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Cellulose Dissolution, Modification, and the Derived Hydrogel: A Review

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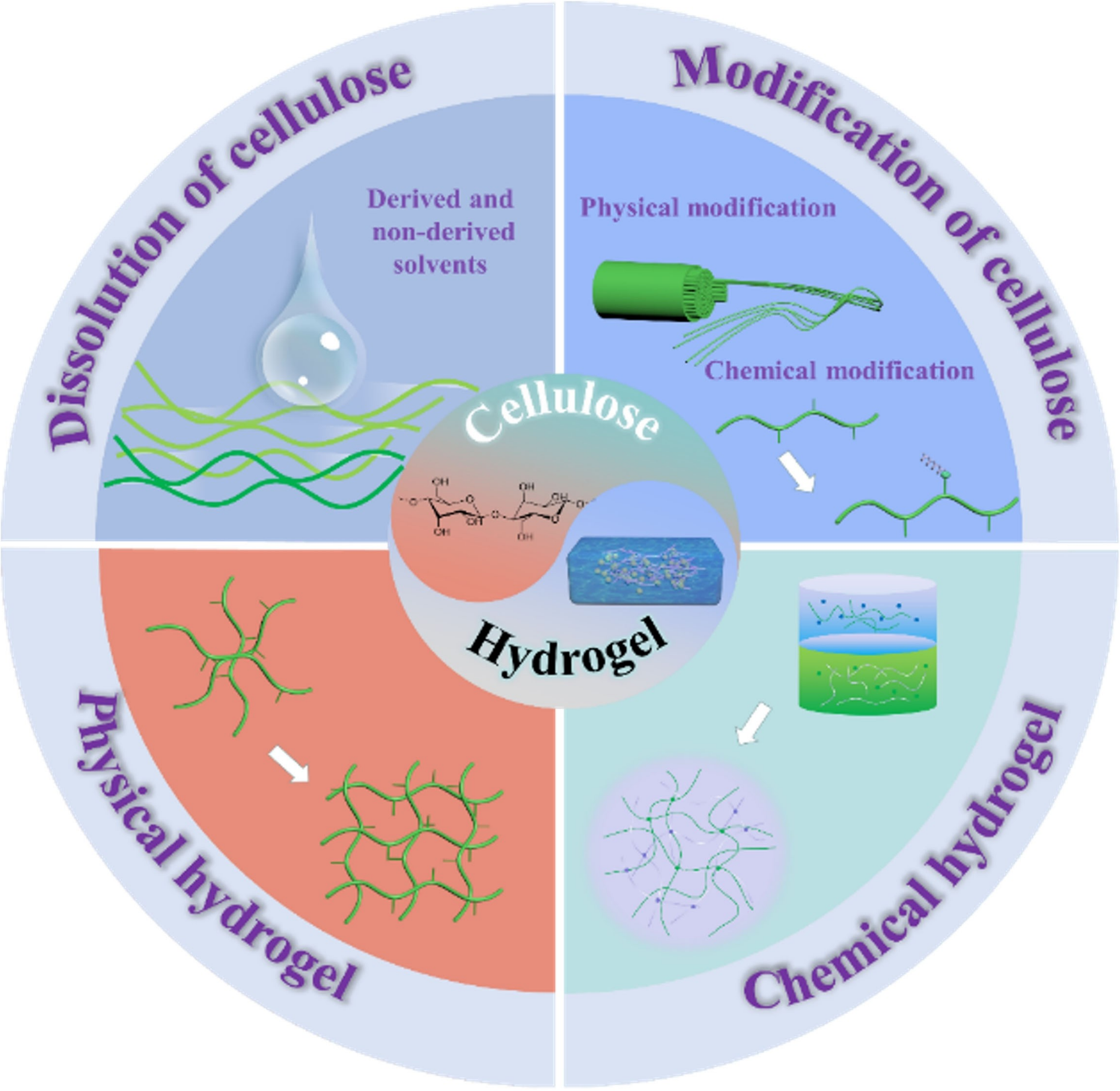

The cellulose-based hydrogel has occupied a pivotal position in almost all walks of life. However, the native cellulose can not be directly used for preparing hydrogel due to the complex non-covalent interactions. Some literature has discussed the dissolution and modification of cellulose but has yet to address the influence of the pretreatment on the as-prepared hydrogels. Firstly, the “touching” of cellulose by derived and non-derived solvents was introduced, namely, the dissolution of cellulose. Secondly, the “conversion” of functional groups on the cellulose surface by special routes, which is the modification of cellulose. The above-mentioned two parts were intended to explain the changes in physicochemical properties of cellulose by these routes and their influences on the subsequent hydrogel preparation. Finally, the “reinforcement” of cellulose-based hydrogels by physical and chemical techniques was summarized, viz., improving the mechanical properties of cellulose-based hydrogels and the changes in the multi-level structure of the interior of cellulose-based hydrogels.

1. Introduction

Hydrogels are generally prepared from hydrophilic polymer chains through physical, chemical cross-linking, or combination strategies, in which the three-dimensional (3D) network swells in an aqueous solution until the thermodynamic force of swelling completely neutralizes the shrinkage force exerted by the cross-linking.[1–3] As a result, hydrogels could retain a 3D structure while containing a large amount of water, which endowed hydrogels with biocompatibility, sustainability, and degradation, especially for the natural macromolecules-based hydrogel.

Currently, natural macromolecules have been widely used to form hydrogels that have been used in biomedical engineering, food packaging, surface coating, drug delivery, sensors, etc. (as shown in Figure 1). The physicochemical properties of hydrogels determined their performances in specific fields.[4] Thereinto, mechanical performances are the major for most applications, such as tensile, fracture, compressive, and bending strengths. However, most hydrogels with excellent mechanical properties are prepared from petroleum-based compounds, viz., the mechanical performances of natural polymer-based hydrogels are still inferior to those of synthetic polymers. Thus, how to enhance the mechanical performances of hydrogels is the focus of current research.

Cellulose is one of the most widely distributed renewable resources in nature, and thus, has been widely employed as the precursor for hydrogel. However, the usage of cellulose is limited by the strong intramolecular and intermolecular hydrogen bonding that goes against the dissolution of cellulose in conventional solvents. Thus, proper modification methods and solvents have been developed to obtain cellulose solutions, which significantly affect the physicochemical properties of cellulose-based hydrogels, as well as the applications (Figure 1). For cellulose dissolution, many series of solution systems have been developed based on different dissolution mechanisms, such as alkali/urea, ionic liquid, *N*-methylmorpholine-*N*-oxide (NMMO), etc.[5]

Hydroxyl groups are the sole functional groups that can be facilely modified via oxidation, esterification, etherification, and silanization.[6] As a result, the physicochemical properties (e.g., molecular weights, structures, and chemical characteristics) of cellulose feedstock change and the consequent hydrogels.[7]

The present review summarizes the influence of developed solvents and modification methods on the physicochemical properties of cellulose. Moreover, the strategies that enhanced mechanical performances in cellulose-based hydrogel were emphasized.

2. Overview of Cellulose

Cellulose is an essential substance through the maintenance structure of plant cell walls. It can also be obtained from algae, acetic acid bacilli, rhizobia, etc. Currently, several groups have conducted comprehensive reviews of cellulose.[8–12] Therefore, this section only introduced some information involved in the dissolution and chemical reaction rate of cellulose.

Cellulose is a polysaccharide consisting of β (1→4) linked D-glucose units with a pattern of C1 chair conformation. Intramolecular and intermolecular hydrogen bonding are the dominant forces in the cellulose matrix that limit the dispersion of cellulose in the reaction systems and consequently block contact between the active sites (i.e., hydroxyl groups) and modifying reagents. Moreover, the cellulose chain forms a unique layered structure based on intermolecular hydrogen bonding, covalent bonding, and hydrophobic force.[13] The (200) crystal plane has low hydroxyl group content, which is a hydrophobic interface; and the (100) and (01–10) crystal planes are hydrophilic interfaces. Even so, the combined forces make the cellulose chains closely arranged, enhancing cellulose molecular chains in linear integrity and rigidity and forming a two-phase structure with a high side order of cohesive crystal regions and loosely stacked amorphous regions, which contribute to the mechanical strength.

The hydroxyl group is the substantial functional group in the cellulose chain, which can be derivatized via the typical

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hydroxyl reactions. Distinctively, the hydroxyl group connected with C1 has reducibility (i.e., reducing end), which can be further derivatized via oxidation, carboxymethylation, grafting, and other reactions.[14] Each anhydroglucose unit (AGU) has three hydroxyl groups, which are linked to the C atoms at the C2, C3, and C6 positions of glucose, respectively. The hydroxyl groups at C2 and C3 are secondary alcohols, and those at C6 are primary alcohols. The reactivity of the three hydroxyl groups depends on steric hindrance factors related to the supramolecular structure and isomerization of cellulose. When the cellulose is dissolved, C6–OH is ten times more active than C2–OH and C3–OH secondary alcohols due to the free rotation of C5 and C6 bonds;[15] In other cases, viz., the crystalline region in the cellulose cluster, the reactivity order is $C2{-}OH > C3{-}OH \approx C6{-}OH$, which was induced by the inductive effect. In addition to the hydroxyl groups, the formyl groups at the reducing end undoubtedly have high reactivity but were limited by the low content.

3. Dissolution of Cellulose

For all chemicals, dissolution or dispersion state in a specific solvent is one of the major factors that influence the modification or preparation of materials. Thus, proper solvents that could dissolve cellulose have been developing for a long history.[16] The limiting factors of cellulose dissolution can be classified into (1) the complicated intramolecular and intermolecular hydrogen bonding block the solvent molecules permeating into the crystalline region, let alone undermine its tightly packed structure;[17,18] (2) the hydrogen bonding endows cellulose having a rigid structure (i.e., crystalline region) that limits the freedom of conformational change, and the rotation of AGUs only depends on the glycosidic bond; (3) the hydrogen bonding induced complex aggregation structure, viz., the uniformly distributed hydroxyl groups at different crystal planes, and thus present different hydrophilic/hydrophobic interfaces.[19] Based on the principle of cellulose dissolution, this section explains in detail the changes in cellulose molecular structure during the dissolution process from the perspective of hydrogen bonding and covalent linkages (as shown in Figure 2).

3.1. Destruction of hydrogen bonding

As mentioned above, hydrogen bonding is one of the main reasons for the insolubility of native cellulose. Therefore, the cellulose solution can be obtained by breaking the hydrogen bonding in relevant solvents. These solvents are generally formed complexes via the donor-acceptor interaction that causes intramolecular and intermolecular hydrogen bonding to lose stability and consequently achieve the purpose of dissolution. The ability of a solvent to dissolve cellulose theoretically depends on the ability of the solvent to form hydrogen bonding with the hydroxyl groups in cellulose chains. Another important factor is whether the as-formed hydrogen bonding is stronger and more stable than the native hydrogen bonding among cellulose chains.

3.1.1. Ionic liquids

Ionic liquids (ILs) are organic salts that can melt below the boiling point of water and are composed of anion and cation modules. They are different from traditional solvents and are considered environment-friendly due to the advantages of non-volatility, easy recovery, high polarity, chemical stability, thermodynamic stability, and amphipathicity. ILs have been a new system for the direct dissolution of cellulose through targeted design. Anion modules in ILs play a unique role in destroying hydrogen bonding.[20] In detail, anion modules

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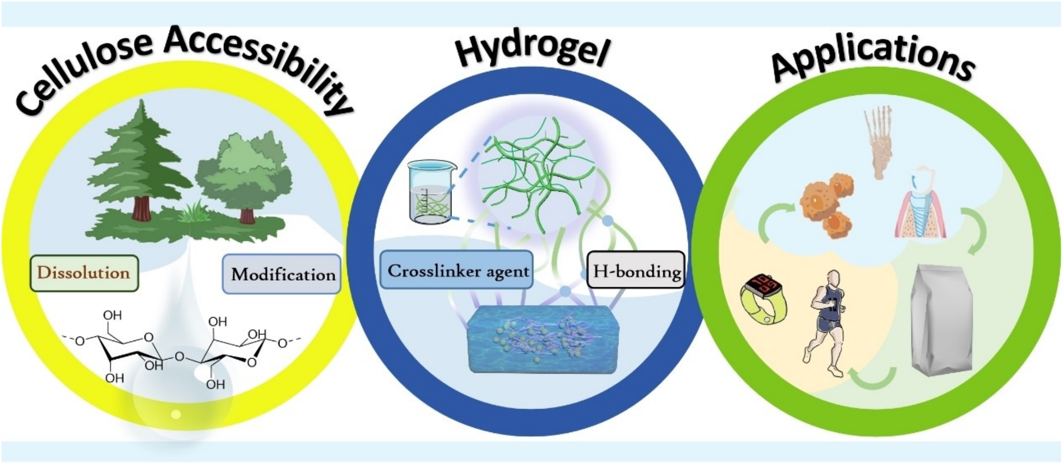

Figure 1. Preparation and application of cellulose-based hydrogel.

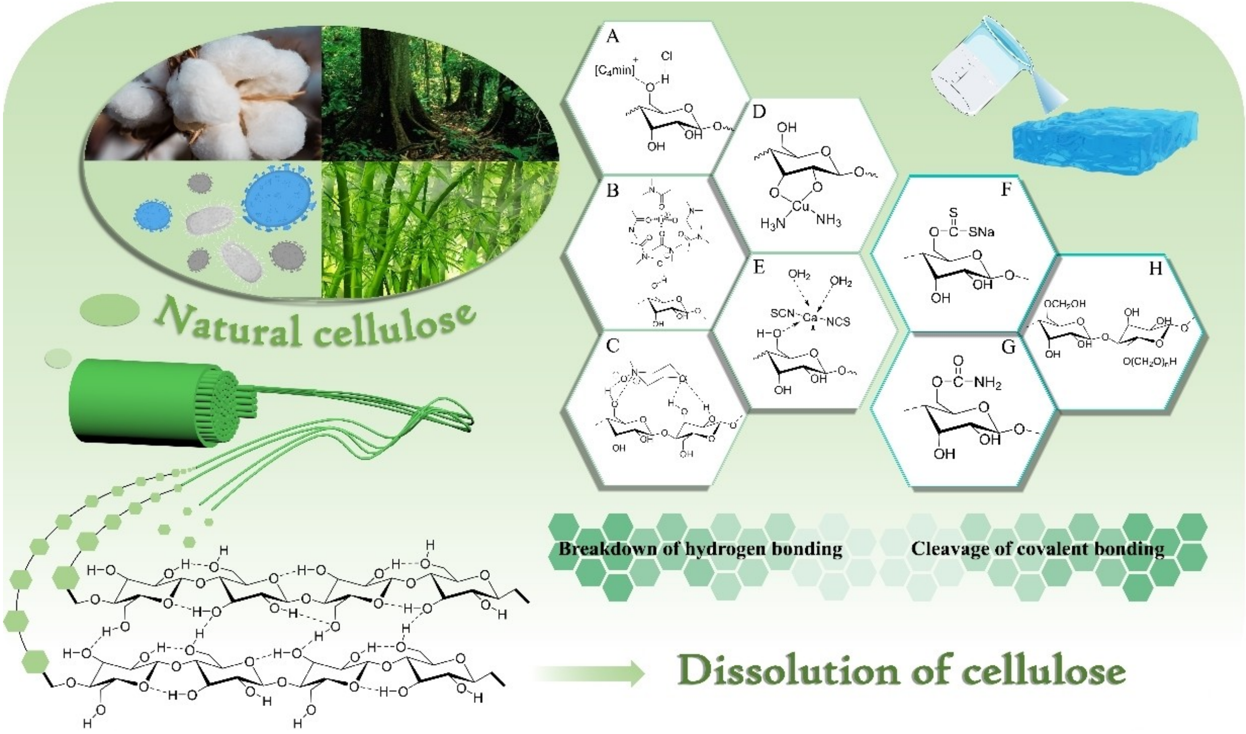

Figure 2. Mechanism of cellulose dissolution, namely, the resultant products in various solutions: A) dissolution in 1-butyl-3-methylimidazolium chloride ionic liquid (IL); B) dissolution in LiCl/DMAc (DMAc = *N,N*-dimethylacetamide) solvent system; C) dissolution in *N*-methylmorpholine-*N*-oxide (NMMO) solvent system; D) dissolution in copper ammonia solution; E) dissolution in molten salt hydrate $Ca(NCS)_2$; F) dissolution to xanthan cellulose ester; G) dissolution to cellulose carbamate; H) dissolution in paraformaldehyde/dimethyl methylate solvent system.

combine with the protons of hydroxyl groups, resulting in a complex structure of electron donor-acceptor, which further destroys the hydrogen bonding (Figure 2A). However, the specific dissolution mechanism still needs to be further studied. It is doubtful that anions in water cannot break hydrogen bonding, while anions in ILs can.[21,22] For cation modules, only those with unsaturated cationic structures contributed to dissolving cellulose. The π-electron delocalization of unsaturated heterocycles makes the interaction between cations and cellulose more active, supporting the formation of hydrogen bonding. In contrast, saturated cations increase steric hindrance, slowing the movement of anions and cations and dramatically reducing cellulose dissolution. Others believed that cationic modules (electron acceptors, such as 1-allyl-3-methylimidazolium ion, $AMIM^+$, 1-butyl-3-methylimidazolium ion, $BMIM^+$, 1-ethyl-3-methylimidazolium ion, $EMIM^+$, etc.) combine with O atoms in hydroxyl groups when cellulose is added to ILs, thus destroying hydrogen bonding.[23] Superbase-derived ILs present a high affinity for protons and supplement the dissolution of cellulose. During the dissolution of cellulose, they will preferentially destroy non-covalent forces on the (200) and (110) crystal surfaces of cellulose. The anion and cation modules in the superbase-derived ILs have shown a significant effect of the steric effect on cellulose dissolution, viz., the modules with smaller steric hindrance favor the dissolution of cellulose, possibly by competing with cellulose to provide hydrogen bonding to anions and cations.[24] Though the studies of ILs on the dissolution of native cellulose have obtained dazzling development, the industry-scale application is still limited by the cost. Moreover, the high viscosity of ILs is still needed to be considered.

The dissolution of cellulose by ILs can be used for homogeneous modification of cellulose. Due to the chemical inertness of ILs, they become suitable reaction media. Cellulose esters, including cellulose acetate (CA), cellulose methyl carbonate, and cellulose levulinate, can be synthesized in the cellulose solutions dissolved by the [DBUH][O_2COCH_3] and Dimethyl sulfoxide (DMSO) mixed solvent.[25–27] Li et al. treated eucalyptus wood with 40 % tetrabutylphosphonium hydroxide ([P 4444][OH]) to obtain cellulose nanocrystals (CNCs).[28] In addition to the dissolution that was similar to other cationic liquids, the "peeling reaction" may also occur due to the strong alkaline of $[P4444]^+$. ILs also act as nano-welding agents by forming a disordered structure on the surface of cellulose, connecting and recombining into a dense network, by which the crystallinity and degree of polymerization are reduced.[29,30]

3.1.2. Deep eutectic solvents

Deep eutectic solvents (DESs) were developed to dissolve cellulose. Much literature has stated DESs green, sustainable, and low-cost advantages but a poor dissolution performance. Moreover, the high viscosity and reclamation were still the defect. Similar to ILs, DESs also dissolve cellulose through hydrogen bonding competition, especially in dissolving pulp, which can significantly reduce viscosity and greatly improve reactivity.[31,32]

The study of DESs mainly focuses on the pretreatment process for lignocellulose, and the dissolution effect is poor, so the subsequent dissolution requires the cooperation of other reagents. Yang et al. pretreated corn cobs with DESs, which effectively removed lignin and hemicellulose and extensively retained cellulose, followed by adding $ZnCl_2/CaCl_2$ for forming hydrogels.[33] The mechanical properties of hydrogels were significantly affected by the content of lignin; viz., the mechanical properties decreased with the increasing content of lignin due to the aggregation effects.[34]

DESs also contribute to the modification of cellulose. Sirvio obtained trimethylglycine cationized cellulose fibers by using DESs (triethylmethylammonium chloride and imidazole) as a solvent and tosyl chloride as a coupling agent, where DESs were used as a solvent and catalyst.[35] Liu et al. used DESs with different carboxylic acids to solubilize cellulose and esterify it to obtain cellulose nanofibers (CNFs) with a high yield (≈88 %).[36] The esterification will form monoesters or cross-linked diesters, which prevent hydrolysis and dissolution of cellulose in DES to obtain high-yield CNFs.[37]

3.1.3. Alkali/urea and NaOH/thiourea system

This system can be said as a completely innovative solvent system, which is contrary to the requirements of traditional solvents for the high-temperature environment and the extensive use of organic solvents.[38] Zhang et al. regulated the fractions of NaOH and urea and controlled the temperature after the cellulose was immersed in a pre-cooled solvent system. The interaction occurred when cellulose formed hydrogen bonding-induced inclusion complexes with alkali and urea in the form of a shell, and the hydroxide breaks the hydrogen bonding among cellulose chains at a lower temperature. The Na^+ could block the recrystallization by forming hydrates.[39,40] Generally, the cellulose could be wholly dissolved by 7 wt % NaOH/12 wt % urea and 4.2 % LiOH/12 wt % urea aqueous solution in only 2 min at −12 °C. However, the KOH presented poor dissolution capacity on cellulose, indicating the critical impact of alkali metal ions in the dissolution process.[41] As an activator, alkali molecules will first penetrate the amorphous zone and reach the outer surface of the crystalline zone to destroy hydrogen bonding. The amorphous zone is swollen to facilitate the solvent to enter the crystalline zone; it also causes the dissolution of part of the crystalline zone of cellulose, exposing more free hydroxyl groups and increasing the accessibility of the modified reagent to the surface and interior of the crystalline zone. It should be noted that the glycosidic bond will be broken in the concentrated alkali system, which leads to the reduction of the degree of polymerization of cellulose, so as to change the mechanical properties of the as-prepared hydrogels.

The regenerated cellulose dissolved by the alkali/urea system affects some physical and chemical properties of the hydrogel. Wang et al. used LiOH/urea system to dissolve bacterial cellulose (BC), formed hydrogel through cross-linking by epichlorohydrin, and explored the effect of urea dosage on the hydrogel. The results showed that the urea content affected the dissolution and regeneration of cellulose, that is, the crystallization ratio of cellulose I and cellulose II, which affected the internal network structure of the hydrogel. When the concentration of urea was 25 wt %, the hydrogel had excellent mechanical properties, with a compressive strength of 3.17 MPa, a value of 56 times that of natural hydrogel.[42] Zhu et al. treated cotton batting with NaOH/urea to form a cellulose solution, in which the hydrolyzed tetrabutyl titanate combined with C2–OH and C3–OH to form a complex.[43] In this process, the $Ti^{[4+]}$ was a crosslinker and expanded cellulose II toward the 11-0 crystal plane to form a homogeneous gel. Lan et al. used NaOH/urea to dissolve microcrystalline cellulose (MCC) and regenerated it in ethanol to obtain high-crystallinity cellulose, and then combined it with ionic conductive polyelectrolyte to get ionic conductive composite hydrogel through the freeze-thaw cycle. The high-crystallinity cellulose skeleton makes the prepared hydrogels have high stability and can resist the erosion of seawater.[44]

3.1.4. LiCl/N,N-dimethylacetamide (LiCl/DMAc) solvent system

Due to its easy operation, the LiCl/DMAc solvent system has been widely used in cellulose solutions. It could dissolve cellulose with a high molecular weight of up to 1,000,000 without degradation. Moreover, the mass fraction of cellulose with a degree of polymerization of 550 could reach 16% in this solvent. However, the dissolution rate was generally low and needed to be pretreated. That is, the cellulose chain is activated by DMAc to reach a relaxed state so that the solvent diffuses into the crystalline region of cellulose, but this process does not change the crystallinity, and this process needs 4–6 hours.[45] Many results have shown the importance of LiCl. Morgenstern et al. proved interactions between Li^+ and cellulose chain, viz., one DMAc molecule in the inner coordination sphere was replaced by a hydroxyl group of cellulose, and the proton in the cellulose chain formed strong hydrogen bonding with Cl^- (Figure 2B).[19] The repulsion between charges and the swelling would force the assembled cellulose chains apart and destroy the non-covalent force between cellulose chains until it was completely dissolved.[46] Zhang extended this mechanism and hypothesized that the Li^+–Cl^- ion pairs worked together, viz., Cl^- formed hydrogen bonding with the proton of cellulose, and solvate was formed from DMAc and Li^+, which can balance the charge,[47] also known as the polyelectrolyte effect. In addition, due to the presence of high osmotic pressure, the solvent will flow in continuously until the cellulose is solvated.[19] However, many aggregates were generated in the dissolution process, which needed mechanical shearing to be temporarily eliminated. Moreover, this solvent system needed high requirements for solvent purity.

The regenerated cellulose dissolved in this solvent can be uniformly dispersed in the system and preserved for a long time;[4] thus, no cellulose degradation occurs, which is conducive to the preparation and composite of cellulose hydrogel film. Zhang et al. prepared a blend film by dissolving cotton cellulose and poly (vinyl fluoride) through LiCl/DMAc.[48] The solvent destroyed the hydrogen bonding of cellulose, followed by generating stronger hydrogen bonding between cellulose and poly (vinyl fluoride) due to the higher electronegativity of fluorine, ensuring the toughness and ductility of the cellulose blend film, and endowing the cellulose film with electrostatic discharge performance. Bianca et al. used LiCl/DMAc to dissolve sisal fiber to prepare hydrogels.[49] The hydrogels had high mechanical strength but low swelling properties; this is because part of the undissolved sisal fiber is filled in the hydrogel network structure, which increases the mechanical properties but also blocks the entry of water.

3.1.5. N-methylmorpholine-N-oxide (NMMO)

NMMO is an ideal solvent for cellulose due to the unique structure of NMMO itself, viz., nitrogen atoms easily form coordination bonding with oxygen atoms, and the resultant nitrogen-oxygen bonding presents more electronegative than the oxygen on other compounds. Oxygen atoms with lone pair electrons form new hydrogen bonding with the hydroxyl groups, general C6–OH, (Figure 2C), thus weakening the interaction among cellulose chains. The hydrogen bonding between NMMO and cellulose first occurred in the amorphous region, which was the most accessible for small molecules because of its loose structure. Following by permeating into the crystalline region, the aggregation structure of cellulose was continuously destroyed. Finally, cellulose chains are movable when all the native hydrogen bonding is replaced by NMMO intermediates. This solvent was significantly influenced by the water content in the system. The water molecules are stronger Brønsted acids compared with cellulose, making NMMO more likely to coordinate with water molecules.[50,51] The competitive relationship between water and cellulose in the formation of hydrogen bonding also limited the development of NMMO. However, the bond energy of N–O was very low and easy to break, which means that NMMO was thermally unstable. It was also sensitive to catalytic impurities, which might lead to unnecessary side reactions.[52] However, it could dissolve cellulose at a high concentration, produce fibers with desirable mechanical properties (e.g., wet and dry strength), and can be almost completely recycled.[53]

Mazhar et al. used NMMO to dissolve the regenerated BC and plant cellulose to prepare hydrogels.[54] They found that the NMMO-treated BC network was more dense and porous due to the crystallization behavior of NMMO in the cooling environment when NMMO was removed with water. The original intermolecular and intramolecular hydrogen bonding framework was changed, reducing the mechanical properties.[55]

3.1.6. Copper-ammonia solution

Copper-ammonia solution, an inorganic metal complex, is one of the early-developed cellulose solvents, consisting of transition metal ions and nitrogen ligands.[56] The primary dissolution mechanism was that Cu^{2+} in copper-ammonia solution preferentially attacked hydroxyl groups on C2 and C3 of the pyran ring, and protons were replaced by $Cu(NH_3)^{2+}$ to form a five-membered chelating ring (Figure 2D). Copper-ammonia solution will oxidize cellulose excessively under aerobic conditions, resulting in a drastic decrease in the polymerization degree of cellulose, which is not conducive to the preparation of high-performance cellulose materials.

3.1.7. Molten salt hydrates

Molten salt hydrates have been found to dissolve cellulose effectively. The cations, a series of Lewis acids, can break the hydrogen bonding and provide the main driving force for cellulose dissolution. Metal cations and water molecules formed coordination complexes, while anions were shielded from cation hydrates, and the as-formed coordination layer also enabled them to dissolve cellulose. Hattori et al. studied the interaction between cellulose and molten salt hydrate $Ca(NCS)_2$ (Figure 2E).[57] They found that saltwater solution with a concentration higher than 48.5 % can dissolve cellulose at high temperatures. This was because calcium ions have a coordination number of 6, and two thiocyanate molecules occupied the coordination layer. When the hydration number of calcium ions was less than 4, there were not enough water molecules to satisfy all coordination of calcium ions. In this case, the hydroxyl group of cellulose entered the unsaturated coordination region of calcium ion, forming a coordination bond between cation and hydroxyl oxygen. However, when the concentration of the salt solution was lower than 48.5 %, all influential coordination of calcium ions will be replaced by water molecules, and cellulose can not be effectively dissolved.[58] Moreover, the regenerated cellulose from the dissolution systems presented lower mechanical properties due to surface fibrillation and resulting low crystallinity. Therefore, only some studies focused on this area. Shi et al. first dissolved lignocellulose fibers by $AlCl_3/ZnCl_2$ aqueous solution to obtain lignocellulose solution to form a cellulose film containing lignocellulose. The mechanical properties of the film increased with the increase of lignin content. When the content of lignin is 3 %, the tensile strength and elongation at break are 81.0 MPa and 17.9 %, respectively. This is mainly because the $AlCl_3/ZnCl_2$ aqueous solution can jointly dissolve cellulose and lignin, which increases the thickness of the film caused by the uniform dispersion of lignin on the cellulose film.[59]

3.1.8. Quaternary ammonium hydroxides

Quaternary ammonium hydroxides (QAH) are recently emerging cellulose solvents. The mechanism is that anions in quaternary ammonium salt aqueous solution react with the proton of the hydroxyl group of cellulose. At the same time, the methylene group on the cation interacts with carbocation (C1) on cellulose through noncovalent forces, forming QAH-cellulose intermediates, thereby breaking intramolecular and intermolecular hydrogen bonding. Such solvents include tetramethylammonium hydroxide (TMAH),[60] tetrabutylammonium hydroxide (TBAH),[61] tetraethylammonium hydroxide (TEAH),[62] tetramethylammoniumhydroxide (TMAH).[63]

Compared with alkali/urea, QAH has the advantage of mild conditions and higher efficiency. TBAH solution (40–50 wt %) can obtain 25 wt % of cellulose solution at 40 °C, which is an outstanding performance for cellulose solvents.[64] Temperature also has an effect on the dissolution of cellulose by TBAH. Wei et al. decreased the temperature to 16 °C and found that the solubility of MCC could be significantly improved.[65] Tian et al. used TMAH to treat poplar holocellulose, and the retention ratio of cellulose could reach 90.2 %.[60] In addition, some solubilizers (e.g., DMSO and urea) can promote the dissolution of cellulose by quaternary ammonium compounds.[66–68]

QAH-dissolved cellulose is also used to prepare hydrogel materials. Cao et al. used the $TBAH/H_2O/DMSO$ system to dissolve cellulose and then aged it in the air to obtain defect-free cellulose hydrogel film with a uniform network. Its mechanical properties, including tensile strength and elongation at break, were about two times higher than those of cellulose film in the general regeneration process. The reason is the coexistence of suitable crystalline proportions of cellulose II and IV during the aging process.[69]

3.2. Derivative method

The cellulose can also be dissolved by covalent bonding in certain solvents. Such systems converted the cellulose into unstable ether, ester, or acetal intermediates that could be treated to produce regenerated cellulose derivatives. As N_2O_4 reacts with cellulose, the nitrite intermediate was obtained, and *N,N*-Dimethylformamide dissolved the derivatives to obtain a cellulose solution. In the late 1800s, cotton and wood pulps were treated with alkali and carbon disulfide (CS_2) to form soluble intermediates, so-called cellulose xanthate, which was also the basis of the adhesive process.[70] Sodium hydroxide reacted with the hydroxyl group to form alkali cellulose that then reacted with CS_2 to form cellulose xanthate (Figure 2F). These intermediates were used to produce regenerated cellulose in an acidic medium. Despite environmental problems associated with by-products and the volatility of CS_2, the viscose process remained the most critical method for cellulose preparation.

Carbamate cellulose was a substitute for viscose.[71] Carbamate intermediates were formed from cellulose and urea, which were then dissolved in a sodium hydroxide solution, followed by obtaining regenerated cellulose fiber by adding sodium sulfate or sulfuric acid as coagulants. More importantly, cyanic acid generated from urea reacted with cellulose to produce cellulose carbamate (Figure 2G). In this process, two by-products (i.e., cyanamide and biuret) were generated, and thus, the original solvents needed to be continuously added.

The paraformaldehyde/DMSO system can also dissolve cellulose. The cellulose reacted with formaldehyde from paraformaldehyde to hydroxymethyl cellulose (Figure 2H), which can be swelled and dissolved by DMSO. The dissolution by DMSO avoided the aggregation of hydroxymethyl cellulose chains, and the swelling of cellulose can promote the reaction between formaldehyde and cellulose.[72] Kasprzak et al. pointed out that the solubility of cellulose presented a positive correlation with temperature in the DMSO system and the regenerated cellulose film showed good uniformity and light transmittance.[73]

3.3. Summary

As abovementioned, the dissolution of cellulose can be classified by the leading role in the dissolution process, i.e., destruction of hydrogen bonding and chemical-derived method. The destruction of hydrogen bonding has been the dominant route due to retaining the original chemical structure of the native cellulose chain to the maximum extent. Though we called these the physical treatment, the chemical reactions can not be avoided due to the abundant ether linkages, in which the carbon presented electropositivity and the nucleophilic reactions occurred between the $C^{\delta+}$ and the nucleophiles (i.e., the negatively charged component of solvents). Thus, the obtained cellulose generally presented a decrease in the degree of polymerization. The degraded cellulose presented better hydrophilia that contributed to adsorbing water inner the 3D network. However, the lower degree of polymerization was opposite to the mechanical strength of the as-prepared hydrogels. Many dissolution processes need metal ions to form hydrated ions that block the recrystallization of cellulose molecular chains. However, the irreversible adsorption of metal ions on the cellulose chain existed due to the complicated noncovalent force, and thus, metal ion-cellulose molecule complexes were formed. The irreversible adsorption induced the loading of metal ions on the cellulose chains, which also limited recrystallization in the regeneration process. The resultant cellulose-based materials generally presented lower mechanical strength than native cellulose-based materials.

4. Modification of Cellulose

Various solvents have been developed to treat cellulose for forming cellulose-based materials. In this aspect, the native cellulose feedstocks (e.g., cotton, wood pulp, and lignocellulose) were first dissolved in the solvents and further regenerated in water. Physical and chemical modifications of cellulose to obtain different substituted cellulose derivatives that can be dissolved in water or conventional organic solvents, which contribute to mass production and still be the current mainstream.

Both the dissolution and modification of cellulose are prerequisites for preparing cellulose-based hydrogels. The dissolution of cellulose has a particular effect on the modification because the physical and/or chemical interactions occurring in the subsequent preparation of hydrogels should be considered. Modification of cellulose has been an option to broaden its application and also a supplement to dissolution. The modification of cellulose can be divided into physical and chemical modifications depending on whether chemical agents were added. Physical modification mainly changed the structure and surface properties of cellulose by external energies (e.g., high pressure, heat, and ultrasonic treatment), which greatly changed the surface properties of cellulose and endowed it with new properties and functions (as shown in Figure 3 and Table 1). Chemical modification was based on the wealthy hydroxyl groups in the cellulose chains, which can be functionalized by various organics on demand. It can be classified into oxidation, esterification, etherification, and silane coupling reaction according to different reaction mechanisms (Figure 3).

4.1. Physical modification

4.1.1. Heat treatment

In the process of cellulose heat treatment, thermal energy can destroy the natural structure of cellulose. When the pyrolysis conditions were reached, cellulose would be pyrolyzed into cellulose triglycan, bioglycan, and levoglucose glycan.[92] As shown in Table 1, the cellulose generally showed an increase in the degree of crystallinity[74–78] and a decrease in the degree of polymerization.[74–76] This change contributed to obtaining a cellulose solution in mild mediums and preparing cellulose-based hydrogel with better mechanical properties. Moreover, this process did not cause a change in cellulose aggregation. However, the results revealed that the fracture of glycosidic bonding in the amorphous region and partial crystallization region affected the overall performance of subsequent hydrogels.[93] Gan et al. prepared hydrogels from thermo-treated cellulose.[94] They found a transformation of cellulose I to cellulose II and the destruction of hydrogen bonding, which improved the solubility of cellulose in an alkali solution and the crosslinking density of subsequent hydrogels. Kikuchi et al. used ionic liquids (ILs) to dissolve cellulose and explored the effect of hydrostatic pressure on the physicochemical properties of hydrogels. Results show that the water-holding capability and the mechanical strength increase with increasing pressure due to the reduced noncovalent force between the ILs and cellulose under high pressure, as well as the blocking of aggregation of cellulose bundles in the cellulose skeleton.[95]

4.1.2. High-pressure treatment

High-pressure treatment generally modified the structure of cellulose to obtain homogeneous and rearranged cellulose[96] that presented a decreased crystallinity.[79–81] Moreover, the thermal stability was consequently decreased.[79–81] The high-pressure modification also led to the aggregation of cellulose crystals, which was caused by the connection of adjacent crystal regions, the mutual penetration of crystal regions, and the transformation of amorphous regions.[97,98] Pirozzi et al. extracted cellulose from tomato residue by high-pressure homogenization with a particle diameter of 600 μm. In this process, lignocellulose became homogeneous defibrillated cellulose due to the synergistic effects of high-speed shearing, high-energy collision, and hole effect.[99]

4.1.3. Ultrasonic treatment

Ultrasonic-treated cellulose manifested changes in structure and properties, viz., the crystallinity increased with

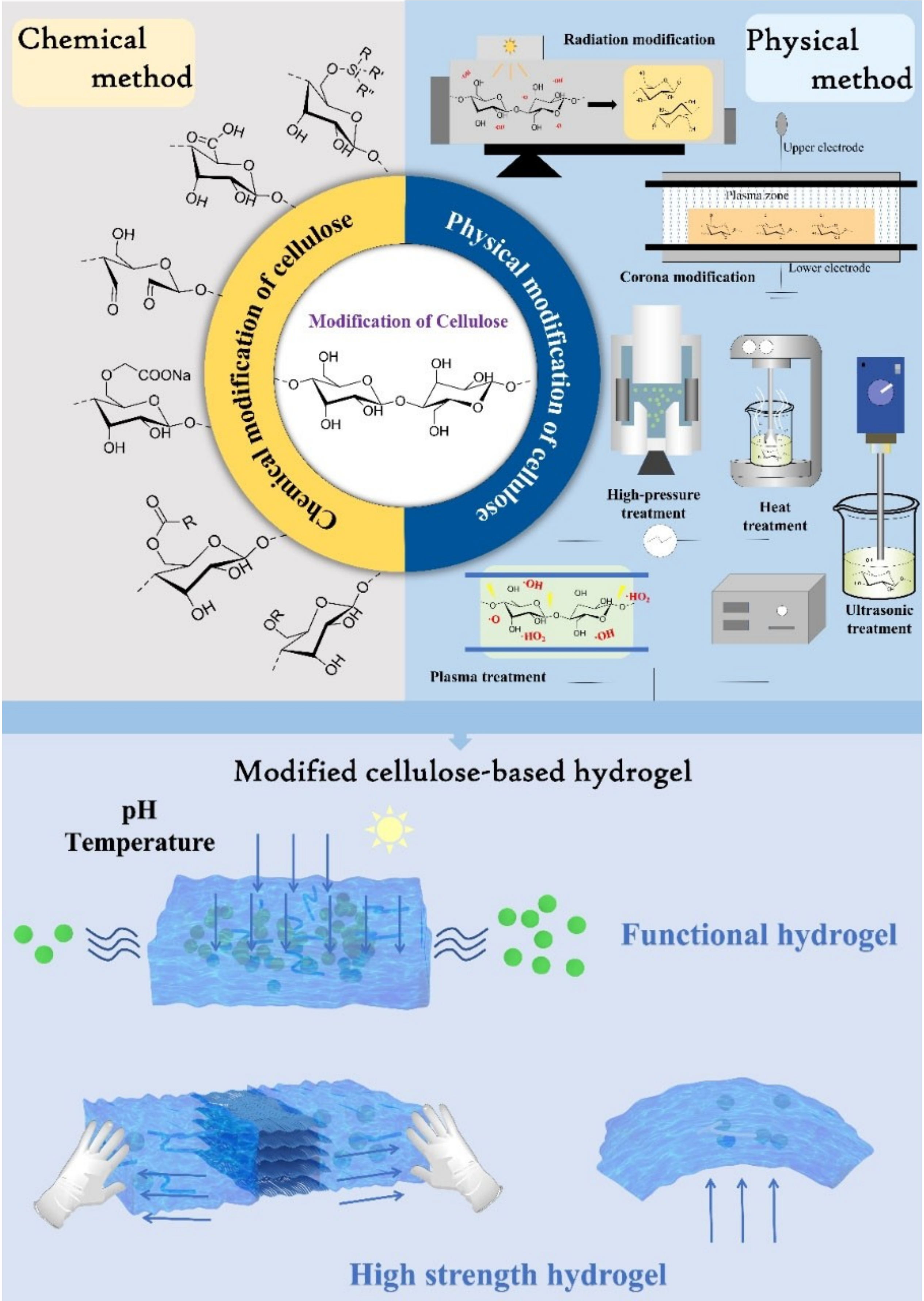

Figure 3. Modification of cellulose.

Table 1. Summary of physical modification methods on cellulose.

Raw Material	Modification Method	Hydrophilicity/ Hydrophobicity	Molecular Weight/Degree of Polymerization	Major Findings	Reference
Chinese parasol wood	silicone oil heat treatment	hydrophobicity	depolymerization	The crystallinity of cellulose and the contact angle of the samples were increased.	[74]
Aspen and Bode chopsticks	high-temperature and high-pressure steam treatment		decreased to 3.4×10^4 (Aspen) and 2.9×10^4 (Bode)	Cellulose nanofiber with high tensile strength; the maximum tensile strength values were 86.9 MPa (Aspen) and 109.9 MPa (Bode).	[75]
Eucalyptus wood	heat treatment		depolymerization	The degree of crystallinity decreased, and the cellulosic I isomerism showed slight distortion in -vivo.	76
Moso bamboo	heat treatment			The degree of crystallinity increased, and cellulose I dominated the action. The cellulose in the fibers was short, fine, and twisted, and the cellulose in the parenchymal cells was shrunken.	77
Buxus plant	high-temperature hydrothermal treatment	hydrophilicity	depolymerization	The structure of cellulose was reorganized, and the stability was increased.	78
bacterial cellulose (BC)	**high-pressure homogenization**			**Cellulose nanofiber was obtained with no change in functional groups with decreased crystallinity.**	**79**
sugarcane bagasse	**high-pressure homogenization**	**hydrophilicity**		**Nanocellulose had a diameter of 10 to 20 nm with decreased thermal stability and crystallinity.**	**80**
Eucalyptus pulp	high-pressure homogenization		decreased to 110 kDa	The thermal stability and crystallinity were reduced.	81
microcrystalline cellulose (MCC)	ultrasonic pretreatment, and sulfuric acid hydrolysis	hydrophilicity	depolymerization	Cellulose nanocrystal (CNC) molecules are rod-shaped with a length of 220–300 nm and a width of 15–22 with increased crystallinity.	82
cellulose	ultrasonic irradiation in NaOH/urea	hydrophilicity	The degree of polymerization was reduced to 150.	The crystal form and crystallinity did not change.	83
natural coir fibers	**plasma treatment**	**hydrophilicity**		**The O_2 plasma-treated fiber possessed increased hydrophilicity; Water absorption increased from 39 % to about 100 %; Oxygen content of samples increased from 18 at% to about 32 at %.**	**84**
cotton	**plasma treatment and NaOH/urea**	**hydrophilicity**	**2.5×10^5 Da (20 min)** **1.5×10^5 Da (40 min)**	**The crystallinity decreased, and the solubility increased.**	**85**
cotton	**plasma treatment**	**hydrophobicity**	**depolymerization**	**Oxidation of the fiber surface reduced water absorption capability.**	**86**
Saccharum officinarum	**cold plasma**	**hydrophilicity**	**depolymerization**	**The surface of cellulose was rough, and pores appeared. The solubility increased and the crystallinity decreased.**	**87**
bleached cellulose pulps	**corona treatment**			**The roughness increased.**	**88**
Kenaf core	electron beam irradiation	hydrophilicity	2.25×10^5 Da	The crystallinity decreased, and the solubility increased.	89
cellulose paper	electron beam irradiation		depolymerization	Cellulose chains were oxidized without significant changes in morphology or crystallinity.	90
bacterial cellulose nanocrystals/CS nanocomposite film	**gamma-ray**	**hydrophobicity**		**The crystallinity and the thermal stability decreased, and the film was dense and uniform.**	**91**

depolymerization.[82,83] The high-frequency sound waves could break the hydrogen bonding and destroy the entanglement and agglomeration behavior of cellulose chains.[100,101] However, the diffused cellulose reunited again if the ultrasonic treatment time exceeded the threshold value.[102,103] The ultrasonic cavitation could interact with cellulose for strong surface interaction that improved the pore structure.[100,104] Wu et al. treated okara cellulose by ultrasonic wave with 600 W power for 30 min, and the strength of as-prepared 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidized cellulose-based hydrogel was increased by 39%. This phenomenon was also induced by the destruction of hydrogen bonding, which contributed to forming a more compact 3D network in the hydrogel.[105]

4.1.4. Plasma treatment

The plasma treatment presented much higher efficiency in improving the hydrophilicity due to the generation of oxygen-containing functional groups such as C–O, C=O/O–C–O, and O–C=O linkages.[87,106] The morphology and structure of cellulose were consequently changed. Zhu et al. treated sugarcane waste with plasma technology and found that the treated cellulose changed from a smooth and complete surface structure to a prominent sunken structure. Cao et al. found that the collision and bombardment of high-energy particles on the cellulose surface caused the broken of the C–C/C–H bond and plasma treatment could introduce oxygen into cellulose molecules to form oxygen-containing functional groups such as C–O, C=O/O–C–O, and O–C=O.[106] An emission spectrum was used to analyze the composition of dielectric barrier discharge plasma and showed that N_2^+ was the primary substance that reacted with cellulose. Although its reactivity was low, it had enough energy to crack chemical bonding and promote the functionalization of cellulose.[107] Also, plasma can initiate the copolymerization of cellulose with monomers in the preparation of cellulose hydrogel.[108] Zhang et al. used glow-discharge electrolytic plasma to treat cellulose at different voltages for preparing hydrogels. The hydrogel obtained at a higher voltage showed a more uniform and relatively complete network structure because more free radicals were generated, which was helpful for the construction of the network structure.[109]

4.1.5. Corona modification

The strong electric field effect of corona technology could interfere with the formation of the layered structure of cellulose. When corona polarization was performed with grid voltage, nanofibers were uniformly generated, and the cellulose chains aligned along the electric field direction.[110] Corona technology was also employed in cellulose-based materials. Cellulose spontaneously formed a double electric layer on the surface of free fiber segments and in the solidification contact. When the cellulose was treated in a unipolar corona discharge, the potential of the double electric layer increased, resulting in increased interaction between cellulose fibers.[110] All these mechanisms led to an increase in the roughness of cellulose, which increased the proportion of the non-crystalline region and facilitated its dissolution.[88]

4.1.6. Radiation modification

The radiation modification of cellulose was based on the free radicals generated from the radiation, which destroyed the chemical bonding of cellulose. However, the macromolecular radicals could occur crosslinking reaction, presenting in fragment recombination and generating new functional groups.[89–91,111] Cellulose fibers could be oxidized by vacuum ultraviolet radiation and introduced carbonyl and carboxylic acid groups onto the fiber surface.[112,113] It was found that the oxidation efficiency of vacuum ultraviolet radiation was similar to that of chromic acid and nitric acid and was better than that of ozone and hydrogen peroxide. In addition, UV irradiation could oxidize the cellulose surface without changing the mechanical properties of the fiber, compared with the oxidation method using acidic reagents.[114] Henniges et al. treated cellulose with plasma, electron beam, and gamma radiation and found that the content of the carbonyl groups was linearly dependent on the dose.[115] Most carbonyl groups were generated from the newly formed reducing end through the cleavage of cellulose chains. Thus, cellulose modification by radiation appeared more feasible, where increased oxidation was partially separated from chain breaking.[90,115] High-energy treatments will cleavage cellulose fragments into macromolecular radicals, such as radiation. However, these radicals can be reorganized into new groups and crosslinked into hydrogels by adding other monomers. Swilem et al. treated carboxymethyl cellulose (CMC) and gelatin with radiation to generate hydrogels via the synergistic effect of radical polymerization and non-covalent forces. By controlling the radiation dose, the compression modulus of the hydrogel can be regulated.[116]

4.2. Chemical modification of cellulose

4.2.1. Oxidation

TEMPO oxidation is one of the main methods for cellulose modification. TEMPO reagents were used to oxidize hydroxyl groups to carboxyl groups. Furthermore, the oxidation process was selective, and only primary hydroxyl groups could be oxidized. Due to the intermolecular and intramolecular hydrogen bonding, the oxidizing agent can not permeate into the crystalline region, and thus, only the hydroxyl groups on the surface were oxidized with low efficiency. Results indicated that the original crystal structure of cellulose did not show a significant change in the TEMPO-mediated oxidation process.[117] To enhance the oxidation efficiency, Tang et al. pretreated cellulose in the NaOH/urea medium, and the degree of oxidation was up to 91.0%.[118] The as-prepared cellulose showed good water solubility due to abundant carboxyl groups, which contributed to the further development of cellulose. However, the TEMPO-mediated oxidation generally induced a decrease in molecular weight. Hassan et al. obtained TEMPO-oxidized cellulose from coconut shells with diameters ranging from 30 μm to 700 nm, which confirmed the depolymerization of cellulose chains.[119] This process was a step-by-step process in which the obtained carboxyl groups on the surface induced the disassembly of the inner crystalline region, and oxidation occurred at the deeper layer.[120] Xing et al. dissolved poplar cellulose in the NaOH/urea system and oxidized the cellulose by TEMPO to obtain a hydrogel.[121] The TEMPO oxidization adjusted the surface charge of cellulose-based hydrogel and consequently increased its adsorption capacity.[122] Moreover, carboxylated cellulose can adsorb heavy metal ions via the coordination reaction. Song et al. found that cellulose extracted from wood by TEMPO oxidation has a high aspect ratio, good water dispersibility, and thermal stability and is suitable for preparing flexible sensing hydrogel/aerogel materials by mingling hypervalent metal ions.[123,124]

Sodium periodate oxidation has been the most widely used method for preparing cellulose-based materials due to the generation of highly reactive formyl groups. In this process, the sodium periodate will split the vicinal diols (C2–OH and C3–OH) on the AGU. The presence of aldehyde groups would increase the reaction activity for further cross-linking or chemical modification. This process also showed similarities to TEMPO oxidation, viz., the original crystal structure of native cellulose would remain,[125] and the diameter of the fibers decreased due to the destruction of complex hydrogen bonding.[126] Moreover, the AGU showed a decrease in rigidity, and the surface-oxidized cellulose chain was unsocial in recrystallization (i.e., the regeneration process). These results induced a loss in the mechanical strength of cellulose as a result. Lee et al. oxidized cellulose with different doses of sodium periodate to explore the influence of the degree of oxidization on morphology, crystallinity, and physicochemical properties of composite polyvinyl alcohol (PVA) films.[127] The increasing oxidation degree significantly decreased the crystallinity, and the cellulose derivatives consequently became soft and curved, which made the oxidized cellulose/PVA film increase in toughness and could be applied to packaging materials.

The Fenton reagent consists of H_2O_2 and Fe (II) salt, and the Fenton oxidation process was similar to the high-energy input process, as expressed in 3.1.4–3.1.6. Hydroxyl radicals were reactive species that can indiscriminately oxidize the C–OH to carboxyl groups.[128] Moreover, the super-high oxidizing ability of hydroxyl radicals could induce the destruction of the surface cellulose chain, which was a photodegradation process. However, the traditional Fenton oxidation process presented a low efficiency due to the compact crystal. Li et al. developed a stepwise process for Fenton oxidation: (1) the Fe (II) was adsorbed, penetrated, and diffused into cellulose feedstock; (2) H_2O_2 was added.[129] In this process, the radical initiation occurred on the surface or inner of the cellulose matrix, which significantly increased the utilization efficiency of hydroxyl radicals. As a result, the hydroxyl groups were all oxidized to carboxyl groups with an increasing content of 43.6 %. Moreover, the improved Fenton oxidation method does not use halogenated compounds such as sodium chloride and sodium hypochlorite, indicating environmental friendliness.

4.2.2. Esterification

The esterification modification of cellulose is one of the most common modification methods, which mainly uses inorganic acid, organic acid, acyl halide, isocyanate, and anhydride reagents. It was clear the modification can be divided into organic and inorganic modification. The obtained cellulose derivatives showed different changes in the wettability according to different modifying reagents.

Inorganic acid modification can be achieved by sulfuric or phosphoric acids that contain multiple hydrolyzed hydroxyl groups. The obtained cellulose derivatives generally showed better hydrophilia due to the existence of strongly dissociated hydroxyl groups, such as CNCs that were obtained in the presence of concentrated sulfuric acid and phosphoric acid. Taking the sulfuric acid-functionalized CNCs as an example, the surface of CNCs possessed sulphate hemi-ester groups that can dissociate and consistently showed excellent dispersion in water.[130] A similar phenomenon can be found in the phosphoric acids derived CNCs. Moreover, hydrolysis in the amorphous region of cellulose occurred.

The organic modification also affects the surface chemistry of cellulose. The dicarboxylic acid and cyclic anhydride could facilely modify cellulose under mild conditions to ensure that the cellulose is not hydrolyzed. Moreover, the remained carboxyl groups endowed cellulose with higher hydrophilicity, and the loss of the hydroxyl groups prevented the re-formation of hydrogen bonding. This characteristic of cellulose modified by dicarboxylic acid and the cyclic anhydride was beneficial to affinity with water, a property that contributed to the preparation of hydrogels. Diisocyanate and multi-isocyanate can also react with cellulose to obtain hydrophilic cellulose derivatives, but a low concentration of isocyanate was needed due to the bifunctionality or multi-functionality, or a crosslinking reaction would occur.

Different from the above-mentioned organic modification, the cellulose could be modified with monofunctional reagents (i.e., monoacyl halides, monoanhydride, and monoisocyanate). These monofunctional reagents generally possessed suspended alkyl groups that were hydrophobe. Thus, the as-prepared cellulose was only used as an additive in the hydrogel. Cellulose acetate was one of the earliest developed cellulose esters. Cellulose acetate was formed by the acetylation of cellulose catalyzed by sulfuric acid under the mixed condition of acetic acid and acetic anhydride.[131] Because the acetylation reaction was random, the hydroxyl groups on cellulose cannot be completely replaced by acetyl groups. The different acetylation degree of hydroxyl groups on cellulose acetate leads to different properties and applications. As a cellulose derivative, cellulose acetate has a high modulus, tensile strength, and sufficient bending resistance.[132]

4.2.3. Etherification

Like the esterification, the degree of substitution (DS) was generally determined by the number of hydroxyl groups on the surface of cellulose that were available for functionalization. However, the accessible hydroxyl groups on the surface of cellulose were only about 0.0318%.[133] Thus, the dissolution of native cellulose was still major. To obtain a high DS, the slurry process was performed to obtain a heterogeneous reaction on an industrial scale. Concentrated NaOH solution and organic solvents (e.g., isopropanol) were used to swell native cellulose. Through the Williamson etherification and hydroxy alkylation, cellulose ether can be prepared gently, quickly, and efficiently. So many cellulose ethers have been prepared and can be classified as ionic ethers (e.g., CMC), alkyl ethers (e.g., methylcellulose, MC and ethylcellulose, EC), hydroxyalkyl ethers (e.g., hydroxyethyl cellulose, HEC and hydroxypropyl cellulose, HPC), and mixed ethers (e.g., hydroxyethyl methyl cellulose, HEMC, carboxymethyl hydroxyethyl cellulose, CMHEC, and hydroxypropyl methylcellulose, HPMC).[134]

Williamson etherification was a bimolecular nucleophilic substitution in which cellulose reacted with halogenated hydrocarbons, and halogenated carbon atoms replaced hydrogen atoms on cellulose hydroxyl groups to produce cellulose ethers. Li et al. modified native cellulose with ethyl iodide in the presence of NaOH.[135] The obtained etherification was generally generated on the surface without affecting the native structure and morphology of cellulose. Moreover, the surface modification introduced hydrophobic alkyl groups, resulting in the reduction of the hydrophilicity of cellulose, which went against the water-holding capability of as-prepared materials. In addition to the Williamson etherification in the presence of concentred alkali, the cellulose also can be etherified in the acidic solution as (1) the hydroxyl groups were first protonated; (2) nucleophilic substitution occurred; (3) the complex was deprotonated to obtain the ether products. Nguyen et al. performed a theoretical study on the etherification of primary alcohols with the hydroxyl groups of cellulose ($n=1$–3) under acidic conditions.[136] During the reaction, reactant and product complexes were formed, and the protons were shared by oxygen atoms in alcohol/ether and water. Moreover, the etherification that obeyed this route needed a high temperature ($\approx 140\,^\circ C$) under acidic and thirsty conditions.

In lab-scale processes, novel methods have been developed based on the above-mentioned theory. The tetrbutyl phosphorus hydroxide was used to catalyze the etherification with a higher DS of cellulose ethers, including EC, cyanoethyl cellulose, HPC, and *N*-trimethyl cellulose. However, the stability and selection of solvents and other problems still needed to be solved in the application.[137] HEC or MC was used in the preparation of hydrogels, which can form a swelling network with chitosan (CS) through hydrogen bonding and obtain good swelling properties.[138] CMC has a negatively charged surface, resulting in excellent dispersion and transparency in water, which contributed to the preparation of hydrogels. Akhlaq et al. isolated cellulose from agricultural wastes (e.g., wheat straw, bagasse, straw, and banana leaf) and further prepared CMC in isopropanol. The DS of obtained CMC was 2.1%.[139] In addition, CMC, a cellulose derivative with carboxyl groups, shrank in an acidic solution and expanded in neutral/alkaline media, which makes it a suitable carrier for peptide delivery.[140]

4.2.4. Silane coupling reaction

Silane coupling agents could facilely modify cellulose according to the desired groups, such as amino group, alkoxy group, isocyanate, etc. Different suspended groups endowed cellulose with other properties. For example, γ-aminopropyl triethoxy silane enabled cellulose with amino groups, and γ-methacryloxypropyltrimethoxysilane enabled cellulose to acquire alkenyl groups. Thus, the silane coupling reactions could be used to directly change the hydrophilia or introduce active sites, which was beneficial to the preparation of hydrogels. These reactions were similar to the above-mentioned chemical modifications. The reaction generally occurred on the surface and did not destroy the crystalline structure of native cellulose. It can promptly complete the coupling reaction in a strong polar solvent system and thus showed poor reaction selectivity. To avoid the defect, an alcohol that was according to the alkoxy was added into the reaction systems to slow the hydrolysis rate. Neves et al. grafted amino silane onto MCC and found that the grafting ratio was proportional to the dosage of silane. The hydrophilic surface was the main reaction site, and the alkyl amine groups played a spacing role between the hydrophilic sides of the cellulose crystal.[141] Silanized cellulose is also commonly used to prepare functional hydrogel materials with a net-like structure for oil-water separation.[142,143]

4.3. Summary

Both physical and chemical modifications presented significant effects on the physicochemical properties of cellulose, which determined the application of cellulose derivatives in the preparation of hydrogels. For physically modified cellulose, the introduction of high energy not only changed the surface chemical properties of cellulose (i.e., wettability) but also caused the degradation of cellulose to a certain extent. The effect of chemical modification on the physicochemical properties of cellulose depended on whether the solvent was mild or not. The surface functional groups of cellulose changed, accompanied by the decrease of cellulose molecular weight, in concentrated acid and alkaline mediums, which had an adverse effect on the improvement of the mechanical properties of cellulose-based hydrogels. The modification performed in mild reagents can not only introduce ideal functional groups on the surface of cellulose but also maintain the original degree of polymerization to the maximum extent, which was beneficial to obtaining cellulose-based hydrogels with excellent mechanical properties.

5. Physical- and Chemical-Derived Hydrogel

Based on the above-mentioned universal solvents and modifiers of cellulose, high-strength and functional cellulose-based hydrogels have been successfully prepared by physical, chemical, or double crosslinking methods and processing strategies (tensile orientation, Hofmeister effect, radiation/enzyme induction, etc.). These make cellulose-based hydrogels able to be widely used based on high-performance materials. This section will be divided into two parts, i.e., physical hydrogel or chemical hydrogel.

Under the interaction of solvents and cellulose, cellulose chains can self-assemble in parallel within the cellulose-based hydrogel to form nanofiber structures by a "bottom-up" approach. Combined with a chemical-physical double cross-linking strategy and a stretching process, it can generate cellulosic materials with highly ordered nanostructures, ultimately achieving high toughness and strength. Cellulose can also be used as a matrix to prepare composites containing other functional components. Cellulose-based composite hydrogels with high performance were constructed by blending with inorganic or organic matter in the presence of organic/inorganic/polymer molecules. Cellulose can also be modified by esterification agents, etherification agents, silane coupling agents, etc., by grafting polymers or acting as cross-linking agents to obtain responsive, functional hydrogels and full-cellulosic hydrogels, which can broaden the application range of cellulosic hydrogels and provide environmentally friendly hydrogels that are more suitable for degradation.

5.1. Physical hydrogels

Cellulose hydrogels can be prepared directly by interacting with solvents. However, this also limits their mechanical properties because the solvents will dissolve inhomogeneously and partially, making the cellulose hydrogels' framework lose or have uneven mechanical properties. It can be enhanced by pre-stretching (changing the arrangement direction of cellulose) and salt ion effect (ionic crosslinking). Mechanical properties can be improved by compounding inorganic/organic polymers as fillers in loose matrices.

The mechanical properties of physical hydrogels depended on the interaction of cellulose, which was usually formed by ionic crosslinking, hydrophobicity, and hydrogen bonding. Ionic crosslinking was the formation of hydrogel networks through electrostatic interactions among precursors with different electrical properties. The hydrophobic action of hydrophobic groups caused the molecular chain to form intramolecular and intermolecular forces to form the hydrogels. Theoretically, the suspended polar groups (e.g., amino, hydroxyl, and carboxyl groups) can spontaneously form hydrogen bonding, resulting in physical hydrogels. It was clear the major role of functional groups that can be obtained by physical and chemical modifications. The groups on the molecular chain of cellulose and cellulose derivatives can form non-covalent linkages to form a crosslinking network, and the mechanical properties of cellulose-based hydrogels can be effectively improved by combining these forces with various methods.

5.1.1. Freeze-thaw method

Freeze-thaw method has been widely used to prepare physical hydrogels, and cellulose derivatives are no exception.[147,148] Pure cellulose hydrogel can be prepared by freeze-thaw processes. The ice crystallographic reduced the interspace among the cellulose chains and increased the concentration of cellulose, resulting in crystal nuclei with hydrogen bonding. The following thawing process made the cellulose chain gain kinetic energy and increased the collision probability. The freeze-thaw cycles induced the constitution of more and more hydrogen bonding, the growth of crystals, and the formation of a solid 3D network. This can be understood as the cellulose accumulation caused by physical constraints in the process of growing ice crystals (as shown in Figure 4A). The hydrogels prepared by the freeze-thaw technique obtained good mechanical properties without affecting the biocompatibility, biodegradability, and toxicity of cellulose, which possessed great significance to the application of hydrogels in biomedical engineering, drug delivery, and environmental protection.[144]

5.1.2. Hydrophobic force

The regenerated cellulose-based hydrogel was obtained from the dissolved native cellulose via the hydrophobic interaction (Figure 4B). In the regeneration process, glucopyranoside rings are stacked through hydrophobic interaction to form monomolecular sheets, followed by forming cellulose II through hydrogen bonding. Xie et al. dissolved cellulose in LiOH/urea aqueous solution and then treated it in $LiBF_4$ aqueous solution as a mild solvent for physical regeneration.[149] BF_4^- anion occupied the hydrophobic water sites of cellulose, slowed down the regeneration process, made a uniform and dense structure, and enhanced the mechanical properties of the as-prepared hydrogel. The researcher investigated the effect of temperature on the tensile strength of hydrogels during regeneration. Results indicated that low temperature contributed to tensile strength ($\approx$14.5 MPa) because the low temperatures decayed solvent diffusion rate between cellulose solution and solvent.[150] In addition, by coating stainless steel mesh on cellulose hydrogel membrane for oil-water separation, oil phases such as soybean oil, petroleum ether, and decane can be separated, and the separation efficiency can achieve more than 98.5 %. After cycling 10 times, the separation efficiency of the decane/water mixture decreases by only 0.4 %, which shows that the hydrogel has great potential in water treatment.

5.1.3. Direction arrangement strategy

Pre-tensioning was a standard method to prepare hydrogels with anisotropy (Figure 4C). The prepared hydrogels have an anisotropic structure and consequent mechanical strength. Chen et al. prepared sodium alginate (SA)/PVA/CMC anisotropic hydrogels by cross-linking $CaCl_2$ with the method of freeze-thaw and pre-stretch.[151] The influence of pre-stretching 50 %

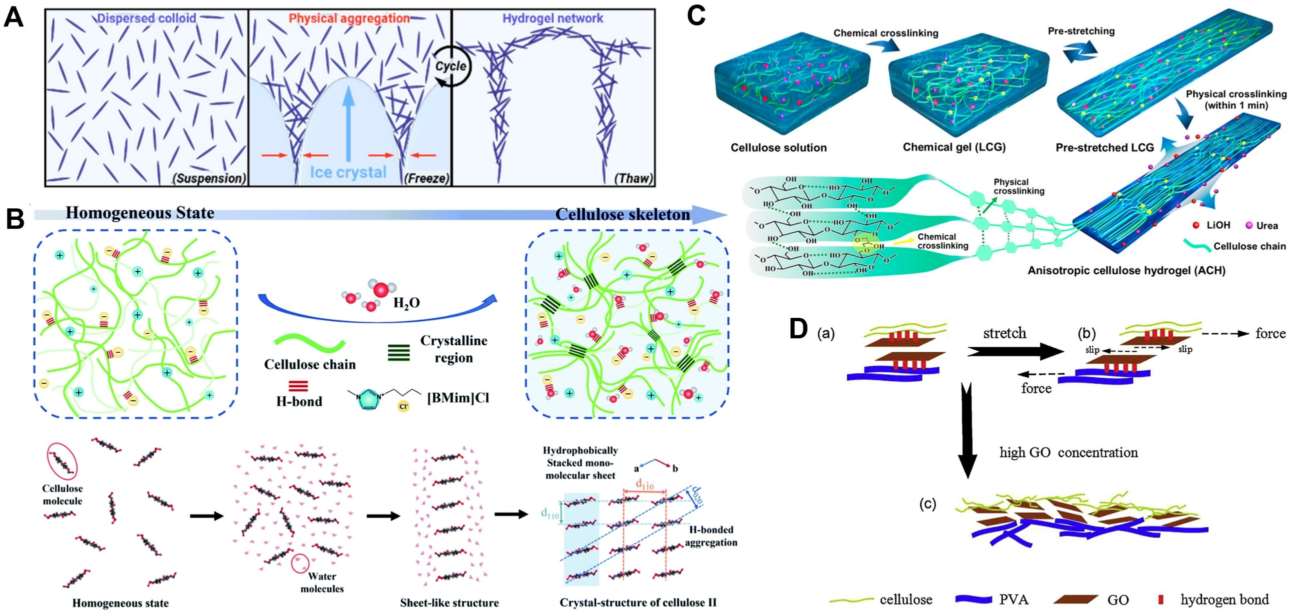

Figure 4. A) Freeze-thaw mechanism of cellulose hydrogels. Reproduced from ref. [144] Copyright (2019), with permission from the American Chemical Society. B) Diagram of self-assembly mechanism of cellulose hydrogel and hydrophobic force between cellulose. Reproduced from ref. [145] Copyright (2022), with permission from the Royal Society of Chemistry (RSC). C) Pre-stretched anisotropic cellulose hydrogel. Reproduced from ref. [146] Copyright (2018), with permission from the American Chemical Society. D) Schematic diagrams of the enhancement of elongation at break of regenerated cellulose/graphene oxide (GO)/polyvinyl alcohol (PVA) composite hydrogel. Reproduced from ref. [167] Copyright (2016), with permission from Elsevier.

and 100% on the mechanical properties of hydrogels was explored. When the pre-stretching was 50%, Young's modulus increased, so the elasticity increased. This phenomenon was due to the ordered arrangement of the internal structure of hydrogels and the densification of porous networks, which was similar to diffusion strengthening. However, the hydrogel showed a slightly lower tensile strength when the pre-stretching was 100% due to the destruction of the internal structure. In addition, cyclic tensile tests were carried out on the hydrogel. It was found that the pore structure of the hydrogel after stretching and drying was similar to that of human tissues such as tendons. The hydrogel had good comprehensive mechanical properties, which could be an ideal biomimetic material. Pre-stretching was also an effective way to prepare biomimetic hydrogels, inspired by the helical structure of lotus roots and supported by BC hydrogel (Figure 4D). BC hydrogel was a biomimetic helix 3D network hydrogel formed by hydrogen bonding. It was pretreated by cutting long strips, then a constant tangential force was applied in the direction of the section. This hydrogel can undergo local plastic deformation and spiral distortion by breaking the hydrogen bonding, and the helical structure of the fibers was reformed when the tangential force was removed. The toughness of biomimetic hydrogel fibers was up to 116.3 $\mathrm{MJ\cdot m^{-3,}}$ which was nine folders than that of BC hydrogel fibers.[152] The good toughness of the material can be used for wound closure. Compared with commercial sutures, it can avoid secondary damage caused by active stretching when sutured at the site of human injury.

Ice crystals formed in the freezing process grew directionally, which can compel the cellulose chains to form an ordered structure.[153] Baccile obtained anisotropic nano cellulose-based aerogel by one-way freezing casting and freeze drying, which had a maximum compressive elastic modulus of 100 kPa in the freezing direction.[154] Moreover, anisotropic hydrogels can also be precisely controlled to prepare the local orientation of bilayer, gradient anisotropic, opposite anisotropic, and adjacent anisotropic cellulose hydrogels. In this process, the primary interaction of cellulose molecules switched between hydrogen bonding and coordination (Ca^{2+}-cellulose complex), which realized the continuous direction adjustment. Results showed an improved fracture stress of 8.7 Mpa due to the aggregation of high-density hydrogen bonding.[155] A regeneration/pre-stretching synergistic strategy can also be used to prepare cellulose-based hydrogel. Guo et al obtained a cellulose-based hydrogel in ethanol that was further uniaxial pre-stretched, fixed, and dried. This process made cellulose fibrosis and limited the length-induced fixed orientation.[156] Moreover, the alcohol molecules reduced the molecular aggregation of cellulose.[157] Though the process was facilely operated, Young's modulus of hydrogel was only 0.8 MPa.

5.1.4. Hofmeister effect

The Hofmeister effect has also been used to obtain a reticular nanofiber structure with high strength. This fact was due to the addition of specific ions that caused the salting-out phenomenon. As a result, the cellulose chains strongly aggregated to form a reticular nanofiber structure and stable crystal structure.[158] According to the Hofmeister effect, Zhou obtained high-orientation and high-strength PVA/HPC hydrogels with a tensile strength of 4 MPa and elasticity of 900 kPa. Moreover, the maximum tensile strain was up to 975% and could fully recover at 100%.[159] In addition, the insertion of HPC enables the hydrogel network to produce a uniform porous structure and achieve the improvement of ionic conductivity, which can be applied to artificial nerves working in 3D-printed robotic hands to ensure the stable transmission of electrical signals and the full recovery of flexible finger movement, which is suitable for the field of flexible electronics.

As an ionic crosslinker, $CaCl_2$ could produce an ionic crosslinking effect with cations because of the active groups in cellulose. In contrast, the high valence cation Ca^{2+} can easily combine with the functional groups to form a relatively stable complex, enhancing the ionic crosslinking effect and improving the gel network's internal crosslinking degree.[160] Phosphate was also an ionic crosslinking agent, which was crosslinked with cellulose or derivatives by electrostatic interaction between anions and cations to form hydrogels.[161] The effects of crosslinker with different proportions on the mechanical properties of hydrogels were also different. Whether Ca^{2+}, HPO_4^{2-}, or other salts were used as crosslinkers of cellulose hydrogel, they are the salting-out effect of the Hofmeister effect. According to the sequence of Hofmeister, we can find that the strength of hydrogel was related to the concentration of salt and the specific properties of ions. The higher the concentration of salt, the stronger the salting out effect, thus promoting the hydrophobic interaction, which led to an increase in the hydrogel strength. Kim et al. have in situ prepared MC-based hydrogels and found that the salting-out effect was $HPO_4^{2-} > H_2PO_4^{-} > Cl^{-}$.[162]

5.1.5. Self-assemble strategy

Cellulose self-assembled hydrogels contained stable networks spontaneously organized or aggregated by non-covalent forces (Figure 4B). Lignocellulose could be dissolved in the DMAc/LiCl solution that broke the hydrogen bonding among cellulose chains, and free cellulose chains existed in the solution. The hydroxyl groups formed a secondary hydrogen bonding with water molecules, which emerged a new strong hydrogen bonding system.[163] MCC was pre-dissolved in 1-butyl-3-methylimidazole ammonium chloride/DMSO, followed by adding freeze-dried CNCs, CNCs of cellulose I, and cellulose II.[164] The resultant hydrogel overcame the chemical incompatibility between MCC and CNC. The CNC I in the hydrogel played a rigid role in the regenerated cellulose matrix and promoted the co-crystallization of CNC II. This operation facilitated the production of tougher hydrogels because a seepage network was formed to avoid the conversion of CNC I to CNC II. In addition, the storage modulus of this all-cellulose hydrogel varied at different humidity levels. It decreased with increasing humidity because water destroyed intermolecular hydrogen bonding, which acted as a plasticizer for dry materials.[165] Such hydrogels can be applied to the preparation of humidity-responsive materials.

5.1.6. Composite with inorganic nanoparticles

For inorganic nanoparticles, electrons and lattice systems have limited freedom degrees; surface defects and the unsaturated surface bond presented excellent affinity for other groups. They can quickly bond directly with organic groups of polymers. Because the surface structure of inorganic nanoparticles was not easy to be destroyed, the nano-size effect between the inorganic nanoparticles and organic polymers was more prominent.

Graphene oxide (GO) seemed to be an almighty additive in forming composite hydrogels due to the wide existence of hydroxyl, carbonyl, and epoxy functional groups on its surface. These functional groups can strongly interact with polar solvents and polymer matrix and ensure the uniform dispersion of GO nanosheets in the polymer matrix.[166] GO has been added as a reinforcer to regenerate cellulose/PVA composite hydrogel. When the tensile strength increased by 40.4%, the elongation at break increased from 103% to 238%. The reason for the significant improvement was that GO could simultaneously form hydrogen bonding with the PVA and cellulose, forming a double network structure (Figure 4Da). When an external force was applied, the stretching of the dual network made the GO sheet slip (Figure 4Db), straightening the coiled molecular chains inside the double network. The strong hydrogen bonding interaction between the GO sheet and regenerated cellulose molecules increased the toughness of the dual network and improved the elongation at break. However, excessing the GO concentration, the increase of elongation at break was not apparent. The superfluous GO combined with regenerated cellulose and PVA to form a relatively rigid region that provided small deformation under external force, and only the molecular chains between the rigid areas could be stretched, preventing the motion of the dual network (Figure 4Dc).[167] Due to the recombination of GO, the hydrogels were pH-responsive and proportional to the swelling rate. Under alkaline conditions, the carboxyl groups dissociated into carboxylic acid anions, which were repulsive to each other in the hydrogel network, resulting in the swelling of the hydrogel.

Carbon nanotubes have unique structures and excellent mechanical properties and also have been used to enhance the mechanical properties of cellulose hydrogel. Lu et al. mixed carbon nanotubes into oxidized cellulose nanofibers/polyacrylamide hydrogels with a 3.5-fold tensile strength and 2.8-fold tensile modulus due to hydrophobic interaction. The entanglement between oxidized cellulose nanofibers and polyacrylamide chains made the internal network structure of hydrogel closer, thus avoiding the collapse of the internal system.[168]

Halloysite nanotubes (HNTs) presented a high aspect ratio and high strength. As the physical crosslinker in hydrogels, HNTs resulted in significant changes in material properties, viz., compressive strength can be significantly improved.[169,170] When the dosage of HNTs was 10 wt%, the compressive strength of dry hydrogels at 70% strain was 120.7 kPa due to the hydrogen bonding between HNTs and the cellulose chain. In addition, CCD-986Sk cells were seeded in the hydrogel for cell viability experiments. The results showed that the cells could spread, grow, and propagate well on the hydrogel, which could be applied to cell soft tissue engineering. In addition to the physical crosslinking, the abundant aluminum elements might support the coordination with the hydroxyl groups of cellulose. Like HNTs, bentonite (BT) was also an inorganic mineral that contained aluminum elements. BT nanoplates had extremely high in-plane elastic modulus and abundant bonding sites on their surface. The compressive modulus of BT/cellulose composite hydrogel increased by 12 times. The coordination interaction between cellulose and BT mainly existed in the form of an Al—O—C bond, which was sufficient to ensure excellent mechanical properties.[171] In addition, the hydrogel impregnated with LiCl had a high ionic conductivity ($25.8\ \mathrm{mS\cdot cm^{-1}}$) and good particle conductivity even at extremely low temperatures since LiCl weakened hydrogen bonding among water molecules, thereby lowering the freezing point and the measured potential of the BT/cellulose hydrogel. It can be inferred that the gap between adjacent BT nanoplates separated by cellulose can quickly pass through cations. The above various effects give the overall hydrogel the advantages of freezing resistance and high ion conductivity, which can be applied in flexible electronics.

In addition, some inorganic particles can be combined into hydrogels to bring some auxiliary functions. Long et al. synthesized a cellulose-based composite hydrogel with ZnO/SiO_2 heterostructure.[172] SiO_2 can form a hydrogen bonding with hydrogels to enhance the mechanical properties and stability of hydrogels and ensure the function of hydrogels in complex environments. On the other hand, defect sites on the SiO_2 surface can be used as electron acceptors. When exposed to light, valence band electrons of ZnO migrated to the impurity layer of SiO_2, which inhibited the recombination of photogenerated carriers and enabled more photogenerated electrons to participate in the reaction (Figure 5), so has high catalytic degradation efficiency (95% in 120 min). In addition, the degradation rate can still reach 90% after 8 cycles of experiments.

5.1.7. Composite with organic small molecules

Ethylene glycol (polyethylene glycol, PEG), glycerin, sorbitol, etc. that contain at least two hydroxyl groups were suitable plasticizers to form cellulose-based hydrogels. The performance of the plasticizers was generally influenced by the number of hydroxyl groups and molecular weight. Higher molecular weight PEGs contributed to the tensile strength of the composite hydrogel. This phenomenon might be related to the strong hydrogen bonding and molecular chain entanglement between PEG and the cellulose chain. The close connection between cellulose and PEG partially broke the crystal structure of cellulose and formed a uniform and dense network, thus improving tensile strength. Moreover, the PEG with higher molecular weight contributed to the elastic modulus.[173] Although plasticizers were beneficial for tensile strength, they only worked at low content. Sun et al. investigated the mechanical properties of HPMC/κ-carrageenan composite film by adding plasticizers, including glycerin, sorbitol, and PEG-400. The results showed that the tensile strength decreased and flexibility increased with the increase in plasticizer content.[174] However, an opposite result was obtained by Chen et al., who prepared cellulose/sorbitol composite hydrogels.[175] When the concentration of sorbitol was 60 wt%, the tensile strength increased to 6.02 Mpa, which may be due to the mutual hydrogen bonding between sorbitol and cellulose.

5.1.8. Composite with natural macromolecules

Natural macromolecules, including SA, CS, gum, collagen, and gelatin, can form physical hydrogels with cellulose through hydrogen bonding, ionic interactions, and molecular entanglement, resulting in enhanced mechanical properties of hydrogels.

Flaxseed gum (FG) consisted of acidic and neutral polysaccharides with a ratio of about 2:1. The hydroxyl and carboxyl

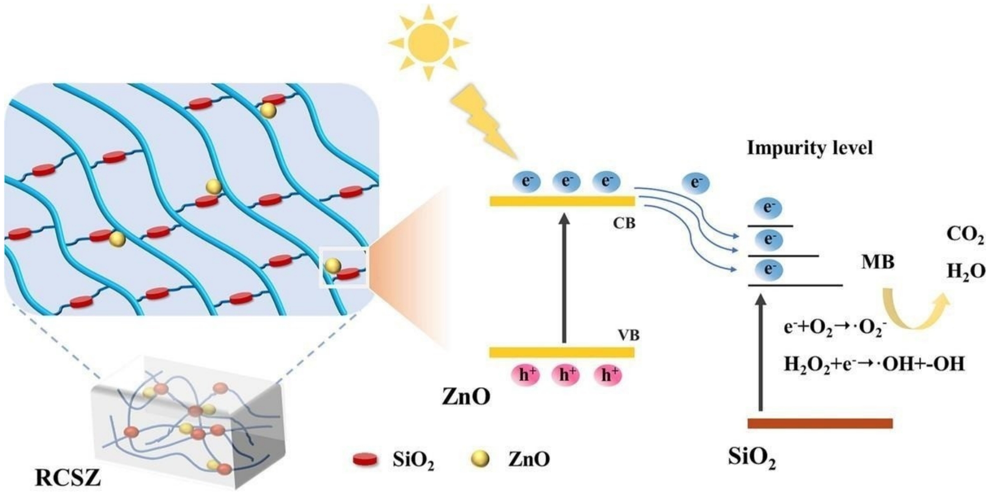

Figure 5. Enhancement mechanism of the separation efficiency of photo-generated carriers for cellulose-based composite hydrogel with ZnO/SiO_2 heterostructure photocatalyst. Reproduced from ref. [172] Copyright (2022), with permission from Elsevier.

groups were the main functional groups that can form hydrogen bonding with cellulose. Thus, Deng et al. developed cellulose/FG composite hydrogel and found that the addition of FG significantly increased the pressure resistance compared with the pure cellulose hydrogels.[176] Flow cytometry and in vivo toxicology analysis proved that the cellulose composite linseed glue hydrogel was biocompatible and could be applied to wound treatment.

SA is an acidic polysaccharide that can be used in hydrogels with the ability to wrap other materials. The addition of SA can improve the mechanical properties of hydrogels.[177] Ma et al. have exploited TEMPO-oxidized cellulose nanofibers (TOCNF)/SA interpenetrating network hydrogel in the presence of acetic acid/$CaCl_2$.[178] The acetic acid restrained the dissociation of carboxyl groups, consequently eliminating electrostatic repulsion and narrowing the distance among the feedstocks. As a result, hydrogen bonding could be facilely formed between the TOCNF and SA. In addition, the "egg-box" model may play a more important role, viz., multiple chelates (i.e., Ca^{2+}–TOCNF and Ca^{2+}–SA complexes) were formed in this process. In addition, the pH-responsiveness of the cellulose hydrogel can be given by adding SA. The release performance at different pH can be explored by loading aspirin, and the sustained release can reach 80 h. It is a good and non-toxic drug carrier.

The amino and acetylamino groups of CS molecules allow protonation to form composite hydrogels through ionic interactions and hydrogen bonding. He et al. dissolved cotton linter pulp and CS in the alkaline/urea system, followed by blending to form cellulose/CS composite hydrogel.[179] The elongation at break increased with the fraction of CS due to the hydrogen bonding between CS and cellulose but declined when it reached 30 %. This phenomenon may be due to the increased proportion of CS leading to the rearrangement in the cellulose hydrogel matrix.[180] The weakening of mechanical properties brought a good antibacterial effect and inhibited the growth of Escherichia coli and Staphylococcus aureus. This may be due to the electrostatic interaction between protonated CS and negatively charged anions, thus limiting the freedom of microorganisms. At the same time, CS restricted microorganisms from hindering the transcription of DNA to RNA, thus hindering reproduction,[181] which can be applied to facial masks to maintain the overall low bacteria environment.[182] Huang et al. obtained nano-cellulose (36–122 nm) by acid hydrolysis, which was further oxidized by sodium periodate.[183] The dialdehyde cellulose with carboxymethyl CS was used to obtain hybrid hydrogel with good biocompatibility, and the compressive strength of the hydrogel was improved.

5.2. Chemical hydrogels

The chemical reaction can not only be used to adjust the physicochemical properties of cellulose but also covalently crosslink hydrophilic cellulose networks to achieve structural stability and effective expansion of cellulose-based hydrogels. The fabrication of different functional or stimuli-responsive cellulose hydrogels through various polymerization reactions with various monomers further broadens the field of hydrogel materials.

5.2.1. Esterification crosslinking

Hydroxyl groups on cellulose or hydroxyl groups and carboxyl groups on its derivatives can be used to prepare cellulose hydrogels by esterification. Isocyanate compounds have been used as crosslinkers for forming covalent bonding with hydroxyl groups to prepare cellulose-based hydrogels (Figure 6A). When cellulose moisture gradually diffused outward from its interior to the surface, it contacted isocyanate and reacted to substituting urea, which slowly gathered to form particles (nuclei). At this time, there was a particular effect, and a random nucleation mechanism controlled the consumption of isocyanate. The diffused water did not completely react with isocyanate on the cellulose surface. The rest crossed the isocyanate coating on the cellulose surface into the air and generated a new interface with isocyanate. In addition, the interfacial reaction between the isocyanate group and cellulose was controlled by the phase interface reaction mechanism, so the total reaction mechanism was between the random nucleation and the phase interface reaction mechanism. Queiroz used polymethylene diisocyanate as a crosslinker to form polyurethane hydrogel with the hydroxyl groups of cellulose, and its compressive modulus increased by 629 %.[49]

Citric acid, a cheap and pollution-free organic polyacid, can occur in crosslinking reactions with cellulose. Citric acid and trisodium citrate can form intermediates due to the ionization in the presence of free water. Oxygen atoms with paired electrons in the formed intermediates showed a relatively strong ability to donate electrons due to high electron density, which can be regarded as Lewis bases. The carbon atom on the carboxylic acid could accept lone pair electrons and can be regarded as Lewis acid. The formed Lewis acid and Lewis base formed a stable C–O linkage through electron rearrangement, and the remaining negatively charged oxygen atom combined with the free H^+ in the system to create a stable hydroxyl group. The generated intermediate was unstable, and the carbonyl group was regenerated while dehydration occurred. Finally, the citric acid molecule existed as a pentacyclic anhydride that appeared high reactivity with hydroxyl groups of cellulose (Figure 6B). The cyclic anhydride then released a carboxyl group that can continue to repeat the process without steric hindrance, resulting in a uniform distribution of chemical cross-linking points within the skeleton. When the addition of citric acid was 5 wt %, the tensile strength increased from 13.35 MPa to 18.30 MPa, and the elongation at break decreased from 18 % to 4.66 % due to the increase in crystallization capacity. Generally, the increased covalently crosslinking density contributed to tensile strength. However, the continued increase in the amount of citric acid caused the opposite effects due to potential submicroscopic cracks.[186] In addition, the prepared hydrogel film has good biocompatibility with HaCaT cells. It has antibacterial effects against gram-positive and

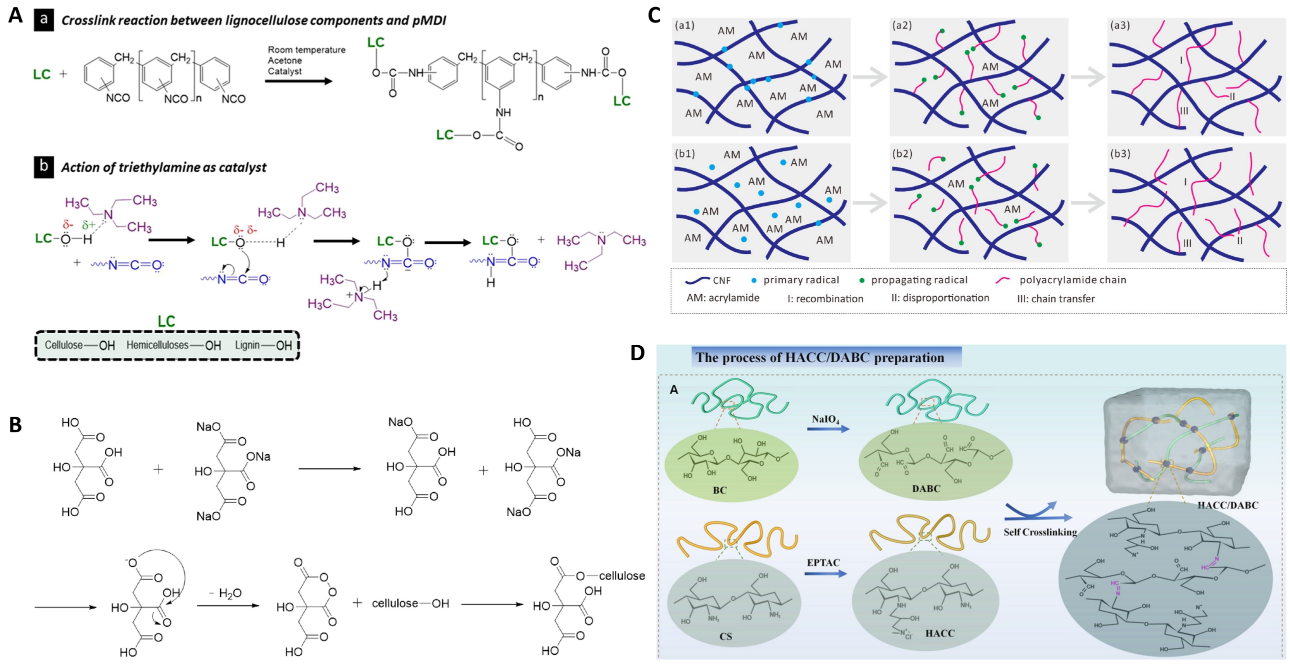

Figure 6. A) Mechanism of crosslinking cellulose and polymeric methylene diphenyl diisocyanate. Reproduced from ref. [49] Copyright (2023), with permission from Elsevier. B) Mechanism of crosslinking cellulose and CA. C) Mechanism of crosslinking polymerization process via UV irradiation (a) and APS initiation(b). Reproduced from ref. [184] Copyright (2021), with permission from the American Chemical Society. D) Mechanism of crosslinking of dialdehyde BC and CS. Reproduced from ref. [185] Copyright (2022), with permission from Elsevier.

gram-negative bacteria, indicating its potential application in wound healing.

5.2.2. Etherification crosslinking

Epichlorohydrin was the representative, which could crosslink cellulose under alkaline conditions corresponding to the following process: (1) The halogenated carbon supplied the electron cloud to halogen (e.g., Cl and Br) and presented as a $C^{\delta+}$, and an S_N2 reaction occurred between $C^{\delta+}$ and the hydroxyl groups of cellulose; (2) Epoxy group, another functional group, could form a C^+, and an S_N1 reaction occurred. Thus, epichlorohydrin has been widely used to prepare cellulose-based hydrogel. The fracture stress and strain of the cellulose hydrogel crosslinked by epichlorohydrin can reach 4.8 MPa and 74%, respectively.[187] Similar reactions can be supported by di/multifunctional glycidyl ether, such as ethylene glycol diglycidyl ether and 1,4-butanediol diglycidyl ether.[188]

5.2.3. Free radical polymerization

Nano cellulose can introduce active groups by grafting reaction to participate in polymerization (Figure 6C). The grafted nano cellulose can enhance its interaction with the polymer chain. Free radical grafting reaction was the most simple and convenient method because many free radicals can be generated on the cellulose backbone before grafting. The copolymerization of *N*,*N*-dimethylacrylamide, and acrylamide compounds to cellulose derivatives was a current method. The cross-linking of the former can improve the compressive strength (about 10 times) and hardness (about 50 times) of the hydrogel. Furthermore, other monomers can be introduced into the matrix, which endowed hydrogel with responsiveness, such as *N*-isopropyl acrylamide.[189,190] Moreover, the mechanical properties of hydrogels can be significantly improved by grafting different polar functional groups, such as the carboxyl and amino groups, with different initiators. Paulo et al. have prepared hydrogels by grafting tryptophan to HPMC, which had a high compression modulus of 201 kPa.[191]

According to the physical modification, the radiation could trigger radicals and thus can be used to form cellulose-based hydrogel (Figure 6C). This was an efficient process without adding chemicals (i.e., monomers and initiators), and the properties of as-prepared hydrogels can be controlled by the radiation dose and time. Ahmed used γ-ray radiation-induced cross-linking to prepare CMC/gelatin hydrogels. By varying the radiation dose, the compression modulus of the hybrid hydrogel can be adjusted from 20 kPa to 100 kPa.[116] Radiation-induced polymerization can also make cellulose polymerize better in hydrogel network structure, thus improving mechanical properties. Gao has prepared cellulose paper-polyamidoxime hybrid hydrogel by polymerization with cellulose, which can adsorb uranium in seawater. Due to the existence of cellulose, its tensile strength increased from 0.066 MPa to 1.10 MPa. This enables the hydrogel to maintain a stable structure in the ocean, resist seawater erosion, and maximize the application of this hydrogel in marine environments.[192]

5.2.4. Stepwise crosslinking

The stepwise crosslinking generally occurred on the cellulose derivatives. Cellulose dialdehyde obtained from sodium periodate oxidation was a typical derivative that can form imine linkage with all the polyamine compounds via Schiff base reaction (Figure 6D). Deng et al. prepared oxidized BC/CS-based hybrid hydrogel with highly efficient self-healing performance.[185] The maximum compressive strain was 50%, and the compressive strength of about 50 kPa. When the molar ratio of $-NH_2$/$-CHO$ was not 1, many cellulose aldehydes tended to agglomerate or formed less crosslinked networks, resulting in the uneven structure of the hydrogel network and gradual reduction of compressive strength. In addition, this hydrogel had potential in tissue engineering due to its structural similarity to the natural extracellular matrix, good biocompatibility, and high water-holding capacity.[193] Kang et al. have also prepared hydrogels from CS and cellulose dialdehyde.[194] With the increased dosage of cellulose dialdehyde, the polymer network became denser, and its mechanical properties consequently improved significantly. The maximum pressure was 30.0 kPa, and the viscoelastic property was enhanced nine times. Moreover, in vitro experiments showed that the hydrogel had good antibacterial activity against Escherichia coli and Staphylococcus aureus, which could be used in food storage and biomedical applications.

Diels-Alder reaction is one of the commonly used reactions for preparing hydrogels. García-Astrain et al. grafted maleimide on CNCs to generate monoenes that further react with furan-modified gelatin to form a stable hydrogel network structure.[195] The most important thing was that the interaction force between modified CNCs was reduced, which reduced the aggregation of CNCs and contributed to good dispersion. Moreover, a strong hydrogen bonding could form between gelatin and cellulose.

The silane coupling agent was also a commonly used crosslinker in hydrogels. Zhang formed cellulose-based hydrogels via 3-aminopropyl ethoxy silane crosslinking. The storage modules of cellulose and lignocellulose hydrogels increased from 276 kPa and 580 kPa to 1110 kPa and 1391 kPa, respectively. The hydrolyzed silane coupling agent can cause mechanical enhancement. The compressive modulus after crosslinking was increased by a factor of 3, confirming the formation of new crosslinking bonds in the gel network.[196] Yang et al. prepared CNCs modified by alkenyl silane, followed by forming a core-shell structure via free radical polymerization with acrylamide.[197] The concentration of CNCs was proportional to Young's modulus and tensile strength of the hydrogel. As a result of the polymerization, a dense shell-like structure formed around the CNCs core. In addition, the crosslinked network structure formed by hydrogel polymerization can inhibit Brownian motion and the topological state of the cellulose chain and ensure the stable structure of hydrogel. Hamedi et al. modified the BC membrane with amino silane and crosslinked it with glutaraldehyde to form a hybrid hydrogel membrane.[198] The mechanical strength of the hydrogel membrane was improved due to the formation of a layer of polysiloxane on the surface of BC. In addition, the amino group of silane and the hydroxyl group of cellulose also formed strong hydrogen bonding.

6. Conclusions and Perspectives

So far, cellulose-based hydrogels have been widely reported. The rapid development of cellulose-based hydrogels benefits from cellulose accessibility. Dissolution and modification of cellulose are two methods by which people can use cellulose directly to the greatest extent. These methods have different influences on the physicochemical properties of cellulose and also on the preparation and performance of subsequent hydrogels. Through physical blending, composite inorganic, organic matter can combine the properties of other substances to develop cellulose hydrogel with non-toxic and excellent mechanical properties; The modification and grafting of cellulose and the polymerization of hydrogels with different crosslinkers can improve the mechanical properties and obtain specific functions (e.g., pH- and thermo-responsiveness) at the same time, which greatly expanded the application of cellulose hydrogels.

Though cellulose has been widely used in the preparation of hydrogels that showed excellent performances, there are still several limitations in the usage of cellulose. The developed solvent showed "high" characteristics, i.e., high concentration, high viscosity, high temperature, and/or high cost. These features induced the destruction of the chemical structure, resulting in the decrease of cellulose-based hydrogels' performance. Moreover, the dissolution and regeneration of cellulose were typically achieved via the broken and rearrangement of hydrogen bonding. These processes involved the adsorption and desorption processes. Thus, irreversible adsorption was inevitable. As a result, the solvent molecules can not be completely removed from the cellulose chains in the regeneration process. Moreover, the remaining solvent molecules can be considered the electrophile or nucleophile that catalysize the cleavage of glycosidic bonds. These results limited the excellent performance of cellulose and the large-scale production of cellulose-based hydrogels. Thus, less use of high electrophilic or affinity reagents will be an important direction for the development of cellulose solvents in the future.

For the cellulose-based hydrogels, most of the published literature declared biocompatibility due to the high water content. It is not accurate due to the introduction of toxic components. Moreover, the recrystallization of the cellulose chain decreased the biodegradation. Thus, the development of cellulose-based hydrogel with real advantages in biocompatibility and biodegradation will be necessary. The preparation of hydrogels by polymerization of cellulose with monomer will remain the mainstream in use for a long time. Highly reactive and biodegradable monomers need to be developed for environmentally friendly cellulose-based hydrogels.

In addition, it is very important to transform cellulose-based hydrogels into recycled materials, which can be completely degradable and pollution-free in the living environment. We hope that cellulose-based hydrogels will have better applications in water treatment, agriculture, biomedicine, biosensing, et al. Just as an enhancer, it can also reduce the use of nonrenewable resources such as fossil energy, alleviate some environmental issues, and help achieve the goal of carbon neutrality and carbon peak.

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Conflict of Interests

The authors declare no competing financial interests.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Cellulose · Hydrogel · Modification · Dissolution · Performance

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