Journal of Polymers and the Environment (2019) 27:871–891
https://doi.org/10.1007/s10924-019-01376-4

REVIEW

Hydrogel Preparation Technologies: Relevance Kinetics, Thermodynamics and Scaling up Aspects

Marwa Mohamed Elsayed[1]

Published online: 11 February 2019

Abstract
Hydrogels are three-dimensional structure composed of organic resources with lightly cross-linked having high to very high swelling ability in aqueous solutions. Due to the special physical and chemical properties of hydrogels, such as: flexibility, swell-ability, softness, and biocompatibility, there are growing research interest in the hydrogel synthesis, developing its properties, and hence increasing the applications in different fields. Both natural and synthetic polymers either physically or chemically cross-linked for producing hydrogels. This review covers definition, classification, application of polymer hydrogels and an also, overview of the different synthesis processes, kinetics and thermodynamics mathematical modeling approaches. A case study related to producing and using hydrogel in various areas has been reviewed.

Keywords Hydrogel · Absorption kinetics · Swelling kinetics · Thermodynamics

Introduction

Hydrogel is a vastly three-dimensional hydrophilic polymer network with the ability for swell huge quantities of water or many other fluids. The hydrogel network may be composed of homo-polymers or copolymers, and there are two types of hydrogel networks, which are physical or chemical network according to the network crosslinks.

Numerous research papers have been published for reviewing hydrogels, each one of these review articles has specific outlook [1]. For example, the preparation and the properties of hydrogel formulation have been reviewed [2]. Hydrogel network sources such as synthetic, semi-synthetic and bio polymeric hydrogels have been discussed [3]. The hydrogel chemistry and different synthetic preparation procedures have been reviewed comprehensively [4]. Another review article has a detailed discussion on the methods for preparation hydrogel networks [5]. Also, the hydrogels prepared from synthetic polymers which used in the field soil conditioners have been illustrated [6]. Furthermore, the natural polymers such as polysaccharides and proteins as raw materials for hydrogels preparation have been surveyed [7]. There was an exclusive article published in 1994, which critically surveyed the water-absorbent polymers in agreement with the patents literature [8]. In the industrial production lookout, a user profile has been published by the Stanford Research Institute; SRI Hydrogels prepared using acrylic monomers family [9]. Two appreciated books on the synthetic hydrogel materials have been published in the period between 1990 and 1998 [10] where the major phenomena related with the synthetic hydrogels have been clearly reflected [11].

Hydrogel preparation technique may undergo using either conventional or radiation techniques. Many authors used the conventional technique for the grafting of vinyl monomers onto different polysaccharides backbone such as starch (St) [12], chitosan (Ch) [13], alginate (Alg) [14] and a blend of polysaccharides [15].

Irradiation is a technique where a mixture composed of monomers and photo initiator have been exposed to a radiation source, the radiation has been absorbed via the photo initiator, which by turn produces an unstable excited species [16]. This excited molecule is capable of transferring energy to the monomer or to the polymer backbone and hence results from the information of free radical. The creation of free radical is followed by the propagation step of polymerization. Initiators may not be required, cross-linked can be used when using vinyl monomer, and both polymerization and crosslinking reactions may be initiated

✉ Marwa Mohamed Elsayed
eng_marwa06@yahoo.com

[1] Chemical Engineering & Pilot Plant Department, National Research Centre, El-Bohouth Street, Dokki, P.O. Box 12622, Giza, Egypt

at room temperatures [17]. Using radiation technique for the biomedical hydrogel has been reviewed by Carenza [18].

Since the first appearance in 1960, some hydrogels undergo continuous or discontinuous changes that are arbitrated by the outside stimuli such as changes in temperature, pH, solvent type, light, ionic strength, both magnetic and electric fields, and the presence of the chelating agent. This response causes increasing the range of hydrogel applications, such as wound dressing [14], tissue engineering [19], soil conditioning [20], drug delivery systems [12], hygienic products [21], and separation science [13].

Free radical graft polymerization of monomer into a polymer chain is one of the known, accessible, and effective methods of hydrogel preparation especially when using natural polymers [22]. Studying the monomer radical graft polymerization kinetics onto polysaccharide chain has been studied [15].

In addition to studying the interaction kinetics of different initiators with polysaccharides promotes also, their search cover the grafting efficiency and the finding the key reactions for the determination of copolymerization grafting rate, and a mathematical model of process kinetics has been developed. The kinetics and mechanism details of styrene grafting onto poly-butadiene have been illustrated [23, 24]. It was notified that the polymerization reaction rate displayed a first-order and a square root relevant to the concentration of monomer and initiator, respectively [25].

In spite of the great number of reviewing articles, to the best of our knowledge, there is no other published review with a comprehensive perspective on hydrogel preparation technologies. This review article aims to provide a summary data for the hydrogel preparation technologies with related polymerization kinetics and thermodynamics. Also, some case studies process and financial considerations pertinent to hydrogel scaling up manufacture.

Hydrogel Classifications

The hydrogel can synthesis via using different raw materials and also different techniques and hence it can be classified along with different points of view as illustrated in Fig. 1.

According to Crosslinking Mechanism

The most known hydrogel classification is physical and chemical based on the type of the crosslinking technique [26]. Physical crosslinking hydrogels are synthesized by one of the following methods: crystallization, ionic interaction, stereo-complex formation, and hydrogen bond. In the case of ionic interactions, hydrogels can undergo cross-linking process at ambient conditions. Polysaccharides such as chitosan, dextran, and carboxy methyl curdle have reported in the literature for the preparation of physically cross-linked hydrogels by hydrophobic modification [27, 28].

Chemical crosslinking involves grafting of monomers on the polymers backbone or using a crosslinking agent to link two or more polymer chains. The crosslinking of natural and synthetic polymers can be obtained via the interaction of functional groups (such as OH, COOH, and NH_2) with a cross linker such aldehyde or methylene is acrylamide. There are a number of methods reported in the literature for obtaining chemically cross-linked "permanent" hydrogels [29].

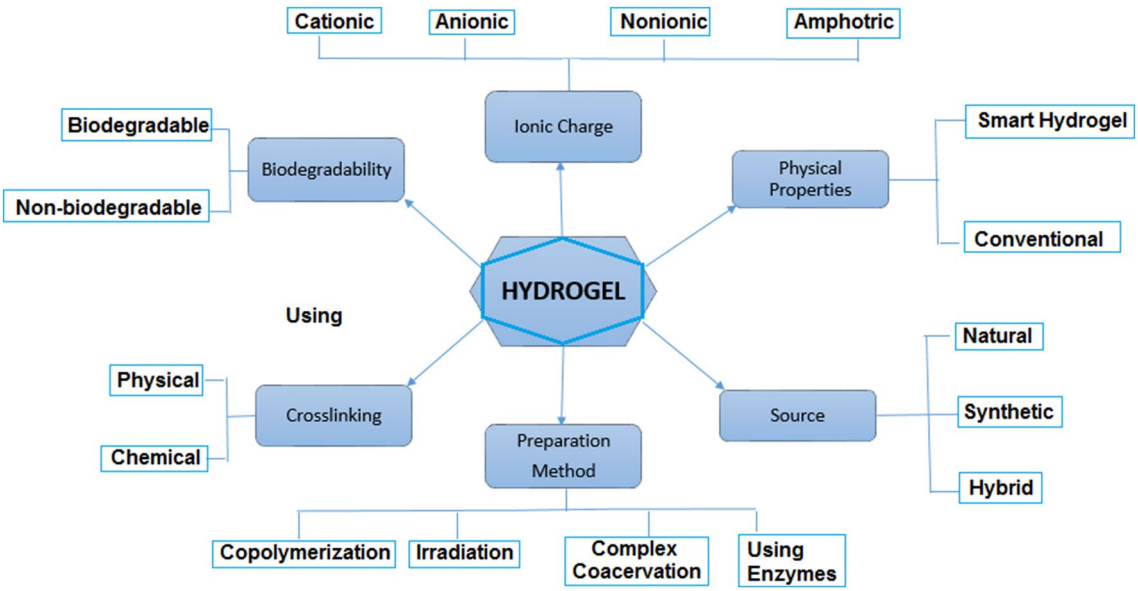

Fig. 1 Classification of hydrogel from different point of view [26]

Classification Based on Source of Preparation

According to their starting materials, hydrogel may be divided into natural, synthetic and "hybrid" combinations of both natural and synthetic [5, 26].

a. Natural Hydrogel

Natural biodegradable polymers have been involved in the hydrogel synthesis, the first one is the protein (fibrin, collagen, and gelatin), and the second one is the polysaccharide (chitosan, starch, and alginate). Regularly, natural polysaccharides are preferred over synthetic polymers because of their low cost, biodegradability, easy availability and non-toxicity [13].

b. Synthetic Hydrogel

Synthetic hydrogels are prepared using chemical polymerization techniques. Examples of synthetic and degradable polymers used in this issue are poly-lactide, poly-glycolide, poly (glycolids-*co*-lactide) and poly (ε-caprolactone).

c. Hybrid Hydrogel

Hybrid hydrogels based on a combination for both natural and synthetic polymers/monomers designed to merge the advantages of synthetic and natural polymers at the same time and permit good control over properties. For example, natural polysaccharides have been grafted with some vinyl monomers to add additional properties onto the polysaccharide network without losing its biodegradable nature [13]. Furthermore, this combination will produce a hydrogel with greater number of functional groups and also will improve the mechanical properties of the natural polymers.

Classification According to Polymeric Composition

a. Homo-polymeric Hydrogels

Polymer network which is built by the linking together of a large number of a single repeating unit "monomer", which is a basic structural unit comprising a single polymer network [8]. Homo-polymers may have cross-linked skeletal structure depending on the nature of the monomer and polymerization technique.

As an example for the hydrogel prepared using one polymer, polyvinyl pyrrolidone has been prepared via irradiation technique using gamma source at a dose rate of 3.2 $Gymin^{-1}$ [16]. Poly-acrylic acid is another example for homo-polymer hydrogel; it is stable with optimal elasticity. Its commercial version contains 2.5% of Poly-acrylic acid and the rest is water [30].

b. Co-polymeric Hydrogels

They are the category of hydrogel comprised of two or more different monomer/polymer at least one of them has hydrophilic property, arranged in a random way [9]. A biodegradable tri-poly (ethylene glycol)-(α-caprolactone)-(ethylene glycol) hydrogel has been investigated for use in the drug delivery system [31, 32]. Polyvinyl pyrrolidone hydrogels have been prepared using different irradiation doses (5–15 KGy) [33].

c. Multi-polymer Interpenetrating Polymeric Hydrogel (IPN)

IPNs defined as the intimate combination of two polymers [34]. This is done via submerging a pre-polymerized hydrogel in monomers and initiator solution. IPNs can be more effectively preserve quick response to pH and/or temperature due to the absence of restricting interpenetrating elastic network, while still have the advantages like modified pore size and slow drug release etc. An example of IPN is the linear cationic poly ally ammonium chloride in acrylamide/acrylic acid copolymer hydrogel, which imparted both higher mechanical strength and fully reversible pH switching [35].

Classification Based on Network Morphology

As shown in Fig. 2 the surface network morphology of the hydrogel may be classified into four categories [26].

a. Non-crystalline "amorphous".
b. Semi-crystalline-structure: a complex mixture of amorphous and crystalline phases.
c. Hydrogen-bonded.
d. Hydrocolloids.

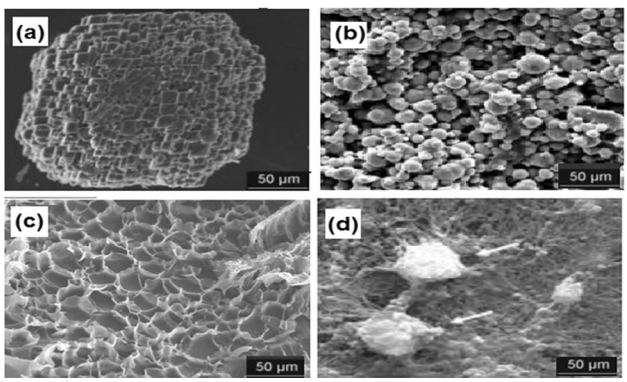

Fig. 2 Hydrogel surface morphology **a** amorphous, **b** semi-crystalline, **c** hydrogen bond and **d** hydrocolloids

Classification Based on Physical Appearance

Hydrogels have different shapes as matrix, film, or microsphere depends on the polymerization technique which involved in the preparation process [36].

Classification According to Network Electrical Charge

a. Non-ionic (neutral).
b. Ionic [anionic (− ve) or cationic (+ ve)].
c. Amphoteric electrolyte (containing both acidic and basic functional groups).
d. Zwitterion (polybetaines) which containing anionic and cationic groups in each unit [37].

Classification According to Sensitivity to the Surrounding Environment

Hydrogels can be sensitive to different surrounding variables such as pH, temperature, enzyme, light, and electric. (Table 1) shows some of the environment sensitive hydrogels and their polymer system [38].

Important Properties of Hydrogel

Swelling Properties

The most significant characteristic of a hydrogel is the ability to absorb large amounts of aqueous solutions which may reach hundreds of times of its dry weight. This phenomenon is known as swelling. The alteration of hydrogel chains by hydration is shown diagrammatically in Fig. 3.

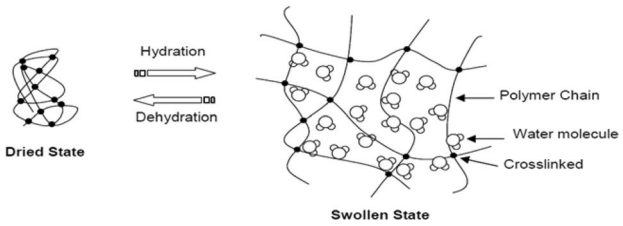

Fig. 3 Volume phase transition of hydrogel by hydration and dehydration

The concentration difference of the mobile ions in the hydrogel interior relative to an external solution (osmotic pressure), changing the solvent's pH causes change ionization degree of the functional groups dictates its swelling profile and hence the volume changes drive the hydrogel volume to change [40]. Mostly, the hydrogels swelling characteristic is recognized as the swelling water ratio (SWR) which is a ratio between the weights of the swollen to the dry hydrogel. Dynamics affecting SWR mainly include the crosslinking ratio, the solvent concentration and quality in addition to the chemical structure [13].

Mechanical Properties

Mechanical properties of hydrogels are very important to determine the suitable field for using the hydrogel. For Example, the evaluation of the mechanical property is essential in different biomedical applications, the matrix for drug delivery, wound dressing material and tissue engineering. The hydrogels mechanical properties should be accepted, that it can maintain its physical consistency during the delivery of therapeutic moieties for the predetermined period of time [41].

Table 1 Shows the name of some hydrogels, crosslinking agents and their applications

Hydrogel	Crosslinking agent	Applications	Refs
Polyvinyl alcohol (PVA)	Sodium borate/boric acid	Packaging	[39]
Chitosan	Oxidized dextrins	Tissue engineering	[40]
Guar gum	Glutaraldehyde	Scaffold of hepatocyte	[41]
Guar gum	Epichlorohydrin	Biomedical application	[42]
Gellan gum	Endogen polyamine spermidine	Drug delivery	[43]
Glycol chitosan	Oxidized alginate	Drug delivery	[44]
Hydroxamated alginates	Zinc	Drug delivery	[45]
Alginate bead	Zinc	Drug delivery	[46]
Scleroglucan	Borax	Drug delivery	[47]
Carboxylmethyl cellulose/starch/SiO_2 nanoparticles	Ethylene glycol dimethacrylate (EGDMA)	Agriculture	[48]
Polyacrylamide	*N,N'*-methylenebisacrylamide	Heavy metal removal	[49]
Polyacrylamide/guar gum graft copolymer	Glutaraldehyde	Heavy metal removal	[50]
Chitosan/poly(acrylamide-*co*-acrylic acid)	*N,N'*-methylenebisacrylamide	Waste water treatment	[51]

By changing the degree of crosslinking the targeted mechanical properties of the hydrogel can be reached. For stronger hydrogel the degree of crosslinking should be increased, a can be obtained through the higher degree of crosslinking decreases the % elongation of the hydrogels creates a more brittle structure [37].

Biocompatible Properties

In order applying the hydrogel products in the biomedical field, they should be biocompatible and nontoxic. Biocompatibility means the material's ability to respond to an appropriate host effect in a definite application. Biocompatibility studies consist of two parameters namely bio-safety and bio-functionality:

a. Bio-safety, for example, appropriate host response not only systemic but also local, the absence of cytotoxicity, mutagenesis, and/or carcinogenesis and
b. Bio-functionality which is the ability of the material to achieve the definite mission for which it is intended. This meaning is particularly related to tissue engineering science since the nature of tissue construct is to continuously interact with the body through the healing process [38].

Hydrogel Applications

Hydrogels are involving in many of our live application. To improve their properties, many researchers tried to copolymerize them with other chemicals, ionize, or treat them with Nano-particles. These techniques make it possible to use them in environmental, medical, biomaterial, pharmaceutical and agricultural applications. Table 1 summarizes different hydrogels and their applications.

Wastewater Treatment

Hydrogels are being used to remove environmental pollutants. For example, tons of swine wastes are produced annually. It results in runoff into surface water systems and hence the degradation of soil-ground water systems. Poly (di-methyl di-allyl ammonium chloride-*co*-acrylamide)-graft-triethylenetetramine–dithiocarbamate (PDCATD) was synthesized and has been used for removing heavy metal from industrial wastewater. Some cationic dyes which are known carcinogens are removed by hydrogels [51].

Medical Field

Smart hydrogels are used in many medical applications due to their responding to some environmental conditions such as pH, temperature, and light as illustrated in Table 2. Many endeavors have been exerted during past 10 years for the treatment of skin wounds and tissue engineering using different hydrogel types [40, 52].

Drug Delivery Applications

In recent times, great efforts have been dedicated to using potential pharmaceutical instruments such as novel drug delivery systems (DDS), since it has an appropriate means of site-specific and controlling the delivery time for therapeutic agents [66].

Agricultural Applications

Because of the hydrogel excellent ability to hold water molecules, it has been applied in the agriculture field more than 60 years ago. These polymers were developed to enhance the soil physical properties via increasing their water use efficiency, water-holding capacity, plant performance and reducing irrigation frequency and reducing compaction tendency [10].

A new slow-release hydrogel fertilizer has been developed which can provide essential plant nutrients including nitrogen, phosphorous, potassium and zinc as well as the organic matrix which acts a soil conditioner [67].

Superabsorbent polymer (SAP) based on graft copolymerization of sodium carboxy methylcellulose and acrylic acid adding potassium per-sulfate as an initiator has been prepared. Experiments were performed at 70 °C for 90 min. The maximum swelling capacity for SAP was 545 g/g in distilled water and 44 g/g in 0.9% w/v NaCl solution [68].

Hydrogel Synthesis Technologies

Preparing hydrogel is spontaneously a combined between polymerization and crosslinking chemical reactions. Different polymerization techniques have used for the hydrogel preparing and synthesis such as solution polymerization or aqueous polymer solution [47], suspension polymerization, radiation polymerization, photo polymerization, and free radical polymerization. According to literature most of the hydrogels were synthesized using step growth and solution polymerization. In these techniques, the products of the hydrogel can be formed or reformed into different shapes and sized. Therefore, these three two techniques are the main focus in this article review [69].

Polymerization Techniques for Producing Hydrogel

According to the chain growth mechanism of the used polymer, polymerizations can be divided into step growth and chain polymerization [14]. Figure 4 represents a simplified

Table 2 Environmental sensitive hydrogel and their polymer system [38]

No	Type of sensitivity	Hydrogel	Reaction summary	Refs.
1	pH	Poly(methacrylic acid-*co*-methyl methacrylate) Hydrogel	22/78 molar %, with two crosslinking degrees (0.3 and 0.5%)	[53]
2	Thermo	Poly(*N*-t butyl acryl amide-coacrylamide)	Prepared using free-radical crosslinking copolymerization	[54]
3	pH	Chitosan-alginate, chitosan carboxymethyl cellulose sodium, and chitosan-carbopol	Polyelectrolyte complexe hydrogels with prolong drug release systems using Diltiazem HCl	[55]
4	Thermo	Poly(*N*-isopropylacrylamide)-poly(ethylene glycol) diacrylate	A major and reversible phase change with changing in temperature and able to release various proteins	[56]
5	Enzyme	Poly(ethylene glycol)	Formed by Thiol-ene photopolymerization technique to fabricate protein delivery vehicles capable of enzyme-responsive protein released at sites of inflammation	[57]
6	pH-thermo	Poly-*N*-isopropylacrylamide	Formed by Electrochemically induced polymerization	[58]
7	pH	Agarose	Highly biocompatible, specifically developed for regenerative medicine applications in spinal cord injury (SCI) repair	[59]
8	pH	Poly (Am-*co*-AA)	Superporous hydrogels with fast responsive properties of system	[60]
9	IR light	*N*-isopropylacrylamide	IR light-responsive hydrogel was used to made liquid-based tunable microlenses	[61]
10	Thermo	Hydroxyethyl methacrylate	Rate controlled rectal Delivery of antipyrine or theophylline. by Cylindrical hydrogels	[62]
11	pH	Chitosan-PVA	Modified pH sensitive swelling	[63]
12	Electro	Polydimethylaminopropylacrylamide	Prepared via crosslinking the water-soluble polymers using radiation or chemical techniques	[64]
13	Electro	Chondroitin4-sulphate	Potential matrices for the electro controlled delivery of peptides and proteins	[65]

block diagram of the hydrogel preparation steps via different techniques.

5.1.1 Step-Growth Polymerizations (Polycondensation)

Step-growth polymerization undergoes by the reactions between monomers/polymers with different types of functional groups, the lifetime of a growing polymer chain may be not exceeded 1 s [70]. Step growth polymerization is exothermic reaction accompanied by increasing the viscosity of the reaction mixture at high conversions. Such as, polyamides can be obtained by the reaction of amino acids with themselves. In addition, polyesters, formed from di-acids and di-ols with removing of water. Thus, any random propagation reaction between two growing polymer chains can be represented schematically as:

$$P_x + P_y \leftrightarrow \quad P_{x+y} + \quad (A)$$

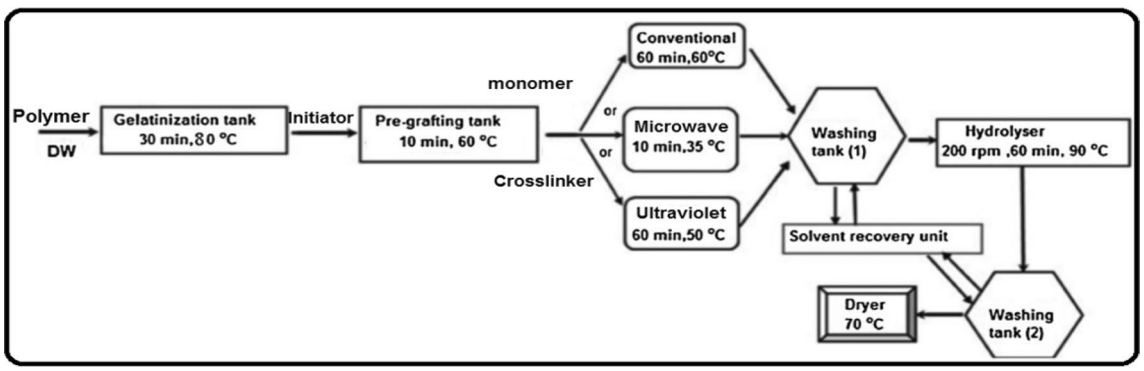

Fig. 4 Simplified hydrogel preparation block diagram

Where P_x, and P_y, denote growing polymer chains with a degree of polymerization x and y, respectively, and "A" denotes a small condensate molecule.

Yunzi et al. [71] provided an overview for step-growth polymerization takes poly(lactic acid) as the example to present new developed polymer synthesis techniques reported in the recent decade (2005–2015) on the basis of industrial technique modifications and advanced laboratory research.

5.1.2 Solution Polymerization/Crosslinking

In solution, co-polymerization/ crosslinking reactions, and ionic or neutral monomers are mixed with the multifunctional crosslinking agents. The polymerization has been initiated thermally, by UV light, or by redox initiator system in the presence of the solvent. The prepared hydrogels need to be washed with distilled water to remove the un-reacted monomers, crosslinking agent, and the initiator [13].

Hydrogel Crosslinking

Crosslinking modifications are improving the mechanical properties and viscoelasticity for applications in different fields. The crosslinking techniques adopted for this purpose are physical crosslinking, chemical crosslinking, grafting polymerization, radiation crosslinking.

5.2.1 Physical Crosslinking

There has been an increased interest in physical or reversible hydrogels due to the relative ease of production and the advantage of not using crosslinking agents "see According to crosslinking the mechanism". These physical crosslinks are not permanent in nature, but they are adequate to make hydrogels insoluble in an aqueous solution. Physical crosslinking gives reversible hydrogels [72]. The various methods reported in the literature to obtain physically crosslinked hydrogels are:

a. Heating/Cooling a Polymer Solution In this method, hydrogels are formed by cooling hot solutions of gelatin or Carrageenan. The hydrogel formation is due to helix-formation and then the formation of junction zones [73]. As shown in Fig. 5 Carrageenan in hot solution above the melting transition temperature is present as random coil conformation, upon cooling it transforms. In other cases, the hydrogel can also be obtained by simply warming the polymer solutions that causes the block copolymerization. Some of the examples are polyethylene oxide-polypropylene oxide, polyethylene glycol-polylactic acid hydrogel [28].

b. Ionic Attraction Figure 6 represents ionotropic gelation formed by the interaction between alginate (COO^-) with

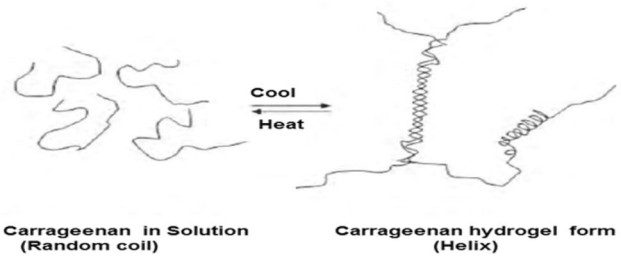

Fig. 5 Hydrogel formation due to aggregation of helix via cooling a hot solution of carrageenan

calcium metal ions (Ca^{2+}). Polymers can cross-link by the addition of di- or tri-valent counter ions. This method causes the gelling of polyelectrolyte solution (e.g. Na^+ alginate-) with opposite charges (e.g. $Ca^{2+} + 2Cl^-$). Other examples are chitosan-polylysine hydrogel [74] and chitosan-dextran hydrogels [75].

c. Complex Coacervation Complex coacervate hydrogels are formed via merging a poly (cation) with poly (anion) as shown in Fig. 7. As polymers with opposite charges attract one another and form both soluble and insoluble complexes depending on surrounding solution. An example is a coacervate xanthan (poly-anionic) with chitosan (poly-cationic) [76].

d. Hydrogen Bonding Hydrogen bonded hydrogel are prepared via lowering the aqueous solution pH of the polymers having the carboxyl groups. Carboxy methylcellulose (CMC) network is an example of the hydrogen-bonded hydrogel. In Poly (CMC) the network dispersing CMC into 0.1M HCl as shown in Fig. 8. The mechanism involves replacing the sodium in CMC with hydrogen from the acid.

Carboxy methylated chitosan (CM-chitosan) hydrogels can also prepare by crosslinking in the presence of acids or poly-functional monomers [77].

5.2.2 Chemical Crosslinking

In the chemical crosslinking is a method for producing a chemically crosslinking hydrogel using radical polymerization of low molecular weight monomers, branched homopolymers, or copolymers in the presence of the crosslinking agent as shown in Fig. 9 [27].

Chemical crosslinking covered in this article involves grafting of monomers onto the polymers backbone or the use of a crosslinking agent to link two polymer chains. The crosslinking of both natural and synthetic polymers have achieved through the reaction between their functional groups (such as COOH, OH, and NH_2) with cross linkers. There are a number of methods reported in the literature to obtain chemically cross-linked permanent hydrogels "see

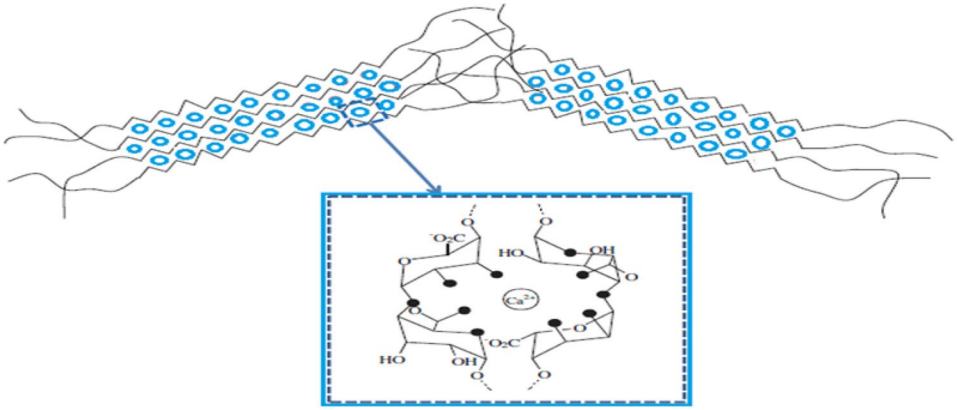

Fig. 6 Ionotropic gelation by the interaction between anionic groups on alginate (COO^-) with divalent metal ions (Ca^{2+})

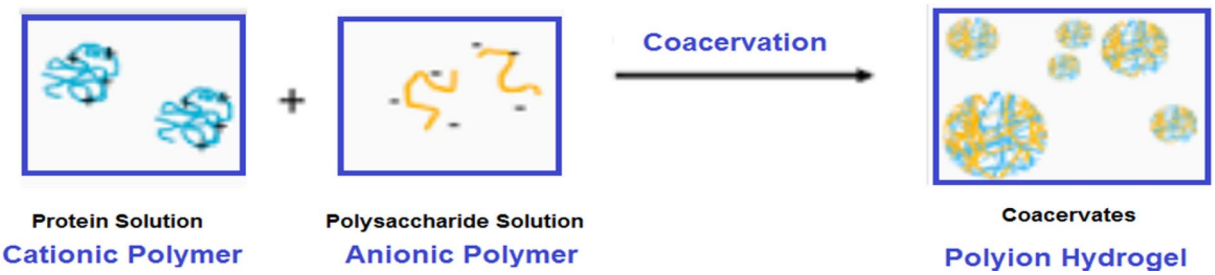

Fig. 7 Complex coacervation between a protein poly-anion and a polysaccharide poly-cation

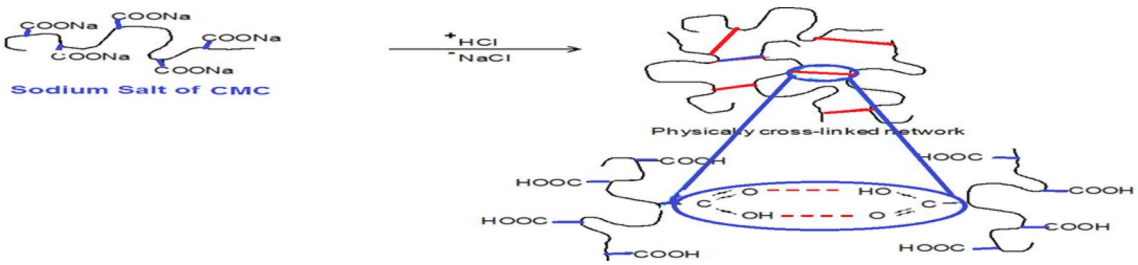

Fig. 8 Hydrogel network formation due to intermolecular H-bonding in CMC at low pH

Table 1". One example is hydrogel prepared by crosslinking of starch and polyvinyl alcohol using glutar aldehyde as a cross-linked [78]. The prepared hydrogel membrane could be used as an artificial skin and at the same time various nutrients/healing factors and medicaments can be delivered to the site of action. Carrageenan and acrylic acid have been cross-linking using 2-acrylamido-2-methylpropanesulfonic acid leading to the development of biodegradable hydrogels with proposed use for novel drug delivery systems [79].

Grafting

Graft polymerization is a novel method for imparting different functional groups into polymer backbone via the attachment of synthetic monomer onto natural polymer and hence modifying the chemical and physical properties of the produced hydrogel as shown in Fig. 10. Graft polymerization can be initiated using various techniques such as conventional and irradiation (MW, UV γ-ray, and e-beam).

Chitosan grafted with acrylamide-*co*-acrylic acid using methylene bis-acrylamide as a cross linker is an example of grafting two monomers into a polymer backbone [51]. Another example is grafting acrylamide (Am) into a backbone of polysaccharide mixture composed of chitosan, alginate, and chitosan to get a wonderful platform may be used in various fields [15].

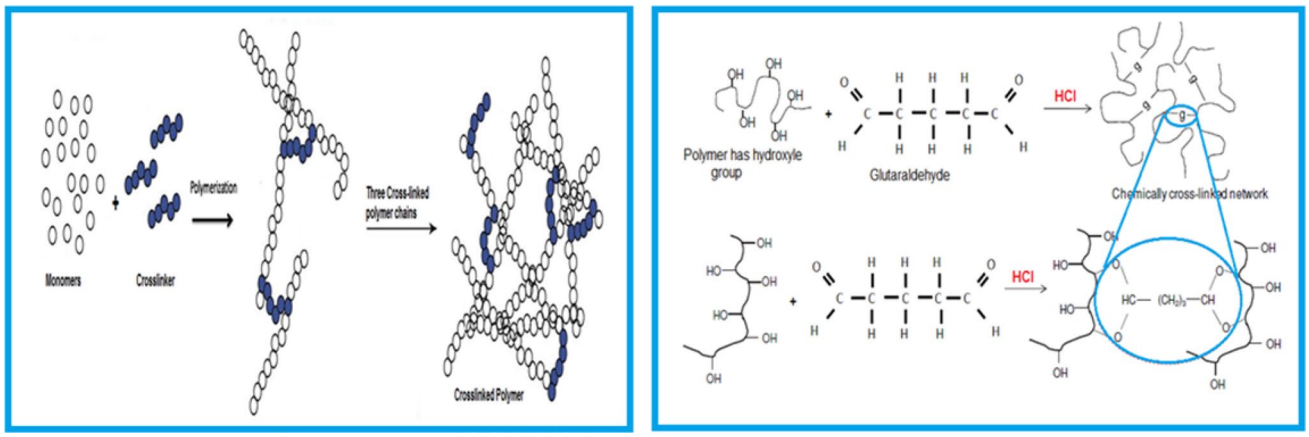

Fig. 9 Schematic illustration of using chemical cross-linked to obtain cross-linked hydrogel network

Fig. 10 Grafting of a monomer on preformed polymeric backbone leading to infinite branching and crosslinking

5.3.1 Grafting Via Conventional Technique

Grafting through conventional method may be achieved through free the radical grafting polymerization in the presence of chemical initiators such as potassium per sulfate (KPS) [13] and ceric ammonium nitrate (CAN) [80]. Many authors prepared hydrogel using the conventional technique for the grafting different vinyl monomers onto polysaccharides such as starch [81], chitosan [51], alginate [55] and cellulose [48].

Reactive extrusion is another conventional method for the grafting technique which has been explored as an alternate process for continuous production of polysaccharide graft copolymers with reduced water requirements. It allows the combination of several chemical processes into a single continuous operation [82].

The starch-g-polyacrylamide hydrogel has been prepared by a reactive extrusion processing resulting in a superabsorbent polymer hydrogel (SAP) with water absorption of 605 g/g. Also, the bentonite clay inorganic filler has been added to the graft copolymer to prepare the SAP composites (SAPC). It was found that new composite has exhibited the water absorption of approximately 730 g/g [83]. Also, grafted polymers of Am and different types starches (corn, waxy maize, wheat, and potato) have been prepared using reactive extrusion in the presence of ammonium per sulfate (APS) as an initiator [84]. The maximum %GY, %GE and SWR of 70%, 89%, and 200 g/g, respectively were obtained when using Am/St (w/w) of 1:2 of potato starch. Furthermore, reactive extrusion has been used for producing starch graft acrylamide, %GY and %GE of 90% and 75% were obtained [85].

5.3.2 Grafting Via Irradiation Techniques

In addition to conventional technique, irradiation technique is well-known methods for modifying the properties of polymeric materials via the grafting process. Photo polymerization is creating initiation sites in a defined area [86]. Polymerization can be done under variable conditions, allowing differences in the monomer structures. The effective grafting has attained according to the number and type of functional groups, temperature, radiation intensity and both the type and the concentration of the applied photo initiator. The major advantage of the radiation initiation over the chemical initiation is that the production relatively pure and initiator-free [87]. For example, microwave and ultraviolet irradiation technique will be discussed in this article review as according to the literature they are the most common in the grafting process.

There are different sorts of irradiation sources such as MW, UV, and gamma-irradiation as illustrated in Fig. 11. For the best to our knowledge, the most common grafting of hydrogel via irradiation has been done via microwave

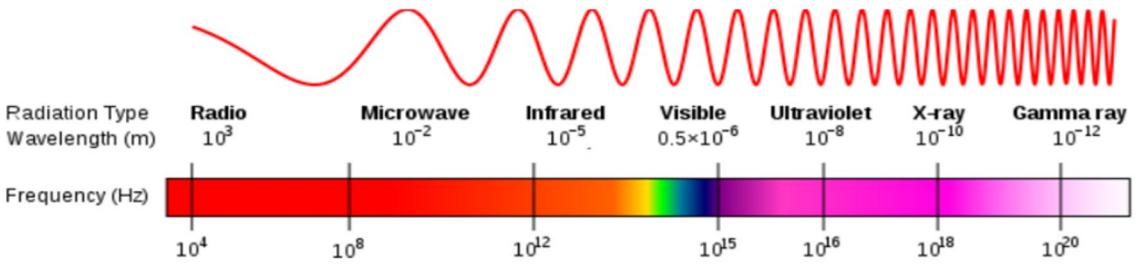

Fig. 11 Electromagnetic Spectrum

and Ultraviolet which will be discussed and summarized in the following section.

i. Microwave Irradiation Technique Microwave (MW) irradiation technique uses electromagnetic waves called micro-waves for heating with a short wavelength ranges between 10^{-4} to 10^{-2} m.

MW is a non-ionizing energy source because it depends on creating heat deep inside the materials; this heat is a consequence of rapid oscillations of the electromagnetic field at high frequency. The main ingredient that enables it to be heated by micro-waves is water, the higher the water content, the faster the heating rate. During the oscillation of the micro-waves, the water molecules also rotate. This is because the attachment of the water negatively charged end to the micro-wave positively charged end, while the water positively end is attracted to the micro-waves negative charged end. The microwaves rotate at an extremely high speed of 2450 revolution per second. This creates friction between water molecules and hence heat is generated [87].

In the literature, many authors used a microwave in the grafting of vinyl monomers onto polymers. For example, acrylic acid and acrylonitrile have been grafted into chitosan [88, 89].

Acrylamide has been grafted into starch and guar gum and chitosan using microwave [90–92].

Singh et al. [93] compared the grafted of methyl acrylamide (MMA) onto chitosan into MW and conventional techniques. Percentage G obtained was 160% using 80% of MW power in 2 min at 0.17 mol/L [MMA], 0.1 g/25 mL. While, %G was 105% using the conventional technique in the presence of KPS/ascorbic acid redox initiator at 35 °C for 60 min.

Singh et al. [94] compared the grafting of acrylonitrile onto starch using MW and conventional technique in the presence of APS. Percentage G and percentage GE of 225% and 98%, respectively have obtained using MW irradiation: 0.17 mol/L acrylonitrile, 0.0014 mol/L APS, 0.1 g starch, 1200 W of MW power and 70 s exposure time. However, under the same conditions at 98 °C (even in the inert atmosphere) raising the concentration of the initiator to 0.0024 mol/L resulted 10% of % G was achieved.

ii. Ultraviolet Irradiation Technique Ultraviolet is electromagnetic radiation with a wavelength shorter than MW and visible light, in the range 10–400 nm. Grafting using UV irradiation is producing unstable excited species on the polysaccharide backbone via absorption of the ultraviolet radiation. Then, the formation of a free radical by rearrangement, fragmentation, and followed by the monomer attacking which leads to grafting [95].

UV-initiated graft copolymerization of MMA onto chitosan has been reported, %G of 300% was obtained [96]. Lee et al. and Mubarak et al. used UV in the presence of benzo-phenone as a photo initiator for the grafting of AA and polyvinyl alcohol onto starch, %G of 120% and 98% were obtained, respectively [97, 98].

Hedin et al. grafted starch into glycidyl methacrylate (GMA) using UV irradiation technique in the presence of KPS, the obtained swelling in distilled water was 280 g/g [99].

5.3.3 Grafting Mechanism

The experiments for studying the grafting mechanism are designed to discover the factors controlling the grafting process using an initiator [25].

Free radicals may be formed in different of methods including; (i) organic peroxides thermal decomposition / hydro-peroxides or azo/diazo compounds. (ii) Light (ultraviolet) (iii) high-energy radiation. The common scenario for the grafting process is the free radical grafting polymerization process which consists of three steps: initiation, propagation, and termination.

Several authors studied the grafting mechanisms for vinyl monomers onto starch using different initiation techniques as follows [100, 101]:

Initiation This step contains the creation of a free radical active center and usually happens in two steps. The first is the formation of free radicals from an initiator.

$$I \xrightarrow{k_d} 2R^{\bullet}$$

$$St + R^{\bullet} \xrightarrow{k_i} RSt^{\bullet}$$

$$St^{\bullet} + M \xrightarrow{k_i} StM^{\bullet}$$

$$M + R^{\bullet} + \xrightarrow{k_i} RM^{\bullet}$$

Propagation The growth of the polymer chain via rapid sequential addition of monomer to the active center:

$$StM_n^{\bullet} + M \xrightarrow{k_p} StM_{n+1}^{\bullet}$$

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}$$

Termination In the case of neglecting all transfer reactions and the present monomer was finished, termination will happen either by combination or by disproportionation.

$$StM_n^{\bullet} + StM_n^{\bullet} \xrightarrow{k_t} graft\ polymer$$

$$StM_n^{\bullet} + St^{\bullet} \xrightarrow{k_t} graft\ polymer$$

$$M_n^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} \text{hom}\, opolymer$$

Where: St•, M•, R• are the free radicals of polymer, monomer and initiator, respectively.

5.3.4 Grafting Kinetics

The main task of all kinetic experiments is to assess the rate of grafting via a variety of experimental methodologies. The experiments done to determine the kinetics rate coefficients could be divided into two areas. The first scheme is the overall polymerization rate accurate measurement, while the second one focuses on the analysis of the resulting molecular weight distributions. If all the polymerizing system rate coefficients are known, it is possible to expect the kinetics of the overall polymerization procedure, including the complete molecular weight distributions as will be discussed here.

Several authors studied the kinetics of graft polymerization of vinyl monomers onto single polysaccharide [80, 100, 102].

The rate of graft polymerization (R_g) is estimated by the following equation [103, 104]

$$Rg(mol/L\ s) = \frac{Amount\ of\ grafted\ monomer}{M_m \times reaction\ time \times reaction\ volume}$$

where M_m represents monomer molecular weight (g/gmol).

The rate of the graft polymerization (R_g) (mole/L sec) depends on the concentrations of polymer, monomer, and initiator as follows:

$$R_g = k\,[P]^a[M]^b[I]^c$$

Where: k is the graft rate constant, P, M and I signifies for the polymer, monomer, and initiator, respectively, and a, b and c are constants.

A grafting rate equation has been derived from methyl acrylate (M) onto sago starch (St) applying the stationary state approximation to the various radical species in the system as follows [25]:

$$\frac{d[St^{\bullet}]}{dt} = kk_d[St][Ce^{4+}] - k_{i1}[St^{\bullet}][M] - k_{i3}[St^{\bullet}][Ce^{4+}] + k_{i4}[St-OX][Ce^{4+}] = 0$$

$$\frac{d[StM^{\bullet}]}{dt} = k_{i1}[St^{\bullet}][M] - k_{t1}[StM^{\bullet}]^2 - k_{t1}[StM^{\bullet}]^2 - k_{it1}[StM^{\bullet}][M^{\bullet}] = 0$$

$$\frac{d[M^{\bullet}]}{dt} = k_{i2}[M][Ce^{4+}] - k_{t1}[M^{\bullet}]^2 - k_{t1}[StM^{\bullet}][M^{\bullet}] = 0$$

$$\frac{d[St-OX]}{dt} = k_{i3}[St^{\bullet}][Ce^{4+}] - k_{i4}[St-OX][SO_4^{-\bullet}]$$

In these equations, M• and STM• represent homo-polymer and graft polymer radicals, respectively. Because there was a little attack of CAN to monomer (M); therefore, k_{i2} [M] $[SO_4^{-\bullet}]$ can omit, and now summing equations the above last two equations yields:

$$kk_d[St][Ce^{4+}] - k_{t1}[StM^{\bullet}]^2 - 2k_{t1}[StM^{\bullet}][M^{\bullet}] - k_{t1}[M^{\bullet}]^2 = 0$$

$$k_{t1}([StM^{\bullet}]^2 + 2[StM^{\bullet}][M^{\bullet}] + [M^{\bullet}]^2) = kk_d[St][Ce^{4+}]$$

$$[StM^{\bullet}]^2 + 2[StM^{\bullet}][M^{\bullet}] + [M^{\bullet}]^2 = \frac{kk_d[St][Ce^{4+}]}{k_{t1}}$$

$$([StM^{\bullet}] + [M^{\bullet}])^2 = \frac{kk_d[St][Ce^{4+}]}{k_{t1}}$$

$$[STM^{\bullet}] + [M^{\bullet}] = (\frac{kk_d[St][Ce^{4+}]}{k_{t1}})^{\frac{1}{2}}$$

The rate of consumption of vinyl monomer is defined by:

$$R_g = k_g[StM^{\bullet}][M] + k_g[M^{\bullet}][M] = k_g[M]([StM^{\bullet}] + [M^{\bullet}])$$

$$R_g = k_g[M](\frac{kk_d[St][Ce^{4+}]}{k_{t1}})^{\frac{1}{2}} = k_p(\frac{kk_d}{k_t})^{\frac{1}{2}}[St]^{\frac{1}{2}}[SO_4^{-\bullet}]^{\frac{1}{2}}[M]$$

The overall rate of grafting (R_g: mole/L s) of a free radical process is simply the rate of chain propagation. The last equation of R_g is the normal kinetic relationship for a simple radical polymerization and shows the first-order dependence of R_g on [M] and the half-order dependence of $[Ce^{4+}]$ and [St] held by this system as follows:

The plot of R_g vs. [P_sB], [I] or [Am] gives the value of k, a, b and c while fixing the other two concentrations. Table 3 a summary for the grafting rate obtained by different authors using different polysaccharides and vinyl.

5.3.5 Studying Some Factors Affect the Grafting Rate

The grafting of ethyl acrylate (EA) onto hydroxyl propyl methylcellulose (HPMC) has been studied, concentrations of EA in the range 0.1–0.4 mol/L, using KPS (2.7 mmol/L) at 60 °C. The G% and GE% have shown an increase trend with the increasing of EA concentration and hence the grafting rate is increasing as shown in Fig. 12 [113].

In another investigation methyl acrylate (MA) has been grafted onto sago starch in which CAN was used as an initiator. A kinetic model of the grafting process has been proposed. An equation of a predicted model relating the graft fraction of MA with the sago starch has been derived, and validity of the predicted model was verified using the experimental results.

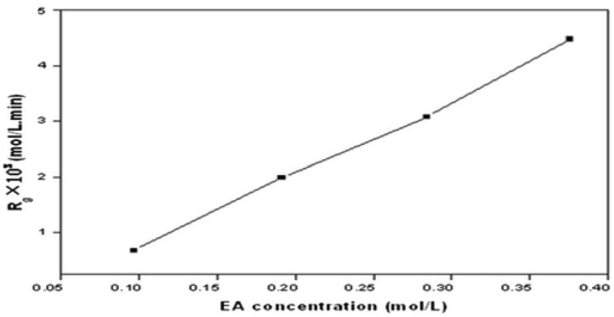

Fig. 12 Relationship between R_g and the monomer concentration of EA

$$\frac{1}{(1-GF)^{0.5}} = 1 + \frac{kk_d[St]}{k_{i2}[M]}$$

Where: k is the equilibrium, k_d is the dissociation constants, and all k_{i2} are initiation constants, (GF) the effect of the methyl acrylate monomer ratio on the graft fraction, [St] starch concentration, [M] monomer concentration [25].

The kinetics and mechanism of styrene grafting to polybutadiene details has been investigated [24]. The polymerization of the monomers appears to follow the

Table 3 Summary for reaction rate equation for grating different vinyl monomers onto polysaccharide chains monomer

No	Polymer	Monomer	Initiator	Reaction rate "Rg"	Refs
1	St	Acrylonitrile 'AN'	KPS	$Rg = k\,[St]^{0.497}\,[AN]^{1.185}\,[KPS]^{0.499}$	[105]
2	St	AN	Potassium permanganate	$Rg = k\,[St]^{1/2}\,[AN]\,[KMnO_4]^{1/2}$	[102]
3	St	AA	CAN	$R_g = k[St]^{0.46}\,[AA]^{0.92}[CAN]^{0.56}$	[80]
4	St	Ethyl methacrylate (EMA)		$R_g = k\,[St]^{0.48}\,[EMA]^{0.92}[CAN]^{0.53}$	
5	St	Acrylamide "Am"	potassium dichromate, Cr(VI) "I"	$Rg = k\,[St]^{0.52}\,[Am]^{0.93}\,[I]^{0.49}$	[104]
6	St	Acrylic acid "AA"		$Rg = k\,[St]^{0.46}\,[AA]^{0.95}\,[I]^{0.44}$	
7	St	Methyl methacrylate "MMA"		$Rg = k[St]^{0.46}\,[MMA]^{0.95}\,[I]^{0.44}$	
8	St	Acrylonitrile "ACN"	Ce(IV) "I"	$Rg = k[ACN]^{0.5}\,[I]^{1.3}$	[106]
9	St	Methyl acrylate	CAN	$R_g\text{-}Kd_d\,[CAN] + Kk_pk_d/k_t\,[S]\,[[MA]^a$	[107]
10	St	Acrylamide	Potassium permanganate	$Rg = k_pd^{-E/RT}[Mn^{7+}]^{0.5}\,[St]^{0.5}\,[MA]^1\,[H_2SO_4]^1$	[108]
11	Starch	2-Hydroxyethyl methacrylate "HMA"	CAN	$Rg = k[HMA]^1$	[109, 110]
12	–	Acrylic acid "AA"	sodium per sulfate	$Rg = k[AA]^{1.5}\,[I]^{0.5}$	[110]
13	Alg	Methyl acrylate "MA"	APS	$Rg = k[Alg]^0\,[MA]^1\,[I]^{0.5}$	[111]
14	Hydroxyl propyl methylcellulose (HPMC)	Ethyl acrylate (EA)	KPS	$Rg = k[HPMC]^{0.5}\,[EA]^1\,[KPS]^{0.5}$	[112]
15	St/Ch/Alg "PsB"	Acrylamide "AAm"	KPS	$Rg = k[AAm]^{0.5}[PsB]^{0.5}\,[KPS]^{0.5}$	[15]

[a] K, k_d, k_p, and k_t are polymerization, dissociation, propagation, and termination constants, respectively

normal kinetics of the reaction. The polymerization rate showed a first-order dependence on monomer concentration and a square root dependence on the used initiator concentration.

The kinetics of polymer particle formation and distribution at the graft polymerization of methyl acrylate onto hydroxyl-ethyl cellulose has investigated. The particle number increases at the first stage of polymerization, then it is constant [114]. The concentration of adsorbed monomer decreases throughout the polymerization reaction as shown in Fig. 13.

The free irradiation graft polymerization of styrene onto polyethylene using has been studied. The dependence on monomer concentration change with increasing dose rate has been investigated. Three different regions of behavior are defined [115]:

(i) a region of low dose rate: $R_g = k\,[dose]^{0.5}\,[M]^{1.5}$
(ii) a region of intermediate dose rate: $R_g = k\,[dose]^{0}\,[M]^{2.5}$ and $R_g = k\,[dose]^{0.5}\,[M]^{2.5}$
(iii) a region of high dose rate: $R_g = k\,[M]^{2.5}$

Huacai and Senkang [116] prepared chitosan- acrylic acid (AA) hydrogel and the effect of reaction time on the grafting yield has been studied. The reaction condition was temperature 80 °C, a ratio of a volume of AA to the mass of Ch 3 mL/g; reaction time was ranging from 1 to 2 h. and the obtained reaction yield was increased from 40 to 80%.

Abd-Alla et. al [117]. studied the effect of polymerization reaction time on G% and GE%. It can be seen from the Fig. 14 that the increase of reaction time from 0.5 to 2 h increased %G and %GE. Increasing the reaction time more than 2 h caused the reaction rate level off. This leveling off can be ascribed to the depletion in monomer and initiator.

Lutfor et al. [118] studied the effect of polymerization conditions on the grafting rate of AN into sago starch. It was found that the optimum reaction temperature and reaction period were 50 °C and 90 min, respectively. The maximum

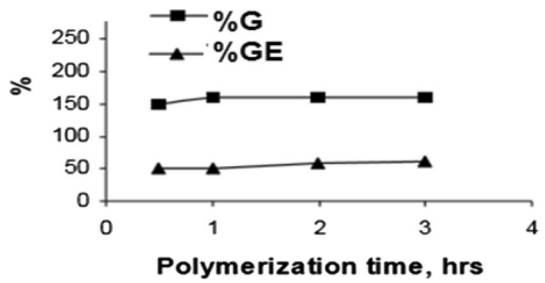

Fig. 14 The Effect of time on the grating parameters, Initiator concentration 0.15%, monomer to cellulose ratio 3:1, Acid conc. 1%, Liquor ratio 25:1, Temp. 20°C

percentage of grafting and efficiency were 83.04% and 95.9%, respectively (Table 4).

Hydrogel Polymerization/Grating Thermodynamics

Thermodynamic models offer simple approaches in order to describe the volume transition behaviors of neutral or ionic hydrogels in equilibrium. The equilibrium state of volume transition of the smart hydrogel in the solvent is obtained when the solvent inside the hydrogels network is in thermodynamic equilibrium with that outside solvent. This can be characterized in terms of the free energy, the chemical potential or the related osmotic pressure [126].

The most extensively used thermodynamic model was derived by Flory [127] for a description of the equilibrium volume transition of the hydrogels. The hydrogel at equilibrium state is preserved as a superior solution system, where the mesh chains cannot move freely to each other, but the chains can become elongated in a non-interacting way during the volume transition process. The hydrogels free energy is considered to be a sum of the mixing free energy which resulted from the mixing course and the elastic free energy due to the rubber elasticity. Furthermore, the osmotic pressure acting on the hydrogel network can be calculated according to the change of free energy.

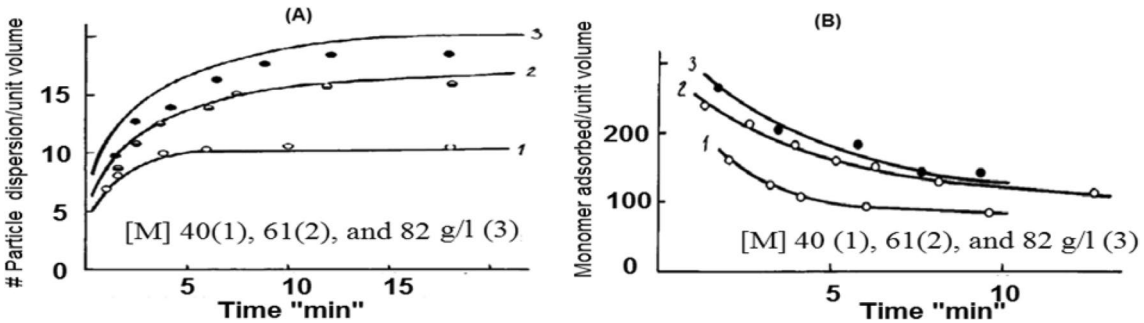

Fig. 13 **a** particle number in unit volumes of dispersion vs. time at [M] 40(1), 61(2), and 82 g/L (3); **b** monomers adsorbed in the unit volume of dispersed cellulose vs. time at the initial monomer concentration 40 (1), 61(2), and 82 g/l (3)

Table 4 Effect of using different grating time on the %G and %GE in the hydrogel synthesis

No	Used technique	Polymer	Monomer	Initiator	Grafting time range "min"	%G	%GE	Ref
1	Microwave	St	Am	KPS	0.08–1.25	120	65	[90]
2	Conventional	Guar	Am	KPS	0.33–1.67	140	49	[119]
3	MW and initiator	Guar	Am	KPS	0.33–1.67	190	66	
4	MW only	Guar	Am	KPS	0.33–1.67	120	42	
5	MW	St	AN	Peroxy di-sulfate	1.66–1.17	100	220	[87]
6	MW	Xanthan	Am	CAN	0.66–1.67	190	67	[76]
7	Conventional	St	Methacrylonitrile	CAN	60–300	105	52	[120]
8	Conventional	St	AN	Potassium permanganate	10–180	140	90	[121]
9	Conventional	St	AN	Potassium permanganate	0–25	55	87	[102]
10	Conventional	St	Butylacrylamide	CAN	60–240	32	–	[122]
11	Conventional	St	AN	CAN	15–180	%GY = 99%		[123]
12	Conventional	St	AN	CAN	0–40	240	95	[124]
13	Ultraviolet	Polypropylene	Glycidyl methacrylate	–	0–240	140	130	[125]
14	Conventional	St	Am	CAN	60–180	26.3%	–	[125]

Potassium per-sulphate has used as efficient initiator for graft copolymerization of the ethyl acrylate (EA) onto hydroxypropyl methylcellulose (HPMC) at 60 °C. The energy of activation needed for the graft copolymerization process has calculated at different temperatures, which have found to be 41.7 kJ/mole within the temperature 50–65 °C. On the basis of the experimental observations, initiating steps have been proposed and a suitable rate expression for graft copolymerization has been derived [111].

Solution graft copolymerization of acrylamide, acrylic acid (AAc) and methyl methacrylate (MMA) onto starch has been carried out using potassium dichromate, as redox initiator, activation energies within temperature 50–55 °C for St-g-PAm, St-g-PAAc and St-g-PMMA syntheses are found to be 48.2, 46.1 and 49 kJ/mol k, respectively. The effect of temperature on the rate of grating have been summarized in the as shown in Table 5 [104].

The changes in thermodynamic value have investigated depending on the change in both temperature and cross linker, which showed the following: Partial Molar Free Energy (ΔG), Enthalpy (ΔH), and Entropy (ΔS) were positive over the used temperature range; all thermodynamic parameters decreased with increasing temperature. When the temperature has increased from 25 to 45 °C, the (ΔG) increased from 0.14 to 13.6 J/mole [126].

As the polymerization temperature has a significant effect the grafting parameters many authors studied this factor and a comparison amongst grafting parameters of reaction between polysaccharides and acrylamides has been summarized in Table 6 [128].

The effect of both initiator concentration (0.003–0.005 mol/L) and solvent (0.05–0.3 mol/L) in the polymerization rate of acrylamide into starch has been

Table 5 Effect of temperature on R_g in optimum conditions

[St] = 50 g/L [AAm] = 0.34 M [I] = 0.032		[St] = 40 g/L [AAc] = 0.31 M [I] = 0.008 M		[St] = 60 g/L [MMA] = 0.34 M [I] = 0.008 M	
T (°C)	$R_g \times 10^5$	T (°C)	$R_g \times 10^5$	T (°C)	$R_g \times 10^5$
25	3.57	40	2.12	40	2.35
30	4.97	50	2.86	45	2.88
35	6.12	60	3.98	50	4.14
40	6.63	70	5.17	55	5.41

evaluated. Keeping all the other parameters constrain "Temperature: 30 °C, AM concentration: 1 .O M, time: 4.5 to 6 h". The rate of acrylamide depletion in the initial stages of polymerization (10 to 15% conversion) was higher than that at the next stages [136].

The free energy of hydrogel with weak chargers can be expressed as a sum of the following terms: the elastic free energy, interaction of the monomer units, the energy gained from ion pairing [137].

By determining the rate of graft polymerization at different temperatures, in the following section, the effect of polymerization temperature on different grafting parameters will be discussed as some investigations have been summarized in Table 7.

Singh et al. studied the effect of the grafting temperature of the acrylonitrile onto starch on the grafting percent and the grafting efficiency for both conventionally and microwave hydrogel preparation techniques as summarized in Table 6 [87]. Using starch (0.1 g/25 mL), acrylonitrile (0.17 M), total reaction volume 25 ml, %G and %E was almost nil using microwave with different initiator

Table 6 A summary of some investigation of the effect of polymerization temperature on the grafting parameters

Polysaccharide	Reaction condition				%G	%E	Refs.
	M/P	Initiator	T (°C)	Time			
Guar gum	2.84	MW	63	20 S	120	57	[119]
	2.84	KPS	60	80 min	140	63	[119]
	2.84	MW/KPS	60	13 S	190	76	[119]
	2	CAN	70	5 h	160	62	[129]
	3.5	CAN	70	5 h	304	75	[129]
	5	CAN	70	5 h	480	83	[129]
	5	CAN	30	24 h	350	58	[130]
Xanthan gum	1.1	BrO_3^-/Fe^{2+}	35	2 h	50	70	[131]
	2.2	BrO_3^-/Fe^{2+}	35	2 h	82	57	[131]
Acacia gum	1	APS	70	2 h	95	47	[132]
	3	APS	70	2 h	278	74	[132]
	5	APS	70	2 h	459	74	[132]
Alg	3.4	CAN	27	24 h	785	94	[133]
Ch	2.84	MW	–	70 S	269	96	[134]
	2.84	KPS	35	1 h	82	47	[134]
Poly(*N*-isopropylacrylamide)	1.5	MW	70	30 min	–	99	[135]

Table 7 Values of the initial rates of grafting (R_g) at various temperatures

Temperature (°C)	$Rg \times 10^5$ (mol/L s)	$1/T \times 10^3$ (K^{-1})	Ln Rg + 10
20	5.56	3.41	0.37
30	6.89	3.3	0.42
40	7.11	3.19	0.450
50	8.31	3.09	0.605

concentration and different polymerization temperatures, while using the conventional method the obtained %G and %GE were 225 and 98%, respectively.

Athawale et. el., [138] studied the polymerization temperature consequence on the grafting of acrylamide onto maize starch. The applied temperature for graft copolymerization was ranger between 30–50°. Increasing reaction temperature has an adverse effect on % GE as well as % G. The % GE decreases from 20% at 30 °C to 8% at 50 °C. While studying the effect of temperature, with the concentrations of monomer and initiator fixed, the decrease in % GE can be explained on the basis of increased rate of homo-polymerization.

Butylacrylamide "BAM" has been grafted conventionally into starch using CAN as an initiator, the initial rates of grafting (R_g) calculated from the reaction temperatures as shown in Table 7. The slope of in R_g vs. 1/T shows that the overall activation energy for grafting of BAm onto starch is 5.67 kJ/mole within temperature ranged from 20 to 50 °C. The activation energy is in good agreement with the reported values for comparable systems Reaction conditions: Starch = 1 g, [BAM] = 0.02 mol/L, [CAN] = 0.91×10^{-3} mol/L in 200 ml solution [122].

Scaling up of Hydrogel Production

Scale up is increasing in the starting raw materials for producing the hydrogel in bench, pilot or industrial scale. Throughout the hydrogel polymerization, heat is released, which is entrapped in the reacting mix due to the insulation property of the pores inside the forming hydrogel structure. To release the heat from the reaction moisture, and the adequate surface should be provided, which is determined by the aspect ratio of the container (diameter/height ratio).

In this section, selected studies and related aspects for the hydrogel production and financial calculations on industrial hydrogel mass production will be illustrated and discussed.

Hydrogel microfibers have considered as a biomaterial to spatiotemporally bio mimic 1D native tissue such as nerves or muscles, which have assembled hierarchically and have the response to external stimuli. Poly(ethylene glycol diacrylate) "PEGDA" oligomer in large scale hydrogel has been produced in the shape of microfibers, a dynamic-crosslinking-spinning (DCS) method is established for direct fabrication of fibers with size-controllable by adjusting the spinning parameters The diameter of fibers can be precisely controlled Anisotropic swelling property is also dependent on inhomogeneous structure generated in spinning process. Comparing with bulk hydrogels, the resulting fibers exhibit superior rapid water adsorption property, which can be

attributed to the large surface area/volume ratio of fiber. This novel DCS process is one-step technology appropriate for large-scale production of anisotropic hydrogel fibers which has a promising application in the area such as biomaterials.

The illustration of DCS is shown in Fig. 15. In this spinning system, PEGDA solution did not dissolve immediately when extruded into the water bath Fig. 15-(Sect. A), but a fiber shape has been formed and aggregate due to the PEGDA solution viscoelasticity. In order to help the monomer rapidly polymerization and hence formed cross-linked polymer and keep the fiber shape during extrusion instantaneously, the UV irradiation has utilized, the PEGDA monomer phase turns to a continuous fiber. Then, a roller was used for fiber collection and provided the drawing force to reduce the fiber diameter Fig. 15-(Sect. B) took place before the UV irradiation point, which was due to the fact that the formed cross-linked structure (Fig. 15-Sect. C) limits the hydrogel network deformation [139].

Marwa et al. Study the starch grafted acrylamide (St-g-Am) hydrogel manufacturing processes using three different grafting techniques (conventional, MW, and UV irradiation) in the pilot plant scale (100 kg/day). Moreover, economics and environmental aspects are addressed using the investigated manufacturing procedures [81].

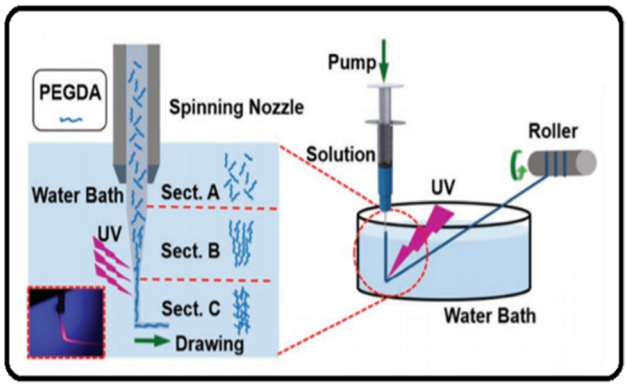

Fig. 15 Fabrication of hydrogel fibers via the dynamic-crosslinking-spinning

Preliminary cost pointers have been done for producing 100 kg/day (30 ton/year) of St-g-Am hydrogel based on the guide of published data [67, 140], budget offers, and Aspen Icarus Process Evaluator Program (version 2006). The author estimated a cost comparison among the three used techniques (conventional, MW, and UV) based on the available cost data. The used equipment specifications and costs are shown in Tables 8 and 9, respectively. Further, annual and unit costs are shown in Table 10. The equipment cost are 1761×10^3, 1526×10^3, and 1474×10^3 (US$) while, the one-ton cost was found to be (US$) 14,250, 12,800, and 12,400 for conventional, MW, and UV hydrogel mini production lines, respectively.

Maaly et. al. [141] investigate an experimental research on the pilot plant scale for the synthesis of an innovative superabsorbent hydrogel. Both powder and gel past hydrogel have been produced using three processes: starch phosphorization, polymerization of a vinyl monomer onto the starch phosphate using either APS or sodium bisulphite (APS/SBS) redox system, or CAN as initiators and finally by incomplete hydrolysis of the copolymerized product. The economic study for producing 3600 ton/year covered two production lines process designed. The total fixed capital costs of

Table 9 Equipment and installation costs for hydrogel production alternatives (100 kg/day)

Item	Cost (US $ 1000)		
	Conventional	MW	UV
Up-stream section	307	307	307
Down-stream section	1147	1147	1147
Reactor system	307	72	20
Total equipment cost	1761	1526	1474
Total installation cost[a]	6492	5539	5350.6

[a]Lang factor is 3.63 [81]

Table 8 Equipment specifications for hydrogel production alternatives

Item	Specifications
Conventional grafting reactor	Stirred tank reactor, 150 L, SS 316 with jacket and reflux condenser, 5.5 KW
MW grafting reactor	Industrial microwave, chamber content: 670 L, 5 KW
UV grafting reactor	Mercury UV light control system, 254–365 nm, 0.5 KW
Hydrolyzed	Stirred tank reactor, 150 L, SS 316 with heating and cooling jacket, 7.5 KW
Rotary filler (1)	Rotary vacuum filter, 8 m^2 filtration area with vacuum pump and filter cake washing system, 5.5 KW
Rotary filler (2)	Rotary vacuum filter, 10 m^2 filtration area with vacuum pump and filter cake washing system, 5.5 KW
Washing tank (1) and (2)	Stirred tank SS 304 1000 L ribbon mixer and variable speed, 7.5 KW
Dryer	Vacuum tray dryer with gas fuel burner, air fans and cyclone for dust collection
Solvent recovery unit	Ethanol recovery unit (250 L/h): distillation column, boiler with electric heater, condenser, 5.5 KW
Storage tanks	SS 316 tanks

Table 10 Annual production and unit costs for hydrogel production (100 kg/day)

Item	Cost (US $ 1000)		
	Conventional	MW	UV
Deprecation cost	317	275	265
Energy cost[a]	18.6	16.5	14.4
Material cost	92	92	92
Total annual cost	427.6	383.5	371
Unit cost (US $ 1000 l ton)	14.25	12.8	12.4

[a]Energy cost ¼ 5.5 cents/KW

hydrogel superabsorbent in both the powder and the gel past forms were investigated. The estimated costs for production of powder and gel paste hydrogel forms, using APS/SBS redox system, were 25,000 LE/ton and 5000 LE/ton respectively, while those using CAN initiator were 29,000 LE/ton and 24,000 LE/ton, respectively [67].

Total fixed direct and indirect costs represent the capital necessary for the installed process equipment with all auxiliaries that are needed. Values of the various percentages used in estimating the fixed-capital investment (F.C.I.) are demonstrated in Table 11.

The different cost factors, directly related to the manufacturing operation are existing in Table 12. Raw materials (commercial grade):maize starch (4000 LE/ton), di-hydrogen sodium phosphate (5000 LE/ton), di-sodium hydrogen phosphate (5000 LE/ton), Egyptology (25 LE/kg), acrylonitrile (12 LE/kg), APS (28 LE/kg), sodium bisulphite (6 LE/kg), 48% aqueous sodium hydroxide (2000 LE/ton), methanol (5000 LE/ton) and 30% aqueous phosphoric acid (7000 LE/ton).

Table 11 Estimation of Fixed Capital Investments for Hydrogel Production Lines

Component	Powder form, cost in 1000 LE		Gel form, cost in 1000 LE	
	APS/SBS process	CAN process	APS/SBS process	CAN process
Purchased equipment cost (E)	5756	4242	2839	3992
Purchased equipment installation (32% E)	1842	1357	909	1277
Instrumentation and control (20% E)	1151	848	568	798
Piping (32% E)	1842	1357	909	1277
Electric equipment and materials (10%E)	576	424	284	399
Building (including services) (20% E)	1,151	848	568	798
Services facilities and Yard improvement (40% E)	2,302	1273	1136	1198
Land (6% E)	345	255	170	240
Total direct cost (D)	14,965	10,604	7383	9979
Indirect cost				
Engineering and Supervision (5% D)	748	530	369	499
Construction expenses and Contractor's fee (7% D)	1047	530	517	698
Contingency (10% F.C.I)	1862	1296	919	1242
Fixed capital investment (F.C.I)	18,622	12,960	9188	12,418
Working capital (15% T.C.I)	3286	2287	1621	2191
Total capital investment (T.C.I)	21,908	15,247	10,809	14,609

Table 12 Estimation of Annual Operating Costs for Hydrogel Production Lines

Component	Powder form, cost in 1000 LE		Gel form, cost in 1000 LE	
	APS/SBS process	CAN process	APS/SBS process	CAN process
Total raw material cost	82,306	102,232	49,816	93,946
Utilities	3087	437	1571	401
Maintenance (3% for buildings including concrete storage tanks and 5% for other installed equipment)	307	225	159	180
Operating labor	900	750	500	675
Labour charges (10% of operating labor)	90	75	50	68
Administrative expenses (20% of operating lab our)	180	150	100	135
Total annual operating cost	86,216	103,869	52,196	95,405

Table 13 Production cost estimates for hydrogel "HGS" and hydrogel enriched with potassium "ESRF" production (10 ton/day)

Annual Cost ($1000/year)		
Cost item	HSG (10 ton/day)	ESRF (10 ton/day)
1. Operating cost		
1.1 Chemicals and materials	6212.2	1147.7
1.2 Electricity	24	14.4
1.3 Maintenances	17.7	7.8
1.4 Labour	45	30
1.5 Others	669.9	133.3
Total operating cost	6998.8	1333.2
2. Depreciation	50.4	22
Total production cost	7049.2	1355.2
Cost per ton($/t)	2349.7	451.7

Talaat et. al. conducted a preliminary techno-economic study for small scale industrial superabsorbent hydrogel production (10 ton /day) affordable gels to improve the farming economics for a. The estimated cost of the prepared hydrogel is about 770 $/ton. It is perceived that the economics of the production could be significantly improved if cheap substrates are used (e.g. waste food grains and other polysaccharide sources) as illustrated in Table 13 [67, 141].

Conclusions

Nowadays, many hydrogel based networks have been prepared and modified to meet the needs of applications in various fields. The evolution of the design of new macromolecular drug delivery systems and biomaterials has been astonishing. Enormous improvements have been made in the hydrogels properties techniques. The favorable property of these hydrogels is either ability to swell when immersed in an aqueous solution. This review demonstrates the literature concerning the classification of hydrogels on different bases, some important properties, and characteristics of these products and technical feasibility of their use. It also involved technologies used for hydrogel production together illustrating the advantages and disadvantages of each technique. An innovated summarization of the kinetics and thermodynamics related to the polymerization/grafting of the hydrogel preparations methods were also discussed in some details.

References

1. Calo E, Khutoryanskiy VV (2015) Biomedical applications of hydrogels: a review of patents and commercial products. Eur Polym J 65:252–267
2. Prinsy Rana G, Ganarajan, Kothiyal P (2015) review on preparation and properties hydrogel formulation. World J Pharm Pharm Sci 4(12):43–57
3. Kulicke WM, Nottelmann H (1989) Structure and swelling of some synthetic, semisynthetic, and biopolymer hydrogels. Adv Chem 223:15–44
4. Peppas NA (1987) Hydrogels in medicine and pharmacy, vol 3. CRC Press, Boca Raton
5. Mathur MA, Shailender KM, Scranton A (1996) Methods for synthesis of hydrogel networks: a review. J Macromol Sci Polym Rev 36 (1996):405–430
6. Bouranis DL, Theodoropoulos AG, Drossopoulos JB (1995) Designing synthetic polymers as soil conditioners. Commun Soil Sci Plant Anal 26,:1455–1480
7. Ichikawa T, Nakajima T, Super absorptive polymers (from natural polysaccharides and polypeptides), In: Polymeric Materials Encyclopedia, Salamone (Ed), CRC, Boca Raton (Florida), 8051–8059, 1996
8. Po R (1994) Water-absorbent polymers: a patent survey. J Macromol Sci Rev Macromol Chem Phys 34:607–662
9. Chin YR, Al-Dayel A, Acrylic acid based superabsorbent polymer, Process economics program review No 85-1-2, Stanford Research Institute, SRI International, Dec. 1985
10. Buchholz FL, Graham AT (1998) Modern superabsorbent polymer technology, Ch 1–7, WileyVCH, New York
11. Brannon-Peppas L, Harland RS (1990) Absorbent Polymer Technology, Ch 1–4, Elsevier, Amsterdam
12. Shalviri A, Liu Q, Abdekhodaie MJ, Wu XY (2010) Novel modified starch–xanthan gum hydrogels for controlled drug delivery: synthesis and characterization. Carbohydr Polym 79(4):898–907
13. El-Sayed M, Sorour M, Abd El Moneem N, Talaat H, Shalaan H, El Marsafy S (2011) Synthesis and properties of natural polymers -grafted- acrylamide. World Appl Sci J 13(2):360–368
14. Straccia MC, d'Ayala GG, Romano I, Oliva A, Laurienzo P (2015) Alginate hydrogels coated with chitosan for wound dressing. Mar Drugs 13:2890–2908
15. El-Sayed M, Sorour M, El Moneem NA, Talaat H, Shalaan H, El Marsafy S (2013) Kinetics of Free Radical Grafting of Acrylamide onto a Blend of Starch/chitosan/alginate. Carbohydr Polym 98:460–464
16. Benamer S, Mahlous M, Boukrif A, Mansouri B, Youcef SL (2006) Synthesis and characterization of hydrogels based on poly(vinyl pyrrolidone). Nuclear Instrum Methods Phys Recourses 12:284–290
17. Güvena O, Sena M, Karadag E, Sarayd D (1999) A review on the radiation synthesis of copolymeric hydrogels for adsorption and separation purposes. Radiat Phys Chem 56:381–386
18. Carenza M (1992) Recent achievements in the use of radiation polymerization and grafting for biomedical applications. Radiat Phys Chem 39:485
19. Pal K, Banthia AK, Majumdar DK (2009) Polymeric hydrogels: characterization and biomedical applications—a minireview. Design Monomers Polym 12:197–220
20. Jin C, Zhou D, Liu H (1985) Huaxue Shijie 26(11):415 Chem. Abstr. 104 89575c 1986
21. Apichart H, Gobwute R, Chamnan R (2017) Preparation of hydroxyapatite hydrogel for bone-like materials via novel self-initiated photocatalytic polymerization. Mater Lett 193:142–145
22. Chien-Chi Lin AT (2006) Metters hydrogels in controlled release formulations: network design and mathematical modeling. Adv Drug Deliv Rev 58:1379–1408
23. Berlin Ad A, Kislenko VN (1992) Kinetics and mechanism of radical graft polymerization of monomers onto polysaccharides. Prog Polym Sci 17:765–825
24. Brydon A, Burnett GM, Cameron GG (1974) Free-radical grafting of monomers to polydienes. II. Kinetics and

mechanism of styrene grafting to polybutadiene. Journal of Polymer Science Polymer Chemistry Ed 12(5):1011–1021
25. Lutfor Mr S, Silong WMdZWan, Yunus M, Zaki Ab, Rahman (2000) Mansor Ahmad, Md Jelas Haron, Kinetics and Mechanism of Free Radical Grafting of Methyl Acrylate onto Sago Starch. J Appl Polym Sci 77:784–791
26. Enas M. Ahmed. H (2015) Preparation, characterization, and applications: a review. J Adv Res 6(2):105–121
27. Maitra J, Shukla VK (2014) Crosslinking in hydrogels —a review american. J Polym Sci 4(2):25–31
28. Hennink WE, Nostrum CF van (2002) Department of Pharmaceutics, Utrecht University. Adv Drug Deliv Rev 54:13–36
29. Yokoyama F, Masada I, Shimamura K, Ikawa T, Monobe K (1986) Morphology and structure of highly elastic poly(vinyl alcohol) hydrogel prepared by repeated freezing-and-melting. Colloid Polym Sci 264:595–601
30. Christensen L, Breiting V, Vuust J, Hogdall E (2006) Adverse reactions following injection with a permanent facial filler polyacrylamide hydrogel (aquamid): causes and treatment. Eur J Plast Surg 28:464–471
31. Gong CY, Shi S, Dong PW, Kan B, Gou ML, Wang XH et al (2009) Synthesis and characterization of PEG-PCL-PEG thermosensitive hydrogel. Int J Pharm 365:8999
32. Kim B, Peppas NA (2003) Poly(ethylene glycol)-containing hydrogels for oral protein delivery applications. Biomed Microdevices 5:333–341
33. Lugao AB, Rogero SO, Malmonge SM (2002) Rheological behavior of irradiated wound dressing poly (vinyl pyrrolidone) hydrogels. Radiat Phys Chem 63:543–546
34. Lipatov YS (2002) Polymer blends and interpenetrating polymer networks at the interface with solids. Progress Polym Sci 27:1721–1801
35. Nilimanka D (2013) Preparation methods and properties of hydrogel: a review. Int J Pharm Pharm Sci 5(3):112–117
36. Sonali BD, Ganesh VD, Sandeep ST, Atul SB, Avinash PT, Hrishikesh AJ, Rajendra NP (2017) Hydrogel new trend in drug delivery system. Rev Eur J Pharm Med Res 4(1):503–512
37. Prinsy Rana G, Ganarajan, Kothiyal P (2015) Review on preparation and properties hydrogel formulation. World J Pharm Pharm Sci 4(12):1069–1087
38. Dwivedi S, Khatri P, Mehra GR, Kumar V (2001) Conceptual hydrogel-A, overview. Int J Pharm Biol Arch 2(6):1588–1597
39. Tsukasa M, Yuuki T, Sachiko A, Takahiko I, Akie H, Keiko E (2010) Role of boric acid for a poly (vinyl alcohol) film as a crosslinking agent: melting behaviors of the films with boric acid Polymer 51(23):5539–5549
40. Kamoun EA, Kenawy ER, Chen X (2017) A review on polymeric hydrogel membranes for wound dressing applications: PVA-based hydrogel dressings. J Adv Res 8:217–233
41. Kawase M, Michibayashi N, Nakashima Y, Kurikawa N, Yagi K, Mizoguchi T (1997) Application of glutaraldehyde-crosslinked chitosan as a scaffold for hepatocyte attachment. Biol Pharm Bull 20(6):708–710
42. Hongbo T, Yanping L (2012) Sun Min and Wang Xiguang preparation and property of crosslinking guar gum. Polym J 44:211–216
43. López-Cebral R, Paolicelli P, Romero-Caamaño V, Seijo B, Casadei MA (2013) Sanchez ASpermidine-crosslinked hydrogels as novel potential platforms for pharmaceutical applications. J Pharm Sci 102(8):2632–2643
44. Xu Xu Y, Weng Lu, Xu (2013) Hao Chen Sustained release of avastin® from polysaccharides crosslinked hydrogels for ocular drug delivery. Int J Biol Macromol 60:272–276
45. Raut NS, Deshmukh PR, Umekar MJ, Kotagale NR (2013) Zinc crosslinked hydroxamated alginates for pulsed drug release. Int J Pharm Investig 3(4):194–202
46. Taha MO, Nasser W, Ardakani A, Alkhatib HS (2008) Sodium lauryl sulfate impedes drug release from zinc-crosslinked alginate beads: switching from enteric coating release into biphasic profiles Int J Pharm 350(1–2):291–300. (Epub 2007 Sep 14)
47. Coviello T, Grassi M, Lapasin R, Marino A, Alhaique F (2003) Scleroglucan/borax: characterization of a novel hydrogel system suitable for drug delivery. Biomaterials 24(16):2789–98
48. Vinay MP, Navneet K, Dataset on the superabsorbent hydrogel synthesis with SiO2 nanoparticles and role in water restoration capability of agriculture soil, Dta In Brief,(2017) article in press
49. Sherr AE, Swift AM (1965) Crosslinked polyacrylamide gel as a dehydrating agent. J Appl Polym Sci 99(12):3929–3934
50. Abdel-Halim ES, Al-Deyab SS (2011) Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion Carbohydr Polym 86(3):1306–1312
51. Marwa M, El-Sayed GhA, Al Bazedi MA, Abdel-Fatah (2017) Development of a novel hydrogel adsorbent for removal of reactive dyes from textile effluents. Res J Pharm Biol Chem Sci 8(3):945–955
52. Raneque MR, Rodriguez A, Carlos PC (2013) Hydrogel wound dressing preparation at laboratory scale by using electron beam and gamma radiation. Nucleus 53:24–31
53. Elizabeth PS, David QG, Briza NZ, Adriana GR, Maria GN, Jose MC (2008) Controlled release of model substances from ph-sensitive hydrogels. J Mexican Chem Soc 52(4):272–278
54. Oguz O, Vildan O (2002) Temperature sensitive poly(N-t-butylacrylamide-coacrylamide) hydrogels: synthesis and swelling behavior. Polymer 43:5017–5026
55. Saleem MA, Azharuddin SK, Ali S, Patil CC (2010) Studies on different chitosan polyelectrolyte complex hydrogel for modified release of diltiazem hydrochlorid. Int J Pharm Pharm Sci 2(4):6467–6479
56. Jennifer JK, William FM (2008) Thermo-responsive hydrogels as a new ocular drug delivery platform to the posterior segment of the eye. Trans Am Ophthalmol Soc 106:206–214
57. Anseth KS, Aimetti AA, Machen AJ (2009) Poly(ethylene glycol) hydrogels formed by thiol-ene photopolymerization for enzyme-esponsive protein delivery. Biomaterials 30(30):1–7
58. Diethelm J, Johanna B (2008) Electrochemically produced responsive hydrogel films: Influence of added salt on thickness and morphology. J Colloid Interface Sci 326:61–65
59. Richard G, Jun C, Haesun P, Kinam P (2000) pH sensitive of fast responsive super porous hydrogels. J Biomater Sci Polym Edn 11(12):1371–1380
60. Xuefeng Z, Hongrui J (2008) Tunable liquid microlens actuated by infrared light responsive hydrogel. Appl Phys Lett 93:151101–151113
61. de Leede LGJ, de Boer AG, Ptirtzgen E (1986) Rate controlled rectal drug delivery in man with a hydrogel preparation. J Control Release 4:17–24
62. Sundaram G, Tao W, Chunxiang C (2006) Swelling of pH-sensitive chitosan–poly (vinyl alcohol) hydrogels. J Appl Polym Sci 102:4665–4671
63. Sudaxshina M (2003) Electro-responsive drug delivery from hydrogels. J Control Release 92:1–17
64. Ruta M, Zuzana C, Zdenka S (2003) Stimuli-sensitive hydrogels in controlled and sustained drug delivery. Medicinal 39(2):19–24
65. Kristi SA, Alex AA, Alexandra JM (2009) Poly(ethylene glycol) hydrogels formed by thiol-ene photo-polymerization for enzyme responsive protein delivery. Biomaterials 30(30):1–7
66. Fariba G, Ebrahim VF (2009) Hydrogels in controlled drug delivery systems. Iran Polym J 18(1):63–88
67. Talaat H, Sorour M, Aboulnour A, Shalaan H (2008) Development of multi-component fertilizing hydrogel with relevant techno-economic indicators. Am Eurasian J Agric Environ Sci 3:764–770

68. Pairote K, Patchareeya K (2017) Research article superabsorbent polymer based on sodium carboxymethyl cellulose grafted polyacrylic acid by inverse suspension polymerization, Int J Polym Sci 2017:1–6
69. Laftah WA, Hashim S, Ibrahim AN (2011) Polymer hydrogels: a review. Polym Plastics Technol Eng 50:1475–1486
70. Handbook Of Radical Polymerization (2002) Krzysztof Matyjaszewski Carnegie Mellon University, Pittsburgh, Pennsylvania. In: Davis TP. University of New South Wales. By John Wiley and Sons, Inc., Hoboken, Sydney
71. Hu Y, Daoud WA, Cheuk KKL, Lin CSK (2016) Newly developed techniques on polycondensation, ring-opening polymerization and polymer modification: focus on poly(lactic acid). Materials 9:133–147
72. Iwona G, Helena J (2010) Review: Synthetic polymer hydrogels for biomedical applications. Chem Chem Technol 4(4):297–304
73. Varghese JS, Chellappa N, Fathima NN (2014) Gelatin-carrageenan hydrogels: role of pore size distribution on drug delivery process. Colloids Surf B Bio interfaces 113:346–351
74. Zunyang S, Feng L, Hui G, Yunfeng X, Quanjuan F, Dapeng L (2017) Combination of nisin and ε-polylysine with chitosan coating inhibits the white blush of fresh-cut carrots. Food Control 74:34–44
75. Kamila S, Radosław AW, Alicja KO, Janusz MR, Piotr U (2017) Radiation synthesis of biocompatible hydrogels of dextran methacrylate, Radiat Phys Chem 142:115–120
76. Kumar A, Singh K, Ahuja M (2009) Xanthan-g-poly(acrylamide): microwave-assisted synthesis, characterization and in vitro release behavior Carbohydr Polym 76:261–267
77. Ling H, Maolin Z, Jing P, Jiuqiang L, Genshuan W (2007) Radiation-induced degradation of carboxymethylated chitosan in aqueous solution. Carbohydr Polym 67(3):305–312
78. Elif AB, Senem C, Murat K, Muruvvet Y (2011) Synthesis, characterization and in vitro antimicrobial activities of boron/starch/polyvinyl alcohol hydrogels. Carbohydr Polym 83(3):1377–1383
79. Sanju F, Manmohan K, Lalit V (2004) Radiation synthesis of superabsorbent poly(acrylic acid)–carrageenan hydrogels. Radiat Phys Chem 69(6):481–486
80. Taghizadeh M, Mehrdad A (2006) Kinetic study of graft polymerization of acrylic acid and ethyl methacrylate onto starch by ceric ammonium nitrate. Iranian J Chem Chem Eng 25:1–11
81. Sorour MH, El Sayed MM, Abd El Moneem NM, Talaat HA, Shaalan HF, El Marsafy SM (2013) Process and financial considerations pertinent to hydrogel manufacture. Starch 65(5–6):527–534
82. Wissam F, Richard V, Nathalie M, Mohamed T, Frederic B, Ali A (2017) Polysaccharides and lignin based hydrogels with potential pharmaceutical use as a drug delivery system produced by a reactive extrusion process, Int J Biol Macromol 104:564–575
83. Charoen N, Toha W, Azizon K, Suda K (2010) Preparation of cassava starch-graft-polyacrylamide superabsorbents and associated composites by reactive blending. Carbohydr Polym 81(2):348–357
84. Willett J, Finkenstadt V (2006) Initiator effects in reactive extrusion of starch–polyacrylamide graft copolymers. J Appl Polym Sci 99:52–58
85. Victoria L, Julious L (2005) Reactive extrusion of starch-polyacrylamide graft copolymers: effects of monomer/starch ratio and moisture content. Macromol Chem Phys 206:1648–1652
86. Jadranka ŽK, Aleksandra NR, Milica V (2017) Gamma irradiation induced in situ synthesis of lead sulfide nanoparticles in poly(vinyl alcohol) hydrogel. Radiat Phys Chem 130:282–290
87. Singh V, Tiwari A, Pandey S, Singh SK (2007) Peroxydisulfate initiated synthesis of potato starch-graft-poly(acrylonitrile) under microwave irradiation. Express Polym Lett 1(1):51–58
88. Nuchter M, Ondruschka B, Bonrath W, Gum A (2004) Microwave assisted synthesis—a critical technology overview. Green Chem 6:128–141
89. Singh V, Tripathi D, Tiwari A, Sanghi R (2005) Microwave promoted synthesis of chitosan-graft-polyacrylonitrile. J Appl Polym Sci 95:820–825
90. Singh V, Tiwari A, Pandey S, Kumar S (2006) Microwave-accelerated synthesis and characterization of potato starch-g-polyacrylamide. Starch/Stärke 58:536–543
91. Singh V, Tiwari A, Pandey S, Singh SK (2006) Microwave accelerated synthesis and characterization of potato starch-g-polyacrylamide. Starch-Starke 58:536–543
92. Singh V, Tiwari A, Tripathi DN, Sanghi R (2004) Microwave assisted synthesis of guar-g-polyacrylamide. Carbohydr Polym 58:1–6
93. Singh V, Tripathi D, Tiwari A, Sanghi R (2006) Microwave synthesized chitosan-graft-poly (methylmethacrylate): an efficient Zn2CI binder Carbohydr Polym 65:35–41
94. Singh V, Tiwari A, Pandey S, Singh S (2007) Peroxydisulfate initiated synthesis of potato starch-graft-poly(acrylonitrile) under microwave irradiation. Express Polym Lett 1(1):51–58
95. Kyung H, Ning L, Gang S (2009) ,UV-induced graft polymerization of acrylamide on cellulose by using immobilized benzophenone as a photo-initiator. Eur Polymer J 45:2443–2449
96. Jenkins D, Hudson S (2001) Review of vinyl graft copolymerization featuring recent advances toward controlled radical-based reactions and illustrated with chitin/chitosan trunk polymers. Chem Rev 101:3245–3273
97. Lee J, Kumar R, Rozman H, Azemi B (2005)"Pasting, swelling and solubility properties of UV initiated starch-graft-poly(AA)". Food Chem 91:203–211
98. Mubarak A, Bhattacharia S, Kader M, Bahari K (2006) Preparation and characterization of ultra violet (UV) radiation cured biodegradable films of sago starch/PVA blend. Carbohydr Polym 63:500–506
99. Hedin J, Otlund A, Nyden M (2010) UV induced cross-linking of starch modified with glycidyl methacrylate. Carbohydr Polym 79:606–613
100. Taghizadeh M, Mafakhery S (2001) Kinetics and mechanism of graft polymerization of acrylonitrile onto starch initiated with potassium persulfate. J Sci Islamic Republic of Iran 12:333–338
101. Lavallee C, Lemay G, Leborgne A, Spassky N, Robert E (1984) Prud'homme, synthesis and polymerization of racemic and optically active β-monosubstituted β-propiolactones. Macromolecules 17:2512–2526
102. Liming Z, Jianping G, Ruchuan T, Jiugao Y, Wei W (2003) Graft mechanism of acrylonitrile onto starch by potassium permanganate. J Appl Polym Sci 88:146–152
103. Athawale V, Rathi S (1999) Polymer reviews publication details, including instructions for authors and subscription information: graft polymerization: starch as a model substrate. Polym Rev 39(3):445–480
104. Taghizadeh M, .Khosravy M (2003) Kinetics and mechanism of graft copolymerization of vinyl monomers (acrylamide, acrylic acid, and methacrylate) onto starch by potassium dichromate as redox initiator. Iran Polym J 12:497–505
105. Taghizadeh M, Mafakhery S (2001) Kinetics and mechanism of graft polymerization of acrylonitrile onto starch initiated with potassium persulfate. J Sci Iranian Polym J 12:333–338
106. Gugliemelli LA, Swanson CL, Doane WM (1973) Kinetics of grafting acrylonitrile onto starch. J Polym Sci Polym Chem Ed 11(10):2451–2465
107. Mingzhu L, Rongshi C, Jingjia W, Cheng M (1993) Graft copolymerization of methyl acrylate onto potato starch initiated by ceric ammonium nitrate. J Polym Sci Part A Polym Chem 31(13):3181–3186

108. Pan S, Li G, Wang Z, Wang Z (1994) Polymerization: starch as a model substrate. Shiyuo Huagong 22(3):177–189
109. Sandle NK, Singh OP, Verma IK (1987) Graft copolymerization of starch with alkylene methacrylates. Die Angewandte Makromolecular Chemis 154(1):87–97. http://www.tandfonline.com/doi/full/10.1081
110. Egboh SHO, Jinadu B, Egboh SHO, Jinadu B (1988) Angew Makromol Chem 163:93. Angew Makromol Chem 1988; 163:93–99
111. Cutié SS, Smith PB, Henton DE, Staples TL, Powell C (1997) Acrylic acid polymerization kinetics. J Polym Sci 35(13):2029–2047
112. Berlin Ad A, Kislenko VN (1992) Kinetics and mechanism of radical graft polymerization of monomers on to polysaccharides. Progress Polym Sci 17:765–825
113. Lili W, Yongshen X (2006) Graft copolymerization kinetics of ethyl acrylate onto hydroxypropyl methylcellulose using potassium persulphate as initiator in aqueous medium. Iran Polym J 15(6):467–475
114. Kislenko VN (1999) Kinetics of particle formation at the graft polymerization of methylacrylate onto hydroxyethyl cellulose. J Colloid Interface Sci 209(1):136–141
115. Abdelgawad R, George O (1977) Kinetics of diffusion-free radiation graft polymerization of styrene onto polyethylene. J Polym Sci 15(2):468–488
116. Huacai Ge, Wang S (2014) Thermal preparation of chitosan-acrylic acid superabsorbent: Optimization, characteristics and water absorbency. Carbohydr Polym 113:296–303
117. Nada MAA, Alkady MY, Fekry HM (2007) Synthesis and characterization of grafted cellulose for use in water and metal ions sorption, BioResources 3(1):46–50
118. Lutfor MR, Haron ASidik,J, Rahman MZA, Ahmed M (2003) Modification of sago starch by graft copolymerization. Effect of reaction conditions on grafting parameters. Int J Polym Mater 52:189–201
119. Singha V, Tiwaria A, Narayan DT, Sanghib R (2004) Microwave assisted synthesis of Guar-g-polyacrylamide. Carbohydr Polym 58:1–6
120. Athawale VD, Lele V (2000) Syntheses and characterisation of graft copolymers of maize starch and methacrylonitrile. Carbohydr Polym 41:407–416
121. Jianping G, Jiugao Y, Wei W, Liming C, Ruchuan T (1998) Graft copolymerization of starch–AN initiated by potassium permanganate. J Appl Polym Sci 68:1965–1972
122. Fares MM, El-faqeeh AS, Osman ME (2003) Graft copolymerization onto starch–I. Synthesis and optimization of starch grafted with N-tert-butylacrylamide copolymer and its hydrogels. J Polym Res 10:119–125
123. Hashem A, Afifi MA, El-Alfy EA, Hebeish A (2005) Synthesis, characterization and saponification of poly (AN)-starch composites and properties of their hydrogels. Am J Appl Sci 2(3):614–621
124. Sugahara Y, Ohta T (2001) Synthesis of starch graft-polyacrylonitrile hydrolyzate and its characterization. J Appl Polym Sci 82:1437–1443
125. Hwang TS, Park JW (2003) UV-induced graft polymerization of polypropylene-g-glycidyl methacrylate membrane in the vapor phase. Macromol Res 11(6):,495–500
126. Suetoh Y, Shibayama M (2000) Effects of non-uniform solvation on thermal response in poly(Nisopropylacrylamide) gels. Polymer 41:505–510
127. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca
128. da Silva DA, de Paula RC, Feitosa JPA (2007) Graft copolymerization of acrylamide onto cashew gum. Eur Polym J 43:2620–2629
129. Toti U, Aminabhavi TM (1994) Modified guar gum matrix tablet for controlled release of diltiazem hydrochloride. J Control Release 95:567–577
130. Deshmukj SR, Singh RP (1987) Drag reduction effectiveness, shear stability and biodegradation resistance of guar gum based graft copolymers. J Appl Polym Sci 33:1963–1975
131. Behari K, Pandey PK, Kumar R, Taunk K (2001) Graft copolymerization of acrylamide onto xanthan gum. Carbohydr Polym 46:185–189
132. Toti US, Soppimath KS, Mallikarjuna NN, Aminabhavi TM (2004) Acrylamide grafted acacia gum polymer matrix tablets as erosion-controlled drug delivery systems. J Appl Polym Sci 93:2245–2253
133. Tripathy T, Singh RP (2001) Characterization of polymeracrylamide-grafted sodium alginate: a novel polymeric flocculent. J Polym Sci 81:3296–3308
134. Singh V, Tiwari A, Tripathi DN, Sanghi R (2006) Microwave enhance synthesis of chitosan-grafted polyacrylamide. Polymer 47:245–260
135. Zhenxia Z, Zhong L, Qibin X, Hongxia X, Yuesheng L (2008) Fast synthesis of temperature-sensitive PNIPAAm hydrogels by microwave irradiation. Eur Polym J 44:1217–1224
136. Varma IK, Singh OP, Sandle NK (1983) Graft-copolymerization of starch with acrylamide, I. Die Angewandte Macromol Chem 119:I83–I192
137. Aykut E, Monica O, de la Cruz (2015) Energy conversion in polyelectrolyte hydrogels. ACS Macro Let 4(8):857–886
138. Athawale VD, Vidyagauri M (1998) Graft copolymerization onto starch 3: grafting of acrylamide using ceric ion initiation and preparation of its hydrogels. Starch 50(10):426–431
139. Hou K, Wang H, Lin Y, Chen S, Yang S, Cheng Y, Hsiao BS, Zhu M (2016) Large scale production of continuous hydrogel fibers with anisotropic swelling behavior by dynamic-crosslinking-spinning. Macromol Rapid Commun 37:1795–1801
140. Gavin TP, Sinnott RK (2008) Chemicalengineeringdesign: principles, practice and economics of plant and process design. Elsevier Science & Technology, ButterworthHeinemann, p 313
141. Maaly MAK, Azza IH, Hanaa MA, Ahmed IW, Techno-economic investigation for production of innovative hydrogel as superabsorbent polymer, 7(3), (2016), 2689–2700