degradation and economic problems. Thus, the replacement with nature based materials could act as more economical, novel, and environmental friendly substitute to synthetic products. Several reports were available on the synthesis and application of superabsorbent hydrogels for agricultural purpose.^{270–273} Low water retention, moisture leaching, and high evapotranspiration rate, etc. in soils retard the plants and crops growth, along with some times permanent damage to soil biota. In the horticultural industry, superabsorbent hydrogels have been efficiently used as a soil amendment to improve the physical properties of soil accounting to further increasing their water holding capacity and nutrient retention.²⁷⁴ Azzam reported that superabsorbent hydrogels can act as a reclaimer–ameliorator material having the potential to impart nearly all the properties of arable lands to sandy soils and hydroponic substrates.²⁷⁵ Also, it will reduce the erosion rate, water runoff, irrigation frequency, compaction affinity and increase soil aeration and microbial activity.²⁷⁶ The edible polymer based hydrogels are suitable as soil additives for water conservation and moisture retention in tropical and subtropical areas, as well as nutrient and fertilizer carrier, as they are biodegradable and biocompatible.²⁷⁷ The potential applications of hydrogels in agriculture fields includes nutrient carrier, soil moistening, water retention, irrigation water consumption reduction, reduce compaction tendency, prevent erosion and runoff, etc.²⁷⁸ Mostly, polyacrylate based superabsorbent hydrogels has reported as potential contender in agriculture fields and was thoroughly investigated by different researchers for the controlled release of fertilizers like urea, phosphate, potassium, etc.^{279–282} Later on, this idea has been extended to integrate

polysaccharide in the network framework, which further improves its properties. Different types of edible polymers such as starch,^{283,284} cellulose,^{285–287} chitosan,^{288,289} CMC,²⁹⁰ alginate,^{291–293} pectin,²⁹⁴ and so forth have been used to prepare hydrogels for agriculture applications. Starch based superabsorbent hydrogel with moisture prevention property has being reported for the slow release of urea as a fertilizer to improve soil property.^{295,296} The release rate of fertilizer was governed by the gel strength, microstructure, and water absorption capacity. Montesano et al. investigated the effect of cellulose based superabsorbent hydrogel on the water retention capacity (both in soils and soilless substrates), and plant growth in different media.²⁹⁷ The hydrogel increased soil moisture capacity by about 400% as compared to not amended soil at a wilting point of –15 bar similar to the nonamended soil. Cultivation trials on cucumber (in soil) and sweet basil (in soilless conditions) revealed overall improvement of quality and growth of plants without any phytotoxicity. Raafat et al. developed a series of gamma irradiation cross-linked superabsorbent hydrogels based on CMC and polyvinylpyrrolidone (PVP) for agriculture application having potentials as nutrient carriers and a soil conditioner.²⁹⁸ Morphologically hydrogel becomes a highly interconnecting porous network structure with water absorbency ranged between 60 and 144 g of water per gram of dry gel and retains about 50% of its water even after 24 h at 25 °C. The gelation property shows direct relation with gamma irradiation dose and PVP content. Urea release as an agrochemical model from the hydrogel proposed these superabsorbent hydrogels as potential eco-friendly materials as soil conditioner and nutrient retention in sandy soils. A hybrid superabsorbent hydrogel based on chitosan cross-linked with cellulose using thiourea formaldehyde followed by grafting with acrylic acid and their potential as controlled release of soil nutrient was evaluated by Essawy et al.²⁹⁹ The hybrid assembly provides further mechanically robust structures functioning over a wide range of pH pertaining to homogeneous blending of chitosan and poly(acrylic acid) in one entity with water absorbency of about 390 and 39.5 g/g (water and saline/0.9 wt % NaCl sol.), respectively. Guilherme et al. reported pectin based hydrogel as carriers for agriculture nutrients such as phosphate, urea, and potassium.²⁹⁴ The release of nutrients from the hydrogel found to be controlled by a mechanism of non-Fickian type with a tendency to macromolecular relaxation. Besides, these hydrogel helps in water conservation and also show excellent capacity to remove divalent copper (120 mg) and lead (130 mg) per gram of gels from wastewater at pH 5.5. It can thus be concluded, edible polymer based hydrogels proved to be very competent resources for agriculture applications.

5.3. Biomedical and Pharmaceutical Applications. In pharmaceutical and biomedical industries, the biocompatibility and biosafety of the designated material would be a prime objective. The edible polymers are known for their biocompatibility and biosafety features and could be a significant material in biomedical and pharmaceuticals products. Various areas where such hydrogels have being extensively investigated includes, drug delivery, regenerative medicine, protein release, tissue engineering, biosensor, extracellular matrix, cosmetics, repair and reconstruction of soft tissues etc.³⁰⁰ Cellulose derivatives like methyl cellulose have being extensively explored for biomedical application. Methylcellulose exhibit thermo-reversible gelation properties having a temperature range of 60–80 °C and showed low cell

adhesion and protein adsorption.³⁰¹ Stabenfeldt et al. investigated laminin functionalized methylcellulose hydrogel for neural tissue engineering, and the hydrogel displays higher cell viability rates along with neural cell adhesion.³⁰² Methylcellulose based formulation was also reported as a suitable injectable scaffold for the repair of brain tissue.³⁰¹ Chitosan based hydrogel has been studied extensively for its potential in biomedical and pharmaceuticals application due to its biocompatibility, biodegradability, and antimicrobial activity. In the drug delivery system, the advancement in chitosan hydrogels has been directed toward a new drug delivery systems which release their contents under different environmental conditions or also known as stimuli-responsive hydrogels (change in pH, temperature, thermosensitive, photosensitive, electric field, etc.).^{303–308} Such systems were known as intelligent or smart hydrogels and have the ability of more accurate and programmable drug delivery.^{309,310} As a drug delivery device chitosan hydrogel has been investigated for oral drug delivery, ocular drug delivery, nasal drug delivery, intestinal delivery, etc.^{311–313} Chitosan based adhesive films have revealed to adhere with sheep intestine strongly without any chemical modification. Therefore, such types of adhesive film could find potential application in tissue repairing.^{314–317} Chitosan and glycerophosphate based thermosensitive hydrogel were also reported to have potential biomedical applications.³¹⁸ Hyaluronic acid modified chitosan based highly porous hydrogel were investigated as a scaffold for postoperative adhesion prevention.³¹⁹ The hydrogel shown very low cytotoxicity and hemolysis and supported the growth of encapsulated cells (NIH-3T3 and human umbilical vein endothelial, HUVECs). However, it is not favorable for attachment of fibroblasts to surface. The hydrogel degraded within 2 weeks via the action of lysozyme in vivo. Hydrobutyl grafted thermosensitive chitosan hydrogel were also investigated as a barrier for postoperative adhesions prevention.³²⁰ Chitosan based hydrogel were similarly find application in treatment of kidney injury. Gao et al. reported chitosan chloride hydrogel as a carrier for mesenchymal stem cells (MSCs) into ischemia/reperfusion induced acute kidney injury to resolve leading obstacle of cell transplantation.³²¹ Results demonstrate the hydrogel reduces apoptosis of host renal cells and enhance the proliferation activity, along with a significant improvement of the renal function. In myocardial fixing, chitosan hydrogel could improve a myocardial infarction microenvironment, enhance stem cell engraftment, survival, and homing in ischemic heart through reactive oxygen species scavenging and chemokine recruitment.³²² This proves that chitosan hydrogels have potential applications in pharmaceuticals and biomedical fields. Pectin is a plant based polysaccharide has several interesting properties and has received significant attention as a colon targeting carrier, since it suffers degradation by colonic bacteria and not affected by intestinal and gastric enzymes.³²³ Pectin can form hydrogel with divalent cation (Ca^{2+}). Butte et al. used pectin based hydrogel to deliver curcumin to the colon. The system showed pH dependence and biodegradable delivery system of curcumin to colon.³²⁴ Calcium ion (Ca^{2+}) cross-linking and addition of another cationic biopolymer increases the stability of the pectin hydrogel.³²⁵ Pectin has the ability to mimic the extracellular matrix. Munarin et al. investigated the prospective of pectin and modified pectin as an extracellular matrix to immobilize cells for bone tissue regeneration.³²⁶ Dextran is another biocompatible polysaccharide, well documented for its

application in the pharmaceuticals and biomedical fields.³²⁷ Dextran has shown reduction in inflammatory response,³²⁸ decrease vascular thrombosis,³²⁹ improved blood flow, and also assistance in organ transplantation via reactive oxygen species scavenger and excess platelet activation reduction.³³⁰ In an emergency, when blood was now accessible, soluble dextran-hemoglobin complexes can act as a substitute to lost blood.^{331,332} Dextran based hydrogel was investigated for protein delivery,^{333–336} drug delivery,^{337,338} surgical uses,³³⁹ tissue engineering,^{340–342} wound healing,^{343,344} etc. Jin et al. prepared a dextran-tyramine hyaluronic acid conjugate biomimetic hydrogel via enzymatic cross-linking as a scaffold for cartilage tissue engineering.³⁴⁵ These hydrogels exhibit good biocompatibility and induced improved cell proliferation and matrix deposition. Ferreira et al. reported a single step method for synthesis of macroporous dextran hydrogel via a biocatalytic transesterification reaction between dextran and divinyladipate.³⁴⁶ The resultant hydrogel exhibit higher elastic modulus as compared to the chemically synthesized counterpart and morphologically displayed unimodal distribution of interconnected pores with an average diameter ranging from 0.4 to 2.0 μm . The in vivo biodegradability test in rat shows the hydrogel degraded in 5–40 days. Similarly, sodium alginates were also extensively investigated in pharmaceuticals and biomedical applications. Alginates possess a unique mucoadhesive property which makes them ideal formulation excipient in the pharmaceuticals industry.³⁴⁷ Alginate suffers supramolecular assemblage in acid solution (pH below 3) forming gels³⁴⁸ or also binds with multivalent cations (mainly Ca^{2+}) forming an ionotropic physical gel.^{349,350} Alginate hydrogels have a wide range of application in pharmaceuticals and biomedical fields,³⁵¹ including drug delivery,^{352–354} tissue engineering,^{355,356} protein delivery,³⁵⁷ cell encapsulation,^{358–361} wound healing,^{362,363} cell culture,^{364,365} etc. Alginate hydrogels, which carry negative charges, have being used as a carrier for cationic drugs and heparin binding growth factors such as vascular endothelial growth factor (VEGF) and others to promote tissue regeneration.^{366,367} Prang et al. have prepared alginate based highly anisotropic capillary hydrogels to promote directed axon regeneration followed spinal cord injury using adult rat spinal cord lesions, which depends on the longitudinally directed regrowth of transected axons.³⁶⁸ Thus, the alginate based capillary hydrogel successfully promoted directed axon regrowth without any major inflammatory responses. This could be a novel strategy for the functional recovery in humans suffering from spinal cord injury. Recently, The Well Bioscience (Newark, NJ) launched an animal origin free hydrogel system (VitrGel 3D) for 3D cell culture that mimics the natural extra cellular matrix environment.³⁶⁹ This hydrogel system is stable at room temperature and is pH neutral. This allows the cells to grow more closely to their natural behaviors and morphologies, which become very helpful for scientist. Another commercial available polysaccharide based hydrogel in pharmaceuticals is “Vascuderm” hydrogel. This hydrogel is a nonoily mannan polysaccharide based material used for wound healing management.

Protein based hydrogels were also excellently investigated in pharmaceutical and biomedical applications. Gelatin is a water-soluble, nonimmunogenic, and biodegradable polypeptide. Gelatin based hydrogel is the most studied protein in biomedical and pharmaceutical applications due to its thermoresponsive gelation and biocompatibility.³⁷⁰ Its application includes drug delivery,^{371,372} tissue engineering,^{373,374}

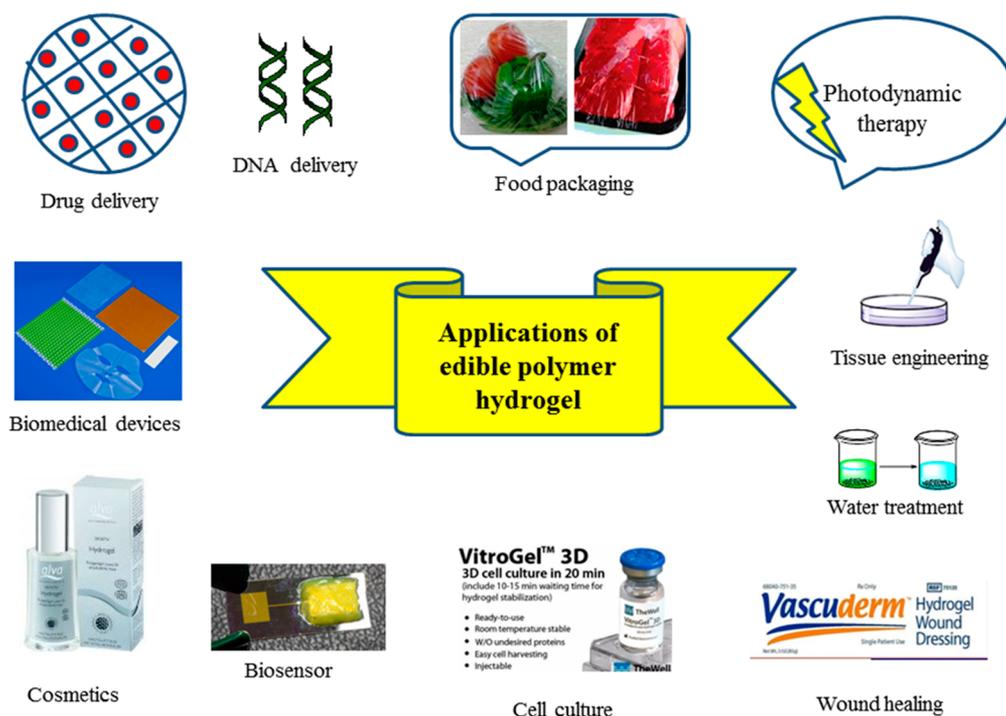


Figure 15. Applications of edible polymer based hydrogel.

contact lenses,³⁷⁵ wound dressing,^{376,377} cell encapsulation,^{378,379} and cell culture,^{380,381} etc. Epichlorohydrin cross-linked carboxy methyl cellulose and gelatin based hydrogels were fabricated as a controlled drug delivery device by Buhus et al. using chloramphenicol as a model drug.³⁸² Zero order kinetics were achieved for drug release having a maximum drug loading of 198.7 mg per gram of hydrogel. The hydrogel also exhibits antimicrobial activity against *S. aureus*. Gelatin hydrogels are proficient tools providing spots for cell adhesion and proliferation and also act as one of the key components of the extracellular matrix.²¹² Due to this characteristic, FDA approved a commercial gelatin based biomaterial “Gelfoam” and has been successfully used in wound healing and tissue engineering.^{383,384} The ability of gelatin derivatives based hydrogel as a sustained carrier for VEGF release to induce angiogenesis were investigated by Li and co-workers.³⁸⁵ Gel formation was carried out using tyramine as a source for providing enzymatic cross-linking points. This gel system was shown a sustained release of VEGF for over 3 weeks. The heparin modified gelatin derivative even exhibit intrinsic ability to induce angiogenesis to some degree without VEGF. In wound healing, the material should deliver a warm and moist environment along with microbe’s free space. An oxidized alginate and gelatin based hydrogel was investigated for wound dressing purpose via in vitro study in a rate model by Balakrishnan et al.¹⁹³ Their hydrogel displays encouraging results with relatively low water vapor transmission rate and good water absorptivity as compared with commercially available material. Figure 15 has shown the applications of some edible polymers based hydrogels in different fields.

5.4. Other Applications. The other areas where edible polymers based hydrogels were assessed for potential application includes wastewater treatment,^{386–389} cosmetics applications,³⁹⁰ personal care products,^{391–393} bioelectronics and biosensors,^{394–396} industrial applications,^{397–399} and so forth. Water is a vital resource for life, with only accounting

0.03% as usable for daily activities out of the total available on earth. However, the over increasing use of water for industrial activity without proper water treatment system releases various toxic pollutants (like metal ions Pb^{2+} , Hg^{2+} , Cd^{2+} , Cu^{2+} , Cr^{6+} , Ni^{2+} , dyes, acids, byproducts, etc.) thereby further escalating the quality of available water.³⁸⁶ Although there are numerous methods available for this purpose, nevertheless they are accompanied by certain disadvantages, such as high cost, generation of secondary pollutants, and incomplete removal of pollutants, etc. Therefore, edible polymer-based hydrogels could be a superior alternative for these applications pertaining to its nontoxicity, abundant availability, low cost, biodegradability, and sustainability, etc. Many reports were available on the application of such hydrogels as absorbent in the treatment of wastewater.^{400–405} The properties of these hydrogels can be tailored easily through various chemical reactions to make it more selective for a particular impurity. Chitosan-based hybrid hydrogel dispersed with Prussian blue nanoparticles showed enhanced photodegradation activity as well as photo-Fenton catalyst for wastewater treatment in the presence of sunlight.⁴⁰⁶ Adhikari et al. reported tripeptides based hydrogels with robust potential for organic dyes removal (Rhodamine B, Reactive Blue 4, and Direct Red 80) from industrial waste.⁴⁰⁷ Furthermore, these gelators can be easily recoverable by changing the pH of the medium. In personal care products and cosmetics products, the use of edible polymer based materials has gained a tremendous growth due to undesirable impact of synthetic chemicals and consumer demands for healthier lifestyles.⁴⁰⁸ A detailed description on the usage of natural polymers in personal care products and cosmetics, their advantages, and present market values were reported by Xian Jun Loh in their book “Polymers for Personal Care Products and Cosmetics”.⁴⁰⁹

To conclude without a doubt, edible polymers based hydrogels hold a number of noteworthy features that qualify and allow them to display extraordinary properties, which

empowers them to be employed as fundamental tools in many fields. This review has focused to bring together an extensive amount of data reported in the literature on edible polymer based hydrogels, their properties, preparation methods, chemical modification, and applications. Edible polymer based hydrogel can act as an alternative to conventional synthetic polymer based hydrogel, having advanced and eco-friendly properties like biodegradability, biocompatibility, and nontoxic and can have potential application in the food industry and pharmaceutical products. Although edible polymers have some issues, like low mechanical strength, flexibility problems, and polymer diffusion; however, chemical modification or blend formation can overwhelm such drawbacks and alter their properties consistent with the application requirement.

For future studies, further attention needs to be paid toward “green synthesis” used for (use of nontoxic solvents, low energy processing, nontoxic cross-linker and chemicals) hydrogels systems. The clarification in complexity and an economical way of hydrogel formulation will be the utmost demanding and needed approach in hydrogel chemistry. Second, the present era is highly dominated by nanomaterials (materials in the nanorange), which gave excellent results as compared to conventional counterparts due to its superior properties. Therefore, nanohydrogels are another important and highly demanding subject, where edible polymers can become suitable contenders. The development of intelligent materials (i.e., responsive to different environmental conditions) is also a new subject in the scientific community with an optimistic prospect in different areas. Addition of other components such as nanofillers, clays, and inorganic nanoparticles to the hydrogel improves the overall properties of the material. In this case, edible polymer-based bionanocomposite hydrogels represent one of the important examples of having advanced properties with immense applications.

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Notes

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