

Guar Gum Based Hydrogels for Sustained Water Release Applications in Agriculture, a Review

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Abstract

In spite of the immense importance of green chemistry synthesis and verification of natural biopolymers is need of time, which reduces the threats to health and environment. Polysaccharides are highly abundant biopolymers with a variation of structure and properties. They are potential substitutes of petroleum-based synthetic products because they are easily available, nontoxic, biodegradable, and biocompatible. Due to their attractive properties, they are used as a rheological modifier in food, pharmaceutical, paper, textile, oil, drilling, and score of other industrial and agriculture sectors. Modification of hydrophilic backbone of these biopolymers spreads and enhances their applications and functionality. Guar Gum is an excellent representative of green, ecofriendly biopolymer. Different methodologies to modify guar properties for agriculture application are available in the literature. This review sheds light on different formulations based on Guar Gum as green biosource and their application in agriculture.

Keywords: Agriculture Guar Gum; Biomedical; Nanocomposites; Smart Hydrogels; Superabsorbent Hydrogels

List of Abbreviations

GG: Guar Gum; SAP: Superabsorbent Polymer; PAA: Poly (Acrylic Acid); CD: B-Cyclodextrin; DX: Dexamethasone; cl-GG-g-PA: Crosslinked Guar Gum-g-polyacrylate; MBA: N, N-Methylene Bis Acrylamide; GG-g-PNaA: Guar Gum-g-poly (sodium acrylate); APS: Ammonium Persulfate; HCST: Higher Critical Solution Temperature; LCST: Lower Critical Solution Temperature; PNIPAAm: GG/poly (N-isopropylacrylamide; APT: Attapulgite Clay; GG-g-PAA/APT: Guar Gum-g-Poly (Acrylic Acid)/attapulgite; AA: Acrylic Acid

Introduction

Guar Gum (GG) is an edible carbohydrate polymer, which belongs to a common group of seed gums, broadly exists in nature, Figure 1. These gums act as food reserves for seed germination. Seed gums are commonly known as galactomannans because

they are chiefly constructed up of mannose and galactose sugar units. They are varied according their mannose/galactose ratio and distribution pattern of the galactose residues within the mannan chain. The backbone of Guar Gum - an extract from the seeds of *Cyamopsis Tetragonolobus*- consists of β -D-mannopyranoses linked 1 \rightarrow 4 with side extensions of α -D-galactose linked 1 \rightarrow 6, Figure 2. The ratio of mannose to galactose unit (M/G) ranges from 1.8:1 to 2:1 due to the geographical origin [1]. Initially, it is believed that galactose side groups are more frequently distributed at regular intervals along the mannose backbone. However, more recent investigations showed random distribution of side branching, Figure 3.

Due to its high molecular weight and the hydrogen bonding formed between the repeating units, Guar Gum is capable of producing highly viscous pseudoplastic aqueous solutions even at very low concentrations. The distinctive ability of Guar Gum to change the rheological properties of different solutions has led to utilization of Guar Gum as valuable candidate in a wide range of applications [2-4].



Guar seed

Guar seed and endosperm

Guar Plant

Figure 1: Guar Plant, Guar seed and Guar endosperm.

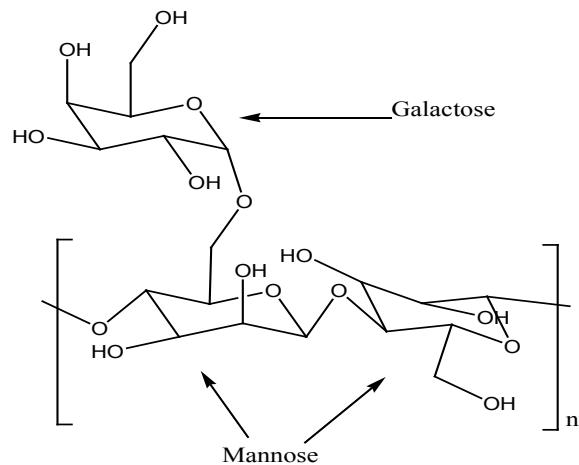


Figure 2: Chemical composition of Guar Gum (GG).

Regular distribution

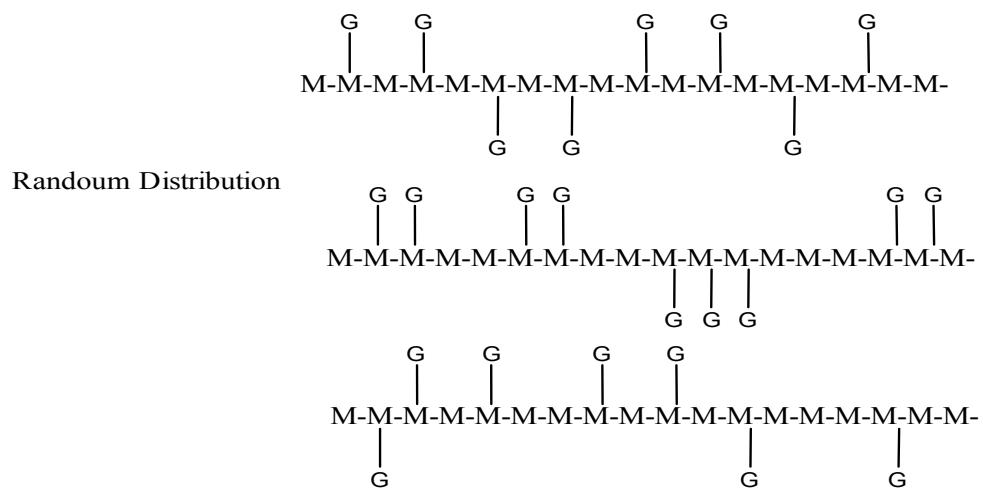


Figure 3: Sequence of galactose and mannose in guar.

GG can be chemically modified by the etherification [5], esterification [6,7], oxidation [8], cross-linking [9], enzymatic hydrolysis [10], and graft [11] in order to advance its applicability.

Properties of Guar Gum

Guar Gum has the following properties that manage its [12-14]:

- It is soluble in hot & cold water but insoluble in most organic solvents.
- Guar Gum solution is highly viscous due to its large hydrodynamic volume in solution and the nature of its specific intermolecular interactions (entanglements).
- Guar Gum products exhibit an obvious temperature thinning effect when their solutions are heated. This is caused by loss of water of hydration around the polymer molecule, which makes Guar Gum the most applicable natural polymer.
- The numerous hydroxyl groups along with the Guar Gum molecule enable different functionalization possibilities. These hydroxyl groups also form strong intramolecular hydrogen bonding all over the molecule.
- It is an excellent thickening and stabilizing agent.
- It is an outstanding emulsifier.

- It has a strong film forming properties.
- At very low concentration, Guar Gum shows excellent settling (Flocculation) properties and it acts as a filter aid.
- It forms neutral solution and maintains a constant high viscosity over a broad range of pH.
- It is highly compatible with a variety of inorganic and organic substances including certain dyes and various constituents of food.
- The viscosity of Guar Gum solution is concentration dependent. Thus, it can be used to control rheology by economic water phase management.

Controlling the physical and chemical properties of Guar Gum by chemical modification such as grafting, blending, and crosslinking with synthetic and natural polymers has been thoroughly investigated [15-18]. In particular, the chemical cross-linking of Guar Gum was introduced to change its swelling power and rheology [19-21]. Therefore, Guar Gum and its derivatives have a wide range of applications in all fields of science. These include dietary fibers, semi-conductors, and sensors, in drug delivery and in pharmaceutical uses [22-25]. Some applications of Guar Gum derivatives are given in Table 1. Despite the extensive efforts made [26,27], a greater effort is still needed to overcome a number of new problems and deal with their effects.

	Guar Gum graft copolymer	Method of initiation	Application (s)	References
1.	Methyl methacrylate onto Guar Gum	Ceric ammonium nitrate-nitric acid	-----	Sharma, et al. (2003) [28]
2.	Polyacrylamide grafted carboxy- methyl Guar Gum	Potassium persulphate solution	Waste water treatment	Pala, et al. (2011) [29]
3.	Guaran Grafted Polystyrene (G-G-Ps) Copolymer	Cerium (IV) in nitric acid medium	Mineral processing and petroleum industries.	Singh and Singh (2010) [30]
4.	Acrylamide (Aam) onto Guar Gum	Potassium bromate/ thiourea dioxide redox system	Removal of hexavalent chromium ion (Cr (VI)) from its aqueous solution.	Abdel-Halim and Deyab (2011) [31]
5.	Guar Gum/polyacrylamide graft copolymer	Potassium bromate/ thiourea dioxide	heavy metal removal	Abdel-Halim, et al. (2011) [32]
6.	<i>p</i> -toluene sulfonate esters hydroxyl propyl Guar Gum	Tosyl chloride in pyridine.	-----	Zhao, et al. (2012) [33]
7.	copolymerization of 4-vinyl pyridine onto Guar Gum	Potassium peroxy-monosulphate/ascorbic acid redox pair	Protecting material against high temperature	Sirivastave, et al. (2007) [34]
8.	carboxymethyl Guar Gum (CMGG) and polyacrylamide (PAM)	Ceric-ion-induced solution	Flocculent material	Adhikary, et al. (2011) [35]
9.	Magnetic Guar Gum grafted carbon nanotube.	-----	Dye removal	Li Yana, et al. (2012). [36].
10.	Guar Gum graft polyaniline	APS (Ammonium Persulphate) in acidic medium	Environmentally friendly conducting materials	Tiwari and Singh (2008) [37]

Table 1: Some applications of Guar Gum derivatives.

These problems include the rapid horrible shortage of irrigation water, potential and continued population growth and industrial activities in most of the countries, which are located mainly in the arid and semi-arid regions of the world. According to the global survey, the heaviest affected areas would be the semi-arid regions of Asia, the Middle East, and Saharan Africa, all of which are already having deep concentration of population living below poverty line. The agricultural sector (irrigation) is one of the chief consumers of water in addition to the demand of from various sectors like domestic; industry etc. due to the population growth and rapid industrialization. The principal method of irrigation commonly practiced is surface irrigation under which crops consume only less than one half of the water released and remaining half gets lost in conveyance, application, runoff and evaporation.

In this regards a detailed review study about the application of Super Absorbent Polymers in the field of agriculture (mainly sustained release and water saving purposes) is introduced herein focusing on those based on Guar Gum as an environmentally friendly, abundant, and cheap natural polymeric material.

Guar Gum Based Hydrogels

Hydrogels are three-dimensional network crosslinked structures with abundant hydrogen bondings between polymeric chains and solvents/water, which help to stabilize the network and keeps its elasticity [38-40]. Hydrogels can be made as super-absorbents and serve to maintain the soil fertility by uptaking tremendous amount of water. The properties of hydrogels are governed mainly by the primary interaction with water molecules via hydrogen-bond formation. Thus, hydrogen-bonding formation has a direct influence on swelling, retention of water, and moisture sorption.

Water absorption by hydrogels is mainly due to the presence of polar groups such as COO^- , OH , CONH_2 , SO_3^- , etc. on the backbone of the polymer. When a hydrophilic polymer is placed in water, it absorbs a large quantity of water and swells as shown in Figure 4 [41-43].

Mode of Action of Hydrogel in Soil

Hydrogels are characterized by negative (anionic), positive (cationic) or neutral charge [44,45]. The charges determine the mode of interaction between hydrogels with solid and solutes. Cationic hydrogels generally bind to the clay components and act as flocculants. Anionic hydrogels can join with the clay and other negatively charged particles through ionic bridges such as calcium and magnesium. The Strong attraction between the gel and

surrounding solutes and soil particles enhances the ability of the gel to absorb water, create aggregates and stabilize soil structure.

The most important problems encountered in the present-day agriculture are low soil fertility and inadequate water retention. However, practicing the proper water management methodologies can increase the productivity of these soils as others. Addition of soil conditioners was found to be more effective than adding clays or organic manures and composts to soils. Soil conditioners keep the soil moisture and thus improve hydro physical properties in such soils. Soil conditioner is a product which is added to soil to improve the soil's physical qualities, especially its ability to provide nutrition for plants and to retain water for longer time in particular in sandy soil [45], Figure 5. Hydrogel soil conditioners modify the hydro physical properties of soils by [46]:

- Increasing the soil holding capacity of water.
- Increasing the soil compactness and reducing erosion and runoff.
- Increasing soil permeability and infiltration.

Hydrogel act as a slow release of water in soil by forming an amorphous gelatinous mass on hydration and thus result in absorption and desorption of water over a long period. Water will be removed from these reservoirs according to the root demand through osmotic pressure difference.

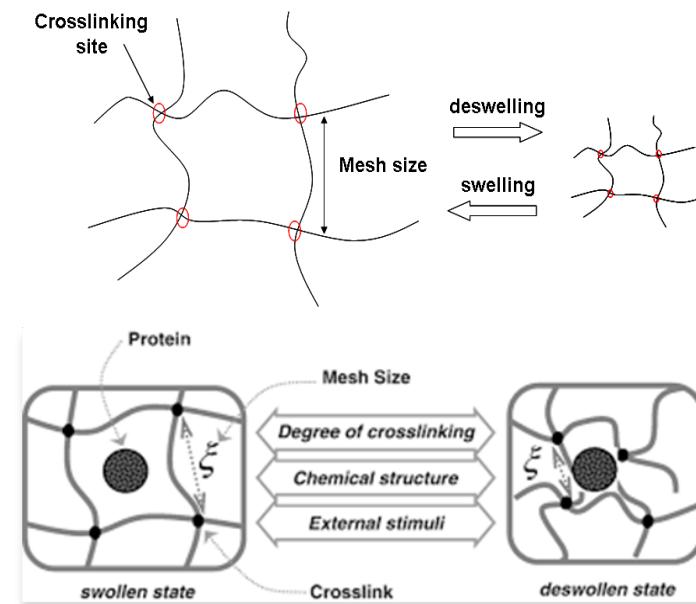


Figure 4: Process of Swelling-deswelling of hydrogels [47].



Figure 5: Hydrogel soil conditioner around the root.

Water Retention of the Sand Treated with the Prepared Hydrogel

The soil moisture is a vital process for plantations. The sandy soil is of very poor water retention due to large pore spaces. Thus, it dries out easily, and leaches precious nutrients past plant roots. The addition of organic materials enhances in water retention and increase nutrient availability. Superabsorbent Polymers significantly increase water-holding capacities in such soils. Furthermore, hydrogels can release the retained water under certain environmental stimuli; these are known as stimuli responsive hydrogels. They will be discussed in more details in the next sections.

Stimuli Responsive Guar Gum Hydrogels

Stimuli-responsive hydrogels are a unique class of hydrogels, which endure large volume phase transitions, large and abrupt changes in their network structure, swelling behavior, permeability on small variation in the environmental conditions [48,49], Figure 6. They can be designed to induce sustained or sudden release of the encaptured liquids according to demand. To attain the desired controlled release characteristics, some naturally occurring, cheaply available, biodegradable, and environmentally friendly matrices have been used. Most of the hydrogel-based formulations involve cross-linking of the matrix in the presence of active agents, or emulsification followed by separation of microspheres without wasting the solvent.

Thus, they are widely applied in biomedical, pharmaceutical and agriculture applications [50-54]. In agriculture, the swelling and water release of the hydrogel are mostly affected by pH, temperature, and salt concentration. They will be discussed in the following sections.

pH and Salt Responsive Hydrogels

Generally, pH responsive hydrogels are also salt responsive. Most pH responsive hydrogels are used in sustained release applications. For instance, Chandrika, et al. [55] prepared pH-Responsive hydrogel materials based on Guar Gum (GG), (PAA) and (CD) by means of a non-toxic crosslinker, tetraethyl orthosilicate for intestinal delivery of (DX). The maximum pH responsive swelling behavior was shown in neutral medium. Furthermore, George and Abraham [56] have reported pH-sensitivity of poly (acrylamide-co-acrylic acid)- based hydrogels. Poorna, et al. [57] introduced superabsorbent hydrogels based on grafting Guar Gum with acrylamide then crosslinking with glutaraldehyde, Figure 6.

GG and APT clay were used as raw materials for preparing Guar Gum-g-poly (Acrylic Acid)/attapulgite (GG-g-PAA/APT) superabsorbent composites through the graft copolymerization of GG, partially neutralized acrylic acid (AA) and APT in aqueous solution. The effects of structure variation such as concentrations of the initiator and crosslinker, APT content, etc. on water absorbency were investigated. Maximum water absorption was attained by the composite prepared under optimal conditions (529 g/g sample in distilled water and 61 g/g sample in 0.9 wt% NaCl solution). It was also demonstrated that swelling behaviors is a pH dependent and high-water absorbency was kept over a wide pH range of 4-11. Furthermore, the developed composites exhibited improved reswelling and water- retention capabilities. The superabsorbent composites can be applied as eco-friendly water- controllable materials for agricultural and horticultural applications [56].

In agriculture, Crosslinked Guar Gum-g-polyacrylate (cl-GG-g-PA) superabsorbent hydrogels were utilized as soil conditioners and agrochemical reservoirs [57]. The hydrogels were prepared by in situ grafting polymerization and crosslinking of acrylamide onto a natural GG followed by hydrolysis, Figure 7. Furthermore, swelling behavior of a superabsorbent hydrogel was studied versus some external stimuli such as salt solutions, fertilizer solutions, temperature, and pH. The GG-SAP exhibited significant swelling in various environments. The effect of GG-SAP on water absorption and the retention characteristics of sandy loam soil and soilless medium were also studied as a function of temperature and moisture tensions. The addition of GG-SAP significantly improved the moisture characteristics of plant growth media (both soil and soil-less), showing that it has remarkable potential for various applications in moisture stress agriculture.

Moreover, a Response Surface Methodology (RSM) was used to prepare Guar Gum- based hydrogel with for enhanced swelling capacity [58]. Maximization of the water absorption capacity of the synthesized hydrogel was achieved through sequential experimental design-based optimization. The variable reaction parameters were:

- (i) Monomer concentration.
- (ii) Initiator concentration.
- (iii) Cross linker concentration.
- (iv) Polymerization time.
- (v) Reaction temperature.
- (vi) Vacuum level.
- (vii) pH of reaction mixture.

The investigated hydrogels were found to be highly pH responsive and should be kept in a narrow range for maximization of percentage swelling. Thus, the sequential experimental strategy was effective in achieving double increase in percentage swelling in an organized way. Synthesized super absorbent polymers can be used as effective water-saving materials for horticultural and agricultural applications.

Wenbo, et al. [59] introduced novel Guar Gum-g-poly (Sodium Acrylate) (GG-g-PNaA) superabsorbent hydrogels by solution graft copolymerization of natural Guar Gum (GG) with partially Neutralized Acrylic Acid (NaA), Ammonium Persulfate (APS) as initiator and MBA as crosslinker. The effects of reaction variables such as the concentration of APS and MBA, the weight ratio of Acrylic Acid (AA) to GG and the neutralization degree of AA on water absorption were studied. The superabsorbent hydrogel prepared under optimal condition showed the maximum absorption of $1107 \text{ g} \square \text{g}^{-1}$ in distilled water and $88 \text{ g} \square \text{g}^{-1}$ in saline solution. pH responsibility of the prepared hydrogels was investigated. The results indicated that the hydrogels exhibited excellent pH-stability in a wide pH range from 4 to 11, and the water-retention capabilities of sandy soils were also greatly improved after utilizing the superabsorbent hydrogels. These superabsorbent hydrogels could be used as prospective eco-friendly water-saving materials and polymeric soil conditioners for agricultural or ecological application.

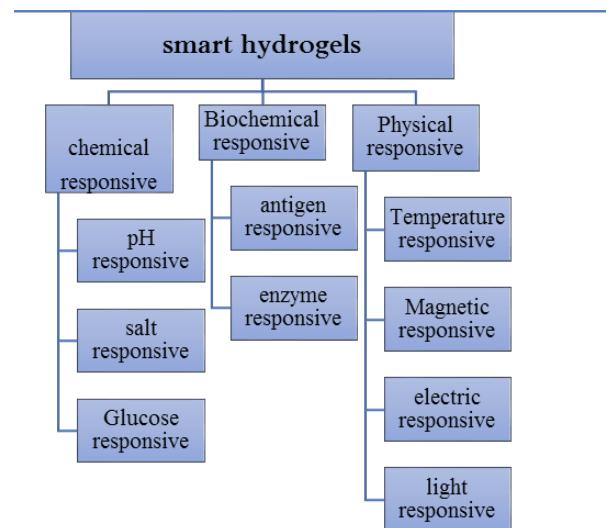


Figure 6: Classification of smart hydrogels, modified from (Alemdar [60]).

Thermo-Responsive Guar Gum- Based Hydrogel

Guar Gum based hydrogels with adaptable Lower Critical Solution Temperature (LCST) characteristics have been extensively investigated for biological applications such as cell patterning, smart drug release, target therapy and DNA sequencing [60-63]. These polymers were prepared by copolymerization of Guar Gum with thermo-responsive acrylate monomers such as N-isopropylacrylamide. They change their phase in the solution at their LCST or HCST. It has been reported that LCST is strongly correlated with many variables including molecular weight, polydispersity index, and the monomer composition of copolymers that controls the hydrophilicity/hydrophobicity balance [64].

Recently, these polymers have been used in agriculture applications. They can absorb huge amount of water under their LCST and start to discharge water when the external temperature approaches their LCST [65]. The important characteristics of the thermo-sensitive hydrogels such as the LCST, rates of shrinking, and permeation rates of substances within the hydrogels can be controlled by suitable selection of the components with the defined hydrophilicity or hydrophobicity of the constituent monomer, variation of the cross-linking density, and/or nature of the medium.

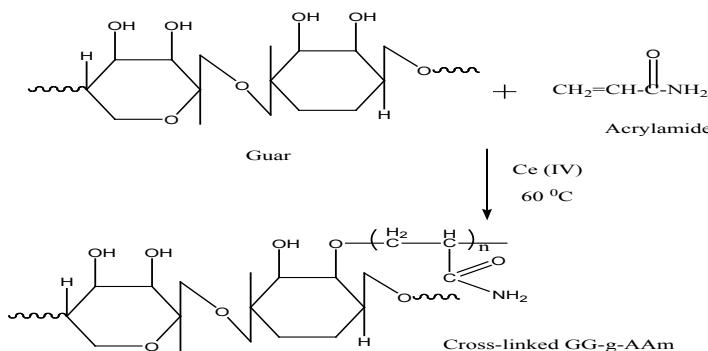


Figure 7: Grafting of acrylamide onto GG and cross-linking of the GG with GA [66].

Several thermo-responsive Guar Gum based hydrogels were prepared and evaluated as superabsorbent hydrogels. Rohini, et al. [66] prepared Guar Gum (GG)-based hydrogel by grafting GG with Acrylic Acid (AAc) using simultaneous gamma radiation technique. The carboxyl groups of poly(AAc) were partially modified to amide groups to generate a network that has pH-sensitive poly (AAc) and temperature-sensitive poly (N-isopropyl acrylamide). Swelling behavior of hydrogels was studied at various temperature, pH, and

the salt sensitivity of the hydrogels was investigated by swelling the hydrogels in 0.9% NaCl solution. The hydrogel synthesized by the post reaction exhibited pH, temperature, and salt sensitivity, while the precursor hydrogel exhibited good salt tolerance.

Stimuli Responsive Interpenetrating Guar Gum Based Hydrogels

Interpenetrating Polymer Networks (IPNs) is an original class of polymeric network hydrogel that has been widely investigated and reported in literature. These polymer networks are resulted from a combination of two or more polymers in network form. These polymers are polymerized either simultaneously or consecutively [67]. Many kinds of IPNs are known. Generally, two different polymers are crosslinked together by chemical reactions in order to obtain a mixed hydrogel [68] or a polymer network is first synthesized and then a second monomer plus the crosslinker and activator are swollen into the first network [69], Figure 8a and Figure 8b. This provides a class of hydrogels with different mechanical, biological, and physico-chemical properties from the native gels, and makes it possible to predict the properties of the IPHs according to the type and relative percentage of each individual native component.

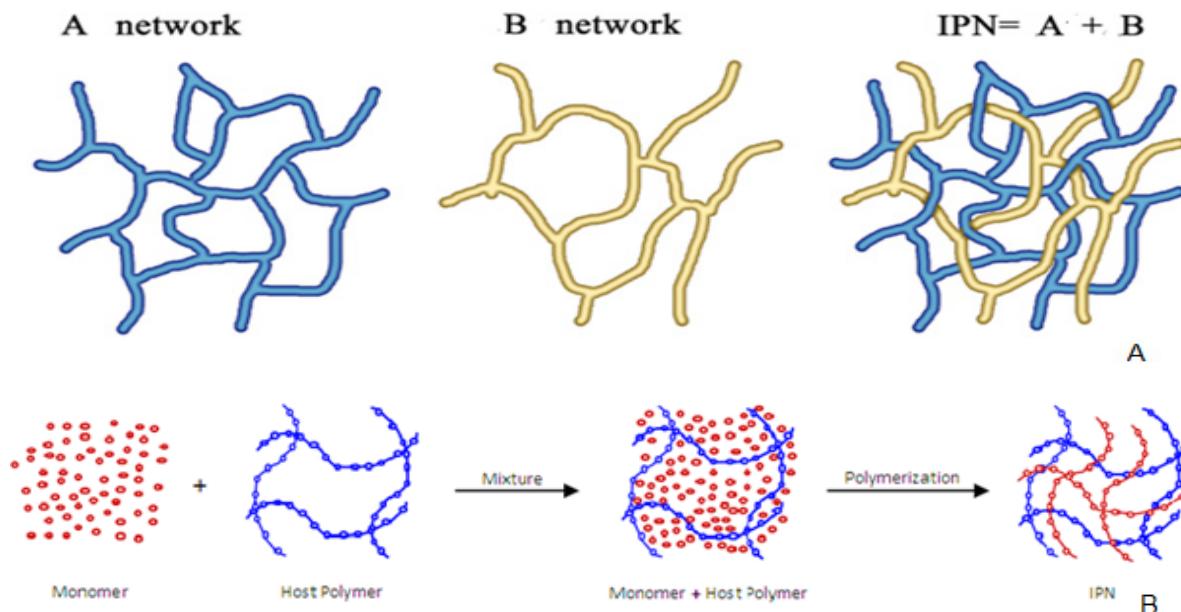


Figure 8: A- two polymer networks are interpenetrated together. B- A second network is synthesized within the first one.

Polysaccharide based hydrogels were also applied in agricultural applications. Hassan [70] prepared polyacrylamide/ sodium alginate (PAAm/ Na-alginate) crosslinked copolymers by using electron beam irradiation. The gel fraction and the swelling behavior of the obtained copolymers were investigated. The thermal properties revealed that the thermal stability of PAAm significantly changed when mixed with Na-alginate. The addition of PAAm/Na-alginate copolymer in small quantities to sandy soil increased its ability to retain water. The growth and other

responses of the Faba bean plant cultivated in a soil treated with PAAm and PAAm/Na-alginate copolymer was investigated. The growth of the bean plant cultivated in a soil containing PAAm/Na-alginate was better than that cultivated in soil treated with PAAm. The data showed that the alginate copolymer exhibits radiolytic and enzymatic degradation to produce oligo-alginate, which acts as a plant growth promoter. The enhanced performance of Faba plant revealed that it is recommended to apply PAAm/Na-alginate copolymer in the agriculture field as a soil conditioner, Figure 9.



Figure 9: Faba bean planted in soil: (a) original (control); (b) treated with PAAm/Na-alginate gel.

Furthermore, two sets of hydrogel materials based on grafting Guar Gum onto acrylic acid/ acrylamide and acrylic acid/ N-isopropylacrylamide copolymers were prepared by free radical polymerization using persulphate radical as an initiator and N,N'methylenebisacrylamide as a crosslinker. The prepared hydrogels were characterized by FTIR Spectroscopy and SEM. The effect of some composition variations on the swelling performance of PA-GG hydrogel was thoroughly studied. Furthermore, swelling behavior was monitored as a function of temperature and electrolyte concentration. (Manar, et al. [71]). The scheme of the synthetic route is given in Figure 10. A lab experiment was conducted in order to investigate the effect of the optimum hydrogels on the growth of guava plant, Figure 11.

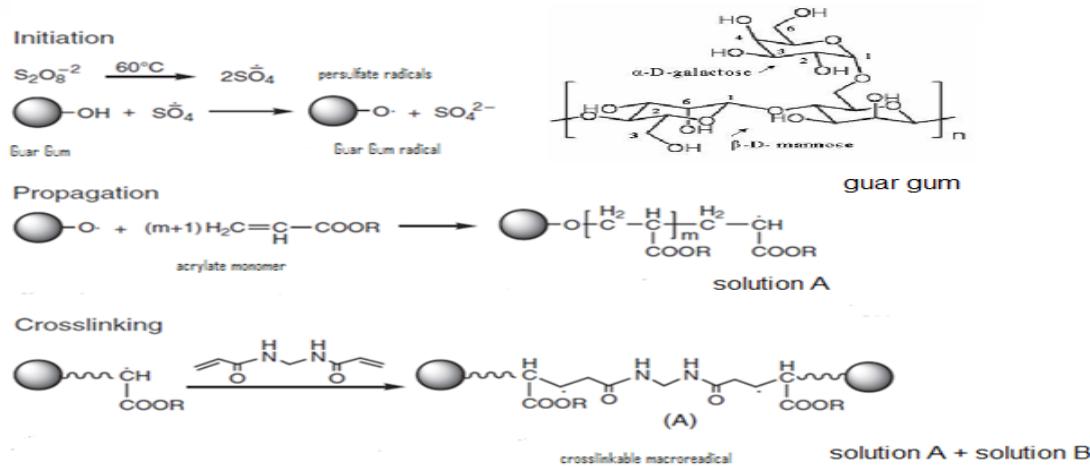


Figure 10: Detailed reaction scheme for modification of Guar Gum into SAH (Manar, et al. [71]).

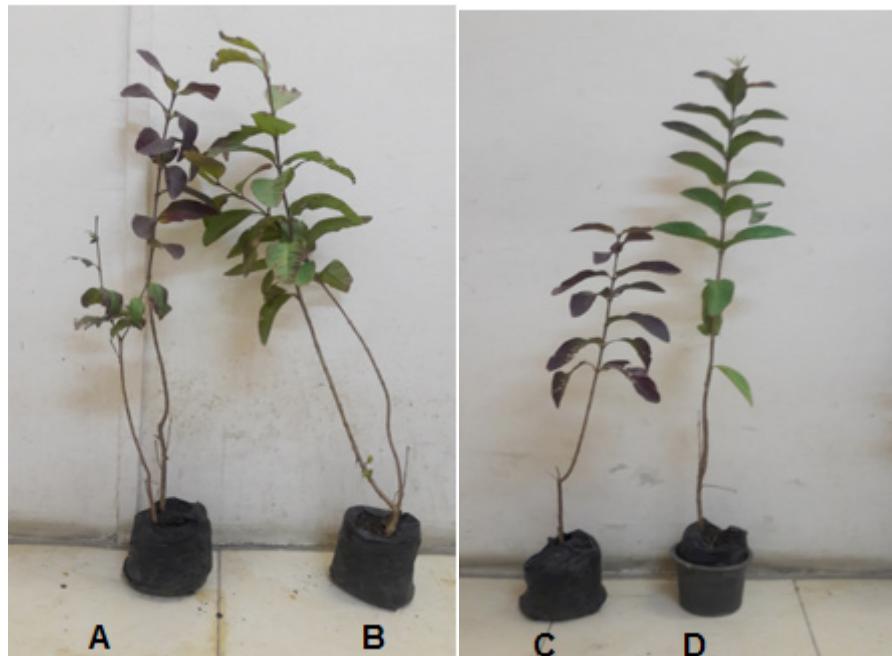


Figure 11: Effect of Guar Gum superabsorbent hydrogels on guava plant after 20 days of implantation (Manar, et al. [67]).

Shuping, et al. [72] modified a degradable nitrogen and phosphorus fertilizer with properties of slow release, water retention, and remediation of saline soil; the nitrogen and phosphorus compounds were coated with starch/poly(Acrylic Acid-Co-Acrylamide) [poly(AA-co-AM)] superabsorbent by reverse suspension radical copolymerization, Figure 12. The variables affecting the water absorbency were investigated and optimized. The data of the structure and morphology characterization showed that poly (AA-co-AM) was grafted moderately from the chain of starch. The pores of the net were affected by the starch content. Moreover, the property of water retention, the behaviors of slow release of nutrient, and the degradation of the superabsorbent hydrogels were evaluated. The results revealed that the water transpiration ratio of soil with the prepared hydrogels was lower by about 8% than that of the blank sample, about 60% nutrient was released within 30 days, and 32 wt % of the hydrogel with a content of starch of 20% was decomposed after 55 days. Moreover, a remarkable decrease in the conductivity was observed, which revealed a sharp decline in the concentration of residual ions for the soil mixed with SAAmF. It may be inferred from these that the product seems to be a promising vehicle for the management of soils, including saline soils.

Furthermore, thermo-responsive interpenetrating Guar Gum (GG)/poly(N-isopropylacrylamide) (PNIPAAm) hydrogels were synthesized (Xiuyu, et al. [74]), Figures 13 and Figure 14. The investigated hydrogels exhibited some reversible thermo-

responsive characteristics at low GG content (below 15 wt%). The introduction of GG component with IPN methodology could develop the temperature sensitivity and permeability of GG/PNIPAAm IPN hydrogels. This property is of specific importance in temperature- induced water release. Thus, these hydrogels can be used in agriculture.

Moreover, Guar Gum/poly (Acrylic Acid) Semi-Interpenetrating Polymer Network (IPN) hydrogels were prepared via free radical polymerization in the presence of a crosslinker MBA. The kinetics of swelling and the water transport mechanism were investigated versus the hydrogel composition and the pH of the swelling medium. Hydrogels showed immense swelling in aqueous medium and displayed swelling characteristics, which were highly dependent on the chemical composition of the hydrogels and pH of the medium in which hydrogels were immersed.

The semi-IPN hydrogels were characterized in the light of different network parameters such as average molecular weight between crosslinks crosslink density and mesh size [75, 76]. The introduction of the anionic functional group COOH by hydrolyzing the CONH group on the microgels of the crosslinked polyacrylamide-g-Guar Gum (pAAm-g-GG) matrix lead to developing of pH-sensitive matrix systems. The polyelectrolyte functional groups introduced provide the pAAm-g-GG matrix into poly anionic polysaccharide networks and the weakly ionic functional groups on the polymeric chains will cause their pH-responsive behavior.

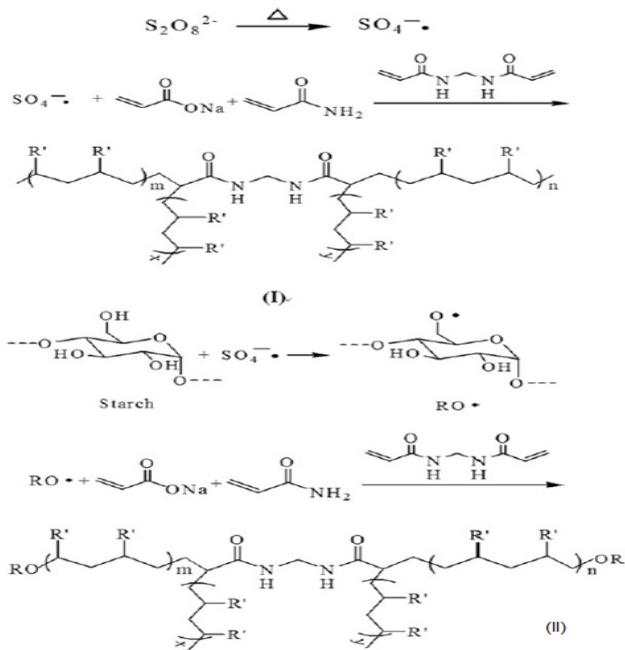


Figure 12: Schematic diagrams of the copolymerization of AA and AM (I) and the graft copolymerization of AA and AM from starch (II) (Shuping, et al. [72]).

Guar Gum Nano-Superabsorbent Composites and Nanocomposites

Superabsorbent composites and nanocomposites have been attracted grand attention in recent years because of their improved properties than conventional hydrogels [77-80]. Due to their ecofriendly and biocompatibility characteristics, their utilization in numerous biomedical applications such as tissue engineering, bone reconstruction, etc. has already been established [81-85].

However, little or no research on their behavior in plant growth environments has been reported. Actually, utilization of raw materials available in nature and their application to derive other useful products without any adverse impact on the environment is of great essence [86-88]. Therefore, the choice of polysaccharide hydrogels was driven by the fact that they are materials with generally well verified biocompatibility and they can be tailored to fit different biomedical applications [89-91]. In this respect, Guar Gum (GG) as an environmentally friendly natural polymer has been modified by several chemical modification reactions into hydrogel composites and nanocomposites for different purposes [92-96].

Wenbo, et al. [95,96] introduced superabsorbent composites based on Guar Gum and Attapulgite (APT) through the graft

copolymerization of GG, partially neutralized acrylic acid and APT in aqueous solution. The effects of reaction conditions such as concentrations of the initiator and crosslinker, APT content, etc. on water absorbency were investigated. The optimized composites retained high water absorbency over a wide pH range of 4-11 and also exhibited improved reswelling and water retention capabilities. The superabsorbent composites can be utilized as eco-friendly water manageable materials for agricultural and horticultural applications.

Likhitha, et al. [97] synthesized superabsorbent nanocomposites of Guar Gum grafted sodium acrylate via both microwave initiation and thermal initiation techniques. The nanocomposites showed high water absorbency within a wide pH range. Preliminary studies on crystal violet dye removal showed promising results. However, the physical properties and water absorbing capability of the prepared hydrogels can also suite agricultural applications. Xiaoning, et al. [98] prepared a series of novel Guar Gum-graft poly (sodium acrylate-co-styrene)/attapulgite (GG-g-P(NaAco-St)/APT) superabsorbent nanocomposites by the simultaneous graft copolymerization of partially neutralized acrylic acid, styrene and attapulgite onto natural Guar Gum, using Ammonium Persulfate as the initiator and N, N'-methylene-bisacrylamide as the crosslinking agent, Figure 15. The grafting of acrylic acid and styrene into Guar Gum was confirmed by Transform Infrared (FTIR). The incorporation of styrene and attapulgite clearly improved the surface porous morphology of the composites as exhibited by Field Emission Scanning Electron Microscopy (FESEM). The effect of St and APT on the swelling properties and the swelling kinetics of the developed nanocomposite were investigated. Results showed that the simultaneous incorporation of proper amount of hydrophobic co-monomer St and inorganic nano-scale APT not only obviously enhanced the swelling capacity but highly improved the swelling rate, and the nanocomposite showed better salt-resistant capability and excellent pH stability in various pH solutions. These advanced properties confirm that the prepared hydrogels are suitable for sustained water release in agriculture application.

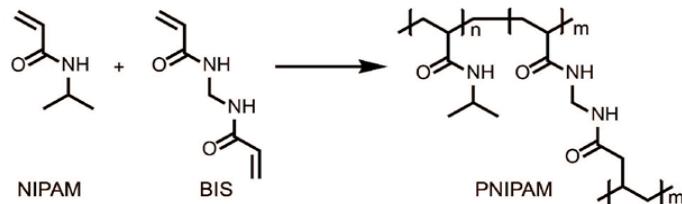


Figure 13: Synthesis of PNIPAM from NIPAM monomer and BIS cross-linker [99].

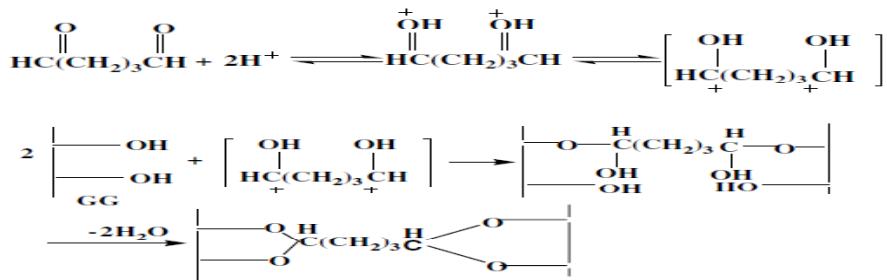


Figure 14: Isomerization of GA at acid environment and the crosslinking reaction of two adjacent hydroxyl groups on GG (Xiuyu, et al. [74]).

Furthermore, Xiaoning, et al. [98] introduced a novel group of Guar Gum superabsorbent composites. These hydrogels were prepared by the simultaneous graft copolymerization of Guar Gum (GG), partially Neutralized Acrylic Acid (NaA), Styrene (St) and Vermiculite (VMT) in presence of Ammonium Persulfate (APS) as an initiator and N, N -Methylene-Bisacrylamide (MBA) as a crosslinker. Fourier Transform-Infrared (FT-IR) and Ultraviolet-Visible (UV-vis) spectroscopies revealed that NaA and St had been grafted onto GG main-chain, and VMT participated in polymerization reaction. The simultaneous incorporation of St and VMT improved the surface pore structure, and VMT led to a better dispersion in the polymer matrix as shown by Field Emission Scanning Electron Microscope (FESEM). Swelling results indicated that the insertion of suitable amount of St and VMT in the network structure induced enhanced swelling capability, rate, and salt resistant performance. Moreover, the composites exhibited good pH-stability in the solution of various pHs, and proved smart swelling-deswelling attribute, which can be used as promising candidate for its utilization in water release application. Figure 15.

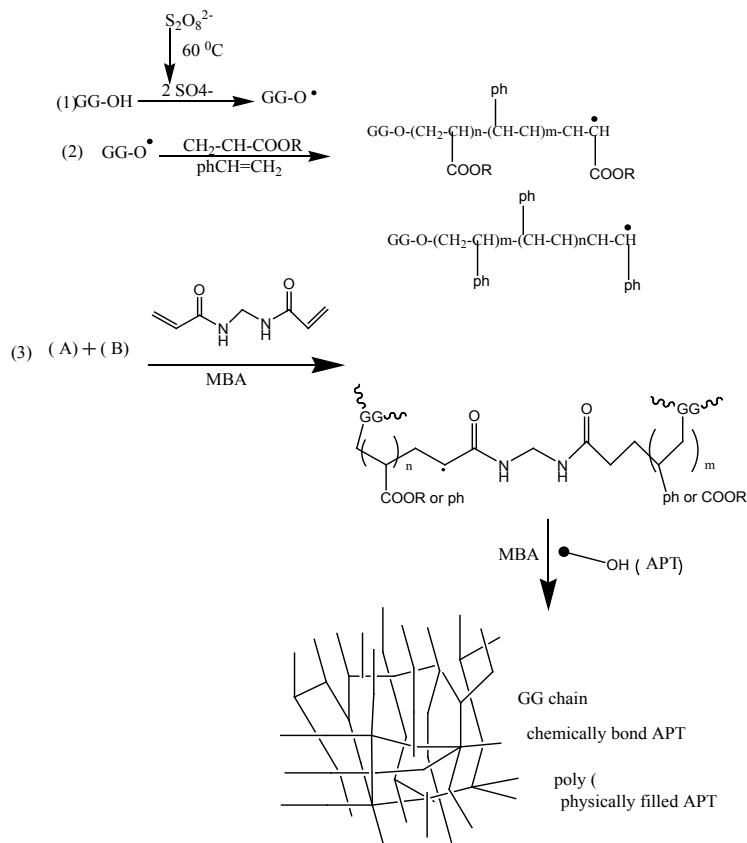


Figure 15: A proposed reaction mechanism for the formation of GG-g-poly(NaAco-St)/APT superabsorbent nanocomposites Xiaoning, et al. [98].

Conclusions

Green biopolymers are now replacing synthetic and petroleum based polymers in most if not all applications due to several economic and environmental issues. Among these polymers, Guar Gum has been extensively used due to its abundance and unique physical properties. It can be easily modified via several chemical protocols into a various number of modified formulations that can suite different applications. Our main concern is agriculture sector and how the modified Guar Gum products can participate in solving some problems in this sector mainly cultivation under desert conditions which require polymers with precisely tailored chemical design and special physical properties. Thus, the present review sheds light on preparation of hydrogels based on modified Guar Gum and their important role in agriculture. Furthermore, Guar Gum composites and nanocomposites were also reviewed.

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