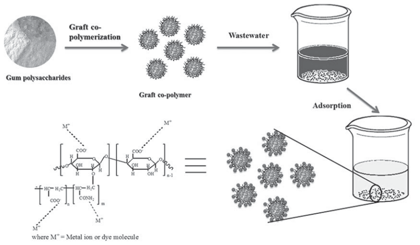
Macromolecular Journals

Recent Progress on the Design and Applications of Polysaccharide-Based Graft Copolymer Hydrogels as Adsorbents for Wastewater Purification

Hemant Mittal, Suprakas Sinha Ray,* Masami Okamoto

Gum polysaccharides are one of the most abundant bio-based polymers. They are generally derived from plants as exudates or from microorganisms and have diverse applications in many industries, especially in the food industries where they are used as emulsifiers and thickeners. In their natural form, gum polysaccharides have poor mechanical and physical properties; therefore, they are frequently modified with various synthetic monomers such as acrylamide and acrylic acid using graft copolymerization. Graft copolymerization is one of the most trusted and widely used synthetic methods for the modification of gum polysaccharides. Gum polysaccharides modified in this way have improved mechanical and physicochemical properties. Furthermore, gum polysaccharides contain a variety of functional groups, for example, carboxylic acid and hydroxyl groups; therefore, they have been used extensively as adsorbents for the removal of different impurities from wastewater such as toxic heavy metal cations and synthetic dyes. Here, the chemical and physical properties of gum polysaccharides, different methods of graft copolymerization, and the use of graft copolymer gum-polysaccharide-based hydrogels are reviewed in detail for the removal of toxic heavy metal cations and synthetic dyes from aqueous solutions.



Dr. H. Mittal, Prof. S. S. Ray
DST/CSIR National Centre for Nanostructured Materials
Council for Scientific and Industrial Research
Pretoria 0001, South Africa
E-mail: resuprakas@csir.co.za; suprakas73@yahoo.com
Dr. H. Mittal, Prof. S. S. Ray
Department of Applied Chemistry
University of Johannesburg
Doornfontein 2028, South Africa
Prof. M. Okamoto
Advanced Polymeric Materials Engineering
Graduate School of Engineering
Toyota Technological Institute
Hisakata 2-12-1, Tempaku, Nagoya 468 8511, Japan

1. Introduction

Gum polysaccharides are comprised of different monosaccharide units joined together by O-glycosidic linkages. The structural diversity of different polysaccharides is due to differences in degree of polymerization, monosaccharide composition, chain shapes, and linkage types. Gum polysaccharides are commonly used in both food and nonfood industries as stabilizers, thickening and gelling agents, crystallization inhibitors, and encapsulating agents.[1] Therefore, they are commonly known as gums or hydrocolloids. In nature, polysaccharide gums occur as storage materials, cell wall components, exudates, and

Macromol. Mater. Eng. **2016**, *301*, 496–522

DOI: 10.1002/mame.201500399

extracellular substances in plants and microorganisms.[1] Gums are frequently produced by higher plants as a protective mechanism following injury. On hydrolysis, simple sugar units, such as arabinose, galactose, glucose, mannose, xylose, and uronic acids are obtained.[1] Natural gums are well known for their swelling characteristics in water, and most of their properties depend on these swelling characteristics. Therefore, gum polysaccharides can be classified (refer to Table 1) on the basis of their origin and gelation properties.

Gum polysaccharides have several advantages over other gel agents, such as environmental friendliness, ease of availability, low cost, and the ease of modification for different end use applications. Besides these advantages, in their natural, unmodified form, gum polysaccharides have several disadvantages, for example, they have very poor mechanical properties, which restrict their range of use. However, these limitations can be overcome by chemical modification of the gums with synthetic monomers, such as acrylic acid (AA), acrylamide (AAM), methyacrylic acid (MAA), and other vinyl monomers.[2–5]

Graft copolymerization of gum polysaccharides with different vinyl monomers is one of the most studied and reliable techniques for the modification of these biopolymers. In last few years, interest has increased concerning the synthesis of graft-copolymer-based polysaccharides, which allows the combination of the advantageous features of synthetic and natural polymers. In this direction, graft copolymerization of vinyl monomers onto polysaccharide chains is the most promising technique because functionalization of the biopolymers imparts desirable properties increasing their potential uses.[6,7] Grafting can be achieved by conventional redox grafting methods,[8] microwave irradiation,[9–11] γ-irradiation,[12] or by electron beams.[13]

Over the last half-century, many gum-polysaccharide-based graft copolymers have been investigated for various applications, such as emulsifiers, drug delivery devices, stabilizers, and thickeners in pharmaceuticals, cosmetics, textiles, and lithography.[14,15] Gum polysaccharides contain many functionalities in their chemical structure, therefore, their graft copolymers and nanocomposites have been widely used as adsorbents for the removal of impurities, such as dyes and heavy metal ions from aqueous solutions.[16–19] The main advantage of using gum-polysaccharide-based graft copolymers as adsorbents is their environmental-friendly nature; however, additional advantages include the ease to which their structure may be tailored according to the nature of the pollutant. Most gum polysaccharides, except chitosan, are anionic in nature, so they efficiently remove cationic impurities such as cationic dyes (e.g., methylene blue, malachite green (MG), rhodamine B, etc.) and heavy metal cations such as Pb^{2+}, Cu^{2+}, Cd^{2+}, and Hg^{2+}.[13,16,18,20–38] On the other hand, chemically modified graft copolymers of gum polysaccharides also show potential for the removal of anionic impurities such as anionic dyes (e.g., Congo red and methyl orange).[31,39–42]

Dr. Hemant Mittal did his Ph.D. in Organic Chemistry from Dr. B R Ambedkar, National Institute of Technology, Jalandhar (India) in 2012. Currently, he is working with Prof. Suprakas Sinha Ray research group as a post-doctoral research fellow. His research work involves the synthesis of gum polysaccharides based hydrogels for the adsorption of different adsorbents from the wastewater. He is also involved in the biodegradation studies of the biopolymers based polymers.

Prof. Suprakas Sinha Ray is a chief researcher in polymer nanocomposites at the CSIR with a Ph.D. in physical chemistry from the University of Calcutta in 2001 and director of the DST-CSIR National Centre for Nanostructured Materials. Ray's current research focuses on polymer-based advanced nanostructured materials and their applications.

Prof. Masami Okamoto received his Ph.D. in 1994 from Tokyo Institute of Technology. Following postdoctoral stay in National Institute of Advanced Industrial Science and Technology, he joined the faculty at Toyota Technological Institute. His recent research interests include nanocomposites, tissue engineering, and regenerative medicine.

Recently, couple of articles summarized the chitosan-[43] and chitin[44]-based adsorbents for the removal of different impurities from wastewater but, to the best of our knowledge, there is no literature available about the grafting and/or blending of gum polysaccharides with synthetic polymers for the development of efficient and environmentally friendly adsorbents for the wastewater treatment. This review aims to give an overview of the chemical properties of different gum polysaccharides, different methods of their graft copolymerization, and examples of their use as adsorbents for the removal of different pollutants from aqueous solutions.

2. Structure and Properties of Gum Polysaccharides

2.1. Gum Xanthan

Gum xanthan is a gram negative, yellow-pigmented, bacterium-derived anionic polysaccharide obtained from the bacterial coat of *Xanthomonas campestris* (*X. campestris*)

Table 1. Classification of gum polysaccharides. Reproduced with permission.[1] 2011, Elsevier Science Ltd.

Basis	Class	Examples
Origin	Seed gums	Guar gum (guar beans), karaya gum (*Sterculia* gum)
	Plant exudates	Gum tragacanth (*Astragalus* shrubs), chicle gum (from Chicle tree), konjac glucomannan (from konjac plant), gum arabic (*Acacia* tree), gum ghatti (sap of *Anogeissus* tree), locust bean gum (carob tree), mastic gum (mastic tree)
	Microbial exudates (fermentation)	Gellan gum, xanthan gum, tara gum (tara tree), spruce gum (spruce tree)
	Seaweed	Sodium alginate, alginic acid
Gelation behavior	Cold-set gels (form gels on cooling the solution)	Gellan gum
	Heat = set gels (form gels on heating the solution)	Konjac glucomannan
	Reentrant gels (from which galactose residues are removed)	Xyloglucan
Chemical structure	Galactomannans	Fenugreek gum, guar gum, locust bean gum
	Glucomannans	Konjac glucomannan
	Uronic acid containing gums	Xanthan gum

and is generally produced by the fermentation of glucose, sucrose, or lactose by the *X. campestris* bacterium. The fermented solution is precipitated using isopropyl alcohol, dried, converted into fine powder, and added to a liquid medium to form the gum. It is highly soluble in water and a very low concentration of xanthan gum leads to a highly viscos solution.

In the xanthan gum main chain, pentasaccharide repeating units of D-glucose are joined through the β-1 position of one unit to the 4-position of the next unit, similar to the chemical structure of cellulose. The main chain of xanthan gum comprised of (1→4)-linked β-D-glucopyranose units, is attached at the C-3 position to trisaccharide side-chains of alternating sugar residues. The side chain is made up of two mannose residues and a glucuronic acid residue. In the terminal portion, β-D-mannopyranose residues are (1→4)-linked to β-D-glucuronic acid residues and these are, in turn, (1→2)-linked to nonterminal α-D-mannopyranose residues.[45–47] Figure 1a shows the molecular structure of xanthan gum. The 6-OH groups of the nonterminal D-mannopyranose residue are present as acetic acid esters, and the pyruvate acetal groups are located on the D-mannopyranosyl end groups of the side-chains. Modification of polysaccharide chain conformation and its characteristics depends upon the different glycosidic linkages in the main chain. Pyruvic acid, attached to the terminal carbohydrate of the side chains, adds another carboxylate group, and xanthan gums with different levels of pyruvate have different rheological properties. The main constituents of xanthan gum are glucose, mannose, glucoronic acid, acetate, and pyruvate, and they are present in the ratio 37:43.4:19.5:4.5:4.4, respectively.[47]

Xanthan gum is mainly used as thickener and stabilizer in industry because of its high viscosity in comparison to other polysaccharides. The viscosity of the xanthan gum solutions is independent of temperature and is virtually constant over a range from boiling to freezing point of pure water. Xanthan gum is completely biodegradable using certain microorganisms under controlled conditions, but it is resistant to degradation using enzymes such as protease, pectinase, and amylase. Due to its extraordinary properties, xanthan gum is used extensively in both food and pharmaceutical industries.[48,49]

Graft copolymers of xanthan gum were prepared with different vinyl monomers, such as AA, MAA, and AAM, and used for different applications.[33,47,50–53] For example, a hydrogel nanocomposite of the graft copolymer of xanthan gum and a copolymer mixture of AA and AAM with Fe_3O_4 magnetic nanoparticles successfully adsorbed MG from aqueous solutions. The prepared hydrogel nanocomposite has a maximum adsorption capacity of 497.15 mg g^{-1}.[24] In another study, a xanthan gum graft copolymer was used for the synthesis of nanosilica within the polymer matrix, and the resultant nanocomposite was used as adsorbent for the adsorption of Pb^{2+} ions and Congo red from the aqueous solution.[51,52] However, the nanocomposite did not have a good adsorption capacity for Congo red (209.205 mg g^{-1}).[51] It did, however, have a high adsorption capacity for Pb^{2+} (537.634 mg g^{-1}).[52] The adsorption

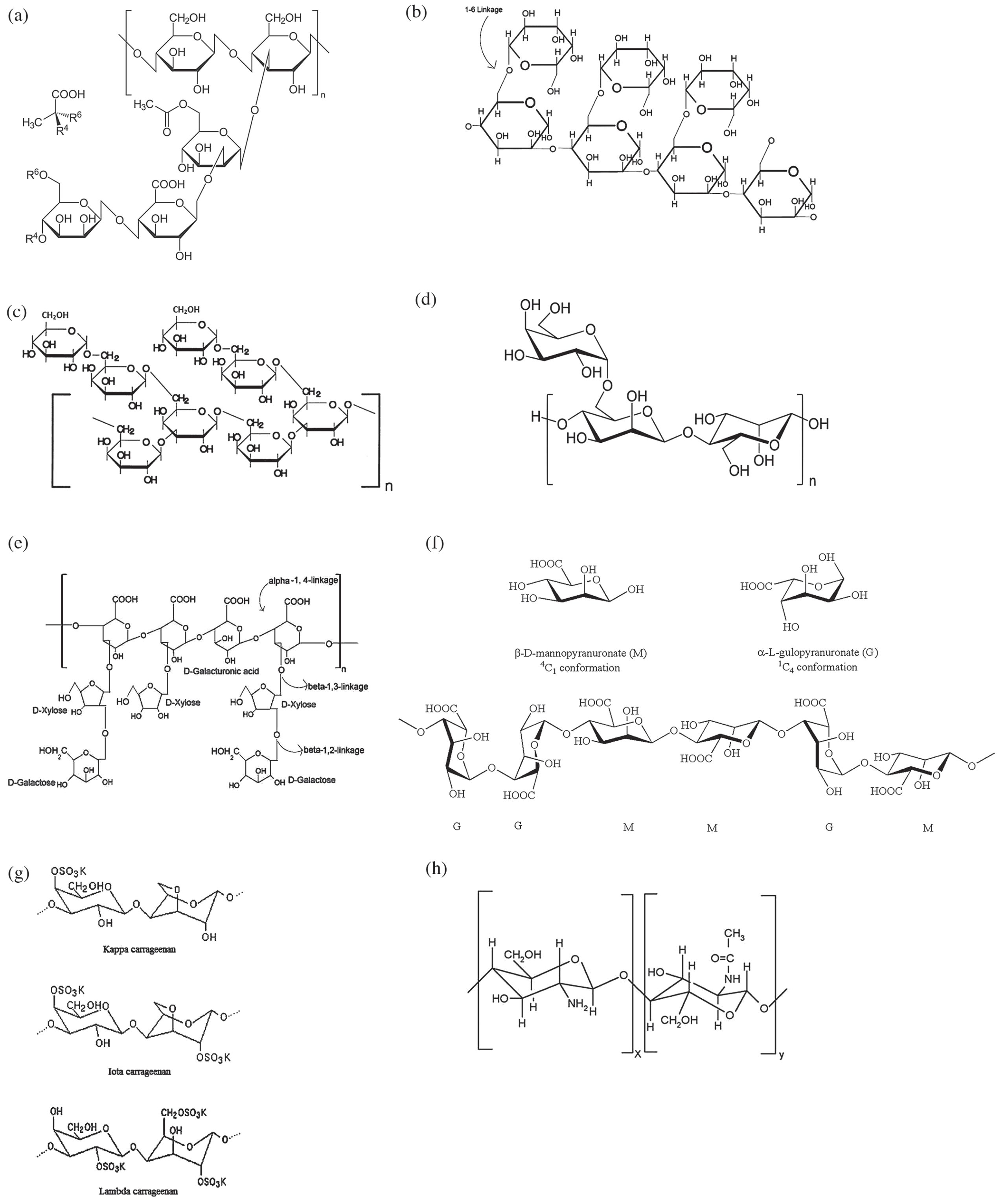


Figure 1. Molecular structure of a) xanthan gum, b) gum ghatti, c) gum arabic, d) guar gum, e) tragacanthic acid, and f) G-block, M-block, and alternating blocks in alginate. Molecular structure of g) different carrageenans and (b) chitosan.

capacity of this hydrogel nanocomposite for cationic pollutants was further enhanced by hydrolysis of its free hydroxyl groups, and the synthesized hydrogel nanocomposite was used for the adsorption of cationic dyes, i.e., methylene blue (MB) and methyl violet (MV) from aqueous solution.[50]

2.2. Gum Ghatti

Gum ghatti is an odour-less exudate of the tree *Anogeissus latifolia* belongs to the *Combretaceae* family and the exudate color varies from very light to dark brown. It is a complex anionic polysaccharide, thus, the exact molecular weight of gum ghatti is not known. The molecular structure [Figure 1b] of gum ghatti contains L-arabinose, D-galactose, D-mannose, D-xylose, and D-glucoronic acid in the molar ratio of 48:29:10:5:10[54] and has alternating 4-O-subsituted and 2-O-subsituted α-D-mannopyranose units and chains of $1\rightarrow6$ linked β-D-galactopyranose units attached to a single L-arabinofuranose residue.[2,55]

Gum ghatti powder has been shown to have huge medicinal benefits including strengthen the immune system.[2] It is a common ingredient in glyconutrient supplements which are used to provide the eight essential sugars used for cell communication including stimulation of the immune system and reduction of the effects of various neurological diseases and autoimmune diseases. Over the past years it has been commonly used to reduce cholesterol levels and accelerate the wounds healing process.[2] in addition, it has the capability to reduce the side effects after chemotherapy and decelerate the consumption of sugars in the intestine of diabetic patients.[56] This substance has also shown the potential to slow down the signs of ageing and can be consumed as a weight loss supplement. No reports of major side effects or drug interactions due to gum ghatti powder have been made, however, it has been reported that excessive use of gum ghatti powder can lead to a laxative effect.[2,54–56]

In our ongoing work, we have synthesized hydrogel polymers of gum ghatti with different vinyl monomers using the free-radical graft copolymerization technique.[2,10,23,27,28] The main advantage of the gum ghatti based graft copolymers is that they are fully biodegradable.[9,55] Moreover, they are highly adsorbent. We have used gum ghatti based hydrogels and nanocomposites with different metal nanoparticles, such as Fe_3O_4, for the removal of different impurities, for example, cationic dyes (i.e., MB, rhodamine B (RB), MG, and MV) and heavy metal cations, such as Pb^{2+} and Cu^{2+}, from aqueous solutions.[22,23,25–28] The graft copolymers of gum ghatti have better adsorption capacities for cationic impurities as compared to the graft copolymers of other gum polysaccharides.

2.3. Gum Arabic

Gum arabic is one of the oldest known plant gum polysaccharides. The name originates from the Arabs who first traded it. It is a highly branched acidic heteropolysaccharide, an exudate of the tree *Acacia*, belonging to the family *Leguminosae*. About 500 species of *Acacia* trees are found to produce the gum arabic and are mainly grown in the tropical and sub-tropical areas of Africa, India, Australia, Central America, and south-west North America. However, the exudate obtained from the *Acacia Senegal* tree is the commercially most valuable because it is produced naturally as large nodules during a process called gummosis to seal wounds in the bark of the tree. It is highly soluble in water, which makes gum arabic unique among the natural gum polysaccharides.[57] This hydrocolloid finds a number of applications, for example, as a flavoring, in confectionery, brewing, pharmaceuticals, cosmetics, lithography, inks, and textiles.[57–63] It is also widely used in the beverage industry to stabilize flavors and essential oils, e.g., in soft-drink concentrates.[64]

Figure 1c shows the molecular structure of gum arabic. It is a complex highly branched polysaccharide with main chain comprised of $(1\rightarrow3)$-β-D-galactopyranosyl units and side chains composed of L-arabinofuranosyl, L-rhamnopyranosyl, D-galactopyranosyl, and D-glucopyranosyl uronic acid units.[60,62] From detailed studies of its structure, it was found to consist of three main fractions:[63] (a) the crucial unit is a highly branched polysaccharide ($M_W = 3 \times 10^5$ g mol^{-1}), made up of β-$(1\rightarrow3)$ galactose backbone with linked branches of arabinose and rhamnose, which terminate in glucuronic acid (found in nature as magnesium, calcium, and potassium salts); (b) less crucial one is a higher molecular weight ($\approx 1 \times 10^6$ g mol^{-1}) arabinogalactan-protein complex (GAGP-GA glycoprotein), which is composed of arabinogalactan ($\approx$13% by mole glucoronic acid) chains covalently bonded to a protein chain through serine and hydroxyproline groups; (c) the least fraction one is a glycoprotein ($\approx$50 wt%) having a different amino acids composition to that of the GAGP complex.[64]

In a recent study, semi-interpenetrating network (IPN) hydrogels of gum arabic were prepared with a copolymer mixture of poly(hydroxyethylmethacrylate-*co*-acrylic acid) (p(HEMA-*co*-AA)) using ammonium persulfate (APS) and *N*,*N*′-methylene-bis-acrylamide (MBA) as the initiator and crosslinker, respectively. The synthesized semi-IPN hydrogel was used for the in situ generation of silver nanoparticles.[64] Smart hydrogels composed of gum arabic with AAM, potassium acrylate, and Fe_3O_4 magnetic nanoparticles were also synthesized, and the stimuli-responsive swelling behavior of the hydrogel in response to changes in a magnetic field was studied.[65] pH and temperature-responsive hydrogels of gum arabic containing AAM were synthesized and used for the treatment of saline water.[66] Gum arabic and Fe_3O_4 magnetic nanoparticle-based adsorbents were used for the rapid and effective adsorption of Cu^{2+} ions from aqueous solution. Equilibrium for the adsorption of 200 mg L^{-1} solutions of Cu^{2+} was reached in only 2 min using this gum-arabic-based magnetic adsorbent. The authors attributed this rapid adsorption rate to external surface adsorption, assuming that all the adsorption sites are present on the exterior of the adsorbent.[30]

In another study, a polymer blend of carboxymethyl cellulose (CMC) and gum arabic was used for the adsorption of basic as well as acidic dyes.[67]

2.4. Guar Gum

Guar gum is a water soluble and nonionic plant polysaccharide, obtained from the seeds of the plant *Cyamopsis tetragonoloba*. It is found to degrade at pH 3.0 and 50 °C but the ionic strength does not have any effect on molecular structure.[68] Figure 1d shows the molecular structure of guar gum, which is composed of (1→4)-linked β-D-mannopyranose units attached with the side chains of (1→6)-linked-α-D-galactopyranose.[69] It is a water-soluble fiber that acts as a bulk forming laxative and is claimed to be effective in promoting regular bowel movements and to relieve constipation and related chronic bowel ailments, including diverticulosis, Crohn's disease, colitis, and irritable bowel syndrome.[70] The graft copolymers of guar gum have also shown their potential as adsorbents for the adsorption of various cationic and anionic impurities from wastewater.[40,70–72] The main advantage of guar gum is that it is non-ionic in nature, therefore, it is very easy to tailor it to a target pollutant by modification. The graft copolymers of guar gum have good adsorption capacities for the removal of different toxic metal cations, such as Pb^{2+}, Cu^{2+}, and methylene blue from aqueous solutions. A graft copolymer of guar gum with PAAM was used for the removal of Cr^{6+} ions from wastewater with a significantly high adsorption capacity of 588.24 mg g^{-1}.[40]

2.5. Gum Tragacanth

Gum tragacanth is a highly branched heterocyclic polysaccharide with a spheroidal molecular shape. It is a gummy exudate of *Astragalus gummifer Labillardiere* or other asiatic species of the genus *Astragalus,* mainly found in Iran and Turkey.[73] It is mainly composed of two components, i.e., tragacanthin, which is a water soluble component, and tragacanthic acid, which is water insoluble.[73–75] When the gum is added to water, water soluble part dissolves to form a viscous solution, whereas insoluable part swells to form soft and adhesive gel-like structure.[76] The molecular structure presented in Figure 1e made up of a main chain of repeating D-galactose residues to which chains of L-arabinose residues are attached. In contrast, tragacanthic acid has a main chain of repeating (1→4)-linked D-galactopyranosyl units with a side chain of substituted xylosyl residues linked at the C-3 position of the glacturonic acid residues.[76,77] Graft copolymers of gum tragacanth formed with different vinyl monomers have been reported and used for different applications, for example, wastewater treatment, flocculation, and drug delivery.[77–80] For example, a graft copolymer based on gum tragacanth and Fe_3O_4/PMMA was used for the highly selective removal of Cr^{6+}.[77]

2.6. Alginate

Alginate is an anionic natural polysaccharide extracted from brown seaweed. It has been used for many industrial and biomedical applications due to its biocompatibility, relatively low cost and toxicity, and its mild gelation, caused by the addition of divalent cations such as Ca^{2+}.[81] Commercially, alginate is extracted by the alkali treatment of brown algae species, including *Laminaria hyperborea*, *L. digitata*, *L. japonica*, *Ascophyllum nodosum*, and *Macrocystis pyrifera*. After alkali treatment, the extract is filtered either with sodium or calcium chloride, leading to the precipitation of alginate salt. Thereafter, the alginate salt is treated with dilute HCl to convert it into alginic acid.[82] The chemical structure of alginate was extensively studied by Fischer and Dörfel[83] and found to have D-mannuronate as the main component. The structure of alginate consists of block copolymers having guluronate and mannuronate in different ratios depending upon the source of the alginate. Alginate consists of blocks of (1,4)-linked-β-D-mannuronate (M) and α-L-guluronate (G) residues. The blocks contain consecutive G residues (GGGGGG), consecutive M residues (MMMMMM), and the alternating G and M residues (GMGMGM) [Figure 1f]. Alginates extracted from different sources have different M and G contents as well as differing lengths of each block, and more than 200 different alginates exists depending upon the length and constitutes of M and G chains.[83]

Hydrogels of the alginates can be easily prepared by crosslinking with cations, and they have potential applications in drug delivery, wound healing, and protein and wastewater treatment.[84] A hydrogel nanocomposite comprising an alginate core shell with the Eu^{3+}-doped $ZnS–SiO_2$ particles was developed and used as a photocatalyst for the degradation of indigo carmine dye.[85] The graft copolymers of alginate have also been used extensively as adsorbents for the removal of different contaminants from polluted water.[34,35,86]

2.7. Carrageenans

Carrageenan is a high-molecular-weight linear polysaccharide exists in three forms: *kappa*, *iota*, and *lambda*. The main chain of carrageenan contains repeating galactose units and sulfated and nonsulfated 3,6-anhydrogalactose (3,6-AG) joined together by the alternating (1,3) and (1,4) glycosidic links. On the basis of their chemical structures, Rees[87] distinguished between different types of carrageenan. *Lambda*, *kappa*, and *iota*, which are considered the main carrageenans, can be synthesized by selective extraction techniques using the *mu*- and *nu*-carrageenans.

Alkali treatment of *mu* and *nu*-carrageenans forms the *kappa*- and *iota*-carrageenans. The molecular structures of carrageenans are shown in the Figure 1g. Basically, these carrageenans differ in the 3,6-anhydrogalactose and ester sulfate content, which influences the chemical, physical, and structural properties of these carrageenans. In *kappa*-carrageenans, the ester sulfate and 3,6-anhydrogalactose content are approximately 25% and 34%, respectively, whereas in *iota*-carrageenans they are 32% and 30%, respectively; however, in the *lambda*-carrageenans the ester sulfate content is 35% with very little or no 3,6-anhydrogalactose content. Carrageenans are high-molecular-weight polysaccharides, and the commercial *kappa*-carrageenan extracts have molecular weights between 400 and 560 kDa.[88] In all carrageenans, 5% of the polysaccharide content is comprised of biopolymers with molecular weights less than 100 kDa, and this is believed to be an inherent feature of native algal weed. Applications of the carrageenans include their use as gelling, thickening, and suspension agents. *Kappa*-carrageenan forms a firm, clear, and brittle gel with poor freezing stability, however, these gels can be softened by addition of locust bean gum. In contrast, *theta*-carrageenan forms soft and elastic gels that have good freeze-thaw stability. *Lambda* carrageenan do not form a gel because of the very low content of 3,6-anhydro groups in the (1→4)-linked α-D-galactopyranosyl residues which are required for the initial formation of a double helix.[89,90] The graft copolymers of carrageenans have been synthesized extensively and used in many applications such as drug delivery and wastewater treatment. Carrageenan based hydrogels have mainly been used in drug delivery applications,[91–97] but some of carrageenan hydrogels have also been used as adsorbents for impurities from wastewater.[98,99] For example, a hydrogel nanocomposite of *kappa*-carrageenan, PVA, and Fe_3O_4 magnetic nanoparticles as used for the adsorption of cationic dyes, e.g., crystal violet, from aqueous solutions.[98] In another study, the carrageenan, alginate, and sodium-montmorillonite-based hydrogel nanocomposites were used for the adsorption of crystal violet and had a maximum adsorption capacity of 88.8 mg g^{-1}.[99]

2.8. Chitosan

Chitosan is a linear cationic polysaccharide in which β-(1-4)-linked D-glucosamine and *N*-acetyl-D-glucosamine units are randomly distributed [Figure 1h].[100,101] It is usually produced by the deacetylation of chitin (> 60%) and is the most abundant biopolymer after cellulose. Chitin is a structural element in the exoskeleton of crustaceans and insects. Chitosan contains nitrogen, and this is responsible for its cationic nature, as well as its capacity to form polyelectrolyte complexes. Hydrogels of chitosan have been prepared with different shapes and formulations.[102–111] Chitosan is the only biopolymer that has cationic functionalities in its chemical structure; therefore, it is very important in water treatment systems. Extensive research has been carried out on the use of chitosan-based graft copolymers or hydrogels as adsorbents for the removal of pollutants from wastewater.[36,42,112] An IPN of chitosan was prepared with poly(acrylamide) (PAAM), and various reaction parameters, such as the ratio of crosslinker, pH of the reaction mixture, and molar mass of the chitosan, were optimized during the formation of semi-IPN. For the preparation of the full-IPN, the chitosan was crosslinked with epichlorohydrin in 2 M NaOH. The full-IPN contained carboxylic acid groups instead of amide groups, formed by the partial hydrolysis of the amide groups in PAAM at high pH. The full-IPN had a cationic network resulting from the cross-linked chitosan and the anionic PAAM network. Also, the swelling and adsorption properties of the synthesized hydrogel polymer were strongly influenced by the presence of the two oppositely charged networks. The semi-IPN with cationic functionalities was found to have a high adsorption capacity for the anionic dyes, in contrast, the full IPN hydrogel polymer containing anionic functionalities had a greater absorption capacity for cationic dyes.[112]

3. Graft Copolymerization of Gum Polysaccharides

3.1. Graft Copolymerization with Vinyl Monomers

Gum polysaccharides have many advantages over synthetic polymers, but they also suffer from disadvantages such as poor mechanical and physical properties. Therefore, gum polysaccharides must be modified with synthetic monomers to improve their property-profile. Graft copolymerization of gum polysaccharides with vinyl monomers, which also act as crosslinking agents, is one of the most studied techniques for modification of polysaccharide gums. The polymerization is initiated by an initiator and can be carried out in bulk, solution, or suspension. The second step comprises crosslinking the linear polymer chains by irradiation or by chemical reactions.[113] Monomers used in the synthesis of the ionic polymer network contain either an ionizable group or a group that can undergo substitution after polymerization is complete. Therefore, the obtained hydrogels contain weakly acidic groups, such as carboxylic acids, or weakly basic groups, such as substituted amines, or a strongly acidic and basic group, such as sulfonic acids and quaternary ammonium compounds. Graft copolymers generally have long polymer chains of one composition (i.e., backbone) and randomly distributed chains of different compositions (i.e., side chains). Different monomers can be grafted onto the polymer chains using three strategies: (a) "grafting through" graft copolymerization of a low-molecular-weight monomer copolymerized with a premade vinyl-functionalized polymeric chain;[114] (b) "grafting from" graft copolymerization requires a macromolecule containing initiating functionalities distributed through the structure. In this method, the side chains grow directly from the polymer backbone; (c) "grafting on" involves the grafting of end-functionalized side chains to the solid surface. The main advantage of graft copolymerization is that the end product can be synthesized with the desired properties for the target application.

The formation of the gum polysaccharides graft copolymerized with different vinyl monomer mixtures can be shown by FTIR spectroscopy by observing the newly formed covalent bonds between different functionalities.[115,116] Graft copolymerization usually occurs through the free hydroxyl groups of the polysaccharides; this can be proven by the shift and decrease in intensity of the —OH IR peak.

The molecular structures of the most common monomers and crosslinking agents, such as AA, MAA, AAM, acrylonitrile (AN), AAM derivatives, divinyl benzene, gluteraldehyde, and MBA, used in the preparation of hydrogels are given in Figure 2. The graft copolymers of different gum polysaccharides, such as gum xanthan,[24,47,50–52] gum ghatti,[2,9,10,27,28,55] guar gum,[70,72] chitosan,[4,38,39,42,102,107,117] etc., with different vinyl monomers have been reported to have potential applications in drug delivery,[81,96] flocculation,[3,9,55] and wastewater treatment.[22–25,29]

3.2. Free Radical Graft Copolymerization without Crosslinking Agent

This is one of the most widely used and oldest techniques for the synthesis of gum-polysaccharide-based graft copolymers. In this technique, the gum polysaccharide is mixed with a monomer and the reaction is started by an initiator such as potassium persulfate (KPS), APS, or a mixture of redox initiators such as ABC-KPS. A good example of a graft copolymers prepared by this method is the preparation of Fe^{2+}/BrO^{3-} initiated graft copolymers of PAAM with xanthan gum.[118] Non-crosslinked polymer networks of gum polysaccharides are advantageous because they are water soluble, and these solutions can be used for further applications. The graft copolymer of xanthan gum with PAAM synthesized using graft copolymerization has been used as a template for the synthesis of silica nanoparticles.[52] In another example, a pH sensitive hydrogel of PAA and glycogen using CuBr as an initiator was synthesized and used as an adsorbent for the removal of Pb^{2+} from aqueous solutions.[37] Initially, the glycogen-Br macroinitiator was synthesized by the homogeneous acylation of the hydroxyl groups of glycogen with 2-bromo-2-methyl propionyl bromide in the presence of pyridine at room temperature. The bromo-ester groups formed hydrogen bonds with glycogen and this resulted in better solubility of glycogen-Br macroinitiator in solvents. This higher macroinitiator solubility facilitated the graft copolymerization, furthermore, the remaining functional groups in the glycogen-Br macroinitiator were used as the binding sites for the formation of new functionalized material. In the second step, the hydrogel was synthesized using CuBr/bipyridine as a catalyst and the glycogen-Br macroinitiator, which was dissolved in DMF. The detailed mechanism for this synthesis is shown in Figure 3.[37] Some of the graft copolymers of gum polysaccharides synthesized without using crosslinking agents are summarized in Table 2, along with their applications.[21,33,51,116,119–129]

3.3. Free Radical Graft Copolymerization with Crosslinking Agents

In this kind of graft copolymerization, the crosslinkers form crosslinks or bridges between different polymer chains through covalent bonding. Crosslinks act as

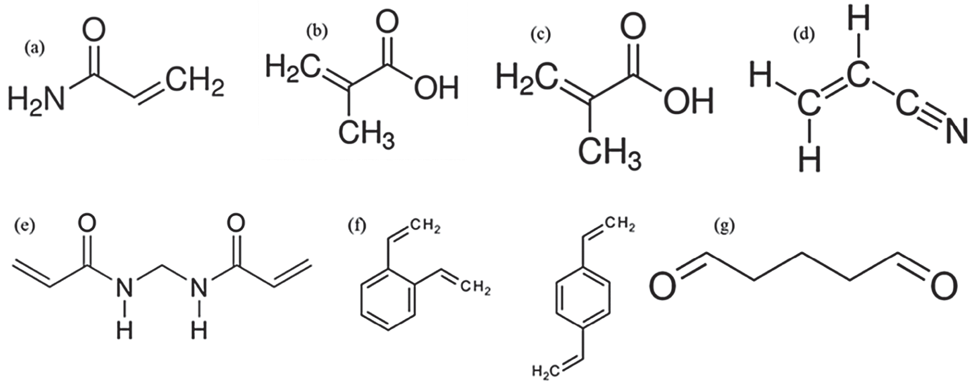
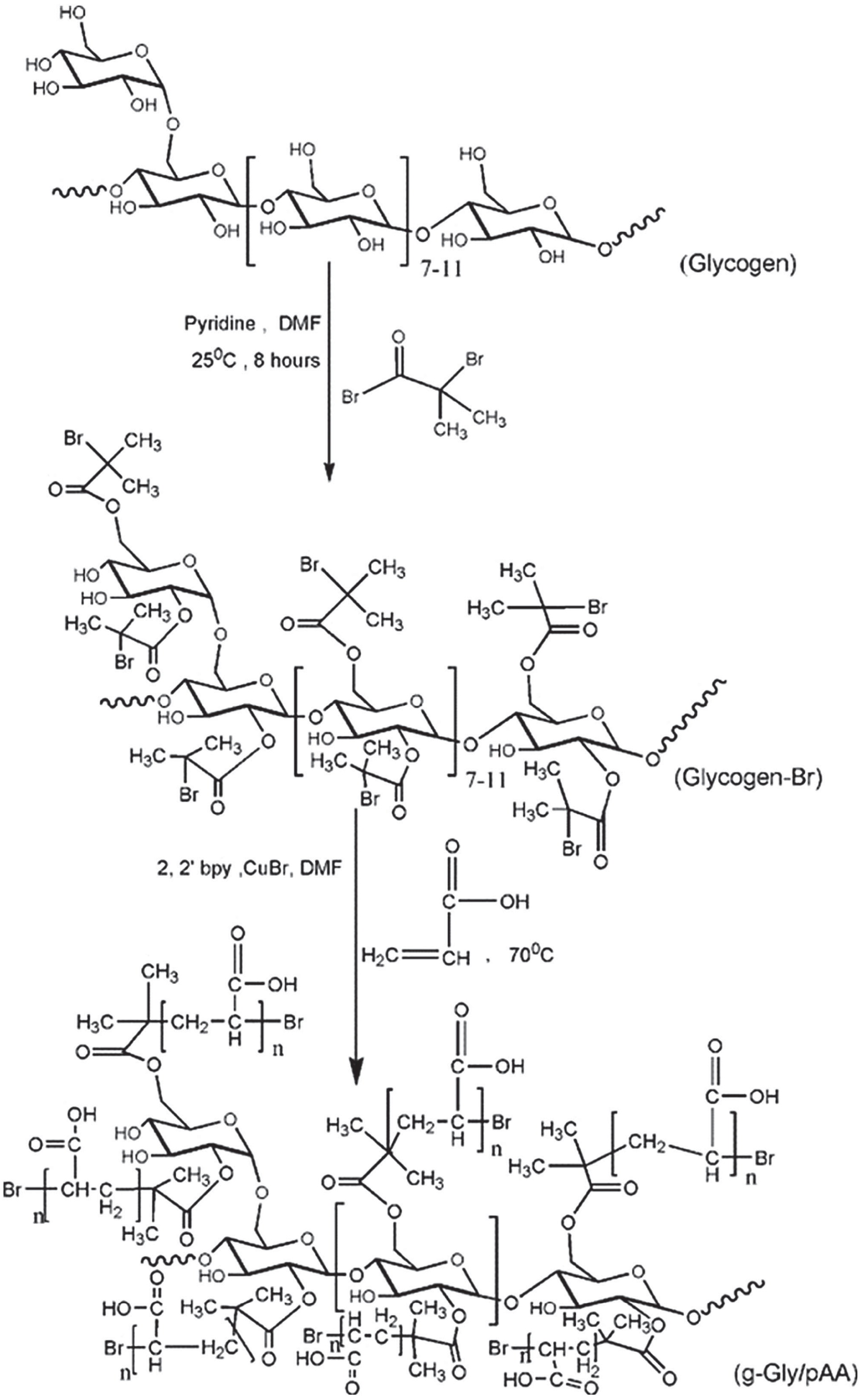


Figure 2. Molecular structures of a) acrylamide (AAM), b) acrylic acid (AA), c) methyacrylic acid (MAA), d) acrylonitrile (AN), e) *N*,*N*′-methylene-bis-acrylamide (MBA), f) divinyl benzene, and g) glutaraldehyde.



■ *Figure 3.* Mechanism of the synthesis of the glycogen-grafted-PAA. Reproduced with permission.[37] 2015, Elsevier Science Ltd.

bridges between polymer chains and form 3D polymeric networks that are practically insoluble in water.[115,130] In this method of preparation, the graft copolymers of gum polysaccharides are prepared with ionic or neutral monomers and multifunctional crosslinking agents. The copolymerization reaction is initiated thermally by

Table 2. Applications of gum polysaccharides based graft copolymers synthesized without crosslinking agents.

Gum polysaccharide	Other polymer/chemicals	Applications	Ref.
κ-Carrageenan	*N*-Vinylpyrrolidone (NVP)	Metal ion adsorption	[116]
Carboxymethyl cellulose	Vinyl sulfonic acid	Metal ion adsorption	[119]
Carboxymethylated guar gum	2-Acrylamidoglycolic acid	Metal ion adsorption	[120]
Aminated guar gum	Fe_3O_4 magnetic nanoparticles	Sustained release of doxorubicin hydrochloride	[121]
Guar gum	Glycidyl methacrylate	Soft tissue engineering	[122]
Cassia javanica seed gum	PAA	Adsorption of Hg^{2+}	[21]
Cassia grandis seed gum	PMMA	Adsorption of Pb^{2+}	[123]
Gum xanthan	PAAM/nanosilica	Adsorption of Congo red	[51]
Gum xanthan	PAAM/nanosilica	Adsorption of Pb^{2+}	[52]
Guar gum	PAA	Controlled release of ketoprofen	[124]
Alginate	PAA	Adsorption of Co^{2+} and Ni^{2+}	[125]
Seed gum from *Ipomoea* and *Cyamopsis* species	PAAM	Coagulation of textile dye solutions	[126]
Chitosan	Policaju/Lactic acid	–	[127]
Starch	PAAM	Soft tissue engineering	[128]
Chitosan	PEG	Wound dressing	[129]

ultraviolet radiation or by a redox initiator. In either process, the solvent acts as a heat sink and minimizes temperature control problems. The synthesized graft copolymers are washed with a suitable solvent, usually distilled water, to remove unreacted monomers, crosslinkers, and initiators. There are two main categories of crosslinked gels, namely, (1) physical hydrogels, in which different polymeric chains are joined together by reversible noncovalent bonding, and (2) chemical hydrogels, in which different polymeric chains are joined together though nonreversible covalent bonding. For physically crosslinked hydrogels, the dissolution of the hydrogel network is prevented by physical interactions between polymeric chains. Because crosslinking agents are avoided during synthesis, this type of hydrogel has attracted the attention of researchers from all over the world, and they are used in a number of pharmaceutical and biomedical applications. The physical crosslink interactions between different polymeric chains can be (a) ionic, (b) hydrophobic, (c) hydrogen bonding, (d) self-assembly of stereo complex formations; (e) coil–coil interactions, or (f) due to specific molecular recognition.[131,132] If the polymeric chains in a hydrogel polymer network are held together by chemical bonds, they are chemically crosslinked hydrogels. Physically crosslinked hydrogels have the advantage of hydrogel synthesis without any chemical modification or crosslinking agent. Despite these advantages, preparation of physically crosslinked hydrogens has some limitations; that is, features or properties of the hydrogels can be difficult to control, e.g., gelation time, pore size, and chemical functionalization. Moreover, chemically crosslinked hydrogels have much better mechanical properties, increasing their property profile and making them more appropriate for a wide variety of industrial applications.

Changes to the morphology of gum polysaccharides grafted and crosslinked with vinyl monomers are usually studied using scanning electron microscopy. In general, the surface of the gum polysaccharide is very smooth and homogeneous, however, after grafting and crosslinking, the smooth surface of the gum polysaccharide becomes very rough and heterogeneous due to the formation of crosslinks between polymeric chains. In one study, Jindal et al.[47] observed that the morphological characteristics of the xanthan gum change after graft copolymerization with different binary vinyl monomer mixtures such as p(AAM-*co*-AA), p(AAM-*co*-AN), and p(AAM-*co*-MAA).[47]

Crosslinker selection during hydrogel synthesis is very important because the swelling capacity of hydrogels is inversely proportional to the crosslinking density. If the crosslinking density is high, the hydrogel will have less swelling capacity and it will be more fragile. Therefore, the role of the crosslinker in synthesis is important and it must be selected based on the desired end-use of the hydrogel. For example, if higher mechanical strength is required, the crosslinking density should also be higher and a larger concentration of crosslinker must be used. In contrast, if greater swelling capacity is required, e.g., in water purification or superabsorbent applications, lower crosslinking density is required and a lower concentration of the crosslinker must be used. The crosslinking density of the hydrogel polymers can be determined using Equation (1)

$$\text{Crosslinking density, network chain per gram} = \frac{-\left(\ln(1-V_\text{p})+V_\text{p}+X\left(V_\text{p}\right)^2\right)}{\left\{D_\text{p}(V_\text{o})\left[(V_\text{r})^{1/3-(V_\text{p})/2}\right]\right\}} \tag{1}$$

where V_p is the volume fraction of the polymer in the swollen polymer, X is the Huggins polymer–solvent interaction constant, $\underline{D}_\text{p}$ is the density of polymer (g cm^{-3}), V_o is the molar volume of the solvent (cm^3 mol^{-1}), and D_o is the density of the solvent (g cm^{-3}). In addition, the value of $\underline{V}_\text{p}$ is calculated by using Equation (2)

$$V_\text{p} = \frac{1}{(1+Q)} \tag{2}$$

where Q is given by Equation (3)

$$Q = \frac{(\text{weight of solvent in the swollen polymer} \times D_\text{p})}{(\text{weight of polymer} \times D_\text{o})} \tag{3}$$

An important property of gum-polysaccharide-based graft copolymers is that they swell up to several hundred times their dry volume in water and biological fluids. The combination of swelling behavior in aqueous environments and biocompatibility means that these copolymers have applications in pharmaceutical, ophthalmology, and tissue engineering.[2,3,10,47,66,74,79,124] The polymer chains in a hydrogel interact with solvent molecules and expand to a fully solvated state. At the same time, the crosslinked structure applies an opposing force, restraining the chains. Equilibrium is achieved when these expanding and retracting forces balance. The equilibrium swelling ratio is given by Equation (4)

$$\text{Equilibrium selling ratio} = \frac{W_\text{swollen}}{W_\text{dry}} \tag{4}$$

Here, W_swollen is the weight of the swollen gel and W_dry is the weight of the dry gel.

The swelling kinetics of hydrogels can also be determined from their swelling kinetic curves. First, W_0, the weight of the dry gel is measured. The equilibrium swelling is achieved by immersing the dried gel in an excess amount of water. W_t, the weight of the wet gel is measured after the removal of surface water. Equation (5) is then used to calculate swelling ratio:

$$\text{Swelling ratio} = \frac{(w_\text{t} - w_\text{o})}{w_\text{o}} \tag{5}$$

The equilibrium and dynamic swelling characteristic in water controls the physical behavior of a hydrogel. The thermodynamic parameter of hydrogel swelling can be calculated using the Flory–Huggins theory.[130] Considering the isotropic crosslinked structure of hydrogel, after swelling, the total Gibbs free energy change of the system, can be described as Equation (6)

$$\Delta G = \Delta G_\text{mixture} + \Delta G_\text{elastic} \tag{6}$$

Here, the value of ΔG_elastic is related to the elastic retractive forces, and ΔG_mixture represents the thermodynamic compatibility of the polymer and the water.

To express the change in chemical potential of swelling medium in terms of elastic and mixing contributions at any swelling time, Equation (6) is differentiated with respect to the water molecules in the system, thus, yielding Equation (7)

$$\mu_1 - \mu_{1,\text{o}} = \Delta\mu_\text{mixture} + \Delta\mu_\text{elastic} \tag{7}$$

Here, μ_1 and $\mu_{1,0}$ are, respectively, the chemical potential of water within the gel and pure water.

At equilibrium, the chemical potentials of water within the gel and pure water must be equal; therefore, the contributions from the elastic and mixing to the chemical potential must be balanced. Since the change in chemical potential upon mixing is related to heat and the entropy of mixing, therefore, the chemical potential of mixing can be calculated using Flory–Huggins equation as described below

$$\Delta\mu_\text{mixture} = RT\left(\ln(1-2v_{2,\text{s}}) + v_{2,\text{s}} + x_1 v_{(2,\text{s})}^2\right) \tag{8}$$

where, x_1 is the interaction parameter between polymer and water, $v_{2,\text{s}}$ is the polymer volume fraction of the gel, T is the absolute temperature, and R is the gas constant. For a particular solvent at a particular temperature the swelling equilibrium attend when thermodynamic and elastic forces become equal. Therefore, the value of Q, the volume degree of swelling, can then be calculated using Equation (9)

$$v_{2,\text{s}} = \frac{V_\text{p}}{V_\text{gel}} = \frac{1}{Q} \tag{9}$$

The swelling behavior of gum-polysaccharide-based graft copolymers shows responsive behavior to the external environment, i.e., the swelling capacity changes with respect to changes in external environmental conditions, such as temperature, pH, electrical stimulus, and magnetic fields. Thus, these materials are also known as smart, environment-responsive, stimuli-sensitive, and intelligent polymers.[2,10,36,47,66,95,108] The swelling capacity of hydrogel polymers depends upon the extent of crosslinking between polymeric chains and the presence of free hydrophilic functionalities in the structure of the hydrogel polymer. The swelling capacity of the hydrogel polymer reduces with increasing crosslinking density. Therefore, during hydrogel formation, a balance between mechanical properties and swelling capacity must be maintained. The swelling capacity of the hydrogel polymer also depends upon the nature of the monomer as well as the biopolymer, e.g., hydrogel polymers of hydrophilic monomers such as AA and AAM have greater swelling capacities than those polymerized from MMA or AN monomers. Furthermore, the swelling capacity of hydrogel polymers formed from binary monomer mixtures of AA and AAM is found to be much greater than the hydrogel polymers of AA or AAM alone.[10]

The thermal stability of the gum polysaccharides is expected to increase after grafting and crosslinking between polymer chains. Usually, the enhancement in thermal stability of the gum polysaccharide is measured by the increase in the IDT and final decomposition temperatures (FDT). However, sometimes changes in IDT and FDT also depend upon the monomer used. For example, when PAAM monomers are used, the IDT of the graft copolymer is less than that of gum PAAM. Furthermore, the FDT is higher than that of gum polysaccharide. Grafting with PAAM lowers the IDT of the graft copolymers because the PAAM are degraded by the formation of imide groups and the loss of ammonia; however, the formation of imide groups leads to an increase in FDT.[118] Moreover, on graft copolymerization and crosslinking, the rate of polymer weight loss decreases with temperature.[115,133] For example, gum ghatti has an IDT of 206.9 °C and FDT of 521.6 °C, in contrast, gum ghatti-*cl*-PAAM has IDT and FDT of 134.7 and 598.7 °C, respectively. Comparison of the TGA data for gum ghatti and gum ghatti-*cl*-PAAM shows that the IDT of gum ghatti was higher, whereas the FDT was lower than that of gum ghatti-*cl*-PAAM. Therefore, on the basis of TGA data we can conclude that the higher thermal stability of gum ghatti-*cl*-PAAM is due the formation of covalent crosslinks between polymeric chains. Results from the TGA analyses are further endorsed by DTA and DTG results. Two exothermic peaks at 483.2 (203 μV) and 492.7 °C (154 μV) were observed in the DTA profile of gum ghatti. In contrast, gum ghatti-*cl*-PAAM had two exothermic DTA peaks at 469.9 (8.5 μV) and 597.3 °C (186.6 μV). The DTA data further indicate that less heat is evolved during thermal decomposition of gum ghatti-*cl*-PAAM than that of gum ghatti. Moreover, in the case of gum ghatti-*cl*-PAAM, degradation occurred at a much higher temperature. The DTG of gum ghatti revealed maximum decomposition at 479.0 °C with a mass loss rate of 2.230 mg min^{-1}. In the case of gum ghatti-*cl*-PAAM, maximum decomposition was observed at 595.9 °C with a weight loss rate of 1.094 mg min^{-1}. Therefore, the DTG results show that maximum decomposition occurs at a higher temperature with less weight loss in gum ghatti-*cl*-PAAM than that of gum ghatti.[133]

In our ongoing work, 3D crosslinked hydrogels comprised of gum karaya and a p(AA-*co*-AAM) copolymer mixture was prepared using the KPS-ascorbic acid as the redox initiator and MBA as a crosslinking agent by free-radical graft copolymerization.[23] Initially, ascorbic acid reacts with KPS to produce SO_4^{*-}, which in turn reacts with water to produce OH^*. Then, these free radicals initiate the graft copolymerization reaction by generating active sites on the backbone and monomers. Then, activated monomers and gum karaya chains propagate the graft copolymerization reaction further. Finally, MBA, the crosslinking agent, leads to the formation of the 3D hydrogel network. The synthesized hydrogel polymer was further used for the in situ generation of nanosilica within the hydrogel polymer matrix. A detailed mechanism of the graft copolymerization of gum karaya with p(AA-*co*-AAM) copolymer and MBA as the crosslinking agent for the generation of nanosilica is shown in Figure 4.[23] Some gum polysaccharide graft copolymers synthesized using chemical crosslinkers are also summarized in Table 3, along with their applications.[3,9,22–29,53,55,71,134–148]

3.4. Graft Copolymerization Through Irradiation

Graft copolymers can also be prepared under different reaction conditions, for example, in air, and with microwave,[20,21,43,114] γ-, and[12,149] UV-radiation.[150] The main advantage of radiation induced graft copolymerization is the reactions are rapid, and the product mainly consists of short chain polymers, which have larger swelling ratios than those of graft copolymers synthesized conventionally in air. Graft copolymerization of polysaccharides using radiation is achieved by three routes: (i) in solution, where all reactants are in the same phase and fully miscible, i.e., a completely homogeneous solution; (ii) in a suspension, where either the backbone polymer and/or monomer/catalyst are immiscible, i.e., the reactants are not fully miscible; and (iii) in systems where the backbone polymer, monomers, and initiator are impregnated on a neutral solid support, i.e., a solid phase.[114]

Generally, irradiation of polymer solutions in water generates radicals on the macromolecular chains. Moreover, under radiation water molecules convert to hydroxyl radicals that can combine with the macromolecular chain radicals, leading to the formation of a number of macroradicals. The formation of covalent bonds occurs through the recombination of macroradicals of different macromolecular chains and, at the end, a crosslinked structured is developed. The macroradicals are generally very active and can easily react with environmental oxygen. To avoid this side reaction, radiation-initiated grafting reaction generally performs in inert environment in presence of either nitrogen or argon.

Generally, irradiation of aqueous polymer solutions results in the formation of radicals on the polymer chains. Moreover, radiolysis of water molecules results

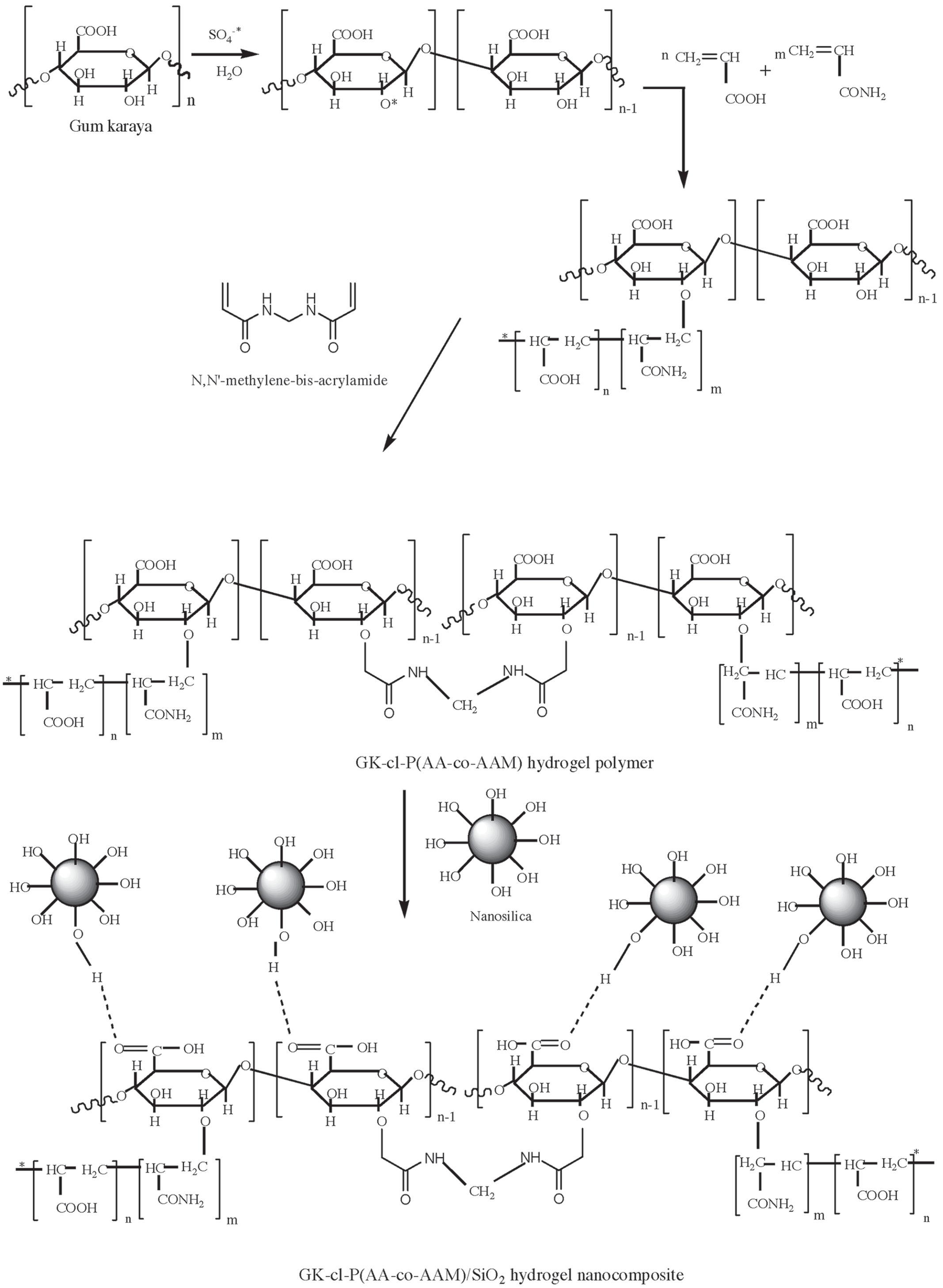


Figure 4. Mechanism for the synthesis of the gum karaya-*cl*-p(AA-*co*-AAM)/SiO$_2$ hydrogel nanocomposite. Reproduced with permission.[29] 2015, Elsevier Science Ltd.

in the formation of hydroxyl radicals that also attack the polymer chains, resulting in the formation of macroradicals. Recombination of the macroradicals on different chains results in the formation of covalent bonds and, finally, a crosslinked structure is formed. During radiation polymerization, macroradicals can interact with oxygen and, as a result, radiation initiated reactions are performed in an inert atmosphere using nitrogen or argon gas. In case of graft copolymerization using microwave radiation, two procedures are used. The first is a

Table 3. Crosslinked hydrogels of different polysaccharides and their applications.

Polysaccharide	Monomer(s)/other polymer	Crosslinker	Application	Ref.
Xanthan gum	P(AAM-*co*-AA)/Fe_3O_4	MBA	Adsorption of MG	[24]
	Starch	Sodium trimethaphosphate	Controlled release of anionic drugs	[134]
	AA/Loess	MBA	–	[135]
	P(HEMA-*co*-AA)	MBA	–	[64]
Gum ghatti	P(AA-*co*-AAM)/Fe_3O_4 NPs	MBA	Adsorption of rhodamine B	[22]
	P(AAM-*co*-AN)	MBA	As flocculent for the removal of colloidal particles	[55]
	P(AAM-*co*-MAA)	MBA	As flocculent for the removal of colloidal particles	[9]
	PAA/Fe_3O_4 NPs	MBA	Adsorption of MB	[27]
	P(AAM-*co*-AN)	MBA	Adsorption of Pb^{2+} and Cu^{2+}	[23]
	AA	MBA	Adsorption of Pb^{2+} and Cu^{2+}	[26]
Guar gum	P(AA-*co*-ANI)	hexamine	–	[136]
	–	MBA	Adsorption of Cu^{2+}	[71]
	PAA	MBA	–	[137]
	–	1,2,3,4-butanetetracarboxylic dianhydride	Release of proteins	[138]
Alginate	Chitosan/ hyaluronate	Ca^{2+}	Synthetic bone substitutes	[139]
	EG	$CaCl_2$	Bone tissue engineering	[140]
	NIPAM	$CaCl_2$	–	[141]
	Dextran-HEMA	Ca^{2+}	Biomedical applications	[142]
	PGMA	$CaCl_2$	Controlled release of riboflavin	[143]
	PVA	$CaCl_2$	Cardiac applications	[144]
	HA	$CaCl_2$	Myocardial tissue engineering	[145]
	Gelatin	$CaCl_2$	Soft tissue engineering	[146]
Starch	P(AA-*co*-SCA)	MBA	–	[147]
N-Succinylchitosan	PAA/Attapulgite	MBA	–	[148]

microwave assisted method, in which microwave radiation is used to initiation the reactions in addition to chemical initiators.[3,21,105,106] The second method is microwave initiated graft copolymerization. Here, the polymerization is initiated solely by microwave radiation.[3] In microwave graft copolymerization, the polysaccharide solution should be either soluble in water or should form a suspension. However, sometimes, even soluble polysaccharides do not form homogeneous solutions, and this loss of homogeneity decreases the overall graft yield. Despite this, hydrogels of gum polysaccharides synthesized using radiation are promising adsorbents due to the short polymer chains formed in this method. Also, because synthesis time is short, a greater number of functional groups remain in the graft copolymers or hydrogels. For example, hydrogel polymers of AA with tara gum (*Caesalpinia spinosa*) synthesized using γ-radiation-induced graft copolymerization have improved mechanical and swelling properties than those of tara gum itself.[149]

4. Stimuli-Responsive Graft Copolymers

4.1. Temperature-Responsive Graft Copolymers

Hydrogels that change their volume phase transition in response to changes in solution temperature are termed “temperature-responsive hydrogels” or “thermosensitive hydrogels.” In the study of smart hydrogels, temperature is the most commonly studied stimulus; however, it can be difficult to control. Generally, the phase transition of the thermosensitive hydrogels mainly depends on the hydrophilic-lipophilic balance (HLB); this, in turn, depends on the size and configuration of hydrophobic moieties in the hydrogels. The swelling/deswelling behavior of the thermosensitive hydrogels is due to the strengthening of hydrophobic interactions and the weakening of hydrogen bonding. Moreover, at elevated temperatures, hydrophobic associations between different polymer chains become stronger because increasing temperatures make hydrophobic interactions more favorable. Therefore, at elevated temperatures, increasing intermolecular forces between hydrophobic chains and the loss of stability of hydrogen bonds results in the shrinkage of the hydrogel network. Some thermosensitive hydrogels have a phase transition at a temperature above their lower critical solution temperature (LCST); this is the temperature above which the hydrogels deswell or undergo a phase transition from a soluble state (i.e., random coils) to an insoluble state (i.e., collapsed or globule form) with an increase in temperature. When the phase transition occurs upon temperature decrease it is called the upper critical solution temperature (UCST) (Figure 5).[151] Temperature-responsive hydrogels that have a LCST are called negative thermosensitive hydrogels.[152] Due to their numerous possible applications in biomedical science, hydrogel polymers that have a LCST are attracting much attention. Generally, polymer solubility increases with increasing temperature, however, the reverse is true for polymers with a LCST. This unusual solubility behavior is due to the predominating hydrophobic interactions. Furthermore, the LCST of the hydrogels can be altered by changing the ratio of hydrophilic and hydrophobic moieties in the structure of the hydrogel polymers.[153,154]

Below the LCST, the polymers form hydrogen bonds with surrounding water molecules. Above the LCST, the hydrogen bonds are weakened and the water molecules move from the polymer network into the bulk solution, leading to partial dehydration and agglomeration of the polymer chains. This phase transformation is associated with polymer conformational changes, and, above the LCST, the hydrated coiled structure of the hydrogel polymer converts into a partially dehydrated, globular structure (Figure 6).[151]

A number of researchers have become interested in poly(*N*-isopropyl acrylamide) (PNIPAM) temperature-responsive hydrogels because they exhibit a LCST phase transition close to human body temperature, i.e., 32 °C.[108,153,154] The LCST of PNIPAM hydrogels can be increased by incorporating hydrophilic monomers such as PAA, which preferentially forms hydrogen bonds rather than hydrophobic interactions.[155] The LCST of PNIPAM increased to 45 °C on incorporation of 18 wt% PAM, however, the LCST decreased to 10 °C on incorporation of 40% of hydrophobic *N*-tBAAM.[156] Wenceslau et al.[157] have synthesized thermoresponsive IPN hydrogels of chemically modified PVA and PNIPAAM with different degrees of substitution. The synthesized IPN hydrogels show both pH and temperature dependent swelling properties. Furthermore, the IPN hydrogels are less cytotoxic than PVA hydrogels, however, the increased PVA/PNIPAAM ratio results in lower cytocompatibility. Wei et al.[158] synthesized Salecan (a microbial polysaccharide) and PNIPAM based thermosensitive semi-IPNs. The synthesized semi-IPNs have good swelling capacities at room temperature as well as excellent thermosensitive properties, having rapid response rates to temperature changes. The IPN of guar gum and PNIPAM has also been reported to have thermo-responsive characteristics, and the IPNs with lower guar gum content had faster deswelling rates and lower water retention. Increasing the guar gum content of the IPN led to better temperature sensitivity.[159]

4.2. pH Responsive Graft Copolymers

pH responsive hydrogels are a class of smart composite hydrogels whose swelling characteristics change in response to small changes in pH. They contain ionizable functional groups that can donate or accept protons on pH

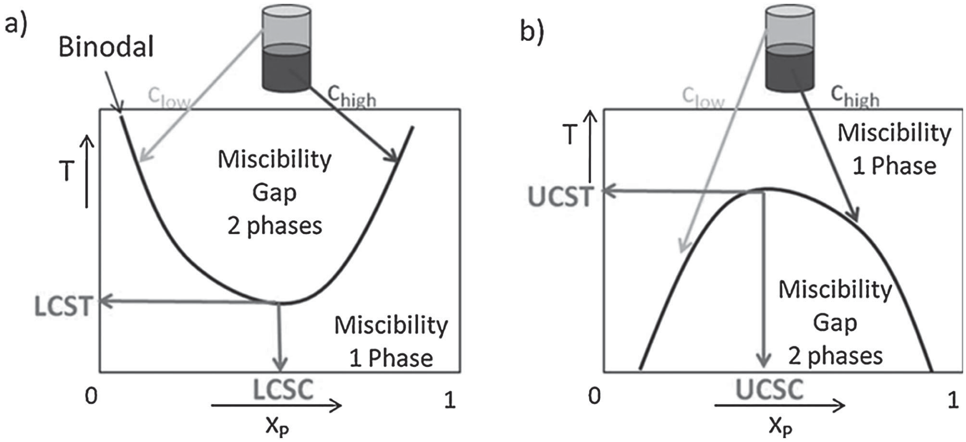


Figure 5. Phase diagram for a binary polymer-solvent mixture exhibiting a) LCST and b) UCST. Reproduced with permission.[151] 2012, Elsevier Science Ltd.

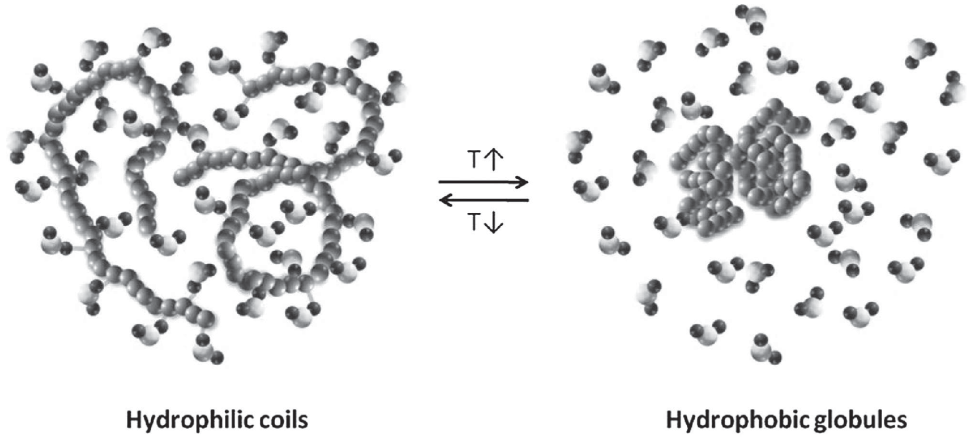


Figure 6. Coil to globule transition of a temperature responsive polymer in aqueous solution. Reproduced with permission.[151] 2012, Elsevier Science Ltd.

changes in the swelling medium. Upon change to environmental pH, the pKa values of the weakly ionizable functional groups in the hydrogel network change, this results in the fast swelling/deswelling of the hydrogels. Consequently, the hydrodynamic volume of the polymer chains changes. This change can be explained using osmotic pressure swelling (π_{ion}) theory, that is, the volume change results from the difference between the mobile ions concentration in the swollen polymer and the external solution.[3,9,55] Macromolecular chains backbones with ionizable groups generate polyelectrolytes in water. Weak polyacids such as PAA act as proton acceptors in acidic media, but they act as proton donors in neutral and basic media. In contrast, polybasic groups act as proton donors in acidic media and as proton acceptors in basic and neutral media. This indicates that the selection of polybases and polyacids must be tailored to the desired application of the hydrogel. In the case of a polyacidic polymer backbone, higher degree of swelling was observed in a neutral medium than that observed in alkali or acidic media. The swelling characteristic of ionic polymers in dilute electrolyte solutions is related to the osmotic swelling pressure between the hydrogel phase and the swelling medium. The osmotic swelling pressure (π_{ion}) is calculated by Equation (10)[3,9,55]

$$\pi_{\text{ion}} = RT\Sigma\left(C_i^g - C_i^s\right) \tag{10}$$

where C_i^g and C_i^s are, respectively, the molar concentrations of mobile ions in the swollen hydrogel and swelling medium, R is the gas constant, and T is the absolute temperature.

In neutral media, π_{ion} is very high because C_i^s becomes almost negligible. In the same vein, electrostatic repulsion between carboxylate ions is responsible for higher degree of swelling. In acidic media, most of the polyacids are protonated; therefore, the value of C_i^g is less as compared to that of mobile ions in solution, resulting in lower π_{ion} values. In contrast, in alkaline solutions, polyacidic groups are completely dissociated, however, at the same time, the higher concentration of Na^+ and ^-OH ions leads to a decrease in π_{ion} and degree of swelling. In addition, the presence of Na^+ ions shield the electrostatic repulsion between the carboxylate anions, results a significant decrease in swelling pressure (π_s).[98,99]

The phase transition of pH-responsive hydrogels is also influenced by the ionic strength of the swelling medium. With an initial increase in swelling medium ionic strength, the concentration of free mobile ions within the hydrogel polymer increases due to exchange of ions in the surrounding solution. Therefore, charge neutrality is maintained, and the osmotic swelling pressure difference between the hydrogel and the solution increases, causing the hydrogel to swell. However, in very high ionic strength solutions (1–10 M), deswelling of the hydrogel networks is observed. This type of swelling/deswelling behavior is due to a decreased osmotic swelling pressure difference. In this case, the osmotic pressure of the hydrogel network is almost equal to the osmotic pressure of the solution (Figure 7).[152] The effect of the ionic strength of different cations on the swelling behavior of gum-ghatti-based hydrogels was studied in solutions of different salt solutions, and it was observed that, after initial swelling, the hydrogels shrank in solutions of higher ionic strength.[160] pH-responsive hydrogels are mainly used for drug delivery applications. A pH-responsive hydrogel of cationic guar gum and AA was synthesized using photoinitiated free radical polymerization. Swelling studies at different pH solutions confirmed the pH-responsive behavior of the synthesized hydrogel. The synthesized hydrogel was used for the sustained release of ketoprofen, and, at pH 7.4, it was found that drug release was mostly due to non-Fickian diffusion. In contrast, in basic conditions, it was due to case II transport.[124] In another study, a pH responsive hydrogel of alginate and guar gum was prepared by crosslinking with gluteraldehyde, and this was used for the controlled delivery of

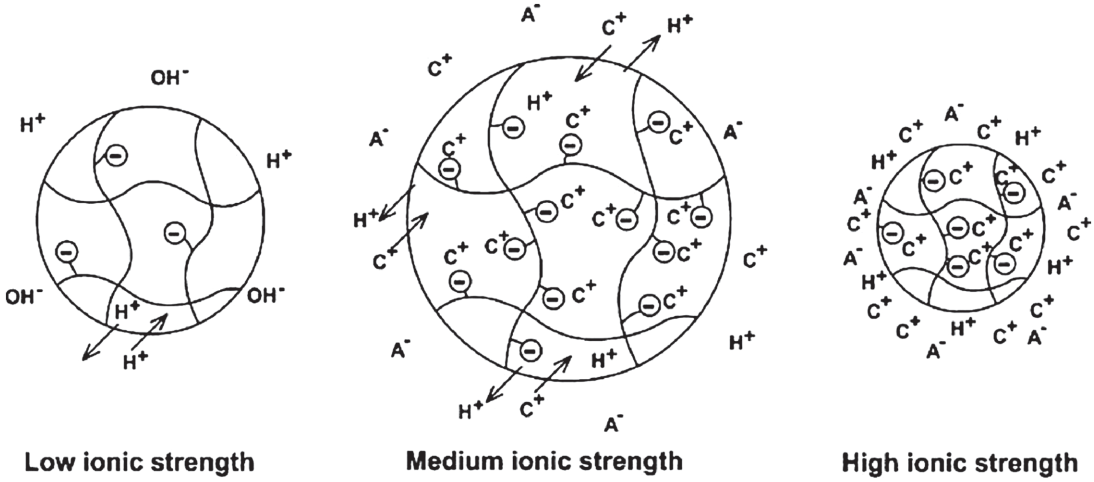


Figure 7. The effect of ionic strength of the swelling behavior of the hydrogels. Reproduced with permission.[152] 2008, Elsevier Science Ltd.

protein drugs. Alginate is pH sensitive and has properties that are favorable for intestinal delivery of protein drugs. However, the leaching of drugs and the rapid dissolution of alginate at high pH values is a significant problem with alginate hydrogels. To overcome these problems and to maximize drug encapsulation, guar gum was added to the polymer matrix and crosslinked with gluteraldehyde. The resultant hydrogel showed much better drug encapsulation and protein release at high pH values. Protein release from test hydrogels was minimal at pH 1.2 (≈ 20%) but rose to approximately 90% at pH 7.4 (Figure 8).[161]

4.3. Magnetosensitive Graft Copolymers

Hydrogels or gum-polysaccharides graft copolymers whose properties change in response to variations in magnetic fields are known as magnetosensitive hydrogels. Magnetically modulated hydrogels are prepared by encapsulation of magnetic particles within the 3D crosslinked polymer matrix of the gum-polysaccharide-based graft copolymers. The development of emulsion polymerization, such as the conventional emulsion polymerization, mini- and microemulsion polymerization, and surfactant-free emulsion polymerization, has led to new synthetic methods for the preparation of magnetosensitive graft copolymers. Magnetosensitive graft copolymers play an important role in health care and biomedical applications, such as gene and drug delivery, cell separation, and the treatment of cancer by magnetic intracellular hyperthermia. Magnetosensitive graft copolymers have also been widely used for the treatment of wastewater.[22,24,30] The ease of separation of graft copolymers from wastewater after treatment is a basic advantage of this method. The hydrogels can be easily separated by application of a magnetic field. Magnetic hydrogels of calcium alginate containing iron oxide nanoparticles have been successfully used for the removal of Cu^{2+} ions from wastewater.[162] In another study, magnetic nanocomposites of gum arabic with iron oxide nanoparticles were successfully synthesized and utilized for the adsorption of Cu^{2+} ions from the waste water, and a maximum adsorption capacity of 38.5 mg g^{-1} was achieved.[30]

A magnetic responsive hydrogel of κ-carrageenan and carboxymethyl chitosan was prepared and used as sustained drug delivery devices. The magnetoresponsive hydrogels were prepared by the interaction of the carboxylate and amine groups of the carboxymethyl

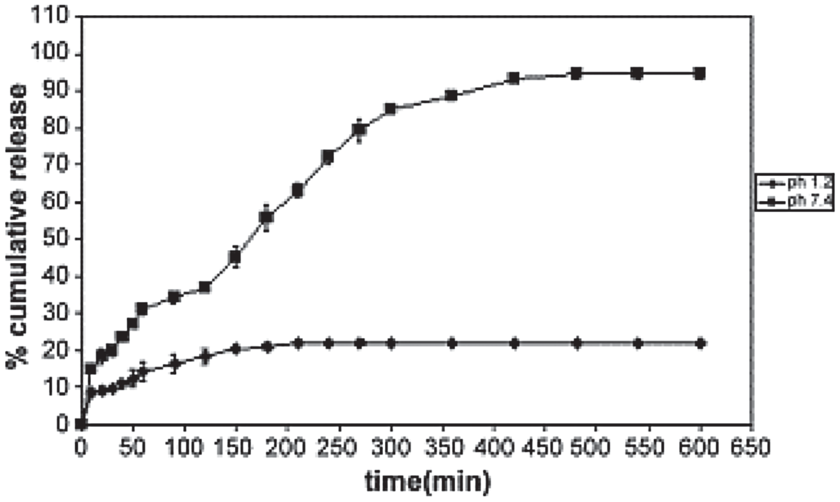


Figure 8. Drug release behavior of an alginate-guar gum hydrogel in different pH solutions. Reproduced with permission.[161] 2007, Elsevier Science Ltd.

chitosan as well as the sulfate pendants of the κ-carrageenan with Fe^{2+} and Fe^{3+} ions. The mechanism of the formation of magnetoresponsive hydrogels of κ-carrageenan and carboxymethyl chitosan is shown in Figure 9.[163]

4.4. Electrical-Stimulus-Responsive Graft Copolymers

Hydrogels that show a phase transition on application of an electric current are known as "electrical-stimulus-responsive" or "electroresponsive" hydrogels. These hydrogels are mainly composed of polyelectrolytes, i.e., hydrogels that contain high concentrations of ionizable functional groups along the polymer backbone.[164] For their function, there must be contact with a voltage source; this is a great disadvantages of these systems. Hydrogels either bend or deswell in the presence of an electric field. This bending or deswelling of the hydrogels depends on the shape of the hydrogel and its position relative to the electrode. The hydrogel bends if the main axis of the hydrogel lies parallel to the electrode but is not touching the electrode. Deswelling occurs when the hydrogel is oriented perpendicular to the electrode.[165] Electrical-stimulus-responsive hydrogels that bend in response to the electric current have been utilized mainly in mechanical devices such as valves, artificial body parts (fingers/hands/muscles), soft actuators, and molecular machines.[165,166] In contrast, electrical-stimulus-responsive hydrogels that deswell in response to electric currents are mainly used as drug delivery devices.[165,167] Importantly, the response of these hydrogels is highly dependent on the experimental set-up and the orientation of the hydrogels. Different experimental set-ups have been used to study the phase transitions of polyelectrolyte hydrogels in response to changes in electrical stimuli. If the electrodes are not connected to each other, a conducting medium is required, however, there is no need for a conducting medium (or nonconducting medium may be used) if the electrodes are connected together.[165] Electrosensitive graft copolymers of gum ghatti and PAA were synthesized and their swelling-deswelling behavior in response to changes in an electrical stimulus was successfully investigated. These hydrogels

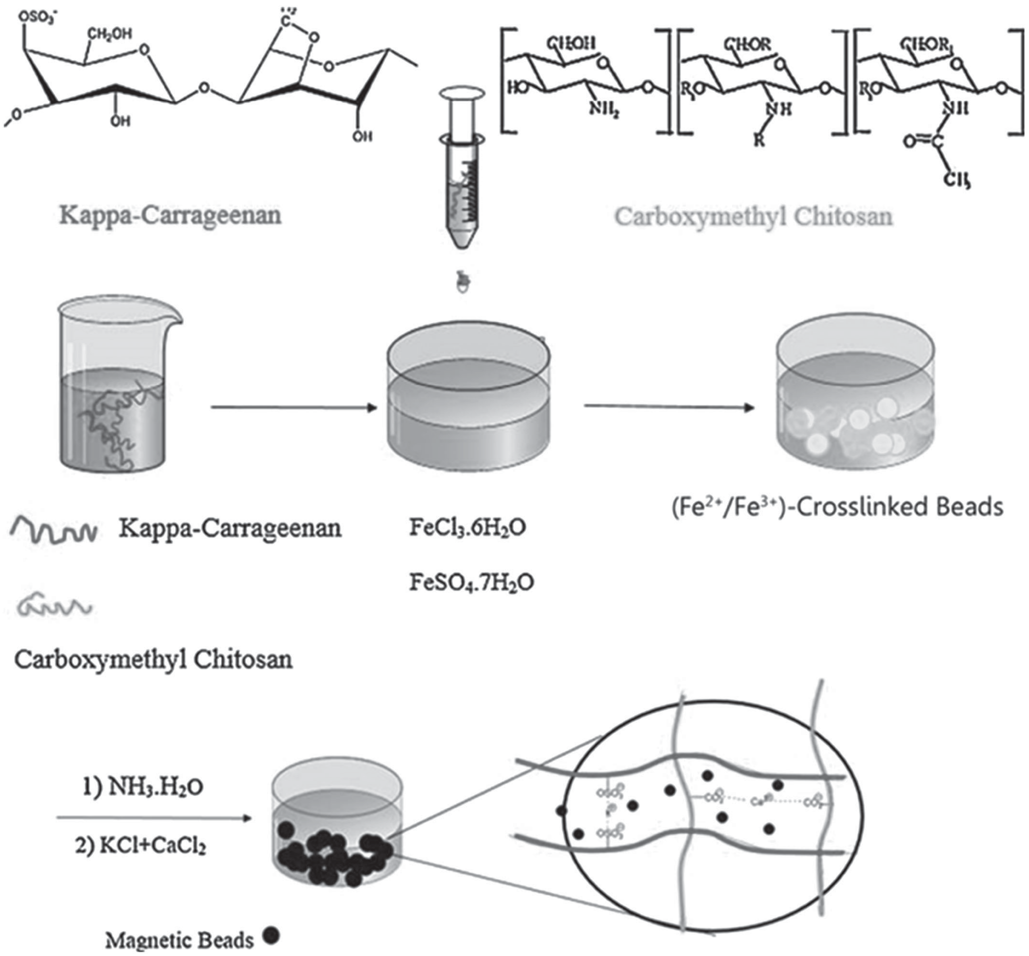


Figure 9. Mechanism of the formation of magneto-responsive hydrogels of κ-carrageenan and carboxymethyl chitosan. Reproduced with permission.[163] 2015, Elsevier Science Ltd.

exhibited remarkable deswelling behavior on the application of an electrical stimulus.[2]

Kim et al.[168] used a polyelectrolyte complex composed of chitosan/hyaluronic acid in NaCl solution at different pH values to study the effect of DC-electric stimulus on the deswelling ratio and bending angle. They found that, in comparison to measurements at neutral pH, the hydrogel bending angle was small at both extremely low and high pH values. They suggested that, in acidic and alkaline medium, the slow diffusion of ions from the crosslinked network was responsible for a small bending angle. The electrosensitive behavior of the calcium alginate/PAA hydrogel was also investigated.[169] Initially, it was expected that the PAA chains would be entangled through the calcium alginate matrix, and the free carboxylic acid groups present in PAA would make the hydrogel pH and electrosensitive. It was found that increasing the concentration of PAA in the hydrogel network increased the pH and electrosensitivity. A similar type of electrosensitive behavior was also observed upon increasing the concentration of ionizable groups in IPN hydrogels of PVA and PAA.[170] Electroresponsive hydrogels were also prepared by mixing of the two aqueous polymer solutions. Over a specific pH range, a polymer complex was formed due to hydrogen or ionic bonding between the two polymer solutions.[171,172] The electrosensitive hydrogel of polyallylamine and heparin was formed over a pH range of 3–11 by mixing their polymer solutions, the complex forms due to the ionic interactions between NH_3^+ groups of polyallylamine and the COO^- and SO_3^- groups of heparin.[172]

5. Biodegradation of Gum-Based Graft Copolymers

One of the biggest advantages of the gum polysaccharide based graft copolymers is their environmentally friendly nature. For example, they can be degraded in both aerobic and anaerobic conditions. Furthermore, modification by graft polymerization to improve mechanical (and other) properties should not affect the biodegradability or environmental friendliness of the gums. However, it was found that graft copolymerization of the polysaccharides and different vinyl monomers did slightly increase resistance to biodegradation. Despite this, according to ASTM standards of biodegradation, they can be still classes as biodegradable. Recently, the biodegradable nature of the gum ghatti and vinyl monomer, such as PAAM, PAA, poly(methacrylic acid) (PMAA), and poly(acrylonitrile) (PAN), based hydrogel polymers was studied, and they were found to be fully biodegradable using the soil composting method.[9,28,55]

It was found that degradation of gum-polysaccharide-based graft copolymers initially starts at polymer backbone of the gum polysaccharide itself. Later, the crosslinks between polymeric chains break, and, finally, the whole 3D polymer network collapses. It was also found that the initial rate of degradation was slow, but this became much faster in the later stages. Initially, time for water absorption is required, but, on reaching equilibrium capacity, the hydrogel polymer begins to degrade due to the action of microorganisms present in the soil compost. Various processes are involved in the degradation of the hydrogel polymers, including enzymatic and chemical degradation. Also, microbe secretion products present in the composting media were found to be involved in the degradation of the gum-polysaccharide-based graft copolymers, which caused the cleavage of chemical bonds aiding bacterial degradation.[9,28,55] Different characterization techniques, such as FTIR and SEM, have been used to monitor biodegradation at different stages of this process. Changes in the intensity and the shifting of some absorption peaks were observed in the FTIR spectra of the grafted polymers at different stages of biodegradation. Moreover, the SEM images of the surfaces of the samples at different stages showed some cracks. For example, the gum ghatti-*cl*-p(AA-*co*-MAA) hydrogel polymer was found to have a smooth, crack-free, continuous and regular morphology, however, in the first stages of biodegradation, the surface morphology became heterogeneous and cracks, fractures, and fissures appeared, indicators of the start of degradation. In the second stage of degradation both the number and size of these fractures and fissures were increased. This observation may be due to the disintegration of grafted polymer chain from gum-polysaccharide backbone. During the last stage of degradation, there was a drastic change in the surface morphology of hydrogel, where the smooth and homogeneous surface of pure hydrogel was transformed into a rough and heterogeneous surface with large cracks, fractures, and fissures.[9]

6. Applications of Gum-Based Graft Copolymers as Adsorbents

Water is a basic resource for life, and only 0.03% of the total water available on earth can be used for our activities. Rapid population and industrial growth has escalated water demand, yet the availability of the useable water remains constant. In addition, lack of proper industrial water treatment has decreased the availability of useable water. Mostly in the developing countries, a large amount of different toxic pollutants such as heavy metal cations (Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, and Cr^{6+}), cationic (methylene blue, rhodamine B, methyl violet, brilliant green, etc.,) and anionic dyes (Congo red, direct red 81, etc.) exists in the industrial wastewaters; for example, mining, battery manufacturing, oil refining, printing and pigments, tanneries, and metal plating. Many methods exist and are used for the treatment of industrial effluent such as coagulation/flocculation, photocatalysis, chemical oxidation, and microbiological or enzymatic degradation. Generally, they have several disadvantages such as the incomplete removal of the pollutant, generation of secondary pollutants, and very high adsorption costs. Adsorption of different pollutants, including dyes and heavy metal ions, onto a solid material is the method of choice for the treatment of wastewater. Gum-polysaccharide-based graft copolymers have shown their potential for the adsorption of different pollutants from the wastewater. The main advantage of using these materials is their low cost, biodegradability, and the ability to tailor the material to the desired application. Graft copolymers of gum polysaccharides can be tailored to absorb a particular impurity to be removed from contaminated water. The main advantage of the polysaccharide-based crosslinked hydrogels is that, first, they do not generate any secondary pollutants; moreover, they can be used repeatedly for adsorption, i.e., they can be recycled (Figure 10).[173]

6.1. Adsorption of Dyes

The textile industry effluents contain a wide variety of toxic dyes, which has serious effect on human health as well as the photosynthetic process of aquatic biota. The majority of synthetic dyes are toxic, carcinogenic, and mutagenic in nature. Because of the high water solubility, dyes are almost nondegradable; furthermore, they cannot be degraded in sludge treatment plants.[174] Gum-polysaccharide-based graft copolymers are promising adsorbents that have been used for the decontamination of wastewater. Recently, numerous gum-polysaccharide-based graft copolymers such as gum ghatti,[22,25,28] gum karaya,[29] xanthan gum,[24,50] and guar gum[72] have been used for the removal of different dyes from wastewater. Most gum polysaccharides contain anionic functional groups, for example, hydroxyl and carboxylic acid groups. Consequently, they adsorb cationic dyes like methylene blue, methyl violet, and rhodamine B well.[22,24,25,29,50,72] Gum-polysaccharide-based hydrogels remove even very high concentrations of cationic dyes.[29] The influence of feed solution dye concentration on the binding mechanism of cationic dyes (methyl violet and basic fuchsine) on a semi-IPN composed of carboxymethyl cellulose and p(AAM-*co*-HEMA) as a matrix has been extensively investigated by Bhattacharyya and Ray.[175] All the hydrogels showed chemical sorption at low dye concentrations and physical sorption at high concentrations. The adsorption capacities of the gum-polysaccharides-based hydrogels have been found to increase tremendously on the addition of metal-oxides and other nanoparticles, for example, Fe_3O_4, SiO_2, TiO_2, graphene, and carbon nanotubes.[22,24,29,30,51,52,64,72,85,99]

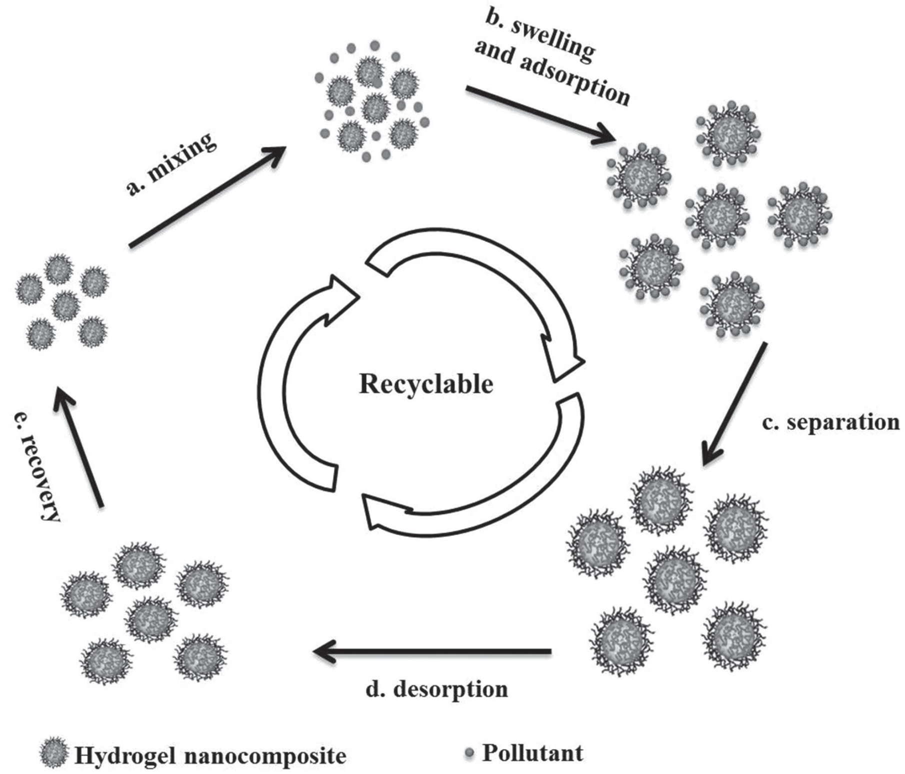


Figure 10. Use of hydrogels as adsorbents. Reproduced with permission.[173] 2013, Elsevier Science Ltd.

Using the graft copolymerization technique, a hybrid hydrogel of the AA grafted starch-*g*-AA and montmorillonite was synthesized using MBA as the crosslinking agent and cerium ammonium nitrate as the initiator. This hydrogel was then used to remove Safranine T from aqueous solution. It was found that increasing the montmorillonite content up to 1% increased the water absorption capacity of the hydrogel, whereas further increase in the montmorillonite content decreased the water absorption capacity.[176] In another study, a hydrogel polymer of sodium alginate and acrylic monomers, such as AA and AAM, was synthesized by graft copolymerization. The synthesized hydrogel polymer was used as an adsorbent for basic fuchsine and methyl violet dyes, and maximum adsorption capacities of the 763 and 550 mg g^{-1}, respectively, were measured.[177] Recently, we have utilized a hydrogel nanocomposite of the xanthan gum and p(AA-*co*-AAM) containing Fe_3O_4 magnetic nanoparticles for the adsorption of rhodamine B from aqueous solution. The synthesized hydrogel nanocomposite has a good adsorption capacity (654.87 mg g^{-1}), especially in comparison with the parent hydrogel polymer (471.69 mg g^{-1}).[22] In another study, a hydrogel nanocomposite of gum karaya and p(AA-*co*-AAM) was used for the in situ synthesis of SiO_2 nanoparticles within the hydrogel polymer matrix, and the synthesized hydrogel nanocomposite was used for the adsorption of methylene blue from aqueous solution; this material was found to have a very high adsorption capacity of 1408.67 mg g^{-1}. The adsorption process was found to be highly pH dependent, and this was subsequently found to be dependent on the value of the point of zero charge on the surface of the adsorbent. The adsorption mechanism was found to follow both external mass as well as intraparticle diffusion processes. The mechanism for the adsorption of methylene blue onto the surface of the hydrogel nanocomposite is shown in Figure 11.[29] The high adsorption capacity of the hydrogel nanocomposite was due to its high surface area and the functionalities present in the chemical structure of the hydrogel nanocomposite.[29] The hydrogel nanocomposite of xanthan gum and PAAM containing SiO_2 was also used to adsorb

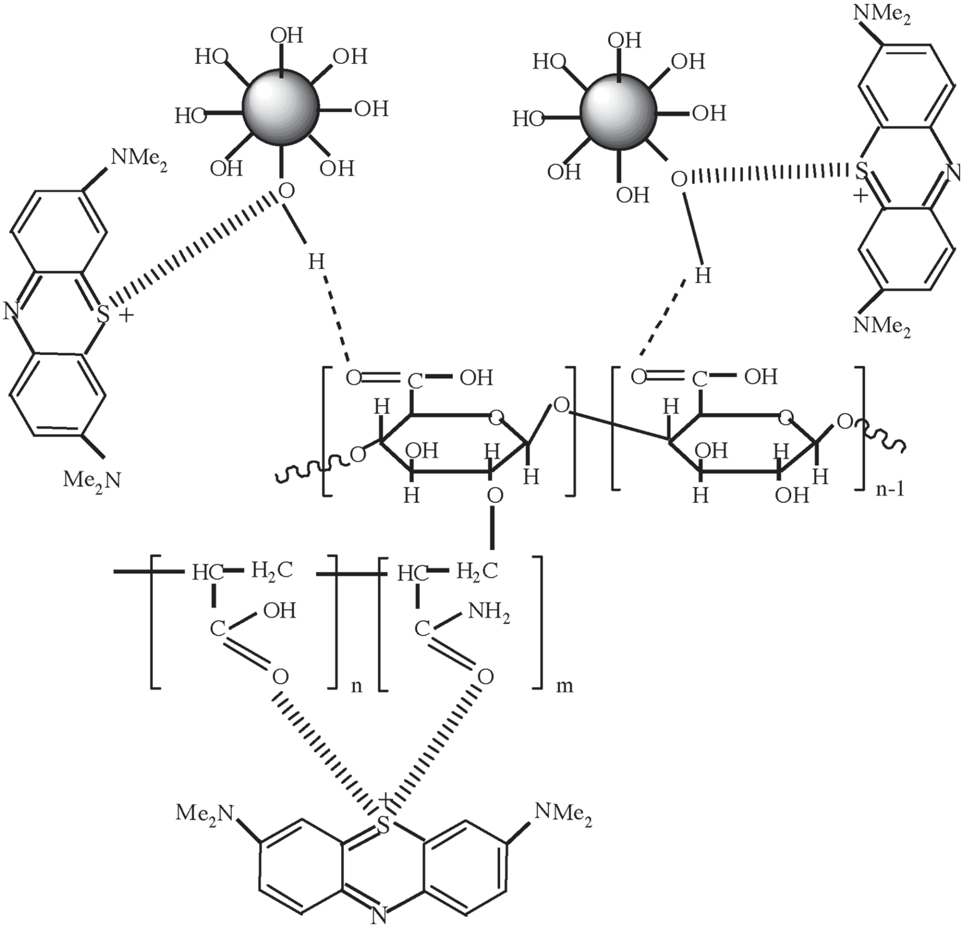


Figure 11. Mechanism of the adsorption of methylene blue onto the gum karaya-*cl*-p(AA-AAM)/SiO_2 hydrogel nanocomposite. Reproduced with permission.[29] 2015, Elsevier Science Ltd.

other cationic dyes such as methylene blue and methyl violet.[50]

Gum-polysaccharide-based graft copolymers were also used for the removal of anionic dyes, such as methyl orange and Congo red.[41] Chitosan-based graft copolymers have been used extensively for the adsorption of anionic dyes from wastewaters. A hydrogel polymer of chitosan and PAAM was used for the removal of remazol brilliant violet and procion yellow MX 8G dyes.[39] A hydrogel polymer of sodium alginate and copolymeric mixture of p(AA-*co*-HEMA) was used for the adsorption of Congo red from aqueous solution. The semi and full-IPN hydrogels and cryogels based on PAAM and chitosan were used for the adsorption of an anionic dye, i.e., direct blue 1, and a cationic dye, i.e., methylene blue.[36,112] The semi IPN hydrogels were found to adsorb the anionic dye because of the presence of positively charged functional groups, however, the full IPN hydrogel adsorbed a greater amount of the cationic dye (methylene blue) because of the abundance of anionic functionalities such as carboxylic acid groups. Both adsorbents were used in six successive adsorption–desorption cycles.[36,112] Some gum-polysaccharide-based adsorbents used for the adsorption of anionic as well as cationic dyes are listed in Table 4.

Table 4. Maximum adsorption capacity of gum polysaccharides based graft copolymers for ionic dyes.

Gum polysaccharide	Monomer/ crosslinker/other chemicals	Pollutant	Adsorption isotherm	Adsorption kinetics	ADSORPTION CAPACITY [mg g^{-1}]	Ref.
Chitosan	PAAM	Remazol brilliant violet and procion yellow MX 8G dyes	Langmuir	Pseudo second order	1428.57 (RV) and 1000 (PY)	[39]
Xanthan gum	P(AAM-*co*-AA)/ Fe_3O_4	Malachite green	Langmuir	Pseudo second order	497.15	[24]
Gum ghatti	P(AA-*co*-AAM)/ Fe_3O_4 NPs	Rhodamine B	Langmuir	Pseudo second order	654.87	[22]
Gum ghatti	P(AAM-*co*-MAA)	Methylene blue and methyl violet	Langmuir	Pseudo second order	694.44 (MB) and 543.47 (MV)	[25]
Gum ghatti	PAA	Methylene blue and Rhodamine B	Langmuir	Pseudo second order	909.09 (MB) and 819.67 (RhB)	[28]
Gum ghatti	PAA/Fe_3O_4 NPs	Methylene blue	Langmuir	Pseudo second order	671.14	[27]
Gum karaya	P(AA-*co*-AAM)/SiO_2	Methylene blue	Langmuir	Pseudo second order	1408.67	[29]
Guar gum	PAAM/SiO_2	Reactive red and Congo red	Langmuir	Pseudo second order	579.01 (RB) and 233.24 (CR)	[41]
Alginate	P(SA-*co*-styrene)/ organo-illite/smectite clay	Methylene blue	Langmuir	Pseudo second order	1843.46	[34]
Chitosan	PAAM	Methylene blue	Langmuir	Pseudo second order	1006.7	[36]
Chitosan	P(EG-*co*-AAM)	Acid orange 7 (AO 7), Methyl orange (MO)	Langmuir	Pseudo second order	243.31 (AO7) and 202.02 (MO)	[42]
Chitosan	PAA/ montmorillonite	Methylene blue	Langmuir	Pseudo second order	1859	[38]
Welan gum	cellulose/carbon tubes	Methylene blue	Langmuir and Sip	Pseudo second order	302.1	[16]
Xanthan gum	PAAM/SiO_2	Congo red	Langmuir	Pseudo second order	209.205	[51]
Xanthan gum	PAAM/SiO_2	Methylene blue	Langmuir	Pseudo second order	497.5	[50]
Xanthan gum	PAAM/SiO_2	Methyl violet	Langmuir	Pseudo second order	378.8	[50]
Carboxymethyl cellulose	P(AAM-*co*-HEMA)	Basic fuchsine	Langmuir	Pseudo second order	920	[175]

6.2. Adsorption of Heavy Metal Ions

Heavy metal cations, such as Pb^{2+}, Cu^{2+}, Cr^{6+}, etc., are highly toxic and even low concentrations of their presence in water have adverse effects on human health as well as on aquatic biota. The untreated effluents from heavy industries and uncontrolled erosion of soils are leading cause for toxic heavy metals presence in surface waters. Over the last few years, a number of techniques such as membrane separation, electrochemical treatment, coagulation–flocculation, etc., have been used to remove toxic heavy metals contaminated water resource, however, the adsorption technique has attracted considerable attention because of its low cost and easy operation as well as its ability to remove even very low concentrations of toxic heavy metals from wastewater. In this direction, bio-based polymers-based adsorbents received great attention because of their low cost, high adsorption efficiency, and environmentally benign nature. Adsorbents based on graft copolymers of gum polysaccharides exhibit superior adsorption capacities and affinities toward metal ions and have been extensively used for the removal of toxic metal cations from contaminated surface water. Recently, graft copolymers of gum polysaccharides have found their place as a potential adsorbents for heavy metal ions.[18,19,21,23,30–33,35,37,40,43,44,52,70,71,86,123,125,162] Chitosan, gum ghatti, xanthan gum, guar gum, alginate, cellulose derivatives, and other polysaccharide-based graft copolymers have shown promising sorption properties for heavy metal ions, and some results are summarized in Table 5.

Table 5. Maximum adsorption capacities of gum-polysaccharide-based graft copolymers for heavy metal ions.

Gum polysaccharide	Monomer/ crosslinker/other chemicals	Pollutant	Adsorption isotherm	Adsorption kinetics	Adsorption capacity [mg g^{-1}]	Ref.
Starch	Poly(ethylacrylate)	Zn^{2+}	Langmuir	Pseudo second order	116	[20]
Cassia javanica seed gum	PAA	Hg^{2+}	Langmuir	Pseudo second order and Intra-particle diffusion model	135	[21]
Gum ghatti	P(AAM-*co*-AN)	Pb^{2+} and Cu^{2+}	Langmuir	Pseudo second order	384.6 (Pb^{2+}) and 203.7 (Cu^{2+})	[23]
Gum ghatti	PAA	Pb^{2+} and Cu^{2+}	Langmuir	Pseudo second order	(310.55) Pb^{2+} and (84.74) Cu^{2+}	[26]
Tragacanth gum	Polyamidoxime	Co^{2+}, Zn^{2+}, Cr^{3+}, Cd^{2+}	Temkin	Pseudo second order	100.0 (Co^{2+}), 76.92 (Zn^{2+}), 71.42 (Cr^{3+}) and 66.67 (Cd^{2+})	[18]
Guar gum	Fe_3O_4 NPs	Cu^{2+}	Langmuir	–	38.5	[30]
Chitosan	PAN	Cu^{2+}, Ni^{2+}, Cr^{6+}	Freundlich	Pseudo second order	(230.79)Cu^{2+}, (385.54)Ni^{2+}, (122.83)Cr^{6+}	[31]
Guar gum	PAAM	Cr^{6+}	Langmuir and Freundlich	–	588.24	[40]
Xanthan gum	PEA	Pb^{2+}	Langmuir	Pseudo second order	142.86	[32]
Xanthan gum	PAAM/SiO_2	Pb^{2+}	Langmuir	Pseudo-second order	1012.15	[33]
Vinyl-functionalized alginate	P(MAA-*co*-IA)	Pb^{2+}	Langmuir	Quasi-second-order kinetic model	423.28	[35]
Cassia marginata seed gum	PMMA	Cr^{6+}	Freundlich and Langmuir	Second order	185.19	[43]
Cellulose	Sodium montmorillonite	Cr^{6+}	Langmuir	Second order	22.2	[44]
Sesbania gum		Cu^{2+}, Cd^{2+}, Pb^{2+}	Langmuir	Pseudo second order	(27.6) Cu^{2+}, (87.1) Cd^{2+}, (22.7) Pb^{2+}	[17]

Cross-linked hydrogel polymer beads of chitosan with AA were used for the adsorption of Cu^{2+} ions. For comparison, the chitosan beads were also prepared without AA. The beads containing AA were found to have much better stability in low pH solutions and had higher mechanical strengths than those without AA. Moreover, the beads with AA also had greater adsorption capacities compared to beads without AA. Carboxylic acid groups in the hydrogel polymer form bidentate carboxylates with metal ions. The desorption of the metal ion was observed in solutions with pH values less than 4. Due to the better mechanical properties of the hydrogel polymer, it could be used for six successive cycles of adsorption–desorption without any loss in adsorption capacity (Figure 12).[173]

In another study, a hydrogel polymer of graphene oxide and chitosan, DNA, and protein was synthesized and used for the adsorption of different dyes and metal ions from aqueous solution. The synthesized hydrogels showed maximum adsorption capacities of 1100 and 1350 mg g^{-1} for methylene blue and methyl violet, respectively.[178] In our recent work, we have used graft copolymers of gum ghatti with different vinyl monomers, such as AAM, AA, and AN, for the removal of different metal cations from wastewater. The graft copolymer of *Cassia javanica* seed gum with poly(acrylic acid) (PAA) was used for the adsorption of Hg^{2+} from aqueous solution. The adsorption was found to follow a pseudo-second-order rate model and Langmuir adsorption isotherm with the maximum adsorption capacity of 135 mg g^{-1}.[21]

7. Conclusions and Outlook

In the last decade, gum-polysaccharide-based graft copolymers have received much attention. They have many advantages over other materials due to their unique value proposition such as low cost, environmentally friendly nature, improved responsiveness, and mechanical properties. The increasing cost of the conventional and commercially available adsorbents has made the low cost polysaccharide based adsorbents very attractive for the wastewater treatment. Furthermore, they can be tailored according to the end-use application. Of the synthetic methods, graft copolymerization gives better control over the properties of the end product. Moreover, the smart behavior of these graft copolymers improves the property profile of this special class of materials. The graft copolymers of gum polysaccharides can be triggered to respond to external environmental conditions such as pH, temperature, and magnetic fields. As adsorbents, gum-polysaccharide-based graft copolymers have potential to remove pollutants like heavy metal cations and synthetic dyes from wastewater. They have also shown very fast adsorption kinetics and very high adsorption capacities. In addition, they can be used repeatedly as adsorbents for four or five cycles of adsorption and desorption. The graft copolymerization of gum polysaccharides with synthetic monomers have helped in overcoming their limitations and made them suitable for use in the industrial scale. However, the graft copolymerization of gum polysaccharides has its own limitations such as the loss of inherent biodegradability of gum polysaccharides. However, a number of

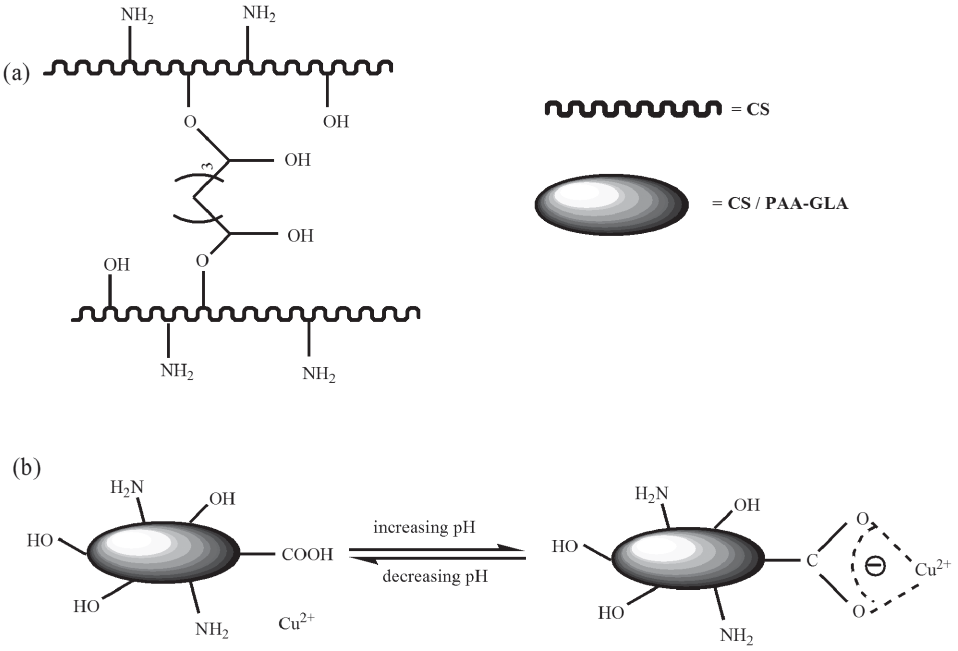


Figure 12. a) The structure of chitosan-gluteraldehyde hydrogel, and b) the mechanism of the adsorption and desorption of Cu^{2+} using the chitosan-gluteraldehyde-PAA hydrogel. Reproduced with permission.[173] 2013, Elsevier Science Ltd.

recent studies have proven that these limitations can be overcome. In addition, different methods of graft copolymerization of gum polysaccharides as well as their unique properties such as stimuli-responsive behavior make them suitable for their use in large scale. Therefore, it can be concluded that gum polysaccharides based graft copolymers have shown a number of benefits over other adsorbents and can be used for commercial applications in future.

Acknowledgements: The authors are grateful to the National Research Foundation (NRF), South Africa, for awarding a postdoctoral research fellowship to Dr. Hemant Mittal. H.M. and S.S.R. also thank the Department of Science and Technology and the Council for Scientific and Industrial Research for financial support.

Received: November 2, 2015; Revised: December 16, 2015; Published online: February 11, 2016; DOI: 10.1002/mame.201500399

Keywords: adsorption; graft copolymerization; hydrogels; polysaccharides; stimuli-responsive

[1] V. Rana, P. Rai, A. K. Tiwary, R. S. Singh, J. F. Kennedy, C. J. Knill, *Carbohydr. Polym.* **2011**, *83*, 1031.
[2] B. S. Kaith, R. Jindal, H. Mittal, K. Kumar, *Chem. Sin.* **2010**, *1*, 44.
[3] H. Mittal, B. S. Kaith, R. Jindal, *Chem. Sin.* **2010**, *1*, 59.
[4] M. Patenaude, N. M. B. Smeets, T. Hoare, *Macromol. Rapid Commun.* **2014**, *35*, 598.
[5] S. Bondalapati, E. Ruvinov, O. Kryukov, S. Cohen, A. Brik, *Macromol. Rapid Commun.* **2014**, *35*, 1754.
[6] G. M. Patel, C. P. Patel, T. C. Trivedi, *Eur. Polym. J.* **1999**, *35*, 201.
[7] A. Pourjavadi, H. Hosseinzadeh, R. Mazidi, *J. Appl. Polym. Sci.* **2005**, *98*, 255.
[8] H. M. Kang, Y. L. Cai, P. S. Liu, *Carbohydr. Res.* **2006**, *341*, 2851.
[9] H. Mittal, R. Jindal, B. S. Kaith, A. Maity, S. S. Ray, *Carbohydr. Polym.* **2015**, *115*, 617.
[10] B. S. Kaith, R. Jindal, H. Mittal, K. Kumar, *Int. J. Polym. Mater.* **2012**, *61*, 99.
[11] G. Sen, R. Kumar, S. Ghosh, S. Pal, *Carbohydr. Polym.* **2009**, *77*, 822.
[12] K. Kumar, B. S. Kaith, R. Jindal, H. Mittal, *J. Appl. Polym. Sci.* **2012**, *124*, 4969.
[13] A. Vahdat, H. Bahrami, N. Ansari, F. Ziaie, *Radiat. Phys. Chem.* **2007**, *76*, 787.
[14] Y. S. R. Krishnaiah, B. P. Srinivas, *Open Drug Delivery J.* **2008**, *2*, 71.
[15] F. G. Prezotti, B. S. F. Cury, R. C. Evangelista, *Carbohydr. Polym.* **2014**, *113*, 286.
[16] C. Deng, J. Liu, W. Zhou, Y. K. Zhang, K. F. Du, Z. M. Zhao, *Chem. Eng. J.* **2012**, *200*, 452.
[17] S. Lan, Z. Leng, N. Guo, X. Wu, S. Gan, *Colloid. Surf., A* **2014**, *446*, 163.
[18] A. Masoumi, M. Ghaemy, *Carbohydr. Polym.* **2014**, *108*, 206.
[19] P. Saravanan, V. T. P. Vinod, B. Sreedhar, R. B. Sashidhar, *Mater. Sci. Eng. C* **2012**, *32*, 581.
[20] V. Singh, S. Maurya, *Int. J. Biol. Macromol.* **2010**, *47*, 348.
[21] V. Singh, S. K. Singh, S. Maurya, *Chem. Eng. J.* **2010**, *160*, 129.
[22] H. Mittal, S. B. Mishra, *Carbohydr. Polym.* **2014**, *101*, 1255.
[23] H. Mittal, A. Maity, S. S. Ray, *J. Phys. Chem. B* **2015**, *119*, 2026.
[24] H. Mittal, V. Parashar, S. B. Mishra, A. K. Mishra, *Chem. Eng. J.* **2014**, *255*, 471.
[25] H. Mittal, A. Maity, S. S. Ray, *Int. J. Biol. Macromol.* **2015**, *79*, 8.
[26] E. Fosso-Kankeu, H. Mittal, S. B. Mishra, A. K. Mishra, *J. Ind. Eng. Chem. Res.* **2015**, *22*, 171.
[27] H. Mittal, N. Ballav, S. B. Mishra, *J. Ind. Eng. Chem. Res.* **2014**, *20*, 2184.
[28] H. Mittal, E. Fosso-Kankeu, S. B. Mishra, A. K. Mishra, *Int. J. Biol. Macromol.* **2013**, *62*, 370.
[29] H. Mittal, A. Maity, S. S. Ray, *Chem. Eng. J.* **2015**, *279*, 166.
[30] S. S. Banerjee, D.-H. Chen, *J. Hazard. Mater.* **2007**, *147*, 792.
[31] P. Shankar, T. Gomathi, K. Vijayalakshmi, P. N. Sudha, *Int. J. Biol. Macromol.* **2014**, *67*, 180.
[32] S. Pandey, S. B. Mishra, *Carbohydr. Polym.* **2012**, *90*, 370.
[33] S. Ghorai, A. K. Sarkar, S. Pal, *Bioresour. Technol.* **2014**, *170*, 578.
[34] Y. Wang, W. Wang, A. Wang, *Chem. Eng. J.* **2013**, *228*, 132.
[35] W. Wang, L. Zong, A. Wang, *Int. J. Biol. Macromol.* **2013**, *62*, 225.
[36] E. S. Dragan, M. M. Lazar, M. V. Dinu, F. Doroftei, *Chem. Eng. J.* **2012**, *204*, 198.
[37] A. Pal, D. Das, A. K. Sarkar, S. Ghorai, R. Das, S. Pal, *Eur. Polym. J.* **2015**, *66*, 33.
[38] L. Wang, J. Zhang, A. Wang, *Colloids Surf. A* **2008**, *322*, 47.
[39] V. Singh, A. K. Sharma, R. Sanghi, *J. Hazard. Mater.* **2009**, *166*, 327.
[40] E. S. Abdel-Halim, S. S. Al-Deyab, *Carbohydr. Polym.* **2011**, *86*, 1306.
[41] S. Pal, A. S. Patra, S. Ghorai, A. K. Sarkar, V. Mahato, S. Sarkar, R. P. Singh, *Bioresour. Technol.* **2015**, *191*, 291.
[42] S. Zhao, F. Zhou, L. Li, M. Cao, D. Zuo, H. Liu, *Composites, Part B* **2012**, *43*, 1570.
[43] G. Crini, P.-M. Badot, *Prog. Polym. Sci.* **2008**, *33*, 399.
[44] W. S. Wan Ngah, L. C. Teong, M. A. K. M. Hanafiah, *Carbohydr. Polym.* **2011**, *83*, 1446.
[45] R. Li, D. L. Feke, *Food Chem.* **2015**, *172*, 808.
[46] É. Paquet, A. Bédard, S. Lemieux, S. L. Turgeon, *Bioact. Carbohydr. Dietary Fibre* **2014**, *4*, 39.
[47] R. Jindal, B. S. Kaith, H. Mittal, *Polym. Renewable Resour.* **2011**, *2*, 105.
[48] A. Palaniraj, V. Jayaraman, *J. Food Eng.* **2011**, *106*, 1.
[49] B. Katzbauer, *Polym. Degrad. Stabil.* **1998**, *59*, 81.
[50] S. Ghorai, A. Sarkar, M. Raoufi, A. B. Panda, H. Schönherr, S. Pal, *ACS Appl. Mater. Interfaces* **2014**, *6*, 4766.
[51] S. Ghorai, A. K. Sarkar, A. B. Panda, S. Pal, *Bioresour. Technol.* **2013**, *144*, 485.
[52] S. Ghorai, A. Sinhamahpatra, A. Sarkar, A. B. Panda, S. Pal, *Bioresour. Technol.* **2012**, *119*, 181.
[53] P. S. Gils, D. Ray, P. K. Sahoo, *Int. J. Biol. Macromol.* **2009**, *45*, 364.
[54] G. O. Aspinall, E. L. Hirst, A. Wickstrom, *J. Chem. Soc.* **1955**, 1160.
[55] H. Mittal, R. Jindal, B. S. Kaith, A. Maity, S. S. Ray, *Carbohydr. Polym.* **2014**, *114*, 321.
[56] M. Jefferies, G. Pass, G. O. Phillips, *J. Sci. Food Agri.* **1977**, *28*, 173.
[57] M. Nakauma, T. Funami, S. Noda, S. Ishihara, S. Al-Assaf, K. Nishinari, G. O. Phillips, *Food Hydrocolloids* **2008**, *22*, 1254.

[58] S.-P. Nie, C. Wang, S. W. Cui, Q. Wang, M.-Y. Xie, G. O. Phillips, *Food Hydrocolloids* **2013**, *32*, 221.
[59] E. Dickinson, *Food Hydrocolloids* **2003**, *17*, 25.
[60] E. Dickinson, *Food Hydrocolloids* **2009**, *23*, 1473.
[61] V. K. Kulshrestha, A. C. Chatterjee, S. N. Mukherjee, *Macromol. Chem. Phys.* **1962**, *54*, 205.
[62] E. Dickinson, D. J. Elverson, B. S. Murray, *Food Hydrocolloids* **1989**, *3*, 101.
[63] M. Elmanan, S. Al-Assaf, G. O. Phillips, P. A. Williams, *Food Hydrocolloids* **2008**, *22*, 682.
[64] P. S. Gils, D. Ray, P. K. Sahoo, *Int. J. Biol. Macromol.* **2010**, *46*, 237.
[65] A. T. Paulino, M. R. Guilherme, L. H. C. Mattoso, E. B. Tambourgi, *Macromol. Chem. Phys.* **2010**, *211*, 1196.
[66] B. S. Kaith, S. Ranjta, *Desalin. Water Treat.* **2010**, *24*, 28.
[67] S. Ibrahim, I. Mousaa, M. Ibrahim, *Bull. Mater. Sci.* **2014**, *37*, 603.
[68] J. C. Brown, G. Livesey, *Am. J. Clin. Nutr.* **1994**, *60*, 956.
[69] K. Behari, R. Kumar, M. Tripathi, P. K. Pandey, *Macromol. Chem. Phys.* **2001**, *202*, 1873.
[70] http://healthyeating.sfgate.com/health-benefits-guar-gum-7855.html (accessed: 2015).
[71] S. Thakur, S. Kumari, P. Dogra, G. S. Chauhan, *Carbohydr. Polym.* **2014**, *106*, 276.
[72] V. K. Gupta, D. Pathania, P. Singh, A. Kumar, B. S. Rathore, *Carbohydr. Polym.* **2014**, *101*, 684.
[73] D. M. W. Anderson, M. M. E. Bridgeman, *Phytochemistry* **1985**, *24*, 2301.
[74] N. Karimi, M. A. Mohammadifar, *Food Hydrocolloids* **2014**, *37*, 124.
[75] F. Chenlo, R. Moreira, C. Silva, *J. Food Eng.* **2010**, *96*, 107.
[76] D. M. W. Anderson, M. M. E. Bridgeman, *Food Hydrocolloids* **1988**, *2*, 51.
[77] S. Sadeghi, F. A. Rad, A. Z. Moghaddam, *Mater. Sci. Eng. C* **2014**, *45*, 136.
[78] Saruchi, B. S. Kaith, R. Jindal, V. Kumar, *Polym. Degrad. Stabil.* **2015**, *115*, 24.
[79] B. S. Kaith, Saruchi, R. Jindal, M. S. Bhatti, *Soft Matter* **2012**, *8*, 2286.
[80] R. Saruchi, B. S. Kaith, R. Jindal, V. Kumar, M. S. Bhatti, *RSC Adv.* **2014**, *4*, 39822.
[81] W. R. Gombotz, S. Wee, *Adv. Drug Delivery Rev.* **1998**, *31*, 267.
[82] M. Rinaudo, *Polym. Int.* **2008**, *57*, 397.
[83] F. G. Fischer, H. Dörfel, *Z. Physiol. Chem.* **1955**, *302*, 186.
[84] O.-S. Lee, B.-J. Ha, S.-N. Park, Y.-S. Lee, *Macromol. Chem. Phys.* **1997**, *198*, 2971.
[85] E. S. Agorku, H. Mittal, B. B. Mamba, A. C. Pandey, A. K. Mishra, *Int. J. Biol. Macromol.* **2014**, *70*, 143.
[86] B. An, H. Son, J. Chung, J. W. Choi, S. H. Lee, S. W. Hong, *Chem. Eng. J.* **2013**, *232*, 51.
[87] D. A. Rees, *J. Chem. Soc.* **1963**, 1821.
[88] V. L. Campo, D. F. Kawano, D. B. d. Silva Jr., I. Carvalho, *Carbohydr. Polym.* **2009**, *77*, 167.
[89] F. van de Velde, S. H. Knutsen, A. I. Usov, H. S. Rollema, A. S. Cerezo, *Trends Food Sci. Technol.* **2002**, *13*, 73.
[90] F. van de Velde, L. Pereira, H. S. Rollema, *Carbohydr. Res.* **2004**, *339*, 2309.
[91] S. Yamazaki, T. Mori, I. Ogino, S. R. Mukai, *Chem. Eng. J.* **2015**, *278*, 122.
[92] H. Hezaveh, I. I. Muhamad, *Chem. Eng. Res. Des.* **2013**, *91*, 508.
[93] R. V. Kulkarni, R. Boppana, G. Krishna Mohan, S. Mutalik, N. V. Kalyane, *J. Colloid Interface Sci.* **2012**, *367*, 509.
[94] A. Pourjavadi, S. Barzegar, F. Zeidabadi, *React. Funct. Polym.* **2007**, *67*, 644.
[95] H. Hezaveh, I. I. Muhamad, *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 182.
[96] J. S. Varghese, N. Chellappa, N. N. Fathima, *Colloids Surf., B* **2014**, *113*, 346.
[97] M. Watase, K. Nishinari, *Macromol. Chem. Phys.* **1987**, *188*, 2213.
[98] G. R. Mahdavinia, A. Massoudi, A. Baghban, E. Shokri, *J. Environ. Chem. Eng.* **2014**, *2*, 1578.
[99] G. R. Mahdavinia, H. Aghaie, H. Sheykhloie, M. T. Vardini, H. Etemadi, *Carbohydr. Polym.* **2013**, *98*, 358.
[100] S. Grant, H. S. Blair, G. McKay, *Macromol. Chem. Phys.* **1989**, *190*, 2279.
[101] R. M. P. da Silva, J. F. Mano, R. L. Reis, *Macromol. Chem. Phys.* **2008**, *209*, 1463.
[102] M. Yazdani-Pedram, J. Retuert, R. Quijada, *Macromol. Chem. Phys.* **2000**, *201*, 923.
[103] T. Seo, H. Ohtake, T. Kanbara, K. Yonetake, T. Iijima, *Macromol. Chem. Phys.* **1991**, *192*, 2447.
[104] Y. Shigeno, K. Kondo, K. Takemoto, *Macromol. Chem. Phys.* **1981**, *182*, 709.
[105] L. Pastorino, S. Erokhina, C. Ruggiero, V. Erokhin, P. Petrini, *Macromol. Chem. Phys.* **2015**, *216*, 1067.
[106] S. L. Jahren, M. F. Butler, S. Adams, R. E. Cameron, *Macromol. Chem. Phys.* **2010**, *211*, 644.
[107] V. E. Tikhonov, I. A. Yamskov, V. A. Davankov, *Macromol. Chem. Phys.* **1993**, *194*, 1863.
[108] F. M. Goycoolea, M. E. Fernández-Valle, I. Aranaz, Á. Heras, *Macromol. Chem. Phys.* **2011**, *212*, 887.
[109] P. Cerrai, G. D. Guerra, M. Tricoli, S. Maltinti, N. Barbani, L. Petarca, *Macromol. Chem. Phys.* **1996**, *197*, 3567.
[110] J. Fangkangwanwong, M. Akashi, T. Kida, S. Chirachanchai, *Macromol. Rapid Commun.* **2006**, *27*, 1039.
[111] H. Saito, X. Wu, J. M. Harris, A. S. Hoffman, *Macromol. Rapid Commun.* **1997**, *18*, 547.
[112] E. S. Dragan, M. M. Perju, M. V. Dinu, *Carbohydr. Polym.* **2012**, *88*, 270.
[113] N. A. Peppas, A. R. Khare, *Adv. Drug Delivery Rev.* **1993**, *11*, 1.
[114] V. Singh, P. Kumar, R. Sanghi, *Prog. Polym. Sci.* **2012**, *37*, 340.
[115] B. S. Kaith, R. Jindal, H. Mittal, K. Kumar, *J. Appl. Polym. Sci.* **2012**, *124*, 2037.
[116] M. M. Mishra, A. Sand, D. K. Mishra, M. Yadav, K. Behari, *Carbohydr. Polym.* **2010**, *82*, 424.
[117] C. T. Tsao, M. H. Hsiao, M. Y. Zhang, S. L. Levengood, M. Zhang, *Macromol. Rapid Commun.* **2015**, *36*, 332.
[118] K. Behari, P. K. Pandey, R. Kumar, K. Taunk, *Carbohydr. Polym.* **2001**, *46*, 185.
[119] A. Sand, M. Yadav, K. Behari, *Carbohydr. Polym.* **2010**, *81*, 97.
[120] A. Sand, M. Yadav, M. M. Mishra, J. Tripathy, K. Behari, *Carbohydr. Polym.* **2011**, *83*, 14.
[121] R. Murali, P. Vidhya, P. Thanikaivelan, *Carbohydr. Polym.* **2014**, *110*, 440.
[122] A. Tiwari, J. J. Grailer, S. Pilla, D. A. Steeber, S. Gong, *Acta Biomater.* **2009**, *5*, 3441.
[123] V. Singh, S. Tiwari, A. K. Sharma, R. Sanghi, *J. Colloid Interface Sci.* **2007**, *316*, 224.
[124] Y. Huang, H. Yu, C. Xiao, *Carbohydr. Polym.* **2007**, *69*, 774.
[125] H. M. Nizam El-Din, M. F. Abou Taleb, A. W. M. El-Naggar, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2008**, *266*, 2607.
[126] R. Sanghi, B. Bhattacharya, V. Singh, *React. Funct. Polym.* **2007**, *67*, 495.

[127] P. A. G. Soares, A. I. Bourbon, A. A. Vicente, C. A. S. Andrade, W. Barros Jr., M. T. S. Correia, A. Pessoa Jr., M. G. Carneiro-da-Cunha, *Mater. Sci. Eng. C* **2014**, *42*, 219.
[128] Y. Tan, P. Wang, K. Xu, W. Li, H. An, L. Li, C. Liu, L. Dong, *Macromol. Mater. Eng.* **2009**, *294*, 855.
[129] S.-H. Chen, C.-T. Tsao, C.-H. Chang, Y.-T. Lai, M.-F. Wu, Z.-W. Liu, C.-N. Chuang, H.-C. Chou, C.-K. Wang, K.-H. Hsieh, *Macromol. Mater. Eng.* **2013**, *298*, 429.
[130] P. J. Flory, *J. Chem. Phys.* **1942**, *10*, 51.
[131] L. E. Bromberg, E. S. Ron, *Adv. Drug Delivery Rev.* **1998**, *31*, 197.
[132] H. Tsuji, F. Horii, M. Nakagawa, Y. Ikada, H. Odani, R. Kitamaru, *Macromolecules* **1992**, *25*, 4114.
[133] H. Mittal, S. B. Mishra, A. K. Mishra, B. S. Kaith, R. Jindal, *Int. J. Biol. Macromol.* **2013**, *58*, 37.
[134] A. Shalviri, Q. Liu, M. J. Abdekhodaie, X. Y. Wu, *Carbohydr. Polym.* **2010**, *79*, 898.
[135] E. Feng, G. Ma, Y. Wu, H. Wang, Z. Lei, *Carbohydr. Polym.* **2014**, *111*, 463.
[136] B. S. Kaith, R. Sharma, S. Kalia, *Int. J. Biol. Macromol.* **2015**, *75*, 266.
[137] X. Li, W. Wu, J. Wang, Y. Duan, *Carbohydr. Polym.* **2006**, *66*, 473.
[138] H. Kono, F. Otaka, M. Ozaki, *Carbohydr. Polym.* **2014**, *111*, 830.
[139] D. S. Morais, M. A. Rodrigues, T. I. Silva, M. A. Lopes, M. Santos, J. D. Santos, C. M. Botelho, *Carbohydr. Polym.* **2013**, *95*, 134.
[140] Y. Man, P. Wang, Y. Guo, L. Xiang, Y. Yang, Y. Qu, P. Gong, L. Deng, *Biomaterials* **2012**, *33*, 8802.
[141] H. K. Ju, S. Y. Kim, S. J. Kim, Y. M. Lee, *J. Appl. Polym. Sci.* **2002**, *83*, 1128.
[142] L. Pescosolido, T. Vermonden, J. Malda, R. Censi, W. J. A. Dhert, F. Alhaique, W. E. Hennink, P. Matricardi, *Acta Biomater.* **2011**, *7*, 1627.
[143] M. A. Abd El-Ghaffar, M. S. Hashem, M. K. El-Awady, A. M. Rabie, *Carbohydr. Polym.* **2012**, *89*, 667.
[144] F. Gnanaprakasam Thankam, J. Muthu, V. Sankar, R. Kozhiparambil Gopal, *Colloids Surf. B* **2013**, *107*, 137.
[145] J. Dahlmann, A. Krause, L. Möller, G. Kensah, M. Möwes, A. Diekmann, U. Martin, A. Kirschning, I. Gruh, G. Dräger, *Biomaterials* **2013**, *34*, 940.
[146] C. Wen, L. Lu, X. Li, *Macromol. Mater. Eng.* **2014**, *299*, 504.
[147] J. Zhang, L. Wang, A. Wang, *Macromol. Mater. Eng.* **2006**, *291*, 612.
[148] P. Li, J. Zhang, A. Wang, *Macromol. Mater. Eng.* **2007**, *292*, 962.
[149] S. G. Abd Alla, M. Sen, A. W. M. El-Naggar, *Carbohydr. Polym.* **2012**, *89*, 478.
[150] M. N. Abu Seman, M. Khayet, Z. I. Bin Ali, N. Hilal, *J. Membr. Sci.* **2010**, *355*, 133.
[151] C. Weber, R. Hoogenboom, U. S. Schubert, *Prog. Polym. Sci.* **2012**, *37*, 686.
[152] A. K. Bajpai, S. K. Shukla, S. Bhanu, S. Kankane, *Prog. Polym. Sci.* **2008**, *33*, 1088.
[153] S. Chaterji, I. K. Kwon, K. Park, *Prog. Polym. Sci.* **2007**, *32*, 1083.
[154] H. Iwata, M. Oodate, Y. Uyama, H. Amemiya, Y. Ikada, *J. Membr. Sci.* **1991**, *55*, 119.
[155] H. Feil, Y. H. Bae, J. Feijen, S. W. Kim, *Macromolecules* **1992**, *25*, 5528.
[156] A. S. Hoffman, P. S. Stayton, V. Bulmus, *J. Biomed. Mater. Res.* **2000**, *52*, 577.
[157] A. C. Wenceslau, F. G. dos Santos, É. R. F. Ramos, C. V. Nakamura, A. F. Rubira, E. C. Muniz, *Mater. Sci. Eng. C* **2012**, *32*, 1259.
[158] W. Wei, X. Hu, X. Qi, H. Yu, Y. Liu, J. Li, J. Zhang, W. Dong, *Colloids Surf. B* **2015**, *125*, 1.
[159] X. Li, W. Wu, W. Liu, *Carbohydr. Polym.* **2008**, *71*, 394.
[160] H. Mittal, S. B. Mishra, A. K. Mishra, B. S. Kaith, R. Jindal, *Int. J. Biol. Macromol.* **2013**, *58*, 37.
[161] M. George, T. E. Abraham, *Int. J. Pharma.* **2007**, *335*, 123.
[162] S.-F. Lim, Y.-M. Zheng, S.-W. Zou, J. P. Chen, *Chem. Eng. J.* **2009**, *152*, 509.
[163] G. R. Mahdavinia, H. Etemadi, F. Soleymani, *Carbohydr. Polym.* **2015**, *128*, 112.
[164] Y. Samchenko, Z. Ulberg, O. Korotych, *Adv. Colloid Interface Sci.* **2011**, *168*, 247.
[165] S. Murdan, *J. Control. Release* **2003**, *92*, 1.
[166] Y. Osada, J.-P. Gong, *Adv. Mater.* **1998**, *10*, 827.
[167] K. Sawahata, M. Hara, H. Yasunaga, Y. Osada, *J. Controlled Release* **1990**, *14*, 253.
[168] S. J. Kim, S. G. Yoon, K. B. Lee, Y. D. Park, S. I. Kim, *Solid State Ionics* **2003**, *164*, 199.
[169] S. H. Yuk, S. H. Cho, H. B. Lee, *Pharm. Res.* **1992**, *9*, 955.
[170] S. Y. Kim, Y. M. Lee, *J. Appl. Polym. Sci.* **1999**, *74*, 1752.
[171] I. C. Kwon, Y. H. Bae, S. W. Kim, *Nature* **1991**, *354*, 291.
[172] I. C. Kwon, Y. H. Bae, S. W. Kim, *J. Controlled Release* **1994**, *30*, 155.
[173] G. Jing, L. Wang, H. Yu, W. A. Amer, L. Zhang, *Colloid. Surf., A* **2013**, *416*, 86.
[174] K. Kumari, T. E. Abraham, *Bioresour. Technol.* **2007**, *98*, 1704.
[175] R. Bhattacharyya, S. K. Ray, *Polym. Eng. Sci.* **2013**, *53*, 2439.
[176] E. Al, G. Güçlü, T. B. İyim, S. Emik, S. Özgümüş, *J. Appl. Polym. Sci.* **2008**, *109*, 16.
[177] R. Bhattacharyya, S. K. Ray, *J. Ind. Eng. Chem.* **2015**, *22*, 92.
[178] C. Cheng, J. Deng, B. Lei, A. He, X. Zhang, L. Ma, S. Li, C. Zhao, *J. Hazard. Mater.* **2013**, *263*, 467.