Int J Pharm Bio Sci 2015 Jan.; 6(1): (P) 622 - 638

Review Article **polymer sciences**

International Journal of Pharma and Bio Sciences **ISSN 0975-6299**

GRAFTING ON GUAR GUM - ITS DERIVATIVES: AN OVERVIEW

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ABSTRACT

Guar gum, a naturally occurring polysaccharide, is being widely used in graft copolymerization with vinyl monomers. In the present article, an attempt has been made in reviewing the literature based on guar gum, particularly related to its derivatization and graft copolymerization. This article exhaustively reviewed the efforts of various workers in the field of graft copolymerization of Guar gum and its various derivatives with various vinyl monomers and the potential effect of process parameters on graft copolymerization. It has been noted from the literature that the extent of grafting is greatly influenced by the process parameters such as initiator, monomer and gum concentrations and also influenced by the reaction time and temperature up to certain limit beyond which it shows decreasing trend.

KEYWORDS: **Guar gum, Guar gum derivatives, Grafting, Grafting parameters.**

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INTRODUCTION

In recent years there has been considerable thrust in the development and utilization of polysaccharides isolated from natural sources such as guar gum, starch, cellulose, alginate, chitosan for the variety of applications like in biomedical and pharmacology, due to their sustainability, biodegradability and biosafety The primary aim of this review article is to survey the literature on Guar gum (GG) particularly focused on its derivatization and grafting. GG is a naturally occurring non-ionic polysaccharide of high molecular weight (approximately 50,000-8,000,000). It is derived from the Guar seed *Cyamopsis tetragonolobus*. This leguminous plant is grown mainly in India and Pakistan and is being used as an edible food item. It also finds application in various industries as viscosity builder, stabilizer, emulsifier and water binder. Guar gum is a member of the class of galactomannans, which consist of α (1–4)-linked β-D-mannopyranosyl backbone partially substituted at O-6 with α-D-galactopyranosyl side groups attached by (1-6) linkages, possessing hydroxyl groups available for the attachment of biologically active compounds (Fig.I). The ratio of mannose to galactose units ranges from 1.6:1.0 to 1.8:1.0, apparently because of climatic variation [1-3].

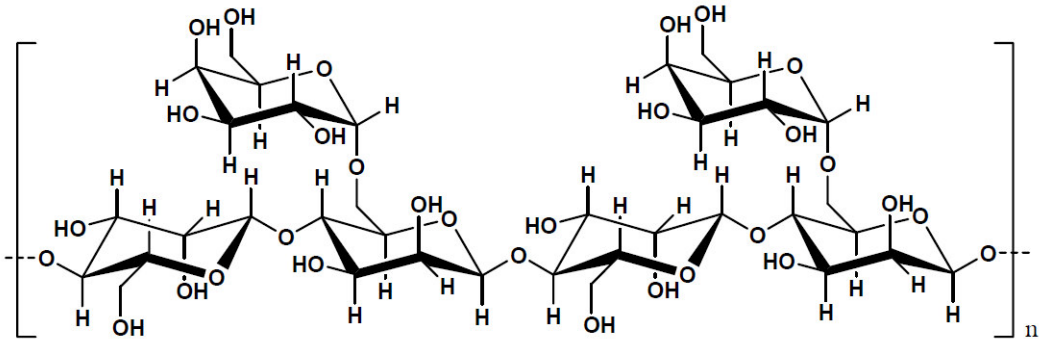

Figure I
Chemical structure of Guar gum

1.1 Manufacture of Guar gum

Guar gum, also known as *Gum cyamopsis* or guar flour, is derived from the ground endosperm of the seed of the guar plant. The guar kernel is composed of several layers, namely the husk (16-18%) on the outer side, the germ (43-46%) and the endosperm (34-40%), which is composed of guar gum. Guar splits are obtained after separation of the husk and the germ. The hull is separated by heat treatment either by attrition milling or various types of impact mills. The endosperm is recovered by sieving from the finer germ and hull fractions, and then milled to obtain powdered guar gum. The GG may be further purified and clarified by dissolution in water, precipitation and recovery with ethanol or isopropanol. It is called as clarified (purified, extracted) guar gum. Clarified guar gum in the market is normally standardized with sugars. The clarified GG has higher galactomannans content. [1,4]

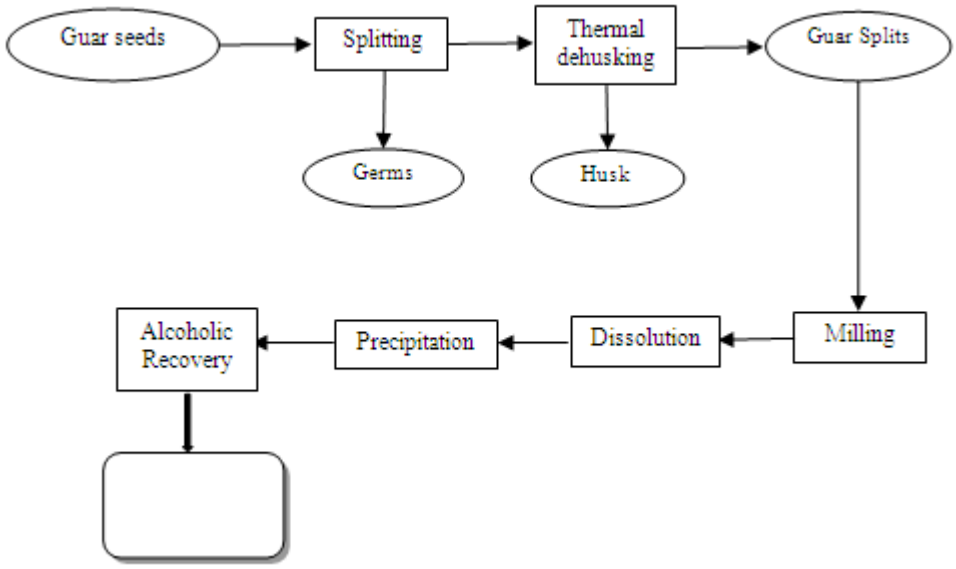

Figure II
Guar gum manufacture flow chart

1.2 Applications of GG/its derivatives

GG and its derivatives such as hydrolyzed, hydroxyalkyl, carboxyalkyl, oxidized, sulphated, borated, cationic and various combinations of these are commercially useful for a number of industrial applications (Fig. III). The functions of GG/its derivatives in various industrial applications are listed in Table II.

Table I
Intrinsic Properties of GG [1,5]

Physical and chemical properties

- Soluble in hot and cold water but insoluble in organic solvent
- GG solutions have buffering capacity and are very stable in the given pH solution.
- Gel forming ability
- Film forming ability
- Excellent thickening properties which makes it an efficient thickening agent
- Higher viscosity even in small quantity
- Resistant to oils, solvents and greases
- Excellent water binding capacity
- Efficient functionality even at low temperatures
- Numerous reactive hydroxyl groups for hydrogen bond formation, chemical modification and crosslinking

Biological properties

- Biocompatibility
- Biodegradable
- Non toxic

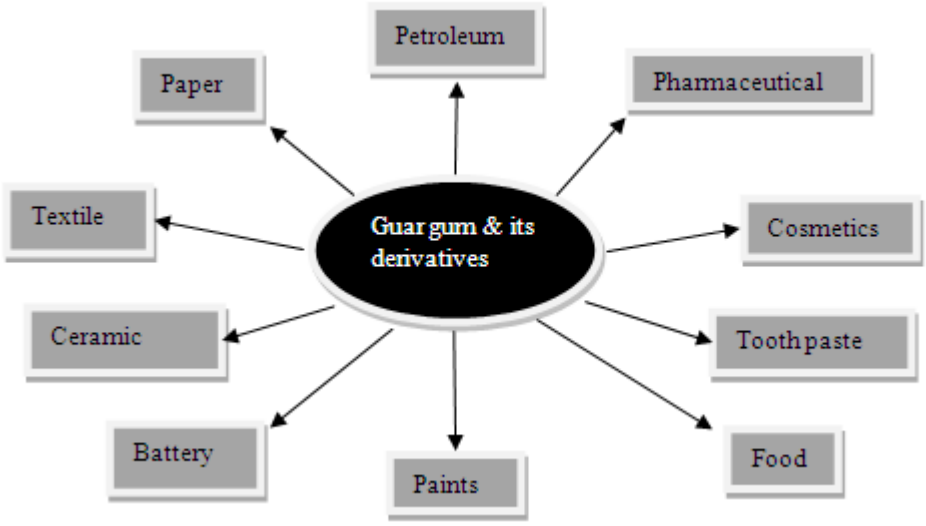

Figure III
Applications of Guar gum and its derivatives

Table II
Functions of GG/its derivatives in various industries

Industry	Function
Petroleum	Thickener for hydraulic fracturing of rock formations to enhance the oil recovery (i.e. hydraulic fracturing fluid)
Paper	Dispersant and suspending agent
Textile	Pigment dispersing aid and also as thickening agent for color printing pastes
Ceramic	Binder, thickener and fixing agents for enamels, porcelain etc.
Food	Thickening agent for products like pudding, ice cream, salad dressings, bakery and confectionary products, sausages, cheese spread etc.
Battery	Electrolyte thickener
Paints	Thickening agent
Tooth paste	Imparts slip so that paste can be extruded form the tube without applying excess pressure
Shaving Cream	Stabilizes the system and impart slip in extrusion
Pharmaceutical	Dry GG as disintegrant and in solution as a binder in compressed tablet manufacture. GG helps in lowering blood sugar, blood pressure and cholesterol levels. It also creates a sense of fullness in stomach so it is also used in manufacture of diet pills. Due to its hydrophilic property and ability to form jelly like mass, it is used in appetite depressants and also in gastric ulcer treatment

The numerous advantageous properties make it the most widely used thickening agent in various industries like food, pharmaceutical, cosmetics, health care, paper & pulp and textile. The GG seeds is very useful in petroleum and drilling industry due to which the seeds are highly in demand in the petroleum industry of USA and the oil fields in the Middle East. Apart from the above mentioned uses, GG was also reported to have specialized application as temperature sensor. [5-8]

2. GG derivatives

GG can be chemically modified into various derivatives by abstracting Hydrogen from free hydroxyl groups along the macromolecular backbone with the reactive functional groups. GG contains on an average three hydroxyl groups per D-mannose unit for derivatization. The primary C-6 hydroxyl position is highly active but the secondary hydroxyls are also sites for substitution. The maximum theoretical degree of substitution in such molecule is three. The chemical modification of GG includes etherification, esterification and crosslinking reactions of hydroxyl groups. The hydroxyl groups when substituted with ethers allow side groups extension which may change the solubility and other important characteristics of the GG. The complex forming reactions lead to cross linking of the molecules resulting in a three dimensional network which manifests itself in gel formation. For example, copper salts form insoluble gel-like complex with galactomannans. Similarly salts of Ca, A1, and Cr have the same gel forming ability at certain pH levels. These chemical processes involving galactomannans are designed to bestow the natural gums with a variety of desired properties - including anionic and cationic whereas galactomannans are neutral and nonionic in character. This chemical modification of GG is done not only to remove its inherent deficiencies (such as decrease in viscosity due to uncontrolled rate of hydration, pH-dependent solubility, turbidity in aqueous dispersion and high susceptibility to microbial attack which limits its long term application) but also to improve its water solubility and multifunctional characteristics. Thus chemical modification of GG broaden its perspective in numerous applications such as paper and pulp, textile, paints and pigments, oilfield, mining, water treatment, food, health care and pharmaceutical industries.[9-12]The GG derivatives reported in the literature are discussed below:

2.1 Carboxymethyl derivative

Carboxymethylation is the most widely studied modification of GG and other bio polysaccharides to produce commercially important biopolymers with promising properties. Carboxymethylated derivatives of GG are widely used in in paper and oil industry.[13]Carboxymethylation of GG involves the reaction between the –OH groups of galactomanan chain with caboxymethyl reagents (such as chloroacetic acid, maleic anhydride and succinic anhydride) under alkaline condition. This results into the introduction of –COOH or –COONa groups on the backbone chain of GG. The contribution of some researchers in carboxymethylation of GG is stated below. Carboxymethylguargum (CMG) was prepared by reacting GG with chloro acetic acid in the presence of sodium hydroxide.[14] Parvathy et al reported the cost effective and ecofriendly reaction for the preparation of carboxymethyl derivative of galactomanan using monochloro acetic acid in the presence of sodium bicarbonate as catalyst instead of sodium hydroxide, thereby reducing the possibility of alkaline degradation and the effect of elevated temperature caused by strong NaOH.[15] Partial carboxymethylation of GG was also reported by Pal et al by using sodium salt of monochloroacetic acid (SMCA) as carboxymethylation agent in presence of sodium hydroxide. They also reported that by changing the concentration of SMCA, CMGs with different degree of substitutions were obtained.[16] Gong et al reported the synthesis of CMG with a simple dry and multi-step method for the first time as a product of the reaction of GG and monochloro acetic acid in the presence of sodium hydroxide.[17]CMG nanoparticles in the range 12–30 nm were also synthesized using nanoprecipitation and sonication method by Gupta et al.[18]

2.2 Hydroxypropyl derivative

Hydroxypropyl GG (HPG) was first time synthesized by phase transfer catalysis reaction which involved reaction of GG with propylene oxide, hexadecyltrimethyl ammonium chloride, at pH 10-10.5, temperature 45-50℃ and reaction time 3-4 hours. This derivative was reported to have high viscosity, better solubility and stability, less content of insoluble residue and superior colloid light transparency compared to guar flour.[19] HPG was also

synthesized by alkaline etherification of GG with propylene oxide, which was further etherified with docosylglycidyl ether in isopropyl alcohol in the presence of alkaline catalyst.[20]

2.3 Benzoyl derivative (BGG)

Huang and Xiao synthesized BGG by the reaction of alkali-GG slurry with benzoyl chloride in an ice-bath. The white precipitate of BGG obtained was washed with water and vacuum dried at 50℃. The benzoylation take place at hydroxyl group of GG.[21]

2.4Carboxymethylhydroxypropyl derivative

Pasha et al synthesized sodium carboxymethylhydroxypropyl derivative of GG by adding ice cold solution of sodium hydroxide to GG dispersion in isopropyl alcohol, followed by subsequent addition of monochloro sodium acetate, chilled propylene oxide and sodium borohydride at 58^{o}C.[11]

2.5 Methyl derivative

Singh et al has demonstrated the complete methylation of a GG using dimethyl sulphate and aqueous sodium hydroxide under Microwave irradiation followed by hydrolysis with 70% HCOOH acid and 0.5N H_2SO_4.[22]Risica et al synthesized methyl ether GG by carrying out heterogeneous phase reaction of GG solution in isopropyl alcohol in presence of 50% (w/v) sodium hydroxide aqueous solution followed by adding alkylating agent (dimethyl sulphate or methyl iodide). The introduction of methoxyl groups along the GG chains lowers the hydrogen bonding sites on the polysaccharide backbone and thus reduces their aggregation tendency.[23]

2.6 Methyl carboxymethyl derivative

Bahamdan et al prepared methylcarboxymethyl guar by reacting sodium carboxymethyl GG (NaCMG) or sodium carboxymethylhydroxypropyl GG (NaCMHPG) with dimethyl sulfate at 60^{o}C under nitrogen atmosphere.[7]

2.7 Carboxyethyl derivative

Sholapur et al synthesized sodium carboxyethyl GG (using optimization technique) by dispersing GG in ice cold solution of sodium hydroxide (5-7^{o}C) followed by addition of 2-Chloropropionic acid at 15^{o}C and then the reaction mixture was treated with isopropyl alcohol (as stabilizing liquid) at 75^{o}C.[24]

2.8 Carboxyl derivative

Polyelectrolyte carboxylated GG was synthesized by selective oxidation of C-6 alcohol functions of galactose units side chains first to aldehyde groups and then to carboxylic groups by halogen oxidation.[25]

2.9 Acryloyloxy derivative

Acryloyloxy GG was produced by the esterification of acryloyl chloride with gaur gum using a Schotten-Bauman's reaction, while reserving the double bond on the acrylate for further reaction. The hydrophilic nature of GG was reduced by acrylation and changed the functionality from one solely consisting of hydroxyl groups to one containing terminal carbon double bonds as well as hydroxyl groups, which would be the case in a partially acrylated product.[26]

2.10 Sulfate derivative

Mestechkina et al synthesized galactomannan sulfates using the SO_3–pyridine complex in dimethylformamide as a sulfating agent. The Sulfation was performed at 60°C for 4 h under constant stirring with four galactomannans i.e. *Galegaorientalis*(oriental goat's rue), *Styphnolobiumjaponicum*(sophora), *Cyamopsistetragonoloba* (GG) and *Ceratoniasiliqua* (locust bean).[27]

2.11 Palmitoyl derivative

Guar Galactomannan Ester of Palmitic Acid i.e. Palmitoylated guar galactomannan (PGGM) was prepared by a heterogeneous method using palmitoyl chloride at 80°C for 3.5h. The authors have also noted that water soluble PGGM has good emulsifying activity, even in high salt concentration or in acidic pH and is a kind of good oil in water (o/w) emulsion stabilizer.[28]

2.12 Benzamide derivative

GG benzamide was synthesized by benzoylation with benzoyl chloride in aqueous medium and using propyl amine to impart a high degree of hydrophobicity. This new derivative was reported to be water resistant, soluble in non-aqueous solvent like dimethyl sulfoxide and biocide active.[29]

3. Grafting of GG and its derivatives

The Graft copolymerization of vinyl monomers onto polysaccharides resulting in the formation of hydrogel materials has been well documented in literature. The various hydrogel materials were formed by grafting vinyl monomers onto polysaccharides such as starch, cellulose, GG, chitosan, sodium alginate, carrageenan etc. The grafting of monomers onto the GG generally takes place at –OH groups by radical polymerization mechanism with either thermal or redox initiators. The free radicals are formed by decomposition of thermal initiators such as potassium per sulfate, sodium per sulfate, ammonium per sulfate or the oxide-redox action of redox initiator pairs like K_2SO_4/ascorbic acid, K_2SO_4/Fe^{2+}, H_2O_2/Fe^{2+}. The radical thus formed abstracts H atom of the –OH group and initiate the chain growth by forming macro radicals, which may initiate the vinyl groups of monomers to propagate the chain growth. The most widely used initiation system is redox initiator system because the activation energy for such system is quite low and radicals are formed at ambient temperature with faster reaction rates and low consumption of energy. The radical formation with some of the commonly used initiation system is represented in figure IV. For instance, in case of ceric ammonium nitrate/nitric acid initiation system, a ceric ion–GG complex is initially formed as a result of electron transfer. Then the ceric ion (IV) is reduced to cerous ion (III), and a free-radical is created on the galactomannan backbone. In the potassium peroxymonosulphate/ ascorbic acid (AA) system, AA species reacts with peroxymonosulphate in presence of H^+ ions to give primary free radicals OH· and AA· radicals. The primary free radicals thus formed from various initiators (though by different mechanisms) abstract hydrogen atom from hydroxyl group of glactomanan chain resulting in the formation of macromolecular radicals. These gum radicals initiate the vinyl monomers to propagate the grafting polymerization leading to grafting of vinyl monomers on GG / its derivatives. The effect of initiator, monomer and gum concentration, reaction time, temperature and pH has a major role to play in percent grafting and grafting efficiency. The mechanism by which cerium (IV) generates free-radicals is believed to involve the formation of coordination complex between the oxidant i.e., CAN and the hydroxyl group of biopolymer. The ceric (IV) – biopolymer complex then disproportionate forming a free-radical on the biopolymer chain and cerium (III) ion.[30-32] The detailed summary of the GG and its derivatives grafted copolymers are listed in Table III

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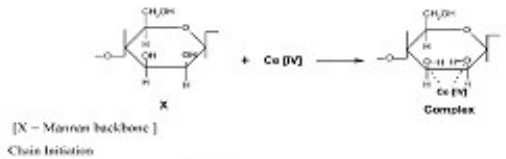
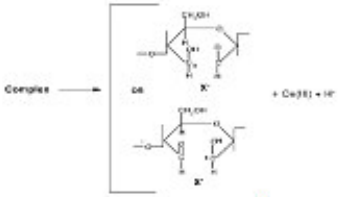
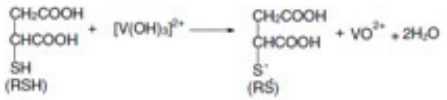




i) Ceric ammonium nitrate/ nitric acid initiation system [32]



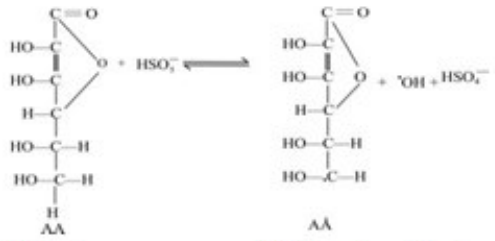
iv) Mercaptosuccinic acid – Vanadium redox pair [34]

$$AA + BrO_3^{\cdot} \rightarrow AA^{\cdot} + BrO_2^{\cdot} + OH^{\cdot}$$

$$AA + BrO_2^{\cdot} \rightarrow AA^{\cdot} + BrO^{-} + OH^{\cdot}$$

$$AA + BrO^{-} \rightarrow AA^{\cdot} + Br^{\cdot} + OH^{-}$$

v) Potassium bromate-ascorbic acid redox pair [35]



ii) Potassium peroxymonosulfate/Ascorbic acid redox pair [31]

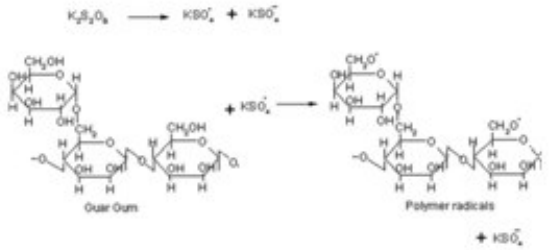
$$H_2P_2O_8^{2-} + Ag^{+} \leftrightarrow H_2AgP_2O_8^{-}$$

Complex

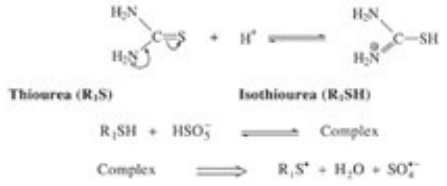
$$H_2AgP_2O_8^{-} + G\text{-}OH \rightarrow G\text{-}O^{\cdot} + HPO4^{\cdot -} + Ag^{+}$$

$$G\text{-}OH + HPO4^{\cdot -} \rightarrow G\text{-}O^{\cdot} + H_2PO4^{\cdot}$$

vi) Peroxydiphosphate–Ag (I) [36]



iii) Potassium per sulfate initiation system [33]



vii) Potassium peroxymonosulfate/Thiourea [37]

$$H_2CrO_4 + CH_2(COOH)_2 + 4H^{+} \rightarrow Cr^{4+} + HO\text{-}CH(COOH)2 + 4H^{+}$$

$$Cr^{4+} + CH_2(COOH)_2 \rightarrow {}^{\cdot}CH_2(COOH)_2 + H^{+} + Cr^{3+}$$

viii) Potassium chromate/malonic acid redox pair [38]

Figure IV
Free radical formation with some of the commonly used initiation system

Table III
Summary of GG/its derivatives grafted copolymers

Comonomer	Initiator system	%G	References
[GG grafted copolymers]			
Acrylic acid	Mercaptosuccinic acid – Vanadium(V)	160.4	[34]
Acrylic acid	Peroxydisulphate– Ag (I)	1237.83	[36]
Acrylamide	Ceric ammonium sulfate	98.2% (GE)	[39]
Acrylamide	Potassium per sulfate		[40]
Acrylamide	Bromate/thiourea		[41]

Acrylamide	Co^{60}γ radiation		[42]
Acrylamide and diallyldimethyl ammonium chloride	Cerrous sulfate and Potassium per sulfate	85	[43]
Methacrylamide	Potassium chromate-malonic acid	185.3	[38]
Methyl methacrylate	Ceric ammonium sulfate-Dextrose		[44]
Methyl methacrylate	Ceric ammonium nitrate-nitric acid	197.86	[32]
Methyl methacrylate	Microwave irradiation		[45]
Ethyl methacrylate	Ceric ammonium sulfate-Dextrose	95.72	[46]
Acrylonitrile	Ceric ammonium nitrate	383	[47]
N-Vinyl formamide	Potassium bromate-ascorbic acid	358.7	[35]
N-Vinylformamide	Bromate-ascorbic acid		[48]
Methacrylic acid	Potassium per sulfate	241	[49]
4-Vinyl Pyridine	Potassium peroxymonosulfate/ Ascorbic acid	560	[31]
Aniline	Ammonium per sulfate	230	[50]
Partially neutralized acrylic acid	Ammonium per sulfate		[51]
Partially neutralized acrylic acidand medicinal stone	Ammonium per sulfate		[52]
Acrylamidoglycolic acid	Potassium per sulfate	550	[33]
Vinyl alcohol	Citric acid as additive		[53]
[Carboxymethyl GG grafted copolymers]			
Acrylamide	Ceric ammonium nitrate		[54]
Acrylamide	Potassium persulfate and microwave irradiation.		[55]
Acrylonitrile	Ceric ammonium nitrate-nitric acid		[56]
Methyl acrylate	Ceric ammonium nitrate-UV radiation	356.58	[57]
Methyl methacrylate	Ceric ammonium nitrate-nitric acid	258.74	[58]
Methacrylic acid	Potassium peroxymonosulphate		[59]
N-isopropylacrylamide	1-(3-(dimethylamino) propyl)-3-ethyl carbodiimide hydrochloride as coupling agent.		[60]
Polyurethane	Calcium chloride		[61]
4-Vinyl Pyridine	Bromate/ thiourea		[62]
[Hydroxypropyl GG grafted copolymers]			
Acrylamide	Ceric ammonium nitrate		[63]
Acrylamide	Ceric ammonium nitrate	241	[64]
[O-Carboxymethyl-O-hydroxypropyl GG grafted copolymers]			
N-isopropylacrylamide	Potassium persulfate and N,N,N,N′-tetramethylethylenediamine		[65]

3.1 Effect of Process parameters on grafting

The detailed survey of literature has revealed that the extent of grafting of vinyl monomers onto GG/its derivatives is greatly affected by various process parameters, which are summarized below.

3.1.1 Effect of initiators

3.1.1.1 Ceric ion induced initiation

Ceric ion-induced redox initiation method has been preferred for grafting polymerization because the redox process initiates free radical sites exclusively on the polysaccharide backbone, which reduces the homopolymerization of participating monomers.[64] Grafting parameters were found to increase by increasing the concentration of ceric ion to certain level and then found to decrease with further rise in ceric ion concentration. The probable reason explained for initial increase in grafting parameters is due to generation of more free primary radicals in presence of Ce^{4+} ions which propagate the graft polymerization. While the subsequent decrease in grafting parameters beyond certain level of Ce^{4+} ions may be due to termination of growing grafted chain and formation of homopolymers which compete with the grafting reaction in presence of excess Ce^{4+} ions. For instance, Grafting efficiency (GE) in case of grafting of methyl methacrylate (MMA) on to GG by using ceric ammonium nitrate (CAN) initiator was found to increase by increasing the concentration of CAN from 0.005 to 0.02 mol/L and then decrease with further rise in [CAN]. [32] Similarly GE increased with increase in the concentration of ceric ammonium sulfate (CAS) up to 18.96 x 10^{-3}mol/L and then decreased in case of grafting of MMA on GG, [44] GE of Ethyl methacrylate (EMA) onto GG was found to be influenced by [CAS] with initial increase in concentration up to 1.26 x 10^{-3}mol/L and then decreased gradually with subsequent rise in [CAS].[46] The effect of photo initiator concentration i.e. [Ce^{4+}] on grafting yield of ultraviolet radiation induced grafting of methyl acrylate on partially carboxymethylated GG (PCMG) was also found to increase with the increase in [Ce^{4+}] from 1.50 x 10^{-3}mol/L to 4.00 x 10^{-3}mol/L and attained its maximum value of 197.29%. The authors reported that the percent grafting (PG) was initially increased with the increase in [Ce^{4+}] from 1.50 x 10^{-3}mol/L to 4 x 10^{-3} mol/L and attained its maximum value of 197.29%. The probable cause for this observation as suggested by authors is that within the aforementioned concentration range of [Ce^{4+}], the complex was formed between the ceric ions and PCMG and the photodecomposition of this complex resulted in greater number of active sites along the backbone which are responsible for grafting polymerization[57,58]. However, in the grafting of acrylamide (AM) onto hydroxy propyl GG (HPG), Nayak and Singh reported that with the increase in [CAN] and keeping [AM] constant, large number of short PAM chains were formed. This resulted in lower hydrodynamic volume of grafted copolymer which was also reflected by high intrinsic viscosity value.[63,64]

3.1.1.1. (a) Effect of Dextrose Concentration in CAS/Dextrose redox pair initiation system

It has been noted from the literature that GE of grafted copolymer increases with initial rise in [dextrose] up to certain value and then decreases with subsequent increase. Chowdhury et al reported similar trend in grafting of MMA on to GG using CAS as initiator [44]. The GE increased with increase in [dextrose] up to 7.57 x 10^{-4} mol/L and then decreased gradually with further increase in dextrose level during grafting of ethyl methacrylate on to GG. The probable explanation for such behavior was explained by the fact that in presence of ceric ions, dextrose forms free radicals that act as an initiator for initiating the graft polymerization while higher concentration of dextrose reduces all the ceric ions to cerous ions.[46]

3.1.1.1. (b) Effect of acid in CAN/Nitric acid redox pair initiation system

It has been observed from the literature that presence of acid at optimum level in CAN/Nitric acid redox pair initiation system is required for efficient grafting of vinyl monomers on to GG/its derivatives. The optimum concentration of acid for maximum PG was found as: 0.2M in grafting of MMA on to GG,[32] 0.20 mol/L in grafting of

methyl acrylate (MA) on to PCMG[57], 0.20 mol/L for MMA on to PCMG,[56] beyond which it decreases. The role of nitric acid in grafting of vinyl monomers on to GG/its derivatives can be explained by the fact that ceric ion exist as Ce^{4+}, $(Ce[OH]_3)^{3+}$ and $(Ce\text{-}O\text{-}Ce)^{6+}$ on reaction of ceric ions with water as shown below:

$$Ce^{4+} + H_2O \rightleftharpoons (Ce\,[OH]_3)^{3+} + H^+ \quad (1)$$

$$2(Ce\,[OH]_3)^{3+} \rightleftharpoons (Ce\text{-}O\text{-}Ce)^{6+} + H_2O \quad (2)$$

The concentration of these ions depend upon the $[H^+]$. The initial rise in PG with respect to optimum value of $[H^+]$ as discussed above favor the concentration of $Ce^{4+}$and $(Ce[OH]_3)^{3+}$ at the expense of $(Ce\text{-}O\text{-}Ce)^{6+}$. Ce^{4+}ions being smaller in size is more capable of forming complex with GG than $(Ce\text{-}O\text{-}Ce)^{6+}$. However, at higher $[H^+]$ i.e. above optimum value, PG decreases because equilibrium (1) and (2) shift towards the formation of $(Ce\text{-}O\text{-}Ce)^{6+}$.[32] Similarly, Trivedi et al also reported the increase in the PG with an increase in the acid concentration was due to a decrease in the termination rate of the growing polymer chain or an increase in the initiation rate. At higher $[H^+]$ the decrease in PG value is attributed to reduction in Ce^{4+}/ PCMG complex and increase in the termination rates.[58]

3.1.1.2 Persulfate initiation

It is observed from the literature that with an increase in the concentration of Potassium persulfate [KPS], PG and GE initially increased, but with further increase in [KPS] beyond certain limit, these grafting parameters showed decreasing trend. This behavior was explained by the fact that with the increase in [KPS] there is simultaneous increase in free radical formation which are able to attack polysaccharide chain of GG/its derivatives. This results in the formation of more macro radicals capable of grafting vinyl monomers on them. On further increasing the [KPS] above threshold value corresponding to maximum grafting, large number of free radicals are formed which may initiate homopolymerization of vinyl monomers at the expense of grafting. This results in decrease in grafting parameters. Similar observations were also reported by several worker, for instance, the optimum value of [KPS] was found to be: 1.1 mmol in grafting of methyl acrylic acid (MAA) onto GG,[49] 0.0011 moles in grafting of acrylamidoglycolic acid on to GG,[33] 0.55M ammonium persulfate (APS)/HCl in grafting of polyaniline onto GG,[50] 0.525 mmol/L for GG-g-poly(sodium acrylate) system.[51] Pal et al reported that low concentration of initiator is favorable for forming small number of longer chains of polyacrylamide to be grafted on CMG whereas higher concentration of initiator results in the formation of large number of short chains. The longer chains on account of their higher hydrodynamic volume, intrinsic viscosity and radius of gyration have better flocculation properties.[55]

3.1.1.3 Peroxymonosulfate initiation

The grafting parameters were found to increase with increase in the concentration of potassium peroxymonosulfate [PMS] up to certain level and then decreased. The initial increase in grafting parameters with respect to [PMS] was attributed to the reduction of PMS in presence of thiourea resulting into the formation of free radicals and the subsequent decrease was attributed to the premature termination of growing grafted chain. The free radicals formed are responsible for propagating grafting chain growth by generating active sites on polymeric backbone. In the grafting of 4-vinylpyridine onto GG, the grating parameters were found to increase up to 10×10^{-4} mol/L and then decreased with increasing the concentration of PMS[31] while in case of N,N dimethylacrylamide grafted onto partially carboxymethylated guar gum, the maximum grafting occurred at 21×10^{-3} mol dm^{-3}.[37]

Table IV
Optimum values of process parameters in GG/CMG grafted copolymers

Comonomer	[Monomer]	[Gum]	Temp.(°C)	Time (min)	References
(GG grafted copolymers)					
Acrylic acid	20.0 x 10^{-2} mol dm^{-3}	121.4 g dm^{-3}	35	120	[34]
Acrylic acid	40.0 x 10^{-2} mol dm^{-3}	97.8 × 10^{-2} g dm^{-3}	45	120	[36]
Methacrylamide	20.0 x 10^{-2}mol dm^{-3}	91.7 × 10^{-2} g dm^{-3}	35	120	[38]
Methyl methacrylate	1.13 mol/L	4 g/L	50	210	[44]
Methyl methacrylate	0.35mol/L	0.05 g/L	30	180	[32]
Ethyl methacrylate	9.57 mol/dL	0.4 g/dL	55	210	[46]
Acrylonitrile	7.5g/400mL	1.5 g/400mL	45		[47]
Acrylonitrile	26 x 10^{-2}mol/L	0.1 - 0.4 g/L	35	90	[66]
N-Vinyl formamide	10.0 x 10^{-2}mol dm^{-3}	2.5 g dm^{-3}	35	120	[35]
Methacrylic acid	0.058 mol	0.5g	60	180	[49]
4-Vinyl Pyridine	20 x 10^{-2}mol/L	1.2 g/L	35	120	[31]
Acrylamide	0.55 mol/L	8 g/L	30	1440	[39]
Aniline	0.15 M	4 g/L	25	75	[50]
Partially neutralized acrylic acid	7.28 g/52.5mL	1.04 g/52.5mL	70	180	[51]
N,N′-dimethylacrylamide	16 x 10^{-2}mol dm^{-3}	1.8 g dm^{-3}	35	120	[37]
(CMG grafted copolymers)					
Acrylamidoglycolic acid	0.091 mol	1.66 mole	60	120	[33]
Methyl acrylate	0.433 mol/L	1 g	35	180	[57]
Methyl methacrylate	0.222 mol/L	1 g	25	240	[58]
Methacrylic acid			40	120	[59]
Acrylamide	0.21 mol (%GE=82%) 0.14 mol) %GE 96%) {mwave method}	0.0061 mol	70		[55]
4-Vinyl Pyridine	25 x 10^{-2}mol dm^{-3}	1.0 g dm^{-3}	40	120	[62]

3.1.2 Effect of Monomer Concentration

The grafting parameters were found to increase up to certain concentration of monomer and then decrease beyond the optimum value. For instance, the optimum value of monomer concentration corresponding to maximum grafting are summarized in Table IV. Various theories have been put forwarded to explain the relationship between GE and concentration of monomer namely,

i) Collision theory

The increase in monomer concentration in grafting polymerization system makes available more number of monomer molecules at the grafting sites.[55] As a result, the chance of molecular collision of the reactants will be greater and the grafting of the monomers on the Polysaccharide backbone is favored. Thus, larger the concentration of monomer more favored will be the reaction between free radicals and the monomer that triggers the grafting process.

ii) Gel effect

This increasesthe viscosity of the medium due to increase in monomer concentration, which causes hindrance in termination, particularly when the termination takes place by coupling of growing grafted chains. The gel effect also causes swelling of backbone chains which facilitates the diffusion of the monomer to the reactive sites of growing grafted chain.[31,66,55] The grafting efficiencies decreased at higher concentration of monomer which is generally attributed to homopolymerization due to which the viscosity of the reaction medium increases. This restricts the diffusion of monomer molecules to the active sites on the backbone.[31,33-35,37,47,49,50,55,66]

3.1.3 Effect of Gum Concentration

The literature data reveals that the grafting percentage increases with an initial increase in the concentration of GG/its derivative up to certain extent and then decreases at higher concentrations above the threshold value. The

initial increase in grafting efficiency may also be due to the availability of more grafting sites. The subsequent decrease in grafting at higher concentration of GG/derivative is due to increase in viscosity of reaction medium causing hindrance in the accessibility of monomer to reactive grafting sites.[31,32,34-37,50,57,58,66]

3.1.4 Effect of Temperature

The percent grafting is found to increase up to certain temperature (as shown in Table 4) and then decreased with further increase in temperature. The explanation put forwarded by many researchers for this response to the effect of temperature is summarized as:

The initial increase in grafting with increase in temperature is ascribed to:

i) Increased free radical formation due to easy decomposition of initiator system with consequent increase in number of grafting sites at the back bone of GG/derivatives by abstracting H^+ ion from the polymer back bone.[31,34,3,49]

ii) Enhanced diffusion of initiator and monomer onto GG/derivatives backbone and their collision with macro radicals.[32,44,46]

iii) Decrease in viscosity of medium at higher temperature.[50]

The decrease in grafting with further rise in temperature beyond the limiting value is attributed to following reasons:

i) Chain-transfer and premature termination of growing grafted chain by excess of free radicals at higher temperature.[33-35,37,57]

ii) Increased collision between monomer free radicals leading to formation of homopolymer.[36,47,50,57]

iii) Volatilization of monomer.[46]

iv) O_2 formed due to decomposition of initiator like peroxymonosulphate act as a scavenger for free radicals and is responsible for depleting all types of radicals.[31,37]

3.1.5 Effect of Time

The grafting of vinyl monomers onto GG/derivatives backbone generally increases with reaction duration and then remains constant thereafter. The explanation provided for initial increase in grafting by different researchers is the availability of more number of grafting sites on polymeric back bone resulting in more and more addition of monomer molecules to the back bone.[31-33,37,44,57,58] However, the subsequent decrease in grafting with increase in reaction time is attributed to the following reasons: Depletion of initiator and monomer concentration with the progress of reaction thereby causing the reduction in number of grafting sites on polysaccharide backbone.[46,49,50,57,58] It may also be due to the termination of growing grafted chain [33] and the mutual annihilation of growing grafted chains.[31,33]

CONCLUSION

The polysaccharide GG is an inexpensive natural bio resource. It can be chemically modified into various derivatives due to the presence of reactive hydroxyl groups on its back bone chain. The derivatization of GG is mainly accomplished in order to get rid of its inherent deficiencies and to improve the desired properties, so as to enable them to be used in variety of industrial applications. The GG and its derivatives find extensive applications in various industries as discussed in this article. The most important aspect of GG modification is the formation of graft copolymer with the vinyl monomers. The grafting of monomers generally takes place at –OH groups by abstraction of H atom. It has been observed from the literature that the process parameters (initiator, monomer and gum concentrations as well as reaction time and temperature) has a major role to play in the grafting efficiency of vinyl monomers onto GG/its derivatives. It can be summarized from this review article that maximum grafting efficiency is achieved at optimum values of these parameters beyond which the grafting parameters are found to decrease. These grafted copolymers based on GG/its derivatives finds unique applications in biomedical, pharmaceutical and waste water treatment.

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