

RECENT APPROACHES TO THE SYNTHESIS OF HYDROGELS FROM LIGNOCELLULOSIC BIOMASS: A REVIEW

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To address the detrimental effects of non-biodegradable wastes on the environment and the health of living organisms, there is a growing interest in valorising renewable resources. Lignocellulosic biomass is an abundant and renewable resource from plants. It is non-toxic, biodegradable and has adjustable mechanical characteristics, making it promising for use in the manufacture of hydrogels. Hydrogels are insoluble water absorbents with a three-dimensional network structure that can hold a considerable amount of water. The production of hydrogels from lignocellulosic biomass is a step toward sustainability. The goal of this study is to highlight current methodologies for the synthesis of hydrogels from various lignocellulosic biomass polymers (cellulose, hemicelluloses and lignin) in their different forms. A variety of techniques have been developed to synthesise various types of hydrogels with specified qualities, such as compressive strength, solvent resistance, water holding capacity, tensile strength, and re-swelling ratios, among others, based on application requirements. The study reports on current methods for the synthesis of lignocellulosic biomass-based hydrogels in order to determine the optimum strategy depending on demand.

Keywords: cellulose, hemicelluloses, lignin, hydrogels, synthesis methods, crosslinking

INTRODUCTION

The excessive usage of non-renewable resources has banefully affected wildlife, soil quality, oceans and atmosphere *etc.*, producing drastic changes in climate by the emission of greenhouse gases.¹ In order to maintain a green earth and healthy life, there is a high demand to explore sustainable and eco-friendly renewable resources as alternative raw materials to develop various products. The most abundantly available or inexpensive source of renewable materials is plant waste biomass, *i.e.* lignocellulose biomass, which has the potential to act as a promising alternative source of matter to address various applications.² This biomass refers to dry plant matter, such as corn stover, corn cobs, rice straw, wheat straw, sugarcane bagasse *etc.*, which are fibrous residues left after crop harvesting.

Cellulose (40-60%), hemicelluloses (20-35%) and lignin (15-20%) are the major components of any lignocellulosic biomass.¹ However, biomass composition varies from crop to crop and it also depends upon variety and production location/conditions, even in the case of the same crop.³ Cellulose and hemicelluloses are polysaccharides, which can be modified by

different degrees of polymerization for biological/chemical utilization.⁴ On the other hand, lignin is a phenolic polymer that helps in the formation of a protective layer around polysaccharides with its constituting three aromatic alcohols, *i.e.* *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.⁵ Cellulose and hemicelluloses have been extensively exploited for their conversion into biofuels and many high value chemicals, including various aromatic and heterocyclic compounds, such as *o*-, *m*- or *p*-xylene, ethylbenzene, 1-methyl-2-*n*-propylbenzene, phenol, *o*-, *m*-, *p*-cresol, isindazole, 1-methylindazole, 1-naphthyl isocyanate, furfural, furfuryl alcohol, 2,5-dimethyl furfural, hydroxymethyl furfural, having diverse applications.^{6,7} Lignin has also been researched for the synthesis of various phenolic compounds for various laboratory and industrial uses.^{8,9}

Besides these applications, a new concept of superabsorbent hydrogels has rapidly progressed and attracted researchers and industrialists.¹⁰ Superabsorbent hydrogels are three-dimensional (3D) hydrophilic networks of polymeric chains,

with high potential for water uptake, which can absorb, swell, and retain aqueous solutions up to hundreds of times their own weights, without disturbing their own structural integrity.¹¹ Hydrogels are synthesized from natural or synthetic polymers. The non-renewable, non-biodegradable and non-biocompatible nature of synthetic polymer hydrogels enhances the problems related to human health and environmental pollution, which limits their wide scope. Therefore, the implementation of lignocellulosic biopolymers for the synthesis of hydrogels has received considerable attention due to their abundance and inexpensive nature.

Hydrogels are cross-linked polymers that can retain excess amounts of water due to their three-dimensional network structure. The nature and positioning of constituent monomers and the synthesis methods have significant effects on the characteristic features of hydrogels, such as biocompatibility, biodegradability, swelling ratio and mechanical strength *etc.*, which enable the use of these polymers in a wide range of applications. There are several methodologies developed for the synthesis of hydrogels such as physical cross-linking, chemical cross-linking, grafting and others, which further include different approaches to fulfil the need of different applications.¹² The preparation of hydrogels most importantly involves the crosslinking of polymeric structures in a fixed network, which can modify its functional properties with a change of the crosslinking technique. The crosslinking between polymeric structures can be formed either by chemical bonds or by physical interactions.¹³ The best results can be obtained from hydrogel synthesis by understanding the concept of different techniques of crosslinking with suitable methods and materials, along with their applications. In this review, different approaches to the synthesis of hydrogels from biomass-derived polymers, *i.e.* cellulose, hemicelluloses and lignin, are discussed.

EXTRACTION OF LIGNOCELLULOSIC BIOPOLYMERS

Before the synthesis of hydrogels from lignocellulosic biopolymers, different polymers need to be extracted from a complex natural network, with the highest possible purity. The extraction of biopolymers from different lignocellulosic sources can be initiated by using different pretreatment methods, such as acidic, alkaline, hydrothermal, wet oxidation,

organosolv, and ionic liquids¹⁴ (Table 1) to remove all hydrophilic and lipophilic non-functional portions¹⁵ and separate biopolymers from the matrix.¹⁶ The extraction can be made more effective by operating different isolation conditions or by changing the solvent, acid or alkali type, with multi-step mechanical-chemical treatments.¹⁵ There are some extraction treatments, such as ultrasound-assisted, micro-assisted and pressurized liquid *etc.*, which can reduce production costs and time, as well as upgrade the quality of bio-compounds.¹⁷

Acidic and alkaline pretreatments involve solubilisation of biomass with a low cost and simple procedure and can be performed at moderate room temperatures. Acids used include HCl, H₂SO₄, H₃PO₄, and HNO₃, while the alkaline solutions used for the process are NaOH, KOH, Ca(OH)₂, Mg(OH)₂, CaO and ammonia.¹⁸ The acidic pretreatment is considered more effective than the alkaline one for lignocellulose biomass, but acidic conditions can cause strong corrosion of the equipment.¹⁹ Alkaline solutions have economic and environmental impacts, but great efficiency in separating biopolymers from the non-functional lignocellulosic matrix. Moreover, ultrasound assisted technology has the potential to combine with acidic and alkaline pretreatments for an enhancement of the extraction process. Ultrasonic waves produce pressure variations within the solution for the intensification of physical and chemical processes.¹⁹

The hydrothermal pretreatment method for extraction purposes is expensive, but it offers the advantages of minimum equipment corrosion, no need of chemicals and simple operation. This method requires elevated temperature and pressure for the hydrolysis of lignocellulosic biomass and can be considered as an eco-friendly fractionation process.²⁰ Wet oxidation involves oxidation of lignocellulosic biomass in liquid medium with dissolved oxygen and elevated temperatures to fractionate the biopolymers.²¹ The organosolv pretreatment method is most often used for qualitative extraction of lignin by involving methanol, ethanol, acetone and ethylene glycol or a mixture of these organic solvents with water for degrading the bonds between polysaccharides and lignin.²¹

Ionic liquid (ILs) are a new category of solvents that can dissolve a huge number of biomolecules, such as cellulose, lignin, pectin, gelatine, silk fibroin and starch, with great

efficiency.²² Ionic liquids are renewable, polar, non-flammable, non-volatile thermally stable, soluble in water as well as in organic solvents. Such unique properties of ionic liquids make them environment-friendly. In this technique, biomass is solubilized in the solvent at 90-130 °C, with ambient pressure, followed by the addition of water to precipitate biopolymers.²¹ Organic cations, namely derivatives of *N*-substituted pyridinium, tetra-alkylated ammonium, *N,N*-substituted imidazolium, tetra-alkylated phosphonium, and anions, either organic or inorganic, are examples of ILs that are usually considered expensive as their production involves

high costs and time consumption.¹⁶ Meanwhile, imidazolium-based ILs, particularly the ones with chloride anions, are considered as excellent solvents for dissolution of different lignocellulosic biopolymers.²³

To sum it up, the acidic pretreatment is the most effective method to extract cellulose and hemicelluloses from lignocellulose biomass. The alkaline pretreatment breaks down the lignin structure, as it increases porosity and the internal surface area of biomass by promoting structural swelling and decreases the degree of polymerization and crystallinity.²⁴

Table 1
Different extraction methods of biopolymers from lignocellulosic biomass

Method	Advantages	Disadvantages	Reaction conditions	Ref.
1. Acid pretreatment	Short reaction time with good yield, overcoming the problem of recalcitrance, allowing the biochemical conversion of lignocellulose	Strong corrosion, formation of toxic compounds, <i>e.g.</i> furfural, hydroxyl methyl furfural	0.2-2.5% diluted acids at 130-210 °C	21,18
2. Hydrothermal pretreatment	Does not require recovery of chemicals, short reaction time, limited corrosion and simple operation	Expensive, causing recalcitrance of lignocellulosic material	Elevated temperature and pressure	20
3. Wet oxidation	High yield of cellulose, does not require costly chemicals	Formation of a large number of by-products, <i>i.e.</i> succinic acid, glycolic acid, formic acid, acetic acid, phenolic compounds, and furfural	20 bar pressure, 195 °C for 10-20 min	28
4. Organosolv pretreatment	High yield of lignin with less formation of fermentation inhibitors	Involvement of costly organic solvents	<200 °C or 200 °C	21
5. Alkaline pretreatment	Requires less severe conditions, improves the mechanical behaviour of polymers	Causes environmental pollution	1-40 wt% NaOH at ambient temperature	29,30, 31
6. Ultrasound assisted with alkaline pretreatment	Improves economic efficiency, thermal stability of polymers, reduces environmental pollution, chemical loadings and reaction time	Loss of acetyl groups	2M NaOH solution irradiated with 500 W power for 10-40 min	14
7. Microwave assisted with alkaline pretreatment	Short reaction time under constant conditions	Low yield	3% NaOH at MW of 180 W power for 12 min	32
8. Ionic liquids	Eco-friendly, high solubility and stability of biomass	High costs and time consumption	Ambient pressure, temperatures of 90-130 °C for 1-24 h	28

The hydrothermal-alkali pretreatment method is commonly used for lignin extraction, can degrade wood fibers by hydrating cellulose, solubilizing hemicelluloses and fractionating lignin.²⁵ The function of alkaline pretreatment is saponification and cleavage of lignin-carbohydrate linkages. Hemicelluloses are extensively broken into monomeric sugars and degraded into organic acids, cellulose is partly degraded, and lignin undergoes both cleavage and oxidation *via* the use of the wet oxidation method.²⁶ Organosolv and ionic liquid pretreatments have proven useful for fractionating and recovering cellulose, hemicelluloses and releasing lignin, with favourable physicochemical properties.²⁷

DIFFERENT APPROACHES TO THE SYNTHESIS OF HYDROGELS

Hydrogels are hydrophilic polymeric networks with 3D configurations, which are cross-linked either physically, or chemically. Hydrogels have the tendency to absorb a large amount of water/biological fluids, and can hold a hundred times their own weight in a swollen state within their network.³³ The absorption capacity of hydrogels depends on their functional groups, water content and density of cross-linked networks.³⁴ Their tendency of absorption is due to the presence of hydrophilic groups, such as $-OH$, $-CONH_2$ and $-SO_3H$, in their polymeric network structures.³⁵ Xerogels are prepared through drying at the room temperature and are characterized by high porosity, large surface area and very smaller pore sizes. Upon contact with water, the volume of a xerogel begins to increase as water molecules infiltrate into the space between the polymer chains, behaving like a hydrogel in its swelling form.³⁶ A hydrogel is formed *via* crosslinking between the chains of polymers, which affects its physical properties, such as viscosity, elasticity, solubility, glass transition, strength, toughness and melting point *etc.* These properties of the hydrogel decide its function, stability and area of application. Higher level of crosslinking restricts the translational movements of polymer chains, which results in decreased swelling degree of hydrogels. However, the amount of solvent that can be absorbed by polymer networks also depends on the density of crosslinking or the number of crosslinks present per unit volume. As crosslinking density increases, the tendency of polymeric chains to absorb solvent molecules decreases.³⁷ Loosely crosslinked hydrogels have great affinity to absorb and retain water, having

great importance in agriculture practices, as they can hold and release water and nutrients or fertilizers required by the plants for their growth.³⁸ Natural polymer-based hydrogels have been used as water absorbents in biomedical devices, *e.g.* contact lens, controlled drug release devices, wound healing, bioactive scaffolds for regenerative medicine due to their biocompatibility and biodegradability.^{39,35} Hydrogels are also applied in the industrial field for the production of sanitary napkins, baby diapers and cosmetics.³³ Hydrogels are also known to be used for adsorbing heavy metal ions, radioactive elements and dyes from contaminated water.^{40,36}

Hydrogels can be synthesized from natural sources, including lignocellulose biopolymers, collagen, agar, alginate, dextran, gelatine, chitosan *etc.*, or from synthetic polyvinyl alcohol (PVA), poly(ethylene glycol)-poly(lactone)-poly(ethylene glycol) (PEG-PL-PEG), poly(ethylene oxide) (PEO), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(acrylic acid) (PAA), and poly(acrylamide) (PAAm) based sources.³³ However, this article has focused only on lignocellulosic biopolymers for the synthesis of hydrogels.

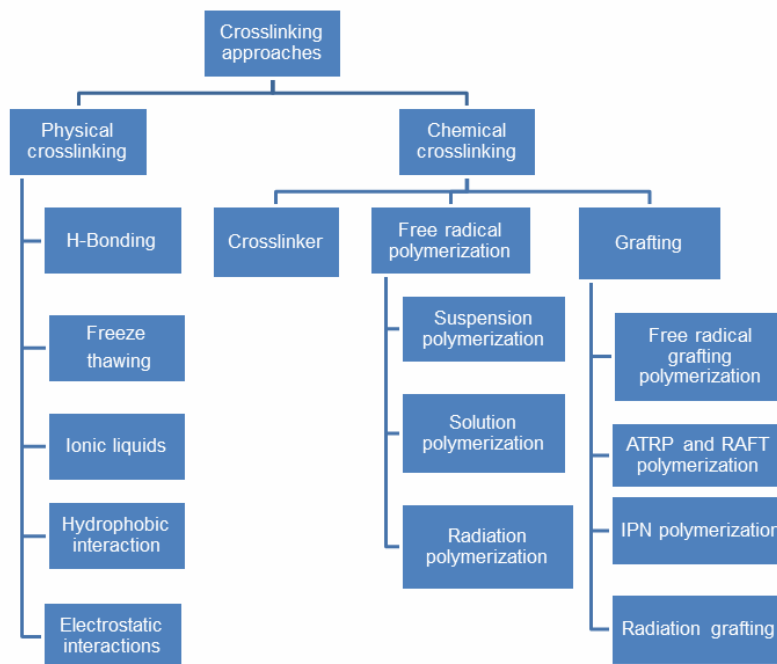
Basically, two approaches, *i.e.* physical crosslinking and chemical crosslinking, have been adopted for the synthesis of hydrogels, and these are further classified into different techniques (Scheme 1).⁴¹ These approaches can improve the mechanical, stability, viscoelastic, shear-thinning, self-healing *etc.*, properties of hydrogels for applications in various fields.⁴²

Physical crosslinking

Physical approaches are highly known as useful, due to their ease of production, without the utilization of high amounts of chemicals and crosslinking agents.⁴² Physically crosslinked hydrogels are also known as self-assembling hydrogels, due to their self-forming capacity through the non-covalent molecular interactions, namely hydrogen(H)-bonding, hydrophobic and electrostatic ones. The formation of the 3D network is due to an entanglement among molecules, and the interaction among ions *via* the increase/decrease of temperature, polymers with random-string state distributed in the solution; the molecular motion increases the deformation of the random-string structure to convert it into a spring-like structure.⁴³ These interactions are reversible in nature, which may cause deconstruction of the

polymeric networks by using a different physical

environment, according to the requirements.⁴⁴



Scheme 1: Classification of crosslinking approaches into physical and chemical crosslinking

Hydrogen bonding

For the synthesis of H-bonded hydrogels, the pH of the aqueous solution containing polymers with carboxyl groups is required to be low. CMC (carboxymethyl cellulose) hydrogels were created by the formation of H-bonds by dissolving CMC in 0.1M HCl and replacing sodium in CMC with hydrogen.⁴² The backbone of lignin contains polar sites that can be used to crosslink hydrophilic polymers, so that H-bond formation was established between lignin and polyurethane hydrogels, which improved the mechanical strength of prepared hydrogels. Hydroxyethyl cellulose (HEC) and polyvinyl alcohol (PVA) hydrogels were physically crosslinked *via* forming H-bonds with borax, and lignin.⁴⁵ Stable intelligent hydrogels prepared by forming strong intermolecular H-bonds between microcrystalline cellulose (MCC) and konjac glucomannan exhibited strong mechanical strength and rapid self-healing properties.⁴⁶

Freeze–thaw

The preparation of hydrogels by the freeze–thaw technique involves phase separation by freezing the solution, which results in ice crystals formation, allowing the concentration of the

polymer solution in regions between the ice crystals and thus, promoting the formation of crystallites. These crystallites act as crosslinking sites for polymer chains causing crosslinking between polymeric networks, followed by thawing the frozen solid to room temperature.⁴⁷ This process is repeated 3–4 times for the refinement of hydrogels and these successive freeze–thawing cycles enhance the polymer crystallization in the gel, resulting in a hydrogel with smaller pore size.⁴⁸ This physical approach has been used for the preparation of hemicellulose-based hydrogels with PVA and chitin nanowhiskers by heating their homogenous mixture slowly up to 800 °C for 1 h, followed by cooling to room temperature and freezing at -20 °C for 10 h. Thawing the solution for 1 h at room temperature and repeating this freeze–thaw cycle three times yields a high-quality hydrogel (Fig. 1).⁴⁹

This technique is also applicable in the case of cellulose nanocrystals (CNCs), the derivative forms of cellulose and lignin. The hydrogel of CNCs can be prepared in 5 repeated freeze–thaw cycles by immersing CNCs into liquid nitrogen or polar organic solvents for 30 s to 10 min, and then warming them up to room temperature for 2

hours.⁵⁰ 1.1 g of PVA was added to 10 mL of 2% NaOH solution, followed by pouring into a silicon mould. Three to five freeze–thaw cycles were repeated, with 16 hours at -20 °C and 8 hours at 28 °C.⁵¹

Ionic liquids

Ionic liquids (ILs) have excellent properties, such as low toxicity, high boiling point, strong polarity, and high stability, which eliminate the need for chemical crosslinkers in the production of biopolymer-based hydrogels. 4% MCC, 2% xylan, and 2% Kraft lignin (the derivative forms of cellulose, hemicellulose and lignin, respectively) were dissolved in 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) at 80 °C for 30 minutes, with stirring every 5 minutes. Sorghum bagasse biomass was added to an ionic liquid solution at 140 °C for 4 hours, with steady stirring, to produce a biopolymer-based hydrogel. The resulting hydrogel solution was transferred to a mould to immerse in an ethanol-water 1:1 (v/v) solution bath for 48 h, with one time replacement of the solution in the mid of the cycle (Fig. 2). Afterwards, it was casted in pure deionized (DI) water twice, within a span of 24 h each for the elimination of any unconsumed ILs.⁴⁷ Lignocellulose material was directly used to form hydrogels by the dissolution in 1-ethyl-3-methylimidazolium chloride (ionic

liquid), which was further processed through freeze–thaw cycles and the solution was then transferred to a coagulation bath of DI water dipped into an ethanol aqueous solution bath for 12 h. Finally, stable gels were obtained and transferred to a tert-butanol bath for 12 h.²³

Electrostatic interactions

Electrostatic interactions occur between ionic polymers by the addition of di- or trivalent counter ions.⁴⁴ Physically crosslinked hydrogels were created by isotropic gelation of the phenoxide anions of alkaline lignin and the protonated cationic amine of chitosan, with electrostatic interactions resulting from simple mixing of both polymers.⁴⁵ Ionic crosslinking was employed to create hemicellulose hydrogels by connecting polyelectrolyte polyvalent ionic bonds with opposing charges (Fig. 3).⁴³ For drug loading and releasing purposes, special cyclodextrin-grafted cellulosic hydrogel beads (CD⁺@HEC-CMC-gel) were prepared through electrostatic and host–guest interactions.⁵² The self-assembled hydrogels, with tunable properties, such as mechanical properties, shear-thinning and self-healing properties, were synthesized by electrostatic interactions between negatively charged biopolymers (hyaluronic acid and CMC) and positively charged cetyltrimethyl ammonium bromide.⁴⁶

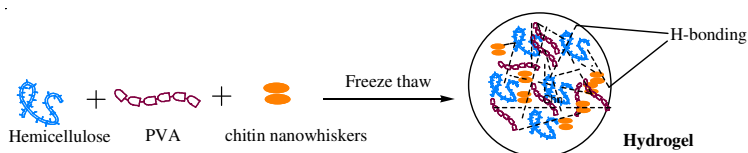


Figure 1: Formation of H-bonded hydrogel *via* freeze–thaw procedure

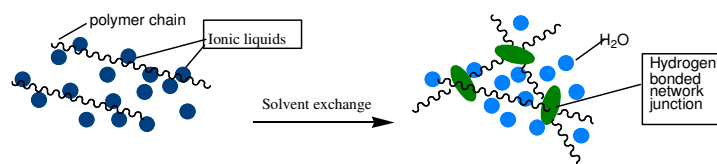


Figure 2: Formation of H-bonded network junction *via* the use of ionic liquids

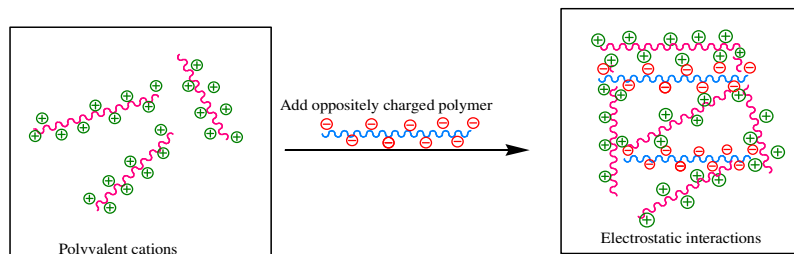


Figure 3: Ionic crosslinking between polyvalent ions *via* electrostatic interactions

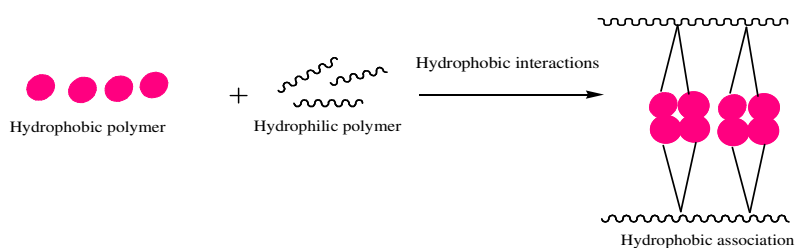


Figure 4: Hydrophobic interactions between hydrophobic and hydrophilic polymers

Hydrophobic interactions

Hydrogels formed by hydrophobic interactions often involve copolymerization of a hydrophilic monomer with a little quantity of a hydrophobic co-monomer through a free-radical process.⁴⁴ At low temperatures, hydrophobic crosslinking includes the hydration of polymeric chains among macromolecule solutions containing alkylated hydroxyl groups. As the temperature rises, macromolecules gradually loosen their state of hydration, the alkylated hydroxyl groups interact with one another, resulting in hydrophobic polymer connections and hydrogel networks.⁵³ Solutions of alkylated cellulose derivatives, such as methyl, ethyl, hydroxyethyl and hydroxypropyl methyl cellulose, were heated above certain temperatures, depending on the cellulose alkylation level, and hydrogels were formed.⁴⁴ Hydrophobic interactions were discovered between hemicellulose molecules, facilitating the creation of a cluster structure of an irregular hemicellulose hydrogel (Fig. 4).⁴³ Due to the hydrophobicity of lignin, hydrogels were prepared by crosslinking lignin with PEG (polyethylene glycol) in aqueous ethanol solution, which was allowed to evaporate at 80 °C for 24 h to carry out polymerization.⁵⁴

Chemical crosslinking

Chemical crosslinking entails grafting functional monomers into the polymer network or using a crosslinker to connect the two polymer chains. Chemical crosslinking is the favoured method for forming persistent hydrogel networks. Chemical gelation (i) disrupts self-association and packing, resulting in decreased crystallinity, (ii) results in a more homogeneous morphology, yielding transparent swollen coagulated hydrogels, and (iii) increases swelling in water and adsorption of water vapours due to the more porous structure. As a result, chemically crosslinked hydrogels have higher potential to load a huge number of pharmaceuticals and have

faster kinetics to release medications than physically crosslinked ones. By adjusting the polymer concentration and the quantity of crosslinker, diverse hydrogels and dry porous networks with regular shape and porosity may be created. Covalent bonding is required for the creation of a 3D network in chemically crosslinked hydrogels.⁵³ For hydrogel production, a variety of chemical crosslinking techniques have been used.

Crosslinkers

Chemical crosslinking primarily includes the employment of crosslinkers, which play an important role in the formation of polymeric networks in hydrogel structures. Various crosslinkers, such as epichlorohydrin (ECH), glutaraldehyde, *N,N*-methylenebis-acrylamide (MBA), vinyl ethyl benzene, ethyldiol-methacrylate and citric acid, have been used for the covalent binding of different polymeric molecules into three-dimensional hydrophilic networks.^{38,43} The interaction between crosslinkers and polymer functional groups, such as OH, COOH and NH₂, generates a chemical connection between polymer chains, resulting in the formation of crosslinked hydrogel polymer networks (Fig. 5).⁴² A number of instances have been described in the literature for the synthesis of biopolymer-based hydrogels. Crosslinking between hydrophilic groups of CMC (carboxymethyl cellulose) and epoxy groups of ECH was shown to be more convenient in an alkaline environment.⁵⁵ In some crosslinking processes, such as free radical polymerization and 3D printing, crosslinkers can be used indirectly to generate unique types of hydrogels with high efficiencies.

Free radical polymerization

Free radical polymerisation is the chemical crosslinking of water-soluble polymeric derivatives with polymerizable groups for the

preparation of hydrogels.⁵⁶ It consists of three primary steps, *i.e.*, initiation, propagation and termination. The first step begins with the introduction of initiator species that produce active radical centres by homolytic dissociation of weak bonds or by redox reactions. Subsequently, hydrophilic monomers, such as acrylic acid series, acrylamide series, vinyl acetate series *etc.*, propagate through their carbon double bonding to form the polymeric network of hydrogels and terminate by combination, transfer or disproportionation of polymerizing radicals (Fig. 6).^{43,44}

Radical polymerisation of hemicelluloses in the form of xylan chains is accomplished by using 2-hydroxyethyl methacrylate (HEMA) as crosslinker to produce HEMA-xylan hydrogel.⁵⁶ CMC and acrylic monomers, such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and acrylamide (AM), are polymerized in the presence of MBA and graphene oxide (GO) nano-sheets as filler to form hydrogels.⁵⁷ The radical polymerization of kraft lignin and isopropylacrylamide (NIPAAm) with MBA in the presence of azobis-isobutyronitrile (AIBN) as initiator has also been reported for the synthesis of hydrogels.⁵⁸

On the basis of producing active radicals, the free radical polymerization technique can be classified as solution polymerization, suspension

polymerization and photo-polymerization. In solution polymerization, initiators, monomers and the polymer of interest are dissolved in the solvent. The concentration of these chemicals is adjusted to initiate the polymerization with most ease. While in the case of suspension polymerization, heat is transferred from droplets (insoluble form of monomer in dispersed aqueous phase) to water.⁴⁴

Photo radical polymerization involves the utilization of high energy X-rays, electron beam or gamma rays to initiate the polymerization of unsaturated substances by ionizing simple molecules either in air or in water.³⁹ Electron-beam radiation induces crosslinking by generating energetic radicals along the sides of polymer strands, which further combine to form a number of crosslinks, resulting in the formation of pure (residue free) hydrogels (Fig. 7).⁴⁴ Hydrogels from carboxymethylated lignocelluloses can be prepared through electron beam induced polymerization with several preconditions to favour the formation of a network over cellulose chain scission.⁵⁹ CMC hydrogels have been prepared using γ -irradiation, which causes free radical crosslinking among polymers.⁴⁴ Microwave irradiation at 600 W for 10 min is also known to contribute to the formation of CMC hydrogels in the presence of methanol, sulphuric acid, acetic acid and glutaraldehyde.⁴⁰

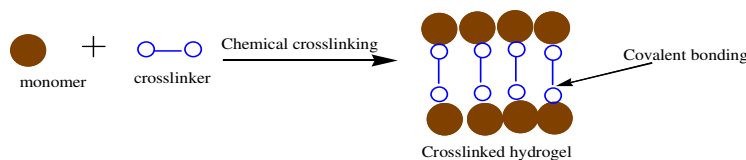


Figure 5: Formation of covalent bond using a crosslinker

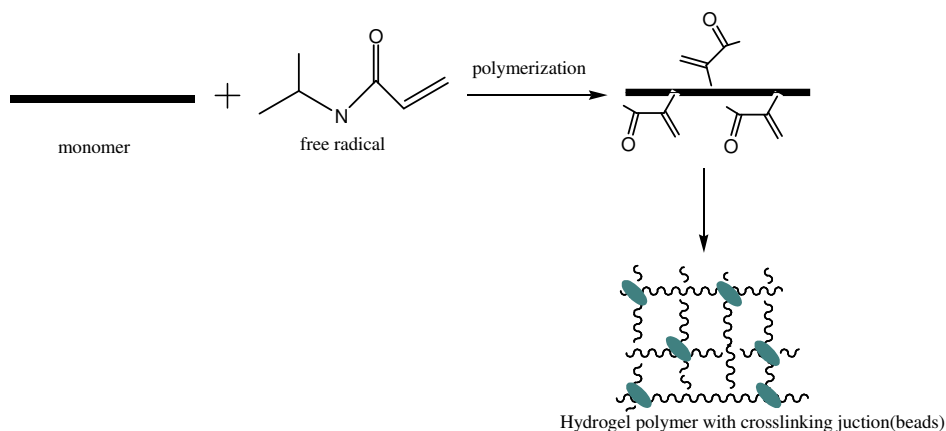


Figure 6: Mechanism of free radical polymerization

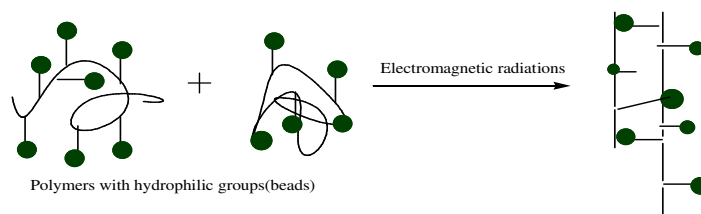
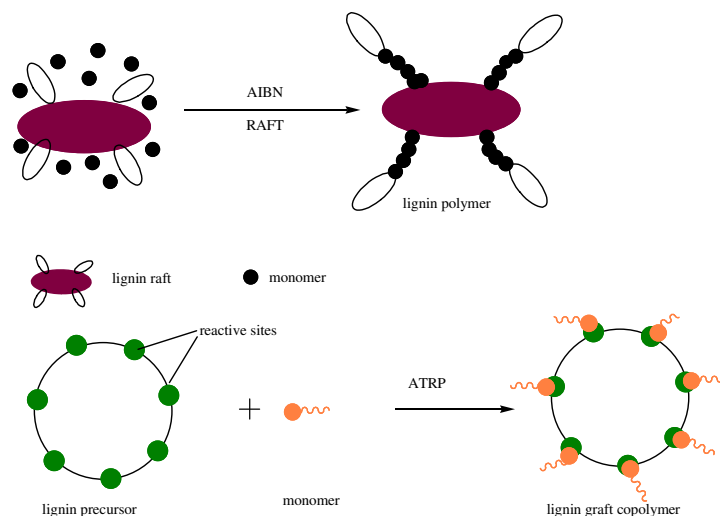
Figure 7: Crosslinking *via* electromagnetic radiations

Figure 8: Polymerization sequence of ATRP and RAFT

Grafting techniques

Grafting involves the polymerisation of α -alkene monomers on active macro radicals, the backbone of the polymer, activated by the action of chemical reagents or high energy radiation treatment.⁴² Vinyl group monomers containing a carboxyl, sulfonic, or nitrile group are often used in the grafting, due to their existence in the polymer backbone for participating in the polymerization.^{43,60} The presence of OH groups on polymers helps facilitate the reactive sites for the grafting reaction.⁵⁴

Free radical grafting polymerization

Different graft copolymerization approaches are developed to synthesize lignocellulose-based hydrogels with acrylonitrile as monomer using different environment-friendly initiation techniques. Grafting can be performed through the hydroxyl radical or persulfate initiation technique, which involves the addition of hydrogen peroxide and thiourea dioxide into the pretreated solution of the lignocellulose material, followed by the addition of acrylonitrile (AN), with a few drops of emulsified soap or with emulsified persulfate salt, to give superabsorbent

hydrogels.⁶⁰ Cellulose-based hydrogels were synthesized by the free radical graft copolymerization technique by reacting cotton with acrylic acid and AM monomers in the presence of MBA as a crosslinker and potassium persulfate as an initiator.⁶¹ Free radical graft copolymerization between xylan (hemicellulose) and acrylic acid could respond to multiple stimuli, and has been reported to synthesize xylan-graft-acrylic acid hydrogels. The acrylic acid acts as a donor of carboxylic acid in the network of hydrogels. Such hydrogels found potential applications in removing heavy metal ions or dyes from wastewater.⁴³

Atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer polymerization (RAFT)

ATRP and RAFT are the most widely used methods of free radical polymerization for the synthesis of designed and controlled polymeric hydrogels. 'Graft-from' and 'graft-onto' are two basic strategies for the fabrication of hydrogels under ATRP and RAFT polymerizations (Fig. 8). The 'graft-from' method synthesizes the polymers from active sites that are located on the backbone

polymer, which, in most cases, is reported to be lignin. The ‘graft-onto’ strategy helps to establish hydrogels by forming covalent bonds between the lignin backbone and the terminal groups of the graft polymers.⁶² The first step of ATRP is the synthesis of lignin-based organic halide as precursor or initiator that will initiate the reaction of lignin with acrylonitrile. The copolymerization of precursor and monomers is the second step. The lignin-based organic halide thus serves as both initiator and polymer backbone in ATRP. In the case of RAFT, the lignin serves as a reaction core followed by initiation through AIBN (azobisisobutyronitrile) for the copolymerization of the monomer onto lignin core. Lignin or cellulose- and hemicellulose-containing lignin could be a starting polymer in ATRP and RAFT techniques for the synthesis of control structure type hydrogels.⁵⁴

Interpenetrating polymer networks and polymerization

Interpenetrating polymer networks (IPN) are alloys of crosslinked polymeric chains that are produced by interpenetration of two or more crosslinked polymers. Interpenetrating polymerization enhances the attributes of one polymer, while keeping the crucial properties of the other. The benefit is that the existing

crosslinked network remains the same in the presence of the crosslinker or initiator.^{54,56} It is a novel strategy for the preparation of complex hydrogels, involving the fabrication of a film first and then polymerization of the monomers or polymers with the film. Polymerization occurs by forming free radicals on monomers or polymers in the presence of the initiator that forms grafting structures with the existing crosslinked network of the film to obtain a hydrogel.⁶² Such reported tough hydrogels are known to be characterised by excellent mechanical properties, stability and high pH sensitivity.⁵⁴ IPNs are of three types, *i.e.* sequential, simultaneous and semi IPNs. Sequential IPNs are formed by more than one IPN in the process, whereas simultaneous IPNs are formed simultaneously. However, semi IPNs are formed by the polymerization of a monomer in the presence of the crosslinked network of the polymer (Fig. 9).⁶³

Semi-IPN hydrogels have been synthesized by the utilization of hemicelluloses and chitosan with glutaraldehyde as crosslinker; however their swelling property can be improved by increasing the hemicellulose content.⁴³ A tough lignin-based hydrogel was prepared by mixing lignin and polyurethane, which was then casted and dried at 60 °C for 3 days, followed by hydration of the dried film to swell up to the equilibrium ratio.⁵⁴

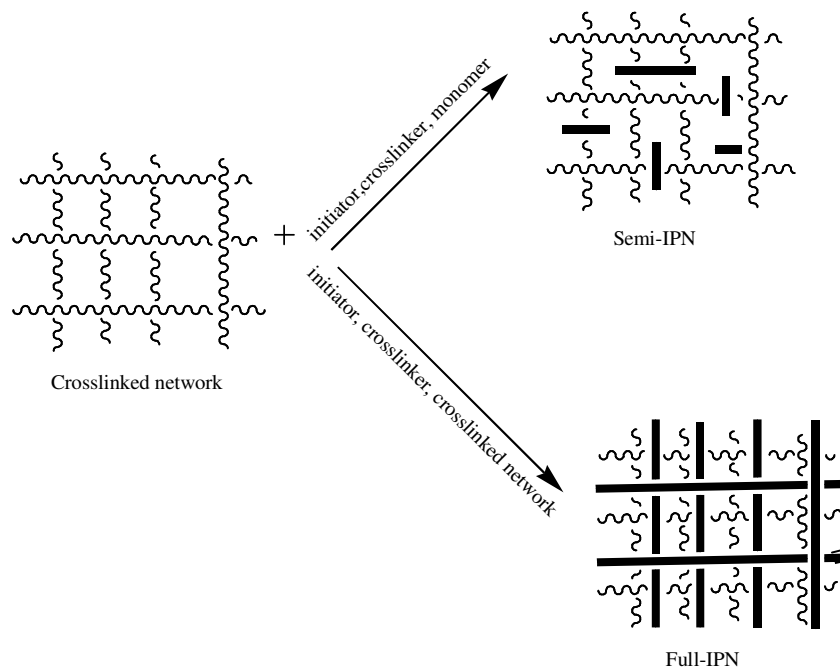


Figure 9: Semi- and full-interpenetrating polymerization

Radiation grafting

Grafting can also be initiated by the use of high energy radiation, including gamma rays and electron beam.⁴² The radiation graft polymerization technique gives the opportunity to make grafted chains by using specific monomers with a fixed amount of irradiation, usually ⁶⁰Co gamma rays, and this technique can control the specific properties of hydrogels.³⁸ A hydrogel of CMC was prepared by grafting CMC and acrylic acid using electron beam irradiation, resulting in the free radical polymerisation of acrylic acid on the backbone of CMC in aqueous solution. The irradiation of CMC and monomer generates free radicals, which combine together to form a hydrogel.⁴²

Other techniques

Instead of physical and chemical crosslinking techniques, there are some other latest techniques reported for the synthesis of hydrogels. Such techniques may be a combination of the above techniques or may be completely different, modern and efficient in forming unique hydrogels, with advanced functionalities.

3D Printing

3D printing technology has been introduced to prepare special hydrogels with their complex and highly customizable scaffold structures, which can support cell adhesion and promote cell infiltration for biomedical applications.⁶⁴ It is based on the layer-by-layer principle for the precise placement of constituents, biochemicals and living cells, and for spatial control of functional constituents to fabricate 3D structures.⁶⁵ 3D printing of hydrogel composites ensures an improvement in their mechanical performance and bio-functionality. The amazing success of 3D printing is mainly due to the possibility of building objects from 3D model data, with complex geometry, accurate resolution and relatively short execution time.⁶⁶ For the

synthesis of hydrogels, the 3D printing technology is mainly categorized into light based, nozzle based and inkjet printer based systems (Table 2), which are further classified according to the different demands of size, shape, and pore and construction mechanism of scaffold structures.⁶⁴

The production of CMC based 3D photocured hydrogels by the 3D digital light projection (DLP) technique requires functionalization of CMC to produce its ink formulation for the production of 3D photocured hydrogels. Hence, CMC was methacrylated to form M-CMC/water formulation in the presence of a fixed amount of lithium phenyl-2, 4, 6-trimethylbenzoylphosphine (LAP) as a photoinitiator. The solution of M-CMC (20 mg/mL) was prepared under magnetic stirring at 50 °C for 1 h. The solution was allowed to cool down, and 2 wt% of bis(acyl) phosphane oxo LAP was added. The solution was placed in the vat of an Asiga UV-MAX DLP, with an XY pixel resolution of 62 μm, using a light-emitting diode light source. The thickness of the layer and the light intensity were fixed, while the exposure time varied for different prints. A post-curing process was performed with a medium-pressure mercury lamp, and then followed the printing process.⁶⁶

The preparation of flexible cellulose nanocrystals (CNCs) based hydrogel, with high speed and accuracy, was done by 3D printing. CNCs, sodium alginate and gelatin were mixed at the ratio of 70/20/10 (wt%) to prepare hydrogel ink, which was used to print the 3D hydrogel scaffold with different structures and then, these printed scaffolds were crosslinked sequentially *via* covalent and ionic reactions with glutaraldehyde and CaCl₂, respectively. Crosslinking results in dimensionally stable hydrogel scaffolds with pore sizes of 80–2125 μm.⁶⁸ By optimising the printing pathways, uniform and gradient pore structures of scaffolds were obtained.

Table 2
3D printing types for the synthesis of hydrogels

3D printing	Methodology	Ref.
Light based	Deposition of light on to the surface of photocurable liquid in a vat	66
Nozzle based	Computer controlled layer-by-layer deposition of polymers through movable nozzle	67
Inkjet printer based	Noncontact technology prints droplets of ink onto a material platform	64

Therefore, 3D printing based hydrogels have been considered as an efficient and promising biomedical scaffold with respect to size, shape, pore structure and orientation for application in tissue repair and regeneration.⁶⁹

Salt bridging

The salt bridging technique involves the polymerization of monomers by the addition of salt electrolytes that form an ionic bridge and increase molecular attraction for the formation of hydrogels with tunable stress-relaxation and excellent stress recovery. Salt addition is known to facilitate the hydrogel formation based on unusual mechanisms of H-bonding, electrostatic interaction, charge repulsion and charge screening.⁷⁰ However, it remains unclear whether this initiates from ionic bridging or charge screening effects.⁷¹ Nanofibrillated cellulose-Ag hydrogels were produced with the addition of AgNO₃ aqueous solution to a nanofibrillated cellulose aqueous dispersion, followed by spontaneous reduction. Complete saturation of available carboxylate groups with silver ions was done by an excess amount of AgNO₃. Gelation occurred quickly upon introduction of AgNO₃. For slow reduction of Ag⁺ to Ag nanoparticles, the hydrogel was kept still for five days and then immersed into water several times to flush the unbound Ag species.⁷² A sodium alginate/cellulose nanofiber hydrogel was also generated by extruding sodium alginate and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO)-oxidized cellulose nanofiber composite solutions into a CaCl₂ solution.⁷³ The hydrogelation of carboxylated cellulose nanofibrils was also carried out with divalent or trivalent cations (Ca²⁺, Zn²⁺, Cu²⁺, Al³⁺ and Fe³⁺) of Ca(NO₃)₂, Zn(NO₃)₂, Cu(NO₃)₂, Al(NO₃)₃ and Fe(NO₃)₃ metal salts.⁷⁴

Synergistic “soft and hard” hierarchical hybrid network

To achieve excellent mechanical performance, reliable self-healing capability, and good self-recovery properties of hydrogels, the synergistic “soft and hard” hierarchical network structures have been demonstrated by combining smooth stress transfer and reversible coordination bonds. Cellulose nanocrystals based hydrogels were prepared by the involvement of “soft and hard” hierarchical networks, in which covalent crosslinked PVA and polyvinylpyrrolidone (PVP)

served as a “soft” homogeneous polymer network and Fe³⁺ crosslinked CNC network as “hard” polymer. CNC-Fe³⁺ ionic coordination bonds were interconnected as nano-reinforcing domains.⁶⁹ The components of Fe³⁺ ions and CNCs were introduced to the homogenous solution of PVA and PVP, and then mixed to obtain functional network hydrogels. These hierarchical porous networks of hydrogels were formed *via* simultaneous host-guest polymerization and ionic coordination triggered by microwave-assisted treatment under acid catalysis. CNC-Fe³⁺ hydrogels exhibit special characteristics, displaying ultrasensitive, stable and repeatable resistance variations upon mechanical deformation, for acting as a flexible and wearable strain sensor.³⁴

Solid-liquid interface contact

The solid-liquid interface contact technology has been developed to prepare unique hydrogels, which exhibited multilayers, high compressive strength, good solvent resistance, and good capacity of cell proliferation for various applications in the biomedical field, such as drug delivery, tissue engineering.⁶⁹ Multi-layered tubular cellulose hydrogels were prepared through a fast contact of the solid-liquid interface in NaOH/urea aqueous solution by using agarose as a template to control the structure of the hydrogels. Firstly, an agarose gel rod was dipped into acetic acid for 1–10 min; afterwards, this acetic acid loaded agarose gel rod was contacted with a cellulose solution on the solution-solid interface for same time to prepare the first cellulose layer. The gel rod with the first layer was dipped again in the acetic acid to form the second layer. The cellulose hydrogel layers were prepared rapidly *via* instant destruction of the cellulose inclusion complex by contact with the acid on the surface of the gel core, which causes quick self-aggregation between exposed cellulose chains.⁷⁵ By repeating this process, onion-like multi-layered tubular cellulose hydrogels with smooth cellulose layers were produced, and the thickness of the cellulose layers could be controlled in a wide range of 36–305 μm, simply by modifying the experimental parameters, such as the soaking time, the cellulose concentration, the amount of loaded acetic acid and the diameter of the agarose gel rod core.⁶⁹

APPLICATIONS OF HYDROGELS

Hydrogels possess unique properties, such as flexibility, versatility, soft surface and rapid swelling in water, which favours its marketing. Hydrogels show extensive and distinguishable uses and the most relevant of them are therapeutic uses, in medical devices and in the controlled release of drugs.⁷⁶ Hydrogels are widely used in contact lens production, as they have been found to be softer than hydrophobic based contact lenses. An alternative of superabsorbent polymers are superporous hydrogels (SPHs), which show similar properties, such as ability to prevent germ colonization, excellent water retention, mechanical strength and elasticity in swollen state.⁷⁷ Hydrogels are also used in cartilage reconstruction and regeneration, artificial organs, drug systems, wound dressings providing the humid environment beneficial for wound healing.³⁵ Hydrogels are also applied industrially in the production of sanitary napkins, baby diapers and cosmetics.³³

Lignin-polyurethane hydrogels were prepared and ammonium sulfate was introduced to generate a slow release fertilizer.⁷⁸ These hydrogels can be implemented as fertilizers by acting as coating materials, and can be used for different agricultural practices. Lignin hydrogels with FeS nanoparticles were used to remove poisonous cadmium metal, due to their suitable properties, such as high swelling capacity, nanoparticle sorption, chemical precipitation *via* chemical reaction and lignin complex formation.^{79,80} Cellulose and lignin based green hydrogels can be used as new materials capable of remediating water pollution by absorbing the contaminants.⁴⁵ Lignin-based hydrogels synthesized from lignin alkali polymers and poly (ethylene glycol) diglycidyl ether (PEGDGE) were noticed to be sustainable, non-phytotoxic with improved swelling properties in both saline and non-saline solutions. Lignin-based hydrogels have been verified to be competent in drought conditions in maize.⁸¹ Such hydrogels have the property to absorb a mixture of alcohol and water, which could be used as delivery vehicle of the alcohol-soluble therapeutic molecules and agricultural chemicals with limited aqueous solubility.⁸²

A hemicellulose-based hydrogel used as rape seed coating material resulted in significant improvement in germination inhibition. The feasibility of softwood hemicellulose-based hydrogels was also investigated as drug carrier of bovine serum albumin (BSA) and caffeine for

controlled release of a high molecular weight drug.⁸² Wheat straw hemicellulose-based hydrogels were prepared with CaCO_3 , which showed high adsorption capacity for methylene blue and smart swelling property, being applicable for wastewater treatment. In another research, macroporous xylan-rich hemicellulose based hydrogels were fabricated *via* free radical copolymerization of xylan and acrylic acid and used for adsorption of Pb^{2+} , Cd^{2+} and Zn^{2+} . Another hemicellulose hydrogel was prepared by the introduction of amidoamine into the biopolymer backbone through water based free radical graft copolymerization and crosslinking, which showed high adsorption capacity for Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} and Co^{2+} .⁸³

Cellulose-based hydrogels are successfully applied in various fields, such as pharmacy, tissue engineering, and regenerative medicine, for drug delivery systems, burn wound regeneration and cardiac, vascular, neural, cartilage and bone tissue regeneration. Cellulose nanoparticles were used in drug delivery systems, or as scaffolds in artificial ligaments or tendon substitutes, with an excellent cytocompatibility. The formulation of cellulose nanoparticles with silver nanoparticles can be used as antimicrobial medication, antibacterial agent in wound dressings, bandages, implants, skin replacements for burnings, face masks, artificial blood vessels, cuffs for nerve surgery, drug delivery, cell carriers and support matrices for enzyme immobilization, cosmetic tissues *etc.*⁵³ Cellulose-based hydrogels prepared by free radical graft copolymerization of cotton with acrylic acid (AA) and acrylamide (AM) showed moderate water retention capacity and can be used as absorbent for agriculture in arid areas.⁶¹ The effects of cellulose-based hydrogels were tested in the cultivation of tomatoes and resulted in much longer plant survival time under stress conditions with 1% hydrogel inclusion, compared to no hydrogel.⁸⁴

Lignocellulose-based hydrogels, due to their excellent biodegradability, water retention capacity and nutrient retention, can be applicable to provide the required water to crops, especially in drought conditions. Sandy soils, upon the addition of small and smart hydrogel beads, acquire the tendency to absorb significant amounts of water for plant growth. The crosslinking conditions allowed imparting important properties to hydrogels, tailoring the quantity of water to be released (increased with decreasing density of crosslinking) and gelation

time,⁸⁵ which could facilitate the retention of a controlled amount of water in hydrogels.⁸⁶ Lignocellulose-based hydrogels have a great impact in the field of agriculture, as they can be used as media for seed germination and may have effects on the physiological traits of plants, influencing their growth. Also they can protect the plant from any microbial or fungal attack, as they have antimicrobial and antifungal properties.⁶²

Hydrogels obtained by different synthesis techniques have their own scope of application, given that each method yields materials with specific properties due to the different nature of binding forces or interactions involved, crosslinking density, supporting chemicals behaviour toward crosslinking. Moreover, the choice of polymers for crosslinking influences the porosity, thermal stability, mechanical strength and liquid retention properties of hydrogels, which also makes the obtained materials suitable for a specific application in a certain field.

CONCLUSION

The valorization of lignocellulosic biopolymers for the synthesis of green hydrogels is a great effort towards sustainability. The crosslinking position and the nature of the constituent hydrogel polymers have a significant role determining their characteristic features, such as swelling ratio, mechanical strength, water holding capacity *etc.*, which make them applicable for the desired purposes in specific areas. In this review, different synthesis approaches, such as physical crosslinking, chemical crosslinking, 3D printing and other modified techniques for the formation of hydrogels and their application in different fields are addressed. Physically crosslinked hydrogels are produced through different mechanisms, *i.e.*, hydrogen bonding, electrostatic interactions and hydrophobic interactions. Chemically crosslinked hydrogels require chemicals or radiation through different polymerization and grafting techniques to produce 3D networks. As a future perspective, advanced and eco-friendly methodologies for the synthesis of green hydrogels, with specialized properties, having full applicability in diverse fields, should be developed.

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