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Microwave-assisted green synthesis of guar gum esters with enhanced physicochemical properties

D. Najaf Iqbal[a], E. Akbar Hussain[b], G. Afshan Soomro[c], H. Rizvi[d], M. Iqbal[a,*], and A. Nazir[a]

a. *Department of Chemistry, The University of Lahore, Lahore, Pakistan.*
b. *Department of Chemistry, Lahore College for Women University, Lahore, Pakistan.*
c. *Institute of Chemistry, Shah Abdul Latif University, Khairpur, Sindh 66020, Pakistan.*
d. *Department of Environmental Sciences and Engineering, Government College University, Faisalabad, Pakistan.*

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Abstract. Several methods have been developed for the modification of natural polymers. Most of the reported methods are expensive, since the chemical reactions are carried out using chemical additives along with stabilizers. Microwave-assisted synthetic strategies have gained significant importance in the synthesis of materials due to their eco-friendly nature. Guar gum is one of the important naturally occurring non-ionic polysaccharides, which has incredible industrial and commercial applications. A rapid method for protecting the hydroxyl group in sterically hindered gum was developed by Microwave-Assisted Synthesis (MAS). An efficient synthesis of different novel guar gum derivatives such as acetate, butyrate, and propionate (GG1-GG3) was performed. Significantly higher yield of ester was achieved after 15 min at 600 W using iodine as a reaction promoter. Gum ester formation was carried out at various concentrations for different reaction intervals. The synthesized products were characterized using FTIR, NMR, and SEM techniques. The efficiency of the adopted synthesis method was evaluated based on swelling ratio, gelation ability, and solubility. The study indicated that the guar gum could be modified using acid anhydride under microwave irradiation with enhanced physic-chemical properties. Moreover, microwave modification is an eco-friendly approach.

1. Introduction

Several methods have been employed for the modification of polysaccharides, but they are expensive and chemical reactions are carried out through chemical additives along with stabilizers, which are the source of toxicity. The commercial modification of biopolymers using conventional methods encounters several limitations [1-3]. In contrast, MAS has shorter reaction time, maximum yields, and reproducibility with reduced side reactions and it has received much attention in recent years. This process is more energy-efficient and has been classified as a greener process. Microwave heating relies on conduction and convection of heat distribution. The materials are heated through much more efficient dielectric heating. Microwaves interact with molecular dipoles and align species with the alternating electric field. By using MAS, biopolymer derivatives with controlled size, disparity, and applications can be synthesized. Microwave irradiation provides rapid and uniform heating for the reaction medium and thus, produces uniform nucleation and growth conditions for biopolymers [4-8]. Since biomolecules are temperature-

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[*] *Corresponding author.*
E-mail address: bosalvee@yahoo.com (M. Iqbal).

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sensitive, more sophisticated techniques are required for the synthesis and fabrication of biomolecules. In this regard, MAS is the best alternative among the conventional synthesis methods. Successful synthesis and modification of biomolecules, e.g., sucrose composite with layered silicates, graft copolymerization of sunn hemp fibers, and chitosan grafted styrene with enhanced physico-chemical properties, using MAS has been reported [9-14]. Different studies have been carried out on the modification of biopolymers like starch and cellulose [15,16]. Polysaccharide is an important biopolymer. Methylation of polysaccharides has previously been reported in the literature [17]. In 2009, Fujioka et al. synthesized acetate, succinate, and octenylsuccinate derivatives of starch using $NaHCO_3$ as catalyst [18]. Synthesis of guar gum succinate was carried out using 4-dimethylaminopyridine as a catalyst [18]. Esterification of hydrolysed Arabic gum with *n*-octenylsuccinic anhydride and oleic acid has also been reported [19]. However, this study reports guar gum esterification by microwave irradiation in the presence of anhydride.

A more recent method involved dissolution of the guar gum in anhydrous DMSO followed by treatment with catalyst and acid anhydride to form desirable derivatives of GG with different degrees of substitutions. DMSO is considered to be an efficient solvent with no hazardous effect on the polymer. Accordingly, DMSO has been used as reaction medium in esterification of a number of guar gum derivatives. Iodine has also been used as a novel, efficient, economical, and convenient catalyst in the modification of polysaccharide for esterification of GG1-GG3 (Figure 1) versus other catalysts, i.e., perchloric acid, sulfuric acid, pyridine, and triethylamine. In the current conditions of environmental pollution [20-33], there is a need to adopt green and eco-benign methods [34,35]. However, the solvent-free iodine catalysed modification of polysaccharides is the best technique for modification of polysaccharides. The aim of this study is solvent-free esterification of guar gum using iodine catalyst under microwave irradiation. This method was adopted in order to eliminate the solvent requirement for making the esterification economical and eco-friendly. Different variables were studied including reactant concentration, catalyst amount, and microwave reaction time. Product formation was confirmed by FTIR analysis. The solubility, rheology, swelling behaviour, and gelation formation were studied in order to evaluate the effect of microwave irradiation on physical properties. Surface modification was monitored by SEM and the modified product was confirmed by ^{1}H-NMR.

2. Materials and methods

Chemicals and reagents of the analytical grade were used. Partially hydrolysed guar gum with molecular weight of 2.3×10^3 g/mol was purchased from National Colloid Industry (NCI), Karachi. All other commercially available reagents were purchased from Sigma Aldrich, Alfa Aesar, Fluka, and Acros Organics.

2.1. Purification of guar gum

Guar Gum (GG) (2.5 g) was dissolved in 100 mL of ultra-pure water with continuous stirring for 12 h at 58°C. Saturated $Ba(OH)_2$ solution was added for precipitation formation. The precipitate was separated by centrifugation acidified with 1 M acetic acid and agitated for 8 h. The supernatant was discarded, and precipitates were washed with 95% ethanol and finally dried at 40°C overnight.

2.2. Synthesis of guar gum esters (GG1-GG3)

For GG esters synthesis, 1.8 g (10-mmole sugar/30 mmol OH) of grinded partially hydrolysed guar powder was mixed with different concentrations of iodine. Domestic microwave oven output of 1000 W with 10 microwave power levels model no. OM-55-B9 orient was used for microwave-assisted transformation of GG via acid anhydrides to fabricate GG1-GG3 guar derivatives via novel routes.

Finally, each mixture was subjected to microwave irradiation in time intervals of 5-15 min with gaps of 30 s on the power level of 600 W. Temperature was noted and reaction progress was monitored by FTIR.

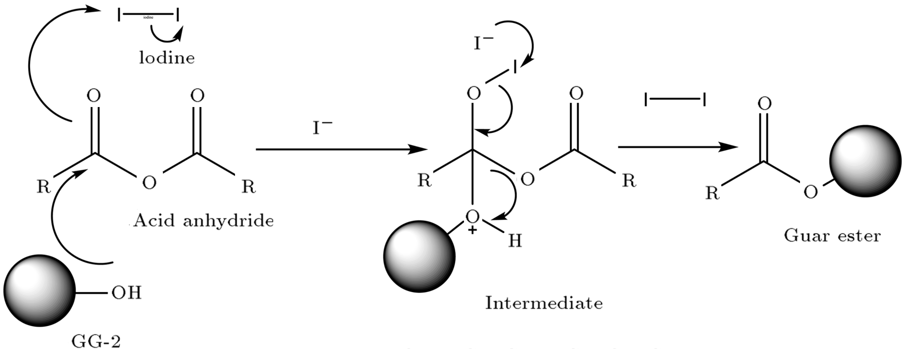

Figure 1. Iodine catalysed esterification of GG via acetic, propionic, and butyric anhydride.

Table 1. Microwave-assisted esterification yield of guar derivative via aliphatic anhydride.

Samples	Anhydride/sugar unit (Moleq)	Time (min)	*DS*	Guar ester yield (%)
GG1-A	1:01	5	0.15	88.2
GG1-B	1:01	10	0.11	87.4
GG1-C	1:01	15	0.16	87.3
GG1-D	2:01	5	0.21	84.2
GG1-E	2:01	10	0.99	85.4
GG1-F	2:01	15	1.33	87.5
GG1-G	3:01	5	1.75	76.5
GG1-H	3:01	10	2.43	69.2
GG1-I	3:01	15	2.64	58.5
GG2-A	1:01	5	–	98.3
GG2-B	1:01	10	0.093	95.4
GG2-C	1:01	15	0.09	89.2
GG2-D	2:01	5	0.13	88.4
GG2-E	2:01	10	0.23	87.4
GG2-F	2:01	15	0.74	87.3
GG2-G	3:01	5	0.98	75.6
GG2-H	3:01	10	1.15	77.2
GG2-I	3:01	13.5	1.33	65.4
GG3-A	1:01	5	–	90.3
GG3-B	1:01	10	–	92.3
GG3-C	1:01	15	0.056	84.4
GG3-D	2:01	5	0.08	83.2
GG3-E	2:01	10	0.095	86.4
GG3-F	2:01	15	0.17	88.4
GG3-G	3:01	5	0.25	79.4
GG3-H	3:01	10	0.98	68.7
GG3-I	3:01	15	1.25	53.2

After the stipulated time interval, the mixture was cooled down to room temperature; washed with 50, 80, and 90% ethanol to remove unreacted acid; and neutralized with 0.5N NaOH solution. Excess iodine was removed by saturated aqueous sodium thiosulfate solution. Finally, the product was dried under vacuum. The time interval, amount of catalyst, and concentration of reagents were studied and optimized for maximum product yield (Table 1).

2.3. Quantitative measurement of substitution degree of guar esters

Unreacted anhydride and liberated acids (filtrate) were titrated with 0.1 M NaOH. DS was calculated (Eq. (1)) from the amount of anhydride consumed [36].

$$\text{Anhydride consumed (m mol)} = \left(\frac{k}{1000}\right)\left(\frac{VCV_x}{V_y}\right), \quad (1)$$

where, k is mol-equivalent weight of anhydride, V is volume (mL) of NaOH consumed, and C is the concentration of NaoH. Vy and Vx are the volume of filtrate taken for titration and total volume of the filtrate, respectively. DS is calculated by Eq. (2):

$$DS = \frac{\text{Anhydride consumed}}{K}, \quad (2)$$

where, K is the equivalent amount of anhydride consumed for a degree of substitution.

2.4. Determination of solubility

The solubility of the guar gum derivatives (GG1-GG3) was determined in different organic solvents at concentration of (1% W/V) with continuous stirring at different temperatures.

2.5. Water holding capacity/swelling ratio of guar gum derivatives

The swelling equilibrium of as-synthesized GG1-GG3 and GG was achieved in ultra-pure water. Samples (1 g) of each compound were dispersed in 50 mL water and kept for 24 hours at 25°C (Japanese Industrial Standard K8150) to establish maximum swelling at equilibrium [37-39]. After the required time, samples were removed, blotted with filter paper to remove excess water, and filtered by a commercial sieve of 681 μm (30-mesh size). The equilibrium degree of swelling index was measured (Eq. (3)).

$$SI=\frac{W_x-W_y}{W_y}, \tag{3}$$

where, SI is swelling index, W_x is the weight of sample after swelling, and W_y is the dry weight of sample before swelling.

Swelling percentage was determined using Eq. (4):

$$PS=SR100. \tag{4}$$

2.6. Gelation study

Gelation study was used to determine the gelation properties of modified samples of GG-1, GG-2, and GG-3 (2-15% w/v) prepared in DMSO (5 mL). The mixture was homogenized by heating at 80°C for 30 min with continuous stirring followed by quick cooling at 4°C for 2 h and tested for gelation property.

2.7. Structural study

Infrared spectra were recorded using Perkin Elmer FT-IR spectrometer. The ^{1}H-NMR spectra were recorded through either a Jeol Eclipse 400 MHz or Varian 400-MR 400 MHz spectrometer. ^{1}H-NMR spectra of native gum were recorded after in situ hydrolysis of guar in deuterated chloride (DCl). Spectra of the derivatives were recorded in DMSO-6 and D_2O. High and Partial Vacuum (10-10^{-4} Pa) Jeol-JSM 5600 LV scanning electron microscopy with secondary electron detector at voltages between 1-30 kV was used for surface morphological evaluation [40].

3. Result and discussions

A plausible reaction mechanism involved the ionization of iodine into corresponding ions I+ and I−, which in turn activated carbonyl groups and converted into acylating agents, further reacting with GG to form guar esters GG1-GG3 with good yield and DS values. Complete substitution of the free hydroxyl groups of guar gum was not achieved by using 1:3 molar ratio of GG/anhydride at medium power level for 15 min. However, organo soluble products were obtained, which yielded better resolved 1H-NMR spectrum.

3.1. Acetylation of GG

Acetylation of polysaccharides can be achieved via different methods [41]. Iodine is considered a good reagent for microwave energy absorbing. In this regard, the method of Biswas et al. [42] was applied for esterification of guar gum. Results revealed that this method was efficient for complete substitution reaction under solvent free-conditions. Proton NMR confirmed peaks at δ3.5-5.4 corresponding to sugar protons. The methyl protons of the acetyl moieties resonated at δ2.03. A distinctive ester peak appeared at 1745 cm^{-1} in FTIR spectrum of the product GG-1, confirming the esterification of hydroxyl groups of guar. Absorption peak of 3300 cm^{-1} was due to the existence of the hydroxyl group, which vanished and indicated the hydroxyl substitution with acetate moieties [43].

The DS was recorded as 2.64 with 88.5% yield. FTIR peaks at 3250 (OH stretch), 2820 (C-H stretch), 1745 (C=O ester), and 1235 (C-O-C ester) and ^{1}H-NMR (400 MHz, D_2O/DCl), ppm = 3.5-5.4 (sugar protons), and 2.03 (3H, CH_3-acetate) confirmed complete esterification of guar.

3.2. Guar propionate (GG-2) and guar butyrate (GG-3) synthesis

In the second phase, GG-2 and GG-3 compounds were synthesized using the same methodology. The yield of GG-2 and GG-3 was low as compared to GG-1, which might be due to low reactivity of propionate and butyrate anhydrides in comparison with acetic anhydride. ^{1}H-NMR spectrum showed resonances at 2.14 and 0.97 ppm due to the methylene and methyl protons of propionate group, respectively. Proton spectra for the GG-3 products were to some extent more complicated. Methyl group of butyl moieties showed resonance of 0.99 ppm and methylene protons resonated at 2.32 and 1.43 due to H-8 and H-9, respectively. All of the expected peaks due to anhydrous sugar units were apparent in the samples. IR data showed characteristic sharp peaks at 1743 and 1726 cm^{-1}, which were due to C=O bond in GG-2 and GG-3, respectively, typically present in esters. Reaction conditions are summarized in Table 2.

GG-2 DS value was 1.33 with 83.4% yield. The FTIR (KBr) peaks of 3256 (OH stretch), 2830 (C-H stretch), 1743-(C=O ester), and 1238 (C-O-C ester) (cm^{-1}) and ^{1}H-NMR (400 MHz, D_2O/DCl): ppm = 3.8-5.6 (sugar protons), 2.14 (2H, 8-H_2), 0.97 (3H, 9-H_3) confirmed the formation of GG-2. The GG-3 DS value was 1.25 with 69.2% yield. The FTIR (KBr)

= 3412 (OH stretch), 2786 (C-H stretch), 1726 (C=O ester), and 1223 (C-O-C ester) (cm^{-1}) and ^{1}H-NMR (400 MHz, D_2O/DCl): ppm = 3.2-6.2 (sugar protons), 2.32 (2H, 8-H_2), 1.43 (2H, 9-H_2), 0.99 (3H, 10-H_3) confirmed the formation of GG-3.

3.3. Effect of catalyst concentration

GG-2 was mixed with acid anhydride (1:3) without any catalyst for 15 min and no change was observed. The catalyst had a pronounced effect on the reaction yield; by increasing the amount of iodine and DMAP, the *DS* value changed considerably. The substitution degree increased by increasing the catalyst, but the yield decreased at higher concentrations of the catalyst due to catalytic hydrolysis of hydroxyl bonds between anhydrous sugar units.

The optimal value of iodine based on the best *DS* value is shown in Table 2(a). For product GG-1, the reaction was performed in triplicate for 15 min with constant molar concentrations of 0.25, 0.50, and 0.75 meq/sugar unit. Products GG1-J, GG2-K, and GG3-L were obtained with maximum degrees of substitution (*DS*) of 1.23, 2.43, and 2.42, respectively. However, *DS* value decreased by increasing the amount of iodine above 0.75 equiv. It seems that excess amount of catalyst has no effect on *DS* value and may hydrolyse the ester. Therefore, the iodine amount needs to be optimized for higher yield during microwave-assisted synthesis of guar derivatives. Similar trends were observed for other compounds with slight variation in *DS* values [43].

3.4. Effect of reaction time

Reaction time showed considerable effect on reaction efficiency since prolonged time increased the interaction of reactants between anhydride and gum. Based on the preliminary assessment, reaction time of 15 min was selected, since beyond this time, the efficiency was decreased, which might be due to cleavage of ester bonds. Therefore, 10-15 min was the optimum reaction time to obtain products with higher *DS* values and yield. The results showed linear relationship between time interval and substitution value at constant (0.25 equivalent) catalyst amount as shown in Table 2(b).

Three different experiments were carried out for product GG1 in the presence of 0.25 equivalent per anhydrous glucose unit and acetic anhydride of 3 equiv-

Table 2(a). Effect of concentration of catalyst on *DS* value.

Sample	Anhydride/sugar unit (Moleq)	Iodine meq/sugar unit	*DS*
GG1-J	3:1	0.25	1.23
GG1-K	3:1	0.50	2.43
GG1-L	3:1	0.75	2.42
GG2-J	3:1	0.25	0.87
GG2-K	3:1	0.50	1.15
GG2-L	3:1	0.75	1.23
GG3-J	2.5:1	0.50	1.11
GG3-K	2.5:1	0.75	0.94
GG3-L	2.5:1	1	1.15

DS: Determined by titration method.

Table 2(b). Linear relationship between time intervals of microwave heating and *DS* value.

Sample	Anhydride/sugar unit (Moleq)	Time (min)	*DS*
GG1-M	3:1	5	0.87
GG1-N	3:1	10	1.01
GG1-O	3:1	15	1.23
GG2-M	3:1	5	0.33
GG2-N	3:1	10	0.99
GG2-O	3:1	15	1.11
GG3-M	2.5:1	5	–
GG3-N	2.5:1	10	0.34
GG3-O	2.5:1	15	0.23

DS: Determined by titration method.

alents in different time intervals (5, 10, 15 min). The resultant products, i.e., GG1-M, GG1-N, and GG1-O, showed *DS* values of 0.87, 1.07, and 1.23, respectively. The reaction yield decreased beyond 15 min reaction time. The same trend of reaction time was observed for other compounds such as GG-3, GG3-M, GG3-N, and GG3-O. By increasing reaction time, reaction temperature also increased, which provided a positive collision between acid anhydride and OH groups. However, further increase in temperature degraded gum structure and led to ester hydrolysis [44]. Increase in temperature facilitated diffusion of acetylating agents and guar gum swelling, which resulted in higher yield of substituted gum. However, as esterification via anhydride was an exothermic reaction, further increase in temperature hydrolysed guar unit and had negative effect on reaction yield.

3.5. Effect of concentration of acid anhydrides

Concentration of acid anhydride affected the degree of substitution of gum linearly. Three different concentrations (10, 20, 30 mmole/sugar unit) of acid anhydride were irradiated for 15 min in the presence of 0.75 equivalent/sugar unit of catalyst. The highest *DS* value (2.23) was recorded for GG1-Q product in the presence of 20 mmole of acetic anhydride. Other products, namely GG2-R and GG3-R, had *DS* values of 1.24 and 1.23, respectively, with 30 mmole of acetic anhydride, as shown in Table 2(c). Higher efficiency of reaction at higher concentrations was due to more interaction among reacting species; as a result, a large number of molecules of carboxylic groups were available to replace with the hydroxyl group of gum.

At optimal reaction conditions, the reaction mixture was homogenous and transparent, which showed normal distribution of anhydrides in the gum granules. Diffusion mechanism plays a vital role in making the inner OH group available to the reaction with anhydrides. At initial stages, the reactants were in heterogeneous form and the OH group on the surface of the gum was preferentially modified; as time proceeded, the gum dissolved in the reaction mixture increases due to increase in reaction temperature. Consequently, other inner OH groups were also replaced with acid groups. It was concluded that microwave induced esterification of GG-2 would be a promising method, which could enhance thermoplastic, mechanical, and morphological properties of the gum.

3.6. Surface morphology of guar gum derivatives

Scanning Electron Microscopy (SEM) was performed to evaluate the surface morphology of synthesized products. High and partial vacuum (10-10^{-4} Pa) Jeol JSM5600 LV SEM with secondary electron detector at voltages between 1-30 kV was used. SEM photomicrographs of the autochthonic gum and modified gum showed remarkable difference in structure and morphology, which was an evidence of variation in gum structure. Significant changes in shape and size of native gum and derivatives indicated modification in guar backbone [45]. The appearance of native guar was portrayed under SEM with distinctive granules and various shapes, namely spherical and cubical with irregular geometry. Most guar granules possessed elliptical shape and a few were spherical in the size range of 8.7 to 30.2 mm. SEM microspheres of guar were non-porous and uniform with high degree of solidification (Figure 2).

GG-1 particles lost their crystallinity and smoothness on modification. GG1-R showed maximum networking and deformation due to greater degree of substitution. Microwave modified compounds GG-2 and GG-3 showed no noticeable changes in their

Table 2(c). Effect of concentration of acid anhydride on DS value.

Sample	Anhydride/sugar unit (Moleq)	Iodine meq/sugar unit	*DS*
GG1-P	1:1	0.75	1.87
GG1-Q	2:1	0.75	2.23
GG1-R	3:1	0.75	1.96
GG2-P	1:1	0.75	0.33
GG2-Q	2:1	0.75	1.23
GG2-R	3:1	0.75	1.24
GG3-P	1:1	0.75	0.23
GG3-Q	2:1	0.75	0.99
GG3-R	3:1	0.75	1.23

DS: Determined by titration method.

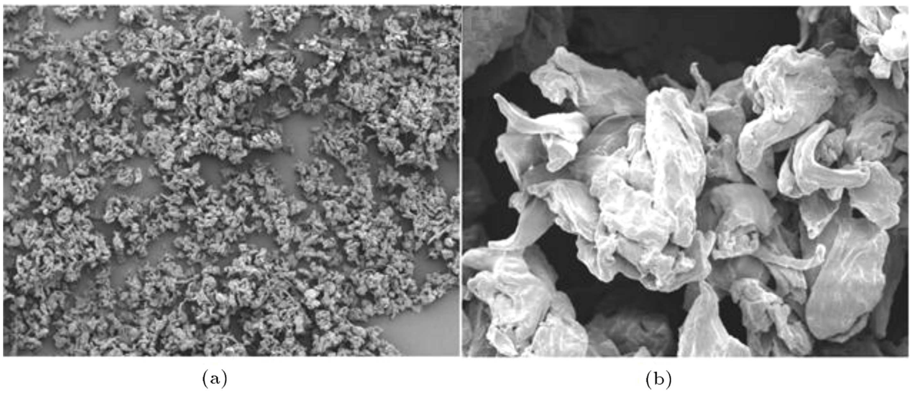
(a) (b)

Figure 2. SEM images of native guar gum.

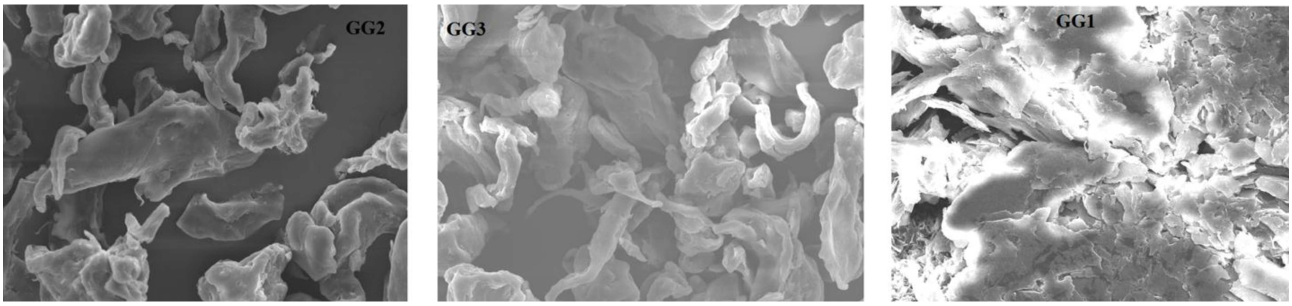

Figure 3. SEM images of modified GG1, GG2, and GG3 (guar derivatives).

microsphere structures (Figure 3). It was concluded that derivatization by microwave irradiation did not change the surface of guar molecules remarkably. The surface remained intact and smooth, and microwaves brought no considerable variation in the microstructure of gum esters. Any change due to modification could occur only in the internal structure of the granules. Inner sections of the guar gum were more susceptible to reactions than the outer surface was.

In the present study, since the substitution occurred to a low degree, the variations might be limited only to the inner regions and the surface morphological studies showed that the upper surface was intact [46].

Guar gum might be distinguished from the gums of other plants by the perfect cold-water solubility, even at very low concentrations. It formed a highly viscous solution, which appeared as a gel-like complex. Water solubility of galactomannans depended upon the mannose to galactose ratio; the greater the α-1-6-D-glucopyranosyl units, the higher the cold water solubility and vice versa [47]. It seemed that the galactose groups maintained the solid-state packing of mannanose backbone and played an important role in the solution state by free rotation of (1→6) linkage due to conformational entropy. Consequently, guar was not organo-soluble and this limited its applications. Therefore, for versatile applications, different methods were employed to increase solubility of guar derivatives in different organic solvents. The introduction of different functional groups into the gum backbone altered the solubility. Such substitutions depend upon various factors like substitution extent, substituent nature, temperature, type of solvent, and molecular weight. Generally, guar derivatives with DS values above 2 show remarkable solubility in organic solvents; on the other hand, commercial guar derivatives are generally available with $DS < 1$ and not soluble in typical solvents [48]. The degree of substitution of GG1 is greater than 2; thus, it has profound effect on solubility. It is soluble in all solvents, whereas GG2 and GG3 have solubility below the normal, which can be increased by heating.

3.7. Water holding capacity and gelation properties

High Water Holding Capacity (WHC) is an important factor that determines industrial applications of polysaccharides. Swelling ratio or WHC is the ability of hydrogels to hold water after the equilibrium attained under certain conditions, resulting in gel formation and loss of granular morphology. Due to hydrophilic nature of GG, it showed greater water uptake capacity than other galactomannan and therefore, could be used to improve texture of products in different industrial formulations. To identify potential applications of guar derivatives in food, pharmaceutical, cosmetics, and many other commercial and industrial sectors, determining their swelling index is a prerequisite [49].

Swelling power leads to better product in the processing and enhances end use performance. WHC of products depends upon gum origin, microstructure, chemical composition, isolation techniques, purity, concentration, temperature, and pH of medium. The degree of swelling was calculated in terms of weight gain percentage. Percentage of swelling ratio for the sample GG1-GG3 was studied and it was concluded that WHC was variable. Variation in swelling ratios among modified samples might be due to the type of the functional group substituted. The relationship between GG swelling and molecular structure is a complex phenomenon. Different studies in the literature have proposed different effects depending upon experimental conditions [50].

Gelation index was determined from the Lowest Gelation Concentration (LGC). The gelation properties of reduced modified gum were due to substitution of hydroxyl groups by different functional moieties. This substitution effects inter-granular association between guar molecules. Formation of gels depends upon intermolecular forces; the stronger the forces, the better the swelling, the higher the hydration rates, and consequently, the stronger the gels. Substitution limits the formation of stronger gels. The LGC value for GG sample was low, which was attributed to high molecular weight, rigidity, and crystalline structure of guar gum. Maximum LGC index was observed for GG3 due to the introduction of hydrophobicity into the guar backbone by induction of fatty acids groups. They caused inter-granular repulsion, which decreased gelation ability. Remarkable change in physical properties of the modified GG1, GG2, and GG3 was observed, which was promising with regards to their applications as binder, water barrier, and emulsifier in industrial formulations. Also, the method adopted for the synthesis is an eco-benign one in comparison with other chemical synthesis techniques and applicable in the modification of other biomolecules for different applications; therefore, it is the best choice to resolve the pollution issue [51-60] among the chemical methods used for the synthesis of organic compounds.

4. Conclusions

Microwave-assisted synthetic strategies have gained significant importance in the synthesis of materials due to their eco-friendly, less expensive, and more efficient nature without using any chemical moieties. A rapid method for protecting the hydroxyl group in sterically hindered gum was developed by MAS. Significantly higher yield of ester was achieved with 15 min MW irradiation at 600 W. The synthesized products were characterized using FTIR, NMR, and SEM techniques. It was concluded that the guar gum could be modified using acid anhydride under microwave irradiation with enhanced swelling ratio, gelation ability, and solubility properties.

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Biographies

Dure Najaf Iqbal completed her PhD in Chemistry with distinction at the Lahore College for Women University, Lahore, in 2014. She is an Assistant Professor (IPFP) in the Department of Chemistry at University of Lahore. Dr. Najaf Iqbal received HEC Scholarship under Indigenous Scholarship Scheme Batch-IV and International Research Support Initiative Program for six months from University of Bristol under IRSIP.

She worked with Prof. Christine Wills at University of Bristol and received training and hands-on operation on different instruments related to her fields of study, e.g., SEM, NMR, and FTIR. She has contributed to several national and international publications and conferences. Her current research interests are organic synthesis, polymeric membranes, FR polymers, and waste water treatment.

Erum Akbar Hussain is currently working as tenured Associate Professor in the Department of Chemistry at Lahore College for Women University. She has also served at PCSIR, Peshawar, and University of Engineering and Technology, Lahore. Dr. Akbar Hussain has over 30 international research publications in well reputed journals of chemistry and supervised 5 PhD and 20 MS students so far. She has also filled two patents in the field of green chemistry and medicinal chemistry. She completed her PhD in the International Centre for Chemical & Biological Sciences, H. E. J. Research Institute of Chemistry, University of Karachi.

Gul Afshan Soomro completed her PhD in Chemistry at the Institute of Chemistry, Shah Abdul Latif University, Khairpur, Pakistan. Currently, she is working in the Department of Chemistry, Shah Abdul Latif University, Khairpur, Pakistan, and her research interest is organic chemistry.

Hina Rizvi completed her PhD in Environmental Science at University of Punjab, Lahore. She is currently working as an Assistant Professor in the Department of Environmental Sciences and Engineering, Government College University, Faisalabad, Pakistan. Her field of interest is treatment of wastewater using physicochemical and biological methods.

Munawar Iqbal received his PhD in Chemistry from University of Agriculture, Faisalabad, Pakistan. Currently, he is working in the Department of Chemistry, University of Lahore, Lahore, Pakistan as an Assistant Professor. He has published 250 research articles with 300+ impact factor and h-index of 25. His research filed is physical chemistry.

Arif Nazir received his PhD in Chemistry from UET, Lahore. He has been teaching at university level since 2003. Currently, he is teaching in the Department of Chemistry at University of Lahore, Lahore, Pakistan. His field of interest envelops biomarkers analysis, petroleum chemistry, biodiesel, toxicity evaluation, adsorption, and method validation techniques.