Current Research in Green and Sustainable Chemistry 5 (2022) 100252

Contents lists available at ScienceDirect

Current Research in Green and Sustainable Chemistry

journal homepage: www.elsevier.com/journals/current-research-in-green-and-sustainable-chemistry/2666-0865

Cellulose hydrogels: Green and sustainable soft biomaterials

Rajen Kundu [a,b,*], Pushpa Mahada [c], Bhawna Chhirang [c], Bappaditya Das [a]

[a] Analytical and Applied Chemistry Division, CSIR-National Metallurgical Laboratory, Jamshedpur, 831007, India
[b] Academy of Scientific & Innovative Research (AcSIR), Ghaziabad, 201002, India
[c] Department of Biochemistry, Central University of Haryana, Mahendargarh, 123031, India

ARTICLE INFO

Keywords:
Biopolymer
Cellulose
Hydrogels
Soft biomaterials
Biodegradable

ABSTRACT

Cellulose is a highly abundant, green, sustainable, and biodegradable polymer. These characteristic features of cellulose make it a useful polymer for the synthesis of bio-based hydrogel/or soft material for various applications. This article is focused on the preparation of biodegradable and biocompatible cellulose-based hydrogels using different methods based on the crosslinking agents used and the solvents used for cellulose dissolution. A study on the classification of different types of hydrogels was also reported. This article also discusses the self-healing cellulose-based hydrogel, bacterial cellulose-based hydrogel and includes the use of cellulose hydrogel in agriculture, biomedical field such as wound healing, wound dressing, and tissue engineering, water purification, removal of heavy metal, and in environmentally beneficial supercapacitors.

1. Introduction

On looking forward to the research of the 21st century, it has become clear that the use of renewable resources and natural polymers for mankind is the sole aim of scientists worldwide. The use of natural polymers like starch, cellulose, keratin, chitin, and gelatine in the research & development sector and commercial sector are widely explored to replace extensively used petroleum-based polymers [1]. By combining both research & development and commercial approaches, it is realized that lignocellulosic biomass is one of the major natural and renewable sources for the extraction of cellulose and further use of the same in preparation of cellulose hydrogel. The renewability of cellulose is not only the solitary characteristic for its use in cellulose hydrogel preparation by scientists but it possesses certain other indistinguishable properties like biodegradability, biocompatibility, and insolubility in most of the solvents [2]. Moreover, cellulose is nontoxic to humans which allows cellulose hydrogels to be used for wound healing, wound dressings, and drug delivery. Whereas the toxicity of the synthetic polymers and/or gelators to humans limits the use of synthetic hydrogels in the medical field [3]. Various applications of cellulose hydrogel are shown in Fig. 1 (see Table 1).

Recently, considerable attention has been given to the utilization of hydrogel in environmental applications [4] such as water purification [5], removal of organic pollutants [6], carbon dioxide capture [7], etc. Affordable environment-friendly process for domestic and industrial wastewater treatment is indispensable challenges. Hydrogel is a well-known adsorbent and can adsorb a large quantity of heavy metals and organic dye/or pollutants from the wastewater. Moreover, cellulose-based hydrogels are a promising adsorbent and have many advantages over synthetic adsorbents owing to their high abundance, biodegradability, non-toxicity, and excellent adsorption capacity. A concise review of the cellulose-based hydrogels for wastewater treatment is discussed elsewhere [8].

Cellulose cannot be used in its natural form like other polymers due to the rich in hydroxyl groups. It is modified with the help of several chemical reactions to form cellulose hydrogel [9]. Cellulose hydrogels are extensively cross-linked and hydrophilic polymers that are extended in three dimensions. Crosslinking strategy for the preparation of cellulose-based hydrogel is shown in Fig. 2. These hydrogels are used in baby diapers and female hygienic products due to their excellent fluid absorbance ability without losing the actual shape [10]. The reason behind retaining the proper shape is the presence of weak (H- bonding, Ionic interactions, and Vander walls interactions) and strong interactions i.e., covalent bonds which held the hydrogel in its intact form. Thus, cellulose is merely not an agricultural or industrial waste but it is involved in a major proportion of our daily utility. In this review, we will discuss the preparation of cellulose hydrogels and their widespread applications based on their properties.

* Corresponding author. Analytical and Applied Chemistry Division, CSIR-National Metallurgical Laboratory, Jamshedpur, 831007, India.
E-mail address: kundurajen@gmail.com (R. Kundu).

https://doi.org/10.1016/j.crgsc.2021.100252
Received 1 August 2021; Received in revised form 27 December 2021; Accepted 28 December 2021
Available online 1 January 2022

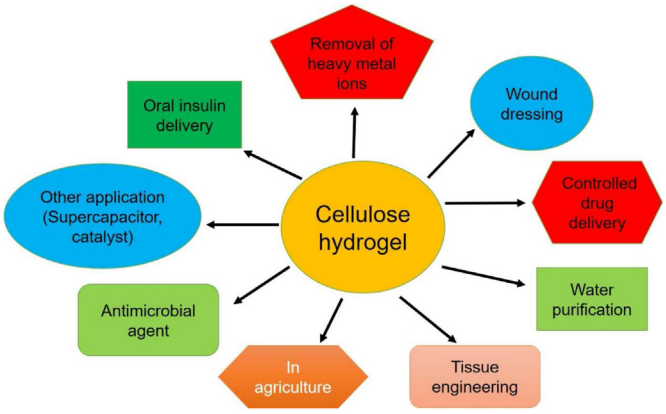

Fig. 1. Various applications of cellulose hydrogel.

Table 1
Cellulose hydrogels for heavy metal removal.

Material	Preparation method	Heavy metals	pH	Temp. (°C)	Ref
CMC/ECH	Chemical cross-linking	Cu, Ni, Pb	7	RT	[47]
CMC-g-poly(NIPAm-co-AA)/MMT	Chemical cross-linking	Cu, Pb	4	RT	[48]
PVC/CMC	Freeze-thaw	Ag, Ni, Cu, Zn	1.5	15	[49]
Chitosan/PVA/GA	Chemical cross-linking combined with Freeze-thaw	Hg, Cu, Cd, Pb	2.00–5.85	30	[50]
PVA/p(AAm-NIPAm)	Chemical cross-linking	Cu, Ni, Pb	6.0	25	[51]
PVA/CMC/GA	Microwave-assisted irradiation	Cu, Cd, Ni, Zn	5–9	RT	[46]

2. Hydrogel

The hydrogel was first synthesized in the 1960s by Wichterle and Lim [11]. This is a miscellaneous mixture of two or more phases. The dispersed phase is water and the solid phase is a three-dimensional network [12–15]. Polysaccharide hydrogels are classified into various types based on (i) preparation method, (ii) types of monomer/polymer involved, and (iii) ionic charge. Based on the preparation method, polysaccharide hydrogels are classified into two subtypes: (a) physically (reversible) crosslinked hydrogels, and (b) chemically (permanent) crosslinked hydrogels [16].

2.1. Physically crosslinked hydrogels

These are reversible and unstable hydrogels where monomers are connected by each other through weak interactions like hydrophobic interactions, ionic interactions, and intermolecular and intramolecular hydrogen bonding. Cellulose exhibits inter-, and intramolecular hydrogen bonding (Fig. 3). Hydrophobic interactions are responsible for the dissolution of cellulose. These hydrogels are frequently used in biomedical fields due to the absence of any external linking. Cellulose-polyvinyl alcohol hydrogel synthesized by the freeze-thaw process is an example of physically crosslinked hydrogel [17].

2.2. Chemically crosslinked hydrogels

These are irreversible and more stable hydrogels than physically crosslinked hydrogels. The hydroxyl and carboxyl groups of cellulose are covalently linked to the amine, carboxyl group, and amide group of cross-linking agents. Cross-linking occurs by free radical polymerization, esterification, Michael Addition, etc (Fig. 4). Citric acid, succinic acid, epichlorohydrin, and divinyl sulfone, etc. are usually employed as crosslinking agents [18].

Based on the types of monomers/polymer involved, hydrogels are of two subtypes. Homopolymer hydrogel contains only a single type of monomer unit which is continuously repeated all over the hydrogel. Cellulose can form homopolymer hydrogel by irradiation with high-energy radiations. It can also be formed by dissolving in NaOH/Urea aqueous solution and crosslinking with epichlorohydrin. Copolymer hydrogels are polymeric hydrogels that are synthesized using polysaccharides along with synthetic units [19].

Ionic hydrogels are polymers of polysaccharides cross-linked with an ionic unit with the help of a crosslinking agent. These are of two types, cationic and anionic. The solely occurring cationic hydrogel is chitosan-based. The chitosan is obtained from partial deacetylation of chitin. Other polysaccharides contribute to anionic hydrogels. The cationic hydrogels have a good property of swelling at low pH because their chains can easily dissociate at low pH while it is vice versa for anionic hydrogels [20]. There are various methods to modify polymers that are essential for the applications of hydrogel like grafting, blending, and curing. Fig. 5 shows the types of cellulose hydrogel based on the cross-linking, configuration, sources, network charge, polymeric compositions.

Smart hydrogel is an interesting class of soft materials that can change its shape and size according to the stimulus provided to them. The stimuli can be temperature, pH, ionic concentration, etc [21]. The superabsorbent hydrogel is a class of smart hydrogel that exhibits several hundred times more water retention capacities than their original dry weight. This type of smart hydrogel is preferred over normal hydrogel due to its high water absorption capacity. Usually, polysaccharide-based hydrogels are prepared through graft polymerization of hydrophilic vinyl monomers with various polysaccharide backbones like cellulose and chitosan. One example of superabsorbent hydrogel is cellulose and chitin-based hybrid hydrogel. In the solution, cellulose and chitin exhibit in the form of entangled chains, random coils, and semi-flexible chains. As the concentration of the cellulose and chitin increases, the solution changes to the gel phase and the hydrogen bonding between cellulose and chitin hybrid increases the stability of the gel formed [22].

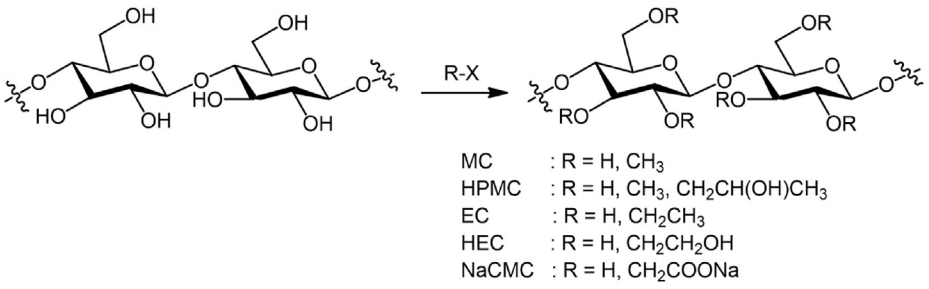

Fig. 2. Crosslinking strategy for the preparation of cellulose-based hydrogel [10]. MC: Methylcellulose, HPMC: Hydroxypropyl methylcellulose, EC: Ethylcellulose, HEC: Hydroxyethylcellulose, NaCMC: Sodium carboxymethylcellulose.

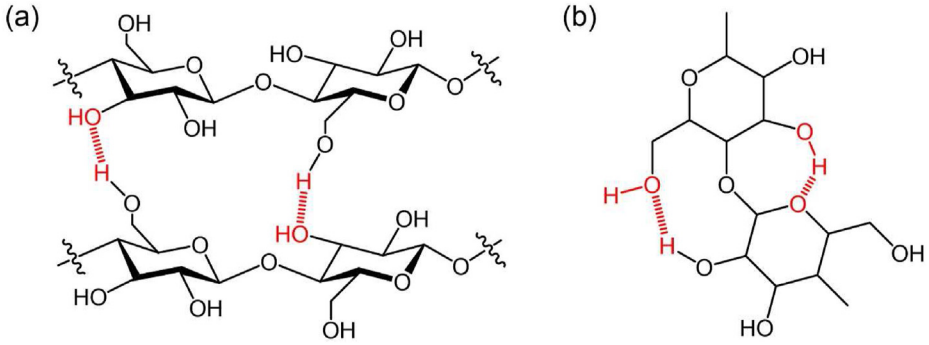

Fig. 3. (a) Inter-, and (b) intramolecular hydrogen bonding of cellulose [12].

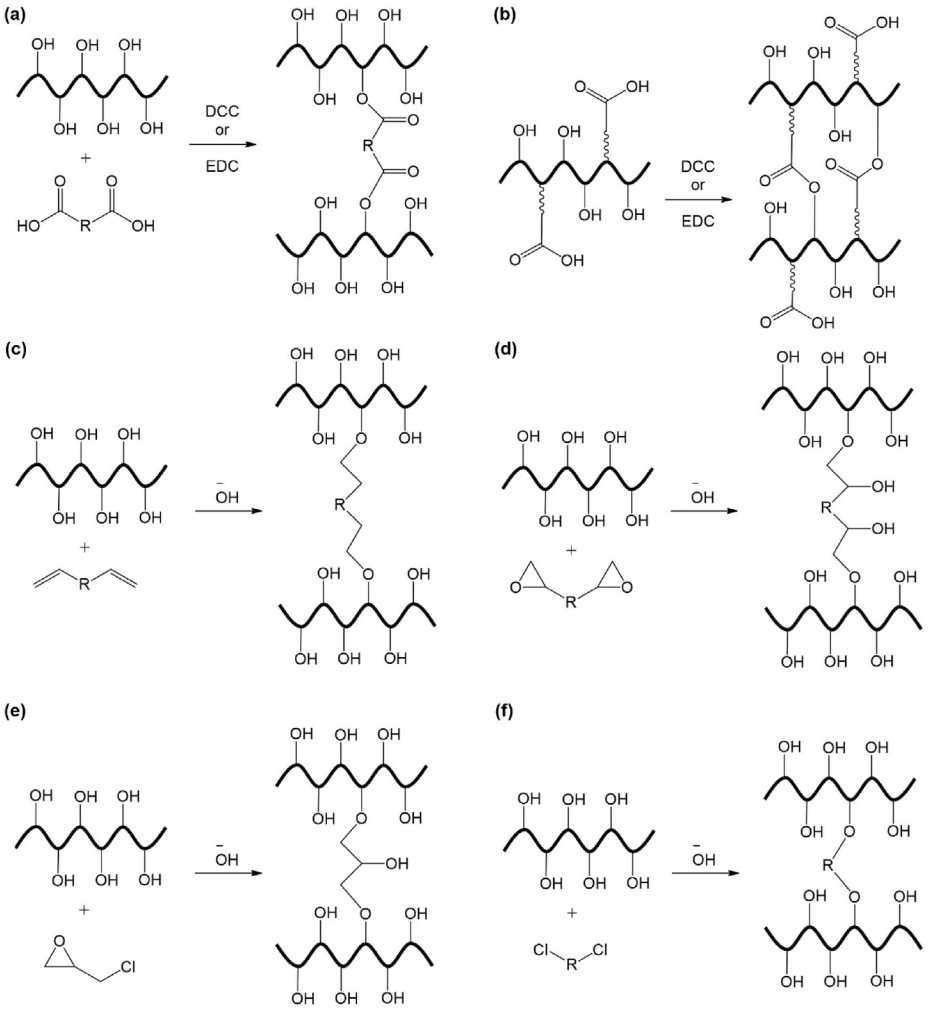

Fig. 4. Various chemical reactions/or crosslinking for the synthesis of cellulose hydrogel; (a) and (b) esterification, (c) Michael addition reaction, (d) and (e) epoxide crosslinking, (f) alkyl halide crosslinking [18].

3. Preparation of cellulose-based hydrogel

Lenny Voorhar et al. described the supramolecular hydrogels and materials. These types of hydrogels and materials are formed through crosslinking by non-covalent interactions such as ionic interactions, hydrogen bonding, metal coordination, and hydrophobic interactions. Metal coordination is used to synthesize stimuli-responsive supramolecular hydrogel [23].

Double network hydrogel is an interesting soft material that is made of two interpenetrating or semi-interpenetrating polymers. These hydrogels have better mechanical properties than single network hydrogels. In a double network hydrogel, one network is strongly covalently cross-linked which contributes to the rigidity. Whereas, the second network is loosely cross-linked curled form and provides flexibility. Cellulose-based double network hydrogels were prepared by the interpenetrating polymer network (IPN) method to get cellulose/poly(N-isopropyl acrylamide) hydrogels with increased thermal sensitivity and mechanical strength [24]. Ying Pei et al. extracted cellulose from cotton and prepared cellulose-based hydrogel with the same. They dissolved the cellulose in NaOH/urea/H_2O (7: 12: 81, weight ratio) solution and

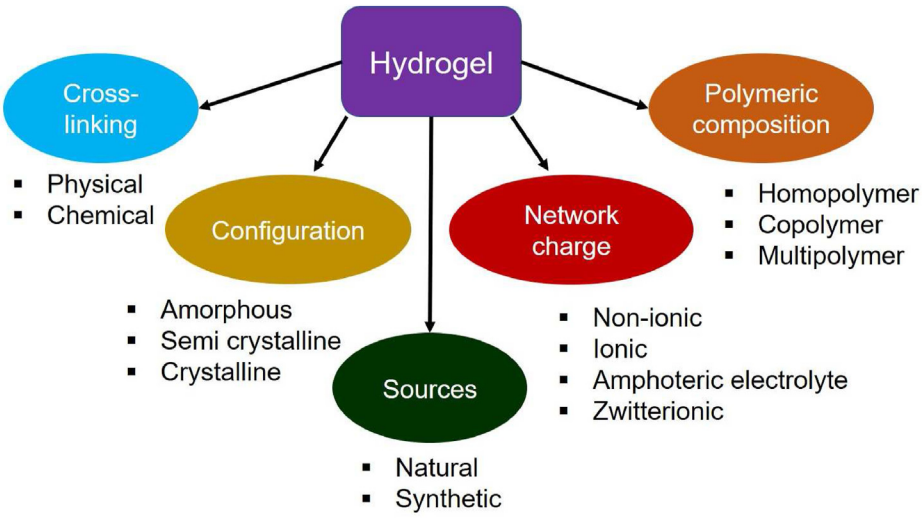

Fig. 5. Classification of cellulose hydrogel [19].

chilled it to −12 °C to obtain a transparent cellulose solution. Next, they added epichlorohydrin (ECH) as a cross-linking agent to form a three-dimensional network which leads to hydrogel formation. After that, they removed the unreacted chemicals such as NaOH, urea, and ECH by placing the hydrogel in deionized water for a certain period [25]. S. Palantoken et al. synthesized cellulose-based hydrogel by using glycine as a network-forming agent. First, cellulose was dissolved in NaOH at 0–4 °C using an ice bath and then glycine alkaline solution (10% w/v) was added to it. Both the solutions were mixed until the mixture became viscous. Finally, the viscous solution was poured into molds for overnight. The synthesized hydrogel was neutralized by acetic acid and frozen at −23 °C [26]. Hiroyuki Kono et al. worked on the synthesis of superabsorbent cellulose/chitin hybrid hydrogel (Fig. 6). They dissolved the cellulose in LiCl/N-methyl-2-pyrrolidinone (NMP) solution at ambient temperature for a period of 48 h. A solution of chitin in LiCl/NMP was added to the cellulose solution and mixed by constant agitation at ambient temperature. After that, 4-dimethyl aminopyridine (DMAP) was added to the cellulose/chitin solution followed by the addition of 1,2,3,4-butane tetracarboxylic dianhydride (BTCA) for esterification. The solution was poured into methanol/water solution and neutralized by NaOH solution. The precipitate was filtered and purified with methanol/water solution [27].

Liang-Yi Wang et al. prepared eco-friendly hydrogel by carboxymethylcellulose (CMC) and polyvinyl alcohol (PVA) through a freeze-thaw process. The synthesized CMC/PVA hydrogel was able to adsorb heavy metal ions. PVA and CMC were dissolved in deionized water at 90 °C and at ambient temperature respectively and then PVA/CMC hydrogel was prepared by repeating the freeze-thaw cycles at different concentrations of PVA and CMC in each cycle [28]. Xiaoye Gao et al. synthesized biodegradable, pH-responsive cellulose hydrogels for oral insulin delivery based on acrylate-grafted carboxymethyl cellulose through coupling reaction (Fig. 7). Acrylic acid (AA), (1-ethyl-3-(3--dimethylaminopropyl) carbodiimide hydrochloride), and 4- dimethyl aminopyridine were dissolved in DMSO to activate the carboxyl group of acrylic acid. CMC solution was added to the activated acrylic acid solution in phosphate buffer and the crosslinking was done by using ammonium persulfate (APS) and N,N,N′,N′-tetramethylethylenediamine (TEMED). The hydrogels were kept in water for seven days with continuous changing of water several times a day to remove all the impurities [29].

Xiong-Fei Zhang et al. synthesized anti-freezing cellulose hydrogels from a $ZnCl_2/CaCl_2$ ionic system. First, they prepared a $ZnCl_2/CaCl_2$ aqueous solution by heating at 80 °C. When the solution became transparent, cellulose was added to this ionic solution and completely dissolved by stirring. Finally, the cellulose/$ZnCl_2/CaCl_2$ aqueous solution was put in molds to prepare a gel network at room temperature [30].

Xiaoning Shi et al. developed superabsorbent hydrogel from super porous hydroxyethyl cellulose (HEC) in anionic surfactant. HEC was uniformly dispersed in distilled water and then a proper amount of sodium n-dodecyl sulfonate (SDS) micelles solution was added to it. The solution

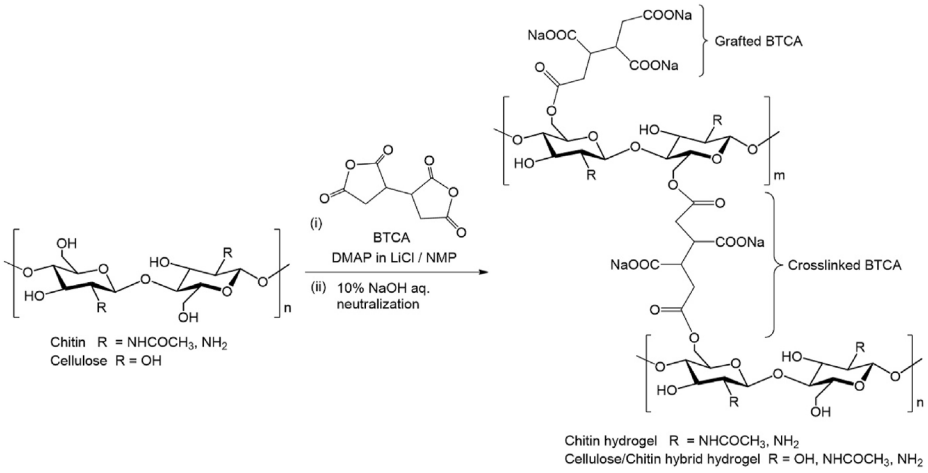

Fig. 6. Chitin and cellulose/chitin hybrid hydrogel synthesized by Hiroyuki Kono et al. [27].

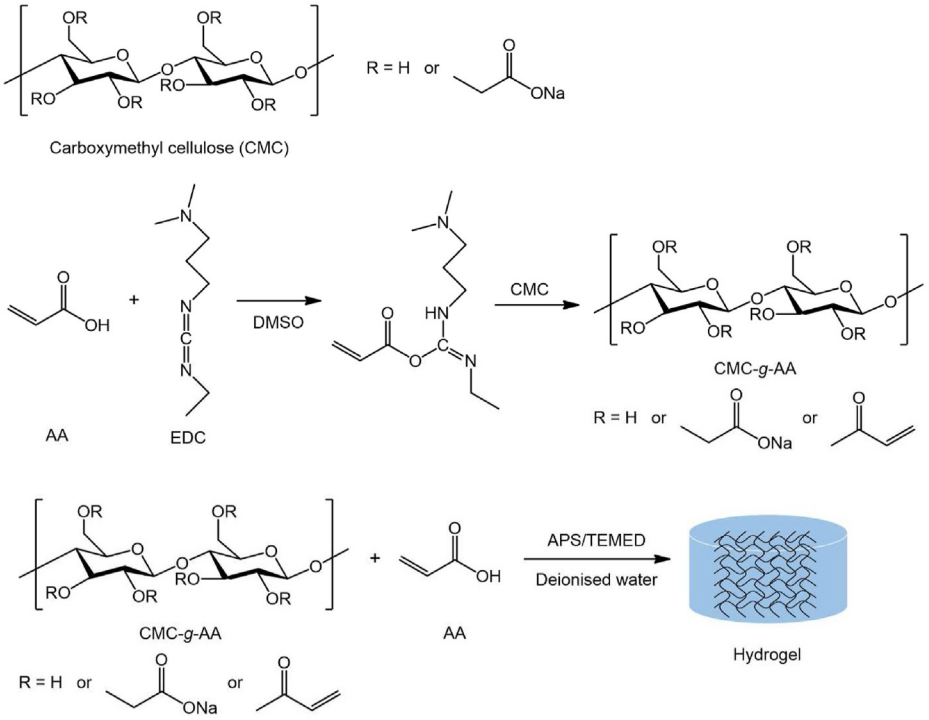

Fig. 7. Synthesis of acrylate-grafted carboxymethyl cellulose (CMC-*g*-AA) hydrogel reported by Xiaoye Gao et al. [29].

was pre-heated in a water bath and nitrogen was flushed to remove dissolved oxygen. Ammonium persulfate (APS) was added to the solution for a radical generation. The reaction mixture was cooled and acrylic acid, attapulgite clay, and N, N- methylenebisacrylamide was added as network forming agent. The temperature of the reaction mixture was raised to accelerate the polymerization. Finally, the synthesized hydrogel was placed in ethanol/water solution to remove SDS and other unreacted chemicals and dehydrated using absolute ethanol [31].

3.1. Characterization and physical properties of cellulose-based hydrogel

Cellulose hydrogel can be characterized by FTIR and morphology analysis. Both the cellulose and cellulose hydrogel showed and absorption at 3410 cm^{-1}, which correspond to –OH stretching vibrations. The signal at 1030 cm^{-1} is assigned to the –C–O– group which is found in both cellulose and cellulose hydrogel (Fig. 8a). However, the signal intensity of –C–O– in cellulose hydrogel is larger than in cellulose which further confirms the increased quantity of –C–O– group due to the crosslinking/or hydrogel formation [32].

Cellulose-based hydrogel exhibits excellent swelling and mechanical properties. Moreover, the swelling and mechanical properties depend on the cross-linker used during the hydrogel preparation. Wei Ning Chen et al. prepared hydrogels by dissolving okara cellulose in LiOH/urea solution followed by adding different amounts of epichlorohydrin (ECH) as a cross-linker into the cellulose solution [32]. The synthesized hydrogel showed a good swelling property and it was found that the water content of okara cellulose hydrogels increased with increasing the molar ratio of epichlorohydrin (ECH) to the anhydroglucose unit (AGU) of cellulose. Cellulose hydrogels exhibited a strain-hardening behavior due to the inter/or intramolecular hydrogen bonds in the cellulose chains. The mechanical/stretching property also increases with increasing the crosslinking between epichlorohydrin and cellulose. Fig. 8 b-c shows the tensile stress-strain curves of okara cellulose hydrogels at different ECH-to-AGU molar ratios. The highest tensile strength (0.245 MPa) at fracture of the okara cellulose hydrogels was found at 0.7:1 ECH-to-AGU molar ratio.

Lew P. Christopher et al. synthesized cellulose-based hydrogel with super absorbing potential. They first reacted the cellulose with sodium monochloroacetate to obtain carboxymethyl cellulose (CMC) and followed by cross-linked with epichlorohydrin (ECH) [33]. Distilled water retention value of the synthesized hydrogel was found to 725 g distilled water/g hydrogel which was comparable to the commercial synthetic (polyacrylate) super absorbing gel(Fig. 9a). Moreover, the synthesized hydrogel was also showed good re-swelling properties (Fig. 9b).

Qianlei Zhang et al. fabricated tough cellulose hydrogels from a LiOH/urea solution of cellulose using epichlorohydrin and subsequent

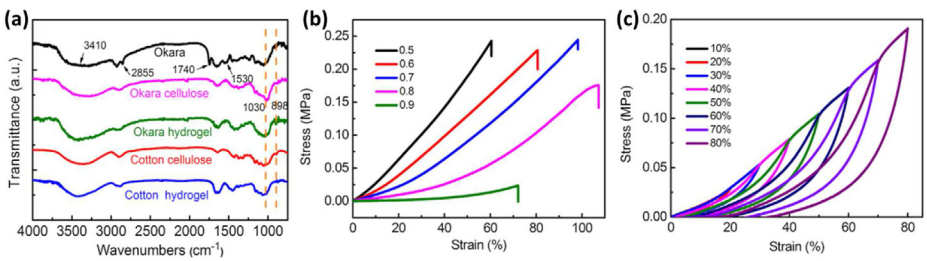

Fig. 8. (a) Fourier-transform infrared spectroscopy (FTIR) spectra of okara powder, okara cellulose, okara cellulose hydrogel, sigmacell cotton cellulose, and cotton cellulose hydrogel. (b) Tensile stress-strain curves of the okara cellulose hydrogels at different ECH-to-AGU molar ratios under tension. (c) Tensile stress-strain curves of the okara cellulose hydrogel (molar ratio of ECH-to-AGU 0.7) during cycles with various maximum stretching. "Reprinted (adapted) from { [32] Cui, X., Lee, J.J.L., Chen, W.N. Eco-friendly and biodegradable cellulose hydrogels produced from low cost okara: towards non-toxic flexible electronics. *Sci. Rep.* 9 (2019) 18166. Copyright © 2019, The Author(s)".

treatment with dilute acid [34]. They studied the mechanical property of synthesized tough cellulose hydrogels carrying a molar ratio of epichlorohydrin to anhydroglucose unit and found the fracture stress and fracture energy about 0.45 MPa and 0.23 MJ m^{-3} respectively from one of the synthesized hydrogel (Fig. 10).

3.2. Self-healing cellulose-based hydrogel

Self-healing hydrogel is a special type of soft material where spontaneous new bonds are formed to restore the three-dimensional network-like structure and function even after damage. Self-healing hydrogel can be synthesized by two major routes. The first one is the dynamic cross-links by inter and intra-molecular noncovalent interaction. The second one is the dynamic covalent bond formation through a reversible chemical reaction. Diels-Alder (DA) reaction is well known reversible chemical reaction which is a potential covalent bond forming reaction for the synthesis of self-healing hydrogel. Jun Yang et al. prepared self-healing cellulose nanocrystal-poly(ethylene glycol) nanocomposite hydrogel via Diels-Alder reaction [35]. In particular, they first synthesized furyl-modified cellulose nanocrystal and maleimideend-functionalized PEG and then these two were cross-linked via a thermally induced Diels-Alder reaction for the self-healing hydrogel synthesis. They found that the gelation time decreases with an increase in temperature which correlates with the Diels-Alder reaction. Moreover, the synthesized hydrogel was biocompatible and exhibited good swelling and mechanical properties. This type of self-healing cellulose hydrogel could be a potential soft material in the biomedical field. Y.M. Chen et al. synthesized self-healing cellulose hydrogels using carboxymethyl cellulose and studied the photoluminescence and mechanical properties [36]. They prepared the self-healing hydrogels by doping an appropriate amount of aluminum (Al^{3+}) ions and photoluminescent citric acid derivatives into carboxymethyl cellulose polymer networks. Self-healing property was attributed due to the reversible ionic coordination between Al^{3+} ions and carboxylate groups ($-COO^-$) dangling both on photoluminescent citric acid derivatives and carboxymethyl cellulose polymer chains. The synthesized hydrogels are self-healed at ambient temperature without any external stimulus and can be stretched approximately 2.5 times of their original length. The hydrogel also exhibited blue-green color under ultraviolet light and could be a potential soft material in biomedical and engineering fields. Liangjiu Bai et al. prepared self-healing nanocomposite hydrogels using modified cellulose nanocrystals by surface-initiated photoinduced electron transfer atom transfer radical polymerization (PET-ATRP) [37]. They first modified the cellulose nanocrystals surface via metal-free PET-ATRP using 4-vinylpyridine as functional monomer, 10-phenylphenothiazine as photocatalyst and ultraviolet light (365 nm) as light source, respectively. Next, the surface-modified cellulose nanocrystals hybrid was reinforced to obtain self-healing nanocomposite hydrogels by electrostatic interactions. The synthesized hydrogels exhibited good mechanical and self-healing properties. Juntao Tang et al. synthesized solvent-free stimuli-responsive self-healing cellulose nanocrystal hydrogels [38]. They first introduced aldehyde groups on cellulose nanocrystal and sodium alginate by oxidizing under mild conditions. Next, they incorporated the amine-containing vinyl functionalized monomers into the surface of oxidized cellulose nanocrystal and sodium alginate via a Schiff-base linkage. Finally, the hydrogels were prepared via a one-pot thermo-responsive in-situ polymerization reaction between modified cellulose nanocrystal and sodium alginate.

3.3. Bacterial cellulose-based hydrogel

Bacterial cellulose is microbial cellulose synthesized by several types of bacteria, including.

Gluconacetobacter xylinus, Acetobacter xylinum, Cluconacetobacter xylinus [39]. The molecular formula of bacterial cellulose is similar to plant-derived cellulose and the diameter of bacterial cellulose fibers is about 20–100 nm. However, due to the crystalline nano-fibrillar structure, bacterial cellulose exhibits a large surface area, excellent mechanical strength, and can retain a large amount of water. Due to these properties, bacterial cellulose is widely used for cellulose-based hydrogel synthesis. V. P. Hoven et al. synthesized bacterial cellulose-based re-swellable hydrogel via deposition of negatively charged polyelectrolyte, carboxymethyl cellulose, into a bacterial cellulose matrix [40]. Due to this non-destructive approach, the material property of the original bacterial cellulose was retained in the resulting cellulose-based hydrogel composite. They further used the synthesized hydrogel as a colorimetric sensor of pH and glucose. Moreover, the hydrogel exhibited wide pH 4.0–9.0 range for detection via color differentiation between each pH and low limit of detection (25 μM) of glucose. As discussed earlier, that owing to the high water holding capacity, easy permeability to gases and liquids, high tensile strength, and flexibility bacterial cellulose hydrogels have been widely used in the biomedical field including wound dressings, tissue engineering, etc. Bacterial cellulose is also a potential material for the synthesis of the antibacterial hydrogel by imparting antibacterial activity. A. Prieto et al. synthesized bacterial cellulose-based antibacterial hydrogel by incorporation of an antimicrobial agent poly(3-hydroxy-acetylthioalkanoate-co-3-hydroxyalkanoate) into the polymeric gel network and studied the bactericidal activity against *Staphylococcus aureus* [41]. Moreover, the synthesized hydrogel showed mechanical and thermal properties in the range of human skin which further suggested to a potential application in wound healing. Guang Yang et al. developed a biology-device interface by using double network bacterial cellulose hydrogel [42]. They produced electroactive hydrogel composite via the deposition of bacterial cellulose and conducting polymer on bacterial cellulose hydrogel surface to cover the bacterial cellulose fibers.

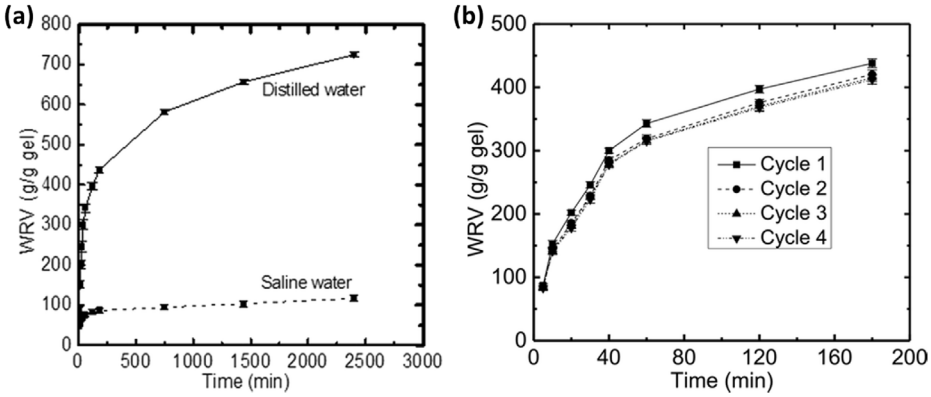

Fig. 9. (a) Water retention value of hydrogel obtained from 3 g/L CMC cross-linked with 4 g/L ECH as a function of time. (b) Water retention value of best absorbing hydrogel (obtained from 3 g/L CMC cross-linked with 4 g/L ECH) following four consecutive re-swelling cycles. "Reprinted (adapted) with permission from { [33] M. N. Alam, M. S. Islam, L. P. Christopher, *ACS Omega.* 4 (2019) 9419–9426}. Copyright {2019} American Chemical Society."

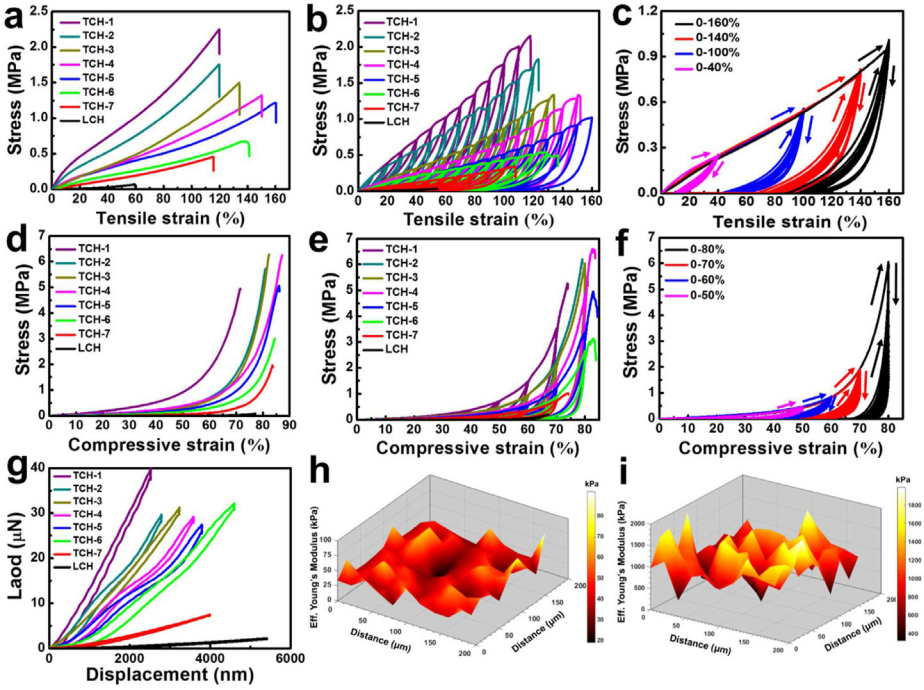

Fig. 10. Mechanical properties of cellulose hydrogels. (a) Tensile stress-strain curves of loose chemical crosslinked cellulose hydrogel (LCH) and tough cellulose hydrogels (TCHs). (b) Corresponding tensile stress-strain tests of LCH and TCHs during loading-unloading cycles of varying maximum stretching. (c) Representative tensile stress-strain curves of TCH-5 hydrogels during 10 times loading-unloading cycles at 40%, 100%, 140%, and 160% strain, respectively. (d) Compressive stress-strain curves of LCH and TCHs. (e) Corresponding compressive stress-strain tests of LCH and TCHs during loading-unloading cycles of varying maximum stretching. (f) Representative compressive stress-strain tests of TCH-4 hydrogels during 10 times loading-unloading cycles at 50%, 60%, 70% and 80% strain, respectively. (g) Force-displacement curves of LCH and TCHs from a displacement-controlled nanoindenter machine. (h–i) Representative effective Young's modulus 3D map of LCH and TCH-5 from nano-indentation measurements, respectively. The grid scan was 10 × 10 points, and the point-to-point pitch is 20 μm "Reprinted (adapted) with permission from { [34] D. Ye, Q. Cheng, Q. Zhang, Y. Wang, C. Chang, L. Li, H. Peng, L. Zhang, *ACS Appl. Mater. Interfaces.* 9 (2017) 43154–43162}. Copyright {2017} American Chemical Society."

The conducting polymer facilitates the composite to respond with current and voltage. This type of electroactive composite could be useful for biology-device interfaces to produce implantable medical devices. M. C. I. M. Amina et al. reported thermo- and pH-responsive bacterial cellulose/acrylic acid hydrogels for drug delivery [43]. They synthesized the hydrogel by combining bacterial cellulose with different amounts of acrylic acid with exposure to accelerated electron-beam irradiation at different doses. The grafting of acrylic acid onto the cellulose fibers was confirmed by the FTIR analysis. Overall studies revealed that the synthesized thermo- and pH-responsive hydrogels could be a promising candidate for control drug delivery systems. M. C. I. M. Amin et al. developed a bacterial cellulose/acrylic acid hydrogel cell carrier for full-thickness wound healing [44]. They studied the ability to deliver human epidermal keratinocytes and dermal fibroblasts for the treatment of full-thickness skin lesions. Overall findings suggested that the synthesized hydrogel could be a potential soft material for cell carrier and wound dressing application.

4. Applications of cellulose hydrogel

4.1. Oral insulin delivery

When a secondary compound is inserted into the hydrogel network in different concentrations, the diffusion properties of the hydrogel are changed. Over the years, insulin is injected into a subcutaneous layer in diabetes patients. This type of administration causes low patient body capacitance. Oral administration of this hormone is avoided due to the acidic behavior of the gastrointestinal tract. To prevent the degradation of the drugs from an acidic environment, they can be supplied via drug-loaded gel. Xiaoye Gao et al. prepared a cellulose-based pH-responsive hydrogel for drug delivery. The active drug from the hydrogel is released through the swelling diffusion method controlled by the pH of the surrounding environment [29].

4.2. Removal of heavy metal ions

Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, etc. ions are termed as heavy metal ions and can be removed by adsorption. Liang-Yi Wang et al. synthesized PVA/CMC hydrogel for the removal of heavy metal ions [28]. Arsenic is a major water pollutant. Iryanti Fatyasari Nata et al. prepared amine-rich magnetite/bacterial cellulose nanocomposite for removal of arsenate by adsorption. The thermal and mechanical properties of this cellulose nanocomposite were greatly improved by the presence of amine surface-functionalized magnetite nanoparticles on the surface of cellulose nanofibrils. This type of amine-rich bacterial cellulose magnetite hydrogel can be used as a reusable adsorbent for the removal of arsenate [45]. Chanathip Baiya et al. reported the selective adsorption of Cu^{2+} ions by carboxymethyl cellulose hydrogel. They extracted the cellulose from sugarcane bagasse and synthesized the hydrogel by microwave-assisted radiations using glutaraldehyde as a crosslinking agent. After adsorption, the metal ions can be recovered from the adsorbent by treating the hydrogel in an aqueous solution of 0.1 M HCl, saturated NaCl, or 0.1 M EDTA [46].

4.3. Wound dressing

Skin acts as the external barrier to various types of microorganisms. Minor cuts on the skin can be easily healed by the body and deep wounds can be further infected by microbes which could result in serious infection. Therefore, wound dressing soft materials having antibacterial properties is of great significance. Cellulose-based hydrogel exhibits water absorption properties and provides suitable moist conditions for wound healing. Antibiotic hydrogels can absorb tissue exudates and kill bacteria in wounds. Bacterial cellulose has high water uptake potential and high porosity. Hence this type of hydrogel can be used for the treatment of burn wounds/or as skin substitutes [52]. Eva Pinho et al. prepared composite hydrogel from cotton textiles and cyclodextrin-hydroxypropyl methylcellulose by crosslinking. This composite hydrogel can accommodate water and thus can be used in wound healing [53]. They further studied the antimicrobial activity of the above-synthesized cellulose hydrogel against *Escherichia coli* and *Staphylococcus aureus* bacteria. Moreover, this composite hydrogel could release drugs such as gallic acid encapsulated within their gel structure. Gallic acid exhibits good antimicrobial and anti-inflammatory activity. Thus, the above drug composite can be used in curing chronic wounds [54]. Zhe Sun et al. prepared hemostatic hydrogel from keratin-catechin nanoparticles (KE-NPs) and cellulose. Keratin is a fibrous protein and it

was isolated from human hair which contains adhesion sequence Arg-Gly-Asp (RGD) and Leu-Asp-Val (LDV). The composites of keratin have the property of bone regeneration, wound healing, and cancer therapy. Polyphenols are used for better adhesion properties. Catechins is a natural polyphenol extracted from tea and the main ingredient is Epigallocatechin-3-gallate (EGCG) which have anti-inflammatory property. Studies have shown that KEC accelerates thrombin activation and platelet aggregation which increases the haemostatic effect [55].

4.4. Controlled drug delivery

Conventional drug delivery (CDD) system has various disadvantages and the commonly practiced conventional method is the oral delivery method. These methods can immediately release the drug but do not maintain the adequate concentration of drug required for treatment. Controlled drug delivery has several advantages over CDD. However, controlled methods are used for maintaining the safe and effective release of drugs [56]. Natural hydrogels are employed in drug delivery because of their high water absorption, large porosity, and non–toxicity. Synthetic hydrogels are avoided because of the toxic cross-connection agent in them. Natural pH-sensitive hydrogels are used for the delivery of protein drugs with 97.6% efficiency [57]. Diana Ciolacu et al. prepared hydrogel from cellulose and lignin by cross-linking with epichlorohydrin (ECH) having high swelling properties. Lignin was incorporated for the regulated release of drugs [58]. Sultan Butun et al. synthesized carboxymethyl cellulose (CMC) hydrogel using divinyl sulfone as a cross-linking agent via a single step using the reverse micelle microemulsion polymerization method. These hydrogels were further used for drug delivery due to their biodegradability and biocompatibility [59]. Acyclovir (Ac) is a herpes virus that was used for testing the controlled release of CMC particles. They also synthesized m-CMC particles which had higher release capacity. They further described that multistep drug loading increases release efficiency. Joachim E Arikibe et al. prepared bacterial cellulose/chitosan-based semi-interpenetrating hydrogels (semi-IPN) crosslinked with genipin. The synthesized hydrogel exhibited pH-responsive swelling properties and was used for drug release study. The swelling of the non-crosslinked hydrogels decreased with the increase of pH. Whereas, swelling of the crosslinked hydrogels increased as the chitosan ratio increased at low pH. It was reported that non-crosslinked structure released drugs faster than cross-linked structure whereas cross-linked structure release-controlled amount of drug [60].

4.5. Water purification

Various materials are available to remove soluble and insoluble pollutants and toxicants from the water by solid-phase extraction. Hydrogel is a soft material and exhibits good absorbency property and hence can be used for the purification of water. Cellulose hydrogel is an immerging soft material for water purification due to its biocompatibility, biodegradability, and non-toxicity. Pollutants enter into the network of cellulose hydrogels and are embedded inside the network through a different kinds of interaction (complexation with the lone pair or electrostatic attraction) with the amine or hydroxyl group of the hydrogel [61]. L. Zhang et al. reported cellulose/chitin hydrogel for Pb^{2+} adsorption. They described that complex formation between Pb^{2+} and N atom in the chitin was the key mechanism of Pb^{2+} removal from solution. Moreover, the hydrophilic and microporous-network structure of cellulose hydrogel also played an important role in increasing adsorption ability [62]. L. Zhang et al. further reported chitin/cellulose blend membranes for efficient removing of heavy metal ions (Hg^{2+}, Cu^{2+}, and Pb^{2+}) from aqueous solution. The uptake capacity of the heavy metal ions increased with the increase of chitin content. The adsorption of metal ions by chitin/cellulose composite was due to the complexation, electrostatic attraction, and metal chelation [63].

4.6. Tissue engineering

Cellulose hydrogel is an important soft material for tissue engineering in the biomedical field. These soft biomaterials are used as a scaffold to provide nutrients and space for new tissue formation such as skin, cartilage, bone, fat, muscle, neurons, artery, ligament, and liver. Moreover, the soft material should be biodegradable and have good cell adhesion properties. The addition of secondary components into the scaffold improves the material properties [64]. Sybele Saska et al. bacterial cellulose-collagen hydrogel for bone tissue engineering. They used glycine-modified bacterial cellulose, type I collagen, and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide as cross-linking agent for hydrogel synthesis. Collagen facilitates cell proliferation and enhances cell adhesion and function [65].

4.7. Agricultural application

Cellulose hydrogels are used in agriculture due to their superabsorbent property, eco-friendly, biodegradability, and biocompatibility. Physical and chemical cross-linking structure imparts super absorbance property in the cellulose hydrogel. Although acrylate-based hydrogels are well-known superabsorbents; however, cellulose hydrogels are more promising as they are made from renewable polymer and biodegradable in nature. Whereas, acrylate-based hydrogels are a synthetic soft material and are not easily degradable [66]. C. Demitri et al. synthesized biodegradable cellulose hydrogel using carboxymethyl cellulose sodium salt and hydroxyethylcellulose. They used carbodiimide as a non-toxic cross-linker. The synthesized hydrogel was used in agriculture as a water reservoir where water scarcity is the major problem. Hydrogel releases the absorbed water without adding additional water from external sources. It also behaved as a soil conditioner which increases the physical and chemical quality of soil and also improves its fertility rate. There are two methods to load hydrogel with nutrients: (a) During the hydrogel processing (in situ loading), and (b) After the hydrogel processing (ex-situ loading). Certain polyacrylamide crosslinked structures have more tendency to absorb water than their dry weight and this property of hydrogel helps in the growth of seedlings in dry soil [67]. Maha M. Ibrahim et al. prepared cellulose-based hydrogel from lignocellulosic biomass and used in agriculture for optimizing water resources. They synthesized this hydrogel from rice straw cellulose [68]. Hao Zhang et al. synthesized cellulose anionic hydrogel using TEMPO-oxidized cellulose nanofibers in NaOH/urea aqueous solution and epichlorohydrin as crosslinker. Microporous structure and high hydrophilicity of the cellulose hydrogel impart excellent water absorption properties. Moreover, this hydrogel releases water and urea in a controlled manner which is beneficial for seed germination and growth [69]. Rapid use of industrial fertilizers like urea in agriculture for increased yield is practiced in our country over many years. The efficiency of urea is very low as compared to its use due to the high rate of degradation in the atmosphere and volatilization in the atmosphere. So, alternative methods are developed to efficiently use urea. Shahin Mohammadi-Khoo et al. synthesized biodegradable cellulose hydrogel crosslinked with urea and used it in the slow release of urea fertilizer (Fig. 11). They studied the urea fertilizer release along with swelling behavior and water retention of hydrogel in tap water, distilled water, and 0.9% NaCl solution [70].

4.8. Antimicrobial agent

Hydrogels are widely used as antimicrobial soft materials. Yong Liu et al. synthesized silver nanoparticles loaded bacterial cellulose hydrogel and used it as an antimicrobial agent. They first synthesized cellulose hydrogel and then immersed the same into the silver nitrate solution. Silver ions were adsorbed on the surface of nanofibers of bacterial cellulose by interacting with the –OH group. Next, the silver ion adsorbed hydrogel was treated with $NaBH_4$ to form the silver nanoparticle. This type of hydrogel exhibits a long-term antibacterial response and is used in controlled drug delivery [71].

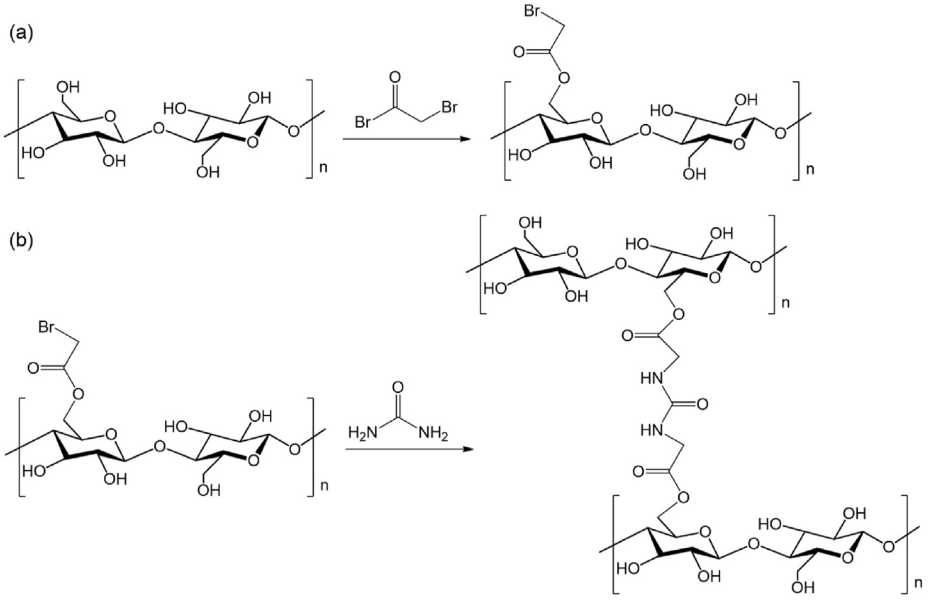

Fig. 11. (a) Bromoacetylation reaction of cellulose, and (b) crosslinking reaction of bromoacetyl cellulose with urea for cellulose hydrogel preparation [70].

4.9. Other applications

Recently, hydrogels find a wide range of applications due to their predictable and tunable material properties. Composites of cellulose hydrogels were found to be used as catalysts for several reactions [72, 73]. Ebrahim Mehdipour et al. prepared palladium nanoparticles using cellulose composite hydrogels and used these to carry out Mizoroki–Heck reaction for aryl halides with olefins. Polysaccharides (chitosan NPs and dialdehyde cellulose nanowhiskers) and graphene oxide nanosheets were used to prepare the hydrogel and used the same as a support to prepare palladium nanoparticles [74]. Ines Cunha et al. synthesized cellulose-based hydrogel electrolyte and used it as a gate dielectric in paper electrolyte-gated transistors. The hydrogel electrolyte film was synthesized by the dissolution of microcrystalline cellulose in an aqueous LiOH/urea solution followed by the addition of carboxymethyl cellulose. This film possesses unique features like flexibility, high capacitance, and transparency. Therefore, it is applicable as flexible electrical appliances like electrolyte gated transistors or as biosensors [75].

5. Conclusion

Hydrogels are a promising material for application in drug delivery, wound dressing, tissue engineering, contact lenses, hygiene products, water purification, removal of heavy metal ions, supercapacitors, the agricultural sector (control release of fertilizer). Cellulose has several advantages such as high abundance, biocompatibility, biodegradability, and high mechanical strength. Due to these advantages, cellulose becomes a unique biopolymer for hydrogel synthesis. Cellulose hydrogel can be synthesized either from plant-based cellulose or from bacterial cellulose. However, due to the crystalline nano-fibrillar structure, bacterial cellulose hydrogel has several advantages over plant cellulose hydrogel. Cellulose is insoluble in water, hence various factors dissolution and derivatization of cellulose are two important factors for cellulose hydrogel synthesis. Cellulose hydrogel is mostly synthesized by dissolving cellulose is in NaOH/urea/H_2O or LiOH/urea/H_2O medium followed by the addition of cross-linker agent as epichlorohydrin (ECH). Both physical crosslinking and chemical crosslinking are utilized to prepare cellulose hydrogel. Cellulose hydrogel is an environmentally sustainable material and a promising alternate for the replacement of hazardous petroleum-based hydrogels.

Consent for publication

Not applicable.

Declaration of competing interest

There are no conflicts to declare.

Acknowledgements

RK is thankful to the CSIR-National Metallurgical Laboratory and Academy of Scientific & Innovative Research (AcSIR), India. BD is thankful to the CSIR-National Metallurgical Laboratory for fellowship.

References

[1] T. Kohnke, A. Lin, T. Elder, H. Theliander, A.J. Ragauskas, Green Chem. 14 (2012) 1864.
[2] S. Athar, R. Bushra, T. Arfin, Nanocellulose and Nanohydrogel Matrices, 2017, https://doi.org/10.1002/9783527803835.ch7.
[3] Z. Bao, C. Xian, Q. Yuan, G. Liu, J. Wu, Advanced Healthcare Materials 8 (2019) 900670.
[4] S. Thakur, B. Sharma, A. Verma, J. Chaudhary, S. Tamulevicius, V.K. Thakur, J. Clean. Prod. 198 (2018) 143–159.
[5] B. Sharma, S. Thakur, G. Mamba, Prateek, R.K. Gupta, V.K. Gupta, V.K. Thakur, J. Environ. Chem. Eng. 9 (1) (2021) 104608.
[6] A. Verma, S. Thakur, G. Mamba, Prateek, R.K. Gupta, P. Thakur, V.K. Thakur, Int. J. Biol. Macromol. 148 (2020) 1130–1139.
[7] A. Verma, S. Thakur, G. Goel, J. Raj, V.K. Gupta, D. Roberts, V.K. Thakur, Current Research in Green and Sustainable Chemistry 3 (2020) 100027.
[8] M. Akter, M. Bhattacharjee, A.K. Dhar, F.B.A. Rahman, S. Haque, T.U. Rashid, S.M.F. Kabir, Gels 7 (2021) 30.
[9] J.V. Rie, W. Thielemans, Nanoscale 9 (2017) 8525.
[10] A. Bashari, A. Rouhani Shirvan, M. Shakeri, Polym. Adv. Technol. 29 (2018) 2853–2867.
[11] P. Thoniyot, M. Tan, A.A. Karim, D.J. Young, X.J. Loh, Adv. Sci. 2 (2015) 1400010.
[12] D.M. Nascimento, Y.L. Nunes, M. Figueiredo, H. de Azeredo, F.A. Aouada, J. Feitosa, M.F. Rosa, A. Dufresne, Green Chem. 20 (2018) 2428–2448.
[13] S. Mondal, S. Das, A.K. Nandi, Soft Matter 16 (2020) 1404–1454.
[14] J. Yang, C. Han, J. Duan, M. Ma, X. Zhang, F. Xu, R. Sun, X. Xie, J. Mater. Chem. 22 (2012) 22467–22480.
[15] Q. Wang, J. Cai, L. Zhang, M. Xu, H. Cheng, C.C. Han, S. Kuga, J. Xiaoe, R. Xiaoe, J. Mater. Chem. 1 (2013) 6678–6686.
[16] S. K. H. Gulrez , S. Al-Assaf, G. O Phillips, IntechOpen. (2011) DOI: 10.5772/24553.
[17] S.D.K. Seera, D. Kundu, T. Banerjee, Cellulose 27 (2020) 6521–6535.
[18] H. Kang, R. Liu, Y. Huang, Macromol. Chem. Phys. 217 (2016) 1322–1334.

[19] R. Borkar, S.S. Waghmare, T. Arfin, Nanocellulose and Nanohydrogel Matrices: Biotechnological and Biomedical Applications, 2017, https://doi.org/10.1002/9783527803835.ch2.
[20] H. He, B. Adzima, M. Zhong, S. Averick, R. Koepsel, H. Murata, A. Russell, D. Luebke, A. Takahara, H. Nulwala, K. Matyjaszewski, Polym. Chem. 5 (2014) 2824–2835.
[21] R. Sanna, E. Fortunati, V. Alzari, D. Nuvoli, A. Terenzi, M.F. Casula, Cellulose 20 (2013) 2393–2402.
[22] M.R. Guilherme, F.A. Aouada, A.R. Fajardo, A.F. Martins, A.T. Paulino, M.F.T. Davi, A.F. Rubira, E.C. Muniz, Eur. Polym. J. 72 (2015) 365–385.
[23] L. Voorhaar, R. Hoogenboom, Chem. Soc. Rev. 45 (2016) 4013–4031.
[24] J. Fu, F. Yang, Z. Guo, New J. Chem. 42 (2018) 17162–17180.
[25] Y. Pei, D. Ye, Q. Zhao, X. Wang, C. Zhang, W. Huang, N. Zhang, S. Liub, L. Zhang, J. Mater. Chem. B. 3 (2015) 7518–7528.
[26] S. Palantoken, K. Bethke, V. Ivanovic, G. Kalinka, J. Kneipp, K. Rademann, J. Appl. Polym. Sci. 137 (2020) 48380.
[27] H. Kono, M. Zakimi, J. Appl. Polym. Sci. 128 (2013) 572–581.
[28] L. Wang, M. Wang, ACS Sustain. Chem. Eng. 4 (2016) 2830–2837.
[29] X. Gao, Y. Cao, X. Song, Z. Zhang, X. Zhuang, C. He, X. Chen, Macromol. Biosci. 14 (2014) 565–575.
[30] X. Zhang, X. Ma, T. Hou, K. Guo, J. Yin, Z. Wang, L. Shu, M. He, J. Yao, Angew. Chem. Int. Ed. 58 (2019) 7366–7370.
[31] X. Shi, Tangjie, A. Wang, J. Appl. Polym. Sci. 132 (2015) 42027.
[32] X. Cui, J.J.L. Lee, W.N. Chen, Sci. Rep. 9 (2019) 18166.
[33] M.N. Alam, M.S. Islam, L.P. Christopher, ACS Omega 4 (2019) 9419–9426.
[34] D. Ye, Q. Cheng, Q. Zhang, Y. Wang, C. Chang, L. Li, H. Peng, L. Zhang, ACS Appl. Mater. Interfaces 9 (2017) 43154–43162.
[35] C. Shao, M. Wang, H. Chang, F. Xu, J. Yang, ACS Sustain. Chem. Eng. 5 (2017) 6167–6174.
[36] Y.M. Chen, L. Sun, S.A. Yang, L. Shi, W.J. Zheng, Z. Wei, C. Hu, Eur. Polym. J. 94 (2017) 501–510.
[37] L. Bai, X. Jiang, Z. Sun, Z. Pei, A. Ma, W. Wang, H. Chen, H. Yang, L. Yang, D. Wei, Cellulose 26 (2019) 5305–5319.
[38] J. Tang, M.U. Javaid, C. Pan, G. Yu, R.M. Berry, K.C. Tam, Carbohydr. Polym. 229 (2020) 115486.
[39] A.F. Jozala, L.C. de Lencastre-Novaes, A.M. Lopes, V. de Carvalho Santos-Ebinuma, P.G. Mazzola, A. Pessoa Jr., D. Grotto, M. Gerenutti, M.V. Chaud, Appl. Microbiol. Biotechnol. 100 (2016) 2063–2072.
[40] T. Siripongpreda, B. Somchob, N. Rodthongkum, V.P. Hoven, Carbohydr. Polym. 256 (2021) 117506.
[41] V. Rivero-Buceta, M.R. Aguilar, A.M. Hernández-Arriaga, F.G. Blanco, A. Rojas, M. Tortajada, R.A. Ramírez-Jiménez, B. Vazquez-Lasa, A. Prieto, Int. J. Biol. Macromol. 162 (2020) 1869–1879.
[42] Z. Shi, Y. Li, X. Chen, H. Han, G. Yang, Nanoscale 6 (2014) 970.
[43] M.C.I.M. Amina, N. Ahmad, N. Halib, I. Ahmad, Carbohydr. Polym. 88 (2012) 465–473.
[44] E.Y.X. Loh, N. Mohamad, M.B. Fauzi, M.H. Ng, S.F. Ng, M.C.I.M. Amin, Sci. Rep. 8 (2018) 2875.
[45] I.F. Nata, M. Sureshkumar, C. Lee, RSC Adv. 1 (2011) 625–631.
[46] C. Baiya, L. Nannuan, Y. Tassanapukdee, O. Chailapakul, K. Songsrirote, American Institute of Chemical Engineers 38 (2018) S157–S165.
[47] A.B. Pitaloka, A.H. Saputra, M. Nasikin, World Appl. Sci. J. 22 (2013) 747–754.
[48] A.M. Das, M.P. Hazarika, M. Goswami, A. Yadav, P. Khound, Carbohydr. Polym. 141 (2016) 20–27.
[49] C.A. Cardona, J.A. Quintero, I.C. Paz, Bioresour. Technol. 101 (2010) 4754–4766.
[50] J.X. Sun, X.F. Sun, H. Zhao, R.C. Sun, Polym. Degrad. Stabil. 84 (2004) 331–339.
[51] Department of Alternative Energy Development and Efficiency, Ministry of Energy, Thailand, Available at, http://biomass.dede.go.th/biomass_web/index.html. accessed September 2017.
[52] L.-H. Fu, C. Qi, M.-G. Ma, P. Wan, J. Mater. Chem. B. 7 (2019) 1541–1562.
[53] E. Pinho, G. Soares, Polym. Adv. Technol. 2 (2018) 3114–3124.
[54] E. Pinho, R.C. Calhelha, I. Ferreira, G. Soares, Polym. Adv. Technol. 30 (2019) 863–871.
[55] Z. Sun, X. Chen, X. Ma, X. Cui, Z. Yi, X. Li, J. Mater. Chem. B. 6 (2018) 6133–6141.
[56] K.J. Skilling, F. Citossi, T.D. Bradshaw, M. Ashford, B. Kellama, M. Marlow, Soft Matter 10 (2014) 237–256.
[57] W. Xu, X. He, M. Zhong, X. Hu, Y. Xiao, RSC Adv. 5 (2015) 3157–3167.
[58] D. Ciolacu, A.M. Oprea, N. Anghel, G. Cazacu, M. Cazacu, Mater. Sci. Eng. C 32 (2012) 452–463.
[59] S. Butun, F.G. Incea, H. Erdugan, N. Sahiner, Carbohydr. Polym. 86 (2011) 636–643.
[60] J.E. Arikibe, R. Lata, K. Kuboyama, T. Ougizawa, D. Rohindra, ChemistrySelect 4 (2019) 9915–9926.
[61] X. Shen, J.L. Shamshina, P. Berton, G. Gurau, R.D. Rogers, Green Chem. 18 (2016) 53–75.
[62] D. Zhou, L. Zhang, S.L. Guo, Water Res. 39 (2005) 3755–3762.
[63] H. Tang, C. Chang, L. Zhang, Chem. Eng. J. 173 (2011) 689–697.
[64] S. Vlierberghe, P. Dubruel, E. Schacht, Biomacromolecules 12 (2011) 1387–1408.
[65] S. Saska, L.N. Teixeira, P. Oliveira, A. Gaspar, S. Ribeiro, Y. Messaddeqa, R. Marchettoa, J. Mater. Chem. 22 (2012) 22102–22112.
[66] P. Calcagnile, T. Sibillano, C. Giannini, A. Sannino, C. Demitri, J. Appl. Polym. Sci. 136 (2019) 47546.
[67] C. Demitri, F. Scalera, M. Madaghiele, A. Sannino, A. Maffezzoli, 2013, International Journal of Polymer Science (2013), 435073.
[68] M.M. Ibrahim, M. Abd-Eladl, N.H. Abou-Baker, J. Appl. Polym. Sci. 132 (2015) 42652.
[69] H. Zhang, M. Yang, Q. Luan, H. Tang, F. Huang, X. Xiang, C. Yang, Y. Bao, J. Agric. Food Chem. 65 (2017) 3785–3791.
[70] S. Mohammadi-Khoo, P.N. Moghadam, A.R. Fareghi, N. Movagharnezhad, J. Appl. Polym. Sci. 133 (2015) 42935.
[71] Y. Liu, S. Wang, Z. Wang, Q. Yao, S. Fang, X. Zhou, X. Yuan, J. Xie, J. Mater. Chem. B. 8 (2020) 4846–4850.
[72] Y. Chen, P. Potschke, J. Pionteck, B. Voit, H. Qi, ACS Omega 4 (2019) 5117–5125.
[73] B. Wang, M. Ran, G. Fang, T. Wu, Q. Tian, L. Zheng, L. Romero-Zerón, Y. Ni, Cellulose 27 (2020) 6995–7008.
[74] S. Ashiri, E. Mehdipour, RSC Adv. 8 (2018) 32877–32885.
[75] I. Cunha, R. Barras, P. Grey, D. Gaspar, E. Fortunato, R. Martins, L. Pereira, Adv. Funct. Mater. 27 (2017) 1606755.