

**GREEN BIOPOLYMER GUAR GUM AND ITS DERIVATIVES****DURE NAJAF IQBAL* AND ERUM AKBAR HUSSAIN***Department of Chemistry, Lahore College for Women University, Lahore***ABSTRACT**

Despite the vast importance of green chemistry synthesis and characterization of natural biopolymers is need of time which eliminates the danger to health and environment. Polysaccharides are widely spread biopolymers with diversity of structure and properties. They are potential substitutes of petroleum-derived synthetic products because they are easily available, nontoxic, biodegradable and biocompatible. Due to their fascinating properties they are used as a rheological modifier in food, pharmaceutical, paper, textile, oil and drilling and score of other industrial and commercial sectors. Modification of hydrophilic backbone of these biopolymers diversifies and enhances its applications and functionality. Guar gum is an outstanding representative of green, ecofriendly biopolymers This Review deals with structure, properties and potential uses of green biopolymer guar gum. Different methodologies to modify guar to enhance and diversify its properties and application range are discussed and reviewed.

KEYWORDS: Biopolymers, Guar gum, Green, Modifications, Hydrophilic backbone**DURE NAJAF IQBAL**

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INTRODUCTION

Guar Gum is a natural water soluble nonionic polysaccharide isolated from the seeds of *Cyamopsis tetragonolobus* (Family leguminous)¹ (Figure.1). This plant is cultivated for centuries in semiarid and subtropical areas of Pakistan and India, and in some areas of North Africa and South America. Guar was introduced into the United States from India in 1903.² Extraction technology of guar gum was commercialized in USA in 1953 by General Mills inc and Stein, Hall & Co. Originally Guar gum introduced as a substitute of locust bean gum during world war (1940) due to the

shortage of locust bean gum for paper industry. Now a day's guar becomes top ranking industrial gums due to its fascinating properties³. Guar has known as "Black Gold"⁴⁻⁶ because demand supply has turned it into cash crop and precious commodity. The world consumption of guar gum reached at 150,000 tons per annum which got a further boost by introduction of different modified forms. About 95 percent of the global market of its guar products is covered by India and Pakistan. US consumption of guar seed and derivatives is estimated to be 40,000 tons per annum⁷.

1 CHEMICAL STRUCTURE AND PROPERTIES OF GUAR GUM

Guar gum, a natural hydrophilic hydrocolloid belongs to the galactomannan family of polysaccharides consisting of mannose backbone and galactose⁸ side branching. Chemically it consist of D-Mannopyranosyl backbone (β -1 \rightarrow 4 glycosidic linkage) along with D -glucopyranosyl side branching (α -1 \rightarrow 6 glycosidic linkage).

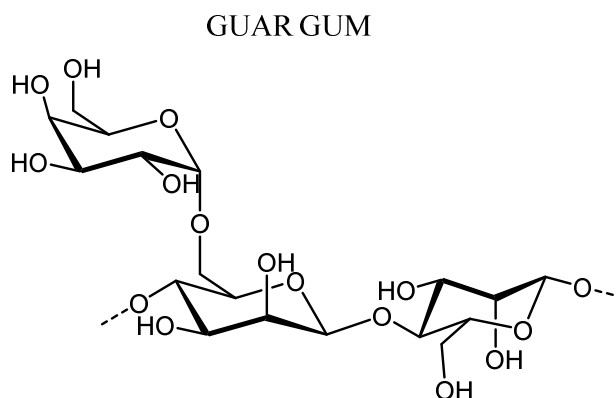


Figure 1
Structure of Guar Gum

The ratio of mannose to galactose unit (M/G) ranges from 1.8:1 to 2:1 due to variation in geographical⁹ origins. Firstly, it believes that galactose side groups are more uniformly distributed at regular intervals along the mannose backbone. But more recent investigations show random distribution¹⁰ of side branching. But there is still debate about exact nature of this interaction (Figure 2). GG is one of the highest molecular weight naturally occurring polysaccharides .Its molecular weight¹¹ ranging from 1-2 MDa. Due to its unique rheology modifying properties, it is being widely used across a broad spectrum of

industries like oil well drilling,¹² textile,¹³ cement,¹⁴ cosmetic,¹⁵ food,¹⁶ paper,¹⁷ paint,¹⁸ pharmaceutical¹⁹ etc. Functional properties of gums depends upon their chemical structure, mannose to galactose ratio, molecular weight and nature of branching so it is better emulsifier, water builder, stabilizer and thickener than locust bean gum . Its water thickening potential is 5-8 times higher than starch.²⁰ Non-ionic nature and stability over wide pH range (5-7) of guar solution is responsible for constant viscosity and compatibility with different salts and other gums. It is insoluble in all organic solvents but

soluble in hot and cold water.²¹ It acts as rheological modifier in many water based systems due to high viscosity even at low concentration (4000+cps, 1% soln at 25°C)

superior to all available naturally occurring gums.²² Guar gum solution show non-Newton, thixotropic, pseudoplastic and shear thinning behaviour.²³

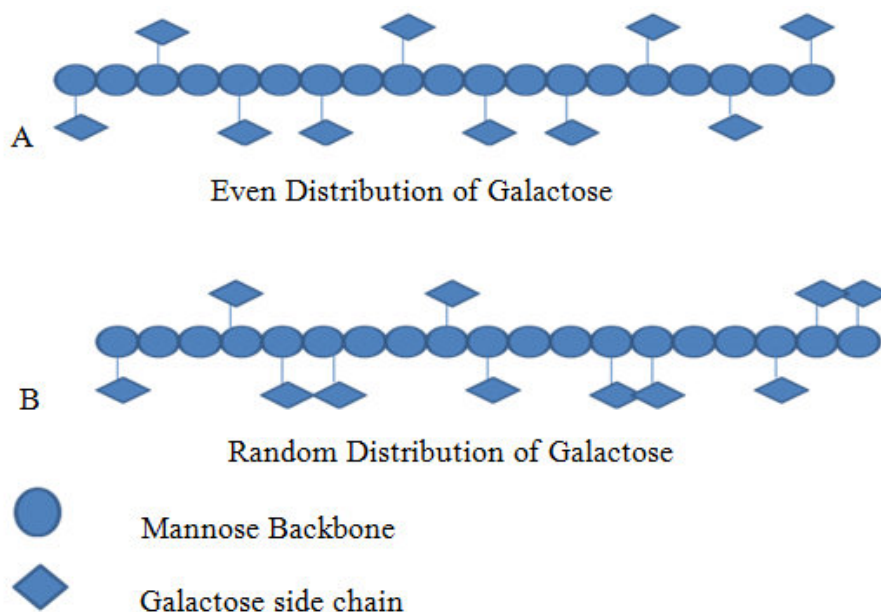


Figure 2
Sequence of Galactose and Mannose in Guar Gum

2 GUAR DERIVATIVES

Modified guar gum was developed in 1960s as an alternative thickener to plain guar gum by General Mills Inc by commercializing hydroxypropyl guar for hydraulic fracturing. Guar gum hydrates well in aqueous solutions, but concerns about solution clarity, alcohol solubility, uncontrolled rate of hydration, decrease in viscosity on prolong stay, microbial contamination susceptibility etc, derivatization of guar gum leads to subtle changes in properties, such as, decreased hydrogen bonding, increased solubility in water-alcohol mixture, improved electrolyte compatibility, increased solution clarity and stable viscosity.²⁴⁻²⁵

On average three hydroxyl groups are available for derivatization per sugar unit in guar gum. The maximum theoretical degree of substitution (DS) in such molecule is three and can be exceed three due to the additional availability of hydroxyl groups.²⁶ DS is defined as average number of hydroxyl groups per sugar unit. Primary hydroxyl group at C6 position is more susceptible to change but C2 and C3 positions are also good reacting sites.

²⁷ Modification of GG is done by two ways

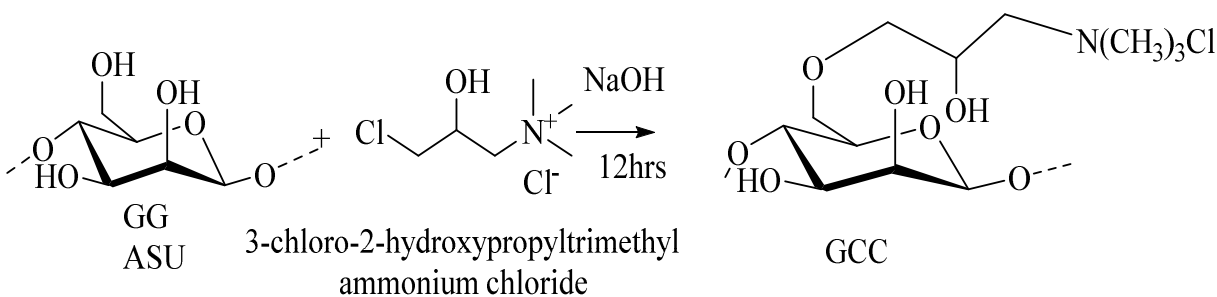
either chemical modification or physical modification to produced different derivatives with variable degree of substitution.²⁸⁻²⁹ The chemical amendments involves replacement of free hydroxyl group of guar backbone by different cationic, anionic, amphoteric and non-ionic groups. Physical alteration means enzymatic, acidic and basic hydrolysis of guar gum to yield low molecular weight gum. Modification enhances properties and applications of guar in broad spectrum of industries. Several techniques may be applied to obtain different derivatives of guar gum with variable DS values.³⁰

2.1 Cationic guar gum

Cationic guar with quaternary ammonium functional group has extensively used in personal care products as substantive conditioning agent. Reagents used for cationization are mostly quaternary ammonium salts with reactive side groups.³¹ They are available in the stable chlorohydrins or reactive epoxide form. Commercially cationic derivatives of guar are available with DS³² lower than 0.1. Oberstar et al.³³ formulated

conditioning shampoo containing cationic derivatives of guar to improve lustre and texture of hairs. Cationic guar samples of variable molar mass and charge density was prepared by Levy et al.³⁴ by reacting cationic reagent 2, 3 epoxypropyltrimethylammonium chlorides to guar molecules in two steps. First step involve synthesis of cationizing reagent and second step involve grafting of cationic group on guar backbone as shown by reaction. Sunil P. Dasgupta³⁵ succeed to prepare cationic derivatives of GG with DS upto 0.1

then higher DS (0.2–1) have been obtained by Cottrell et al.³⁶ in isopropyl alcohol/water media or Pal et al prepared same derivatives in water media for potential use in personal care and food industry. The quaternization of guar using CHPTAC as etherifying agent under the catalytic action of NaOH was studied by Y. Huang et al.³⁷ They investigated the thermal and mechanical stability of hydrogel based on cationic guar gum (CGG) and poly(acrylic acid) (PAA) with maximum DS of 0.35 determined by titration method (Scheme 1).



Scheme 1

The quaternization of GG using CHPTAC as etherifying

Extensive study is done by Bigand et al.³⁸ on cationization of xylan or galactomannan (guar) by using 2,3-epoxypropyltrimethylammonium chloride (ETA) as etherifying agents under alkaline conditions. Reaction conditions were optimized to obtain derivatives with maximum DS value. They succeed to obtain DS value of 1.3 and maximum grafting rate of 48%. Derivatives was characterized by ¹H-NMR, ¹³C-NMR, IR or elemental analysis. Reaction Mechanism is same as shown in Scheme 1.

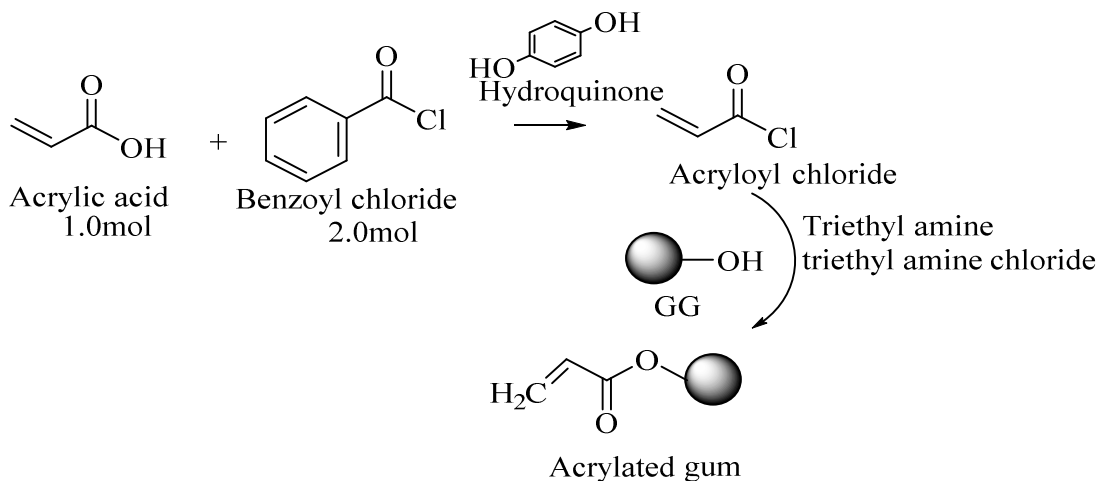
2.2 Grafted Guar Gum

Graft co-polymerization of various monomers onto the backbone of GG and other biopolymers is a field of interest for polysaccharide researchers in last decade. Grafting is done by generating free radicals by chemical initiation on polymer³⁹. Grafting impart important properties to modified polymers which are superior to native one. Grafting is done by thermal, chemical, photochemical methods. These grafted polymers have wide applications in textile printing, paper industry and works as flocculants in oil and drilling industry.

Successful microwave assisted synthesis of guar –g-polyacrylamide; a copolymer was done by V. Singh et al.⁴⁰ without any catalyst. Reaction results concluded greater grafting ratio (66.66%) as compared to (49.12%) grafting obtained by conventional method. Grafted copolymer was characterized using IR, ¹H-NMR, XRD and TGA. O-Carboxymethyl-O-hydroxypropyl guar gum (CMHPG) is a hydrophilic hydrogel commercially available with different DS value to prepare controlled colon drug delivery systems. To enhance its thermal characteristics Shi et al.⁴¹ grafted Poly (N-isopropylacrylamide) (PNIPAAm) side chain on polymer. Solubility phase transfer behaviour, grafting ration of these new polymer graft copolymer was characterized in aqueous media. J. Biswal et al.⁴² discover novel route for grafting of acrylamide on GG using high energy gamma radiations. Comparison of microwave assisted and radiation induced grafting was studied. FTIR, XRD, TGA, SEM results indicated more thermal stability of new grafted co-polymer as compared to native gum. Comparison between conventional redox grafting and microwave assisted grafting of acrylamide on carboxymethylated guar was

done by Sagar Pal et al.⁴³ Novel derivatives CMG-g-PAM synthesis by microwave assisted grafting method showed better flocculation characteristics as compared to conventional redox grafting method. Shenoy and coworkers⁴⁴ synthesis and studied the acrylated guar gum and its effect in acrylic emulsion. Rheological behaviour, film forming ability,

clarity, thermal and mechanical strength of these new derivatives was studied in detail. Result concluded that emulsion with acrylated guar gum has greater tensile strength, lower viscosity, increased elongation and better clarity. Maximum DS value obtained was 0.56 for acrylated guar. Scheme .2



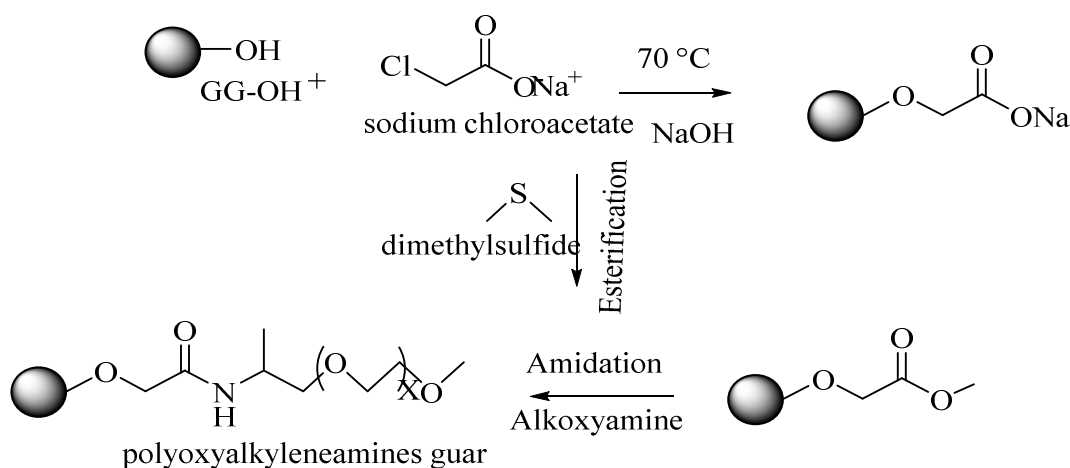
Scheme 2
Reaction Scheme for acrylation of Guar gum

Novel derivatives of guar gum grafted poly (acrylamide-co-diallyldimethyl ammonium chloride) was discovered by Mclean et al.⁴⁵ and studied its behaviour as hydrophobic wood resin adsorbent in paper making. Results showed that GG-g-p(AM-co-DADMAC) act as better polymer fixative as compared to other commercially available fixatives. Wang et al.⁴⁶ and coworkers explore the potential use of guar-grafted (poly-sodium acrylate)/Medicinal stones as pH responsive superabsorbent hydrogels. Characterization of these hydrogels was done by FTIR, XRD, TGA, DTA etc techniques. P. Chowdhury et al.⁴⁷ copolymerized guar and MMA using ceric ammonium sulphate/dextrose as a redox initiators. Modified polymer was analysed by FTIR and TGA techniques. Important discovery was made by Tiwari et al.⁴⁸ by preparing guar gum-methacrylate hydrogels for in situ fabrication of tissue engineering scaffolds. Modification was done by reacting hydroxyl group of guar with glycidyl methyl methacrylate (GMA) water soluble photopolymerizable guar gum-methacrylate (GG-MA). Product was

characterized by NMR techniques. V. Singh et al.⁴⁹ explore the application of GG-g-MA graft copolymer for removal of health hazard Cr (VI) from aqueous system or industrial waste. They fabricated copolymer by using persulfate/ascorbic acid as a redox pair. Same copolymer was synthesis by Tivari et al.⁵⁰ for insitu fabrication of tissue engineering scaffolds. Cerium (IV) incited grafting of polyacrylonitrile on to guar gum was investigated by Thimma et al.⁵¹ Reaction conditions were optimized for each experiment. Effect of temperature, initiator concentration, guar and acrylonitrile molar ratios was investigated on grafting percentage. Hydrolysis of modified GG is done to obtain anionic guar with good water holding capacity. J.H. Trivedi et al.⁵² established a reaction mechanism for grafting of acrylonitrile on partially carboxymethyl guar gum (DS-0.49) to obtain novel derivatives using ceric ammonium sulphate as a catalyst. Reaction conditions were varied such as concentrations of nitric acid, ceric ammonium nitrate, and monomer and time effect to obtain copolymer with

maximum percentage of grafting. For the analysis of grafted polymer FTIR, thermal (TGA/DSC) and scanning electron microscopic (SEM) techniques have been applied. An attempt was made by Behari et al.⁵³ to crosslink environmental friendly monomer N-vinyl formamide on guar gum by using brominated /ascorbic acid initiating system. GG-g-NVF novel grafted copolymer was characterized by IR-spectroscopic, XRD, TGA/DSC thermal techniques. I.Gliko-Kabir et al.⁵⁴ Crosslinked GG with glutaraldehyde (GA). Physicochemical changes or grafting efficiency of modified gum were characterized by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and wide-angle X-ray diffraction (WAXD). Cunha et al.⁵⁵ copolymerized GG with glutaraldehyde to obtain a high molecular weight novel hydrogel which has potential candidate for biomaterials.

Rheological behaviour of these gels was studied along with characterization by GPC, XRD, SEM and TGA techniques. New hydrophobic derivatives of guar were prepared by Ahmad Bahamdan⁵⁶ by reacting hydroxyl functional group of GG with series of polyalkoxyalkyleneamide. Reaction sequence included carboxymethylation, methylation and amidation of guar as shown by scheme 3. Grafting ratio was confirmed by FTIR and NMR techniques. Application of these hydrogels in hydraulic fracturing fluid composition was also studied by Ahmad Bahamdan and William H. Daly.⁵⁷ Cross linking of polyethylene glycol diglycidylether (PEGDGE) to guar polymer was done by G. Leone and R. Barbucci⁵⁸ to create a new hydrogel to use in biomedical field. These hydrogel wer examined by FTIR, AFM and SEM analysis.



Scheme 3
Synthetic Route for Polyoxyalkylamine Guar Derivatives

To increase the hydrophilicity and biocompatibility of carbon nanotubes (CNTs) Li Yan et al.⁵⁹ covalently grafted guar gum (GG) on the surfaces of multiwall carbon nanotube (MWCNT) to obtain GG-MWCNT composite along with iron nanoparticles bounded on the GG-MWCNT to prepare the magnetic GG-MWCNT-Fe₃O₄. Resultant nanocomposites were analyzed by FTIR, TGA/DTA, TEM, UV-vis spectroscopy and X-ray diffraction. Guar gum-g-epichlorohydrin was investigated by T. Hongbo et al.⁶⁰ by reacting epichlorohydrin with guar gum in the alkaline condition .

2.3 Guar gum ethers

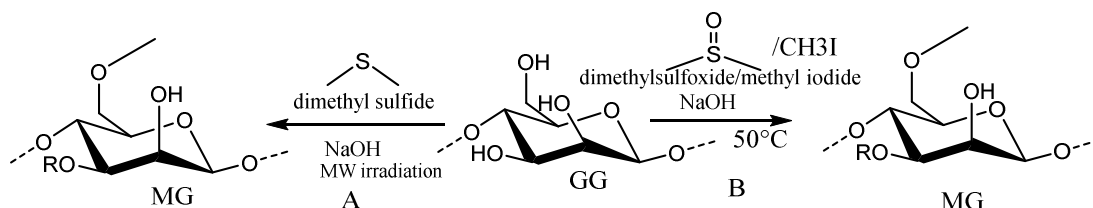
Etherification of polysaccharides is an important mechanism to produce many commercially important derivatives with peculiar properties. Mostly ethers are synthesis via Williamson ether synthesis mechanism. In which free hydroxyl group of guar alkylated in the presence of strong alkali and form alkoxide ions. These ions react with etherifying agents to form guar ether by SN₂ mechanism.

2.3.1 Methylated guar

Methylation of guar gum is an important tool to know about the structure composition and

constitution of polymer. Denham and Woodhouse and Haworth method is considered as standard method for methylation of polysaccharides by using DMS in alkaline condition. Methylation is done by nucleophilic substitution mechanism. V. Singh et al.⁶¹ Fully methylated GG by using the domestic Microwave oven within 4min. They used

dimethyl sulphate as methylating agent and sodium hydroxide as catalyst. Product formed were analyzed by IR spectroscopy. Scheme 4A) D. Risica et al.⁶² performed etherification of Guar by using dimethyl sulfoxide (DMS) and methyl iodide (MI) with excess of sodium hydroxide (NaOH). (scheme 4B)



Scheme 4
Methylation of guar gum by microwave heating/conventional Method

Viscosity measurements, FTIR and H-NMR give important information about DS value of methylated guar.

2.3.2 Carboxymethylated guar

Carboxymethylation is most widely studied conversion of naturally occurring biopolymers to produce commercially important biopolymers with promising properties. Carboxymethylated derivatives of guar gum are widely used in paper and oil industry. B. R. Sharma et al.⁶³ studied carboxymethylation of guar by using acrylamide and sodium hydroxide. The variable was studied for each experiment and they analysed modified gum by FTIR. Solvent less carboxymethylation of guar gum was discovered by K.S. Parvathy et al.⁶⁴ carboxymethylation was done by using monochloroacetic acid and catalytic amount of NaHCO₃ in dry state. CMG was synthesised with variable DS values ranging from 0.065 to 0.675 at variable reaction parameters. The progress of the reaction was monitored by FTIR and ¹³C-NMR spectral data. Partially carboxymethylated guar was synthesised by Sagar Pal by using sodium monochloroacetic acid in presence of alkaline conditions.⁶⁵ The resulting products were characterized by intrinsic viscosity measurement, molecular weight determination, elemental analysis, and TGA/DTA, ¹³C-NMR and FTIR techniques. Mazhar Pasha and Swamy carried out chemical derivatization of guar gum molecule

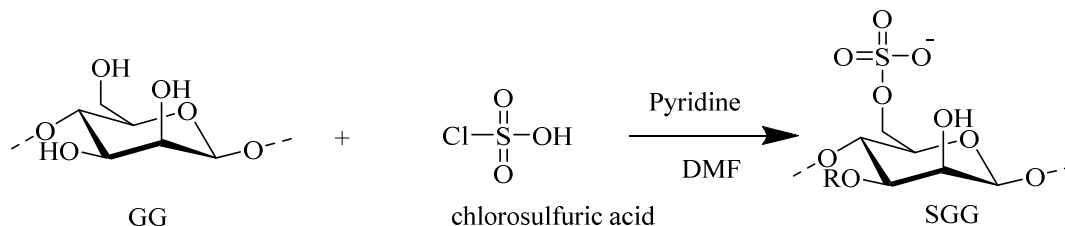
to Sodiumcarboxymethyl hydroxypropyl guar upto DS 1.5.⁶⁶ Effect of PH, electrolytes, viscosity measurements and spectral analysis indicated higher thermal stability, controlled rate of hydration as compared to native gum. Application of carboxymethyl guar gum for colon target drugs was studied by V. Kumar et al. and Sullad et al.⁶⁷⁻⁶⁸ in two different studies. Dodi et al.⁶⁹ also achieved chemical modification of guar by derivatization of carboxymethyl group for biomedical applications especially for oral drug delivery of hydrophilic macromolecules. The resulting products were characterized by NMR and FTIR spectroscopy and by thermal gravimetric analysis (TGA).

2.3.3 Sulfated guar gum

Sulfonation of polysaccharides imparts diverse biological activities to polymer backbone which have wide spectrum of applications in various industries like explosive industry, pharmaceutical industry, paper and pulp industry. Important discovery was made by N. M. Mestechkina et al.⁷⁰ by sulfonating different galactomannan including guar by SO₃.pyridine as sulfonating agent and Dimethylformamide as solvent. They conclude that reaction temperature is an important factor in determination of degree substitution. They succeed to obtain DS 1.4-1.8. Another attempt was made by A.M. Gamal-Eldeen et al.⁷¹ to analyze cancer chemopreventive, antioxidant

and anti-inflammatory properties of sulphated guar gum (SGG). They used SO_3 -formamide complex as sulfonating reagent. They concluded that SGG is an alternative of native guar in food industry to minimize risk of cancer. Xiowang et al.⁷² evaluated antioxidant potential of sulphated guar gum. They

fabricated sulphated gum of different DS value 1.92-2.85 and molecular weight. Product formed was characterized by FTIR and ^{13}C -NMR. Molecular weight determination was afforded by size exclusion chromatography (scheme: 5).



Scheme 5

Sulfation of Guar gum by chlorosulfonic acid

Singh et al.⁷³ formulated guar gum sulfonic acid as an ion exchange resin for removal of toxic metals from steel industry effluent. J. Wang et al.⁷⁴ reported that sulphated guar gum showed significant biological activities. They prepared sulphated guar gum derivatives by Box–Behnken statistical design. Presence of sulphated groups was confirmed by FT-IR, X-ray spectroscopy, size exclusion chromatography (SEC) and laser light scattering (SEC–LLS) analysis.

2.3.4 Hydroxyalkylated guar gum

Hydroxypropyl guar (HPG) is first commercially synthesized guar ether in 1960 by General Mills Inc USA. Hydroxypropyl guar (HPG) is mostly used in oil drilling industry. It has numerous applications in paper/textile industry as sizing agent and pigment printing thickener. Boonstra et al.⁷⁵ prepared non lumping hydroxyalkylated guar derivative with DS value of 0.12 to use as a thickener in textile printing. O-(2-hydroxyethyl), O-(2-hydroxypropyl), O-(2-carboxymethyl) guar gum derivatives were prepared by H. prabhanjan et al.⁷⁶ with variable reaction parameters. Rate of hydration, rheological behaviour, viscosity, moisture contents of resultant products were analyzed. Rheological behaviour of hydroxyethyl guar (HEG) and hydroxypropyl guar (HPG) and its derivatives was studied in detail by Lapasin et al.⁷⁷ under continuous and oscillatory shear flow rate. They summarized that molecular weight and amount of polymer has visible

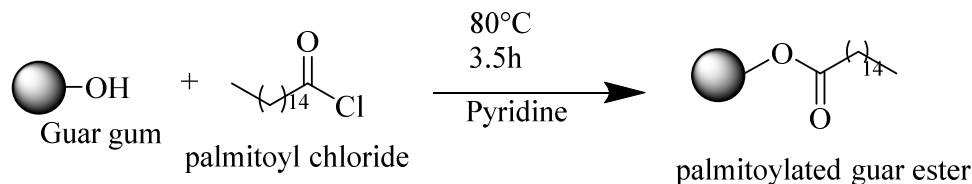
effect on rheology of gum along with temperature. Rong Chun Xiong et al.⁷⁸ developed novel route for synthesis of hydroxypropyl guar by phase transfer catalysis. Typical procedure involves the reaction between guar, propylene oxide and HTAC (hexadecyl trimethyl ammonium chloride) as phase transfer catalyst. Results disclosed that modified guar has higher viscosity, stability and light transparency as compared to native one. G.Wang et al.⁷⁹ improve biocompatible sol-gel silica matrix for the encapsulation of drugs by incorporating a novel water soluble silica precursor, tetrakis(2-hydroxyethyl) orthosilicates (THEOS) and outcome verified rapid sol-gel transition of THEOS in water without any addition of organic solvent and catalyst. Determination of the degree of substitution of Hydroxypropyl guar gum (HPGG) was studied by Yannan Chen et al.⁸⁰ by pyrolysis of gum at C₆ position. Gas chromatography and GC-MS spectrometry was employed for investigated DS of subsequent products. A new chemical method was introduced by Xiaoyan Wua et al.⁸¹ to determine substitution pattern of hydroxypropyl guar. A novel method involve periodate oxidation of gum and product was investigated by IR and NMR techniques. A novel derivative of guar gum hydroxyethyl amino hydroxypropyl guar gum (EAHPG) was prepared by Y. Zhao et al.⁸² by chemical modification of p-toluenesulfonate activated hydroxypropyl guar gum with ethanolamine through nucleophilic

substitution reaction. Results were confirmed by FTIR and NMR spectroscopy.

2.4 Guar gum esters

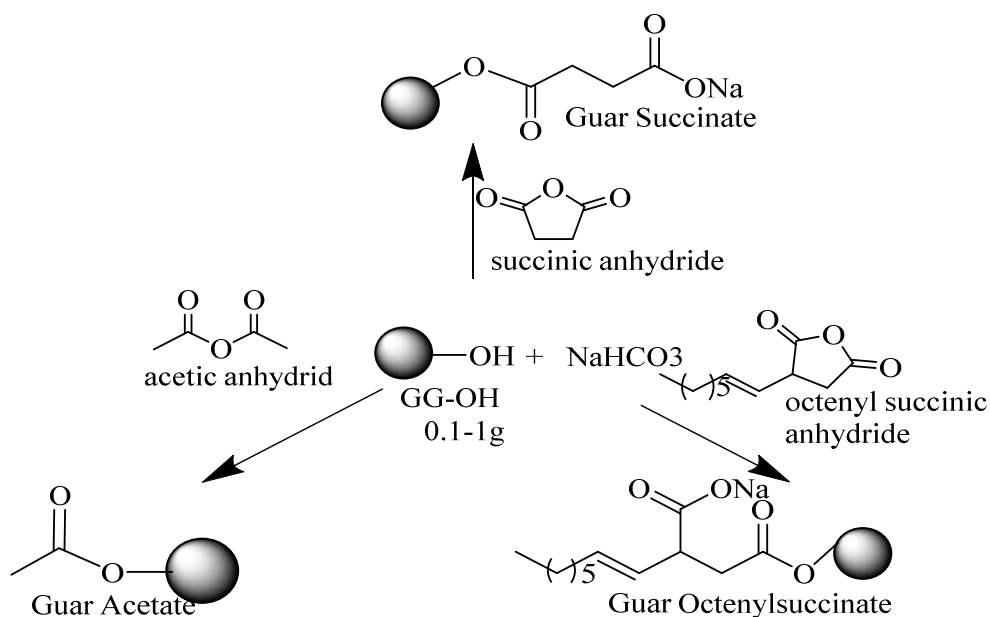
Different synthetic routes are commercialized in recent years to obtain polysaccharides esters with variable properties and applications. Guar gum is used as an emulsifier and thickener in food industry industries because they are non-toxic, biodegradable and having

good emulsifying and antioxidant properties. B. Tian & C. Dong fabricated palmitoylated guar gum derivatives under heterogeneous reaction conditions.⁸³ Reaction procedure involves reaction between guar hydroxyl groups and palmitoyl chloride (Scheme:6) in toluene and pyridine as initiator. Modified gum was characterized by FTIR, XRD and TGA/DTA techniques. Degree of substitution was determined by saponification method.



Scheme 6
Synthesis of palmitoylated guar via palmitoyl chloride

Prashanth et al.⁸⁴ developed eco-friendly method for preparation of three different types of galactomannan esters by reacting polymer with acetic, succinic and octenylsuccinic anhydride under anhydrous condition with mild catalyst NaHCO_3 . Main focus was to avoid strong alkali and far excess of water thus making whole process cost effective. (Scheme: 7)



Scheme 7
Esterification of Galactomannan via Anhydride

An important discovery was made by Rumiko Fujioka et al.⁸⁵ to increase biodegradability of native guar by esterification of succinate group on polymer chain. They designed novel superabsorbent hydrogels in DMSO by action

of succinic anhydride with guar where 4-dimethylaminopyridine was utilized as a catalyst. Resultant hydrogels exhibit excellent water absorbency and biodegradability that establish them as ideal candidate for

biomedical applications. M. A. Shenoy et al.⁸⁶ acetylated the HPG (hydroxypropyl guar) to use it as filler in unsaturated polyester composites. Derivatized guar increased filler-polymer interaction by increasing hydrophobic nature of polymer. Introduction of hydrophobicity in hydrolyzed guar gum (GGH) and gum Arabica was furnished by S.

Sarkar, R. S. Singhal⁸⁷ by reacting gums with n-octenyl succinic anhydride (OSA) and oleic acid. The reaction conditions were optimized for maximum degree of substitution (DS) which was 0.061, 0.072 for guar oleate, guar n-octenyl succinate, respectively. Resultant esters was analyzed as wall materials in microencapsulation.

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