Guar esters of long-chain aliphatic carboxylic acids (fatty acid) were prepared and examined. Esterification was done in two steps, with the first goal to prepare acid chloride by refluxing acid with slight excess of thionyl chloride, and the product was confirmed by elemental analysis. Ten different types of fatty acid (C$_5$-C$_{18}$) were used for derivatization. The reaction mechanism for synthesis of fatty acid ester of guar was studied in detail. Physical properties of the esters were examined as well. The degree of substitution was calculated by titration method and structure elucidation was done using Fourier transform infrared spectroscopy (FTIR), proton-nuclear magnetic resonance (1H-NMR) and scanning electron microscopy (SEM) techniques.
Introduction

Different synthetic routes have been commercialized in recent years to obtain polysaccharide esters with variable properties and applications. Guar gum acts as a potential emulsifier and thickener in the food industry because it is non-toxic, biodegradable and has good emulsifying and antioxidant properties, to increase the emulsifying property of guar [1-5] prepared palmitoylated guar gum derivatives under heterogeneous reaction conditions. Reaction procedure involved reaction between guar hydroxyl groups and palmitoyl chloride (Fig. 1a) in toluene and pyridine as an initiator. Modified gum was characterized by FTIR, X-ray powder diffraction (XRD) and thermogravimetric analysis/differential thermal analysis (TGA/DTA) techniques. The degree of substitution was determined by the saponification method.

An eco-friendly green method [6-11] for preparing three different types of galactomannan esters was developed [12] by reacting polymer with acetic, succinic and octenylsuccinic anhydride under anhydrous conditions with mild catalyst NaHCO3. The main focus was to avoid strong alkali and far excess of water, thus making the whole process cost-effective (Fig. 1b).

An important discovery was made [13] to increase biodegradability of native guar by esterification of the succinate group on a polymer chain. They prepared novel superabsorbent hydrogels in DMSO by reacting guar with succinic anhydride and 4-dimethylaminopyridine as a catalyst. Resultant hydrogels exhibited excellent water absorbency and biodegradability to make them ideal candidates for biomedical applications. Shenoy et al. [14] acetylated the HPG (hydroxypropyl guar) to use as filler in unsaturated polyester composites. Derivatized guar increased filler-polymer interaction by increasing the hydrophobic nature of polymer. Introducing hydrophobicity in hydrolyzed guar gum (GGH) and gum Arabica was done [15] by reacting the gum’s oleic acid and n-octenyl succinic anhydride (OSA). The reaction conditions were optimized for maximum degrees of substitution (DS), which were 0.061 and 0.072 respectively for guar olate and guar n-octenyl succinate. Resultant esters were analyzed as wall materials in microencapsulation.

Novel blends from quaternized polysulfone (QPSF) along with benzoylated guar (BGG) called as QB, and chloromethylated polysulfone (CIPSF) and benzoylated guar (BGG) known as CIB was introduced by Huang et al. [16] by reacted benzoyl guar and quaternized polysulfone. Different techniques were used to confirm the formation of these hydrogels such as FTIR, SEM, AFM and DSC, and tensile tests revealed typical phase separation between blends.

Unsaturated fatty acids have a valuable influence on human health but it cannot be used directly as food additives in their native form. Derivatives of guar-fatty acids might be an interesting substitute of fatty acids. Long-chain fatty acid derivatives of polysaccharides have been intensively studied by many researchers [17]. Green thinking emphasized creating such environmentally friendly biopolymers with promising properties.
Green and Environmentally Friendly...

properties such as thermoplasticity, emulsification, etc. The commercial and academic scientist thoroughly studied synthesis of fatty acid esters of cellulose [18], starch and many other polysaccharides. Products have extensive application in food and non-food industries. However, the knowledge of the higher fatty esters of guar is limited. No considerable work has been done to prepare long-chain fatty acid esters of guar by heterogeneous conditions. The main objective of this study is to prepare a series of fatty acid esters (C5-C18) by the acid chloride-pyridine method [19]. In this work an interesting methodology was reported for the modification of autochthonic guar by reacting hydroxyl groups of mannose and galactose with a variety of fatty acids chloride ranging from C5-C18. A series of fatty acid esters are obtained by this method with variable DS values and physical properties that have the potential for use as emulsifiers and thickeners in a variety of commercial and industrial sectors.

Material and Methods

All commercially available compounds were used without purification except where stated. The standard syringe techniques were used for inert atmosphere. The reactions progress was checked by pre-coated Merck-Kieselgel 60 F254 aluminium-backed TLC plates. The spots were visualized by UV254 light.

Pharmaceutical-grade guar gum (GG-I) was purchased from Pakistan gum industries in Karachi with molecular weight of 1.053×10⁶ g/mol determined by GPC/MALS, and RMS radius of about 55.65 nm. Guar gum was purified by the barium complex formation method [20]. A Perkin Elmer Spectrum One FT-IR spectrometer was used to explore infrared spectra in solid or liquid states. A JEOL Eclipse 400 MHz or Varian 400-MR 400 MHz spectrometer was used to record H-NMR spectra. H-NMR spectra of native gum were done by in situ hydrolysis of guar in DCl. Derivatives spectra were recorded in DMSO-d6 and DCl. 10mg sample per mL of solvent was used for analysis. JEOL-JSM 5600 LV Scanning electron microscopy with secondary electron detector at voltage between 1-30kV (high and partial vacuum 10-10⁻⁴ Pa) was used for surface morphological studies of polymers. Vario EL-III, Germany Elemental analyzer was used for characterizing fatty acid chlorides.

Fatty Acid Chloride Synthesis

A general procedure involves refluxing of fatty acid (10 mM) with excess of thionyl chloride (20 mM) in the presence of catalytic amount of dry DMF (1-2 drops) on a steam bath under inert atmosphere until the consumption of starting material. Reaction was stopped after the required time and the excess of thionyl chloride was removed in vacuum. Corresponding fatty acid chlorides [21] were obtained in the form of yellow oily liquid which was used without further purification. Elemental analysis confirmed the formation of acid chloride.

Fatty Acid Esters of Guar

The procedure described in [22] US patent 5589577 was used with slight modification for esterification of GG-2 (1×10⁻⁴ mM sugar unit/3×10⁻⁴ mM OH) with fatty acid chloride (2×10⁻⁴ mM) under inert atmosphere in DMF and pyridine as a reaction promoter. Reaction temperature varies from 100-140°C for a different time interval (Table 1). General reaction mechanism involves the nucleophilic attack of catalyst pyridine on carbonyl carbon of acid chloride to form a complex. In the next step, free hydroxyl groups of guar back bone made nucleophilic attack on the carbon of intermediate to form a corresponding ester (Figs 2a-b). Reaction can be performed without base, but the resultant product will be of lower yield and substitution value.
Degree of Substitution

Degree of substitution was determined by following the method described in Heinze et al. [23]. 0.15 g guar esters (GG-A to GG-J) were homogenized in 20 ml of acetone-water (50:50% v/v) mixture and kept for 24 hours at room temperature with continuous stirring [24]. De-esterification was done by the addition of 5 ml (1M) ethanolic KOH solution and the mixture was kept for a day at room temperature. Control sample was prepared without guar ester. Then back titration of excess alkali (KOH) was done with aqueous HCl. Percentage substitution and DS were calculated by Eqs. 1-2:

\[
\text{% Substitution} = \frac{V_{\text{blank}} \times V_{\text{HCl}} \times M_{\text{sub}} \times M_{\text{HCl}}}{W_{\text{ester}}} \times 100
\]

\[
\text{DS} = \frac{162 \times M_{\text{sub}}}{M_{\text{HCl}} \times (M_{\text{sub}} - 1) \times \% \text{Sub}}
\]

Swelling Index and Gelation Study of Guar Esters

The swelling equilibrium of synthesized (GG-A to GG-J) and native gum (GG) was carried out in triple-distilled water. The precisely pre-weighed samples (0.5 g) of each compound were dispersed in 50 ml of triple-distilled water and kept for 30 hours at 25°C (Japanese Industrial Standard K8150) to establish equilibrium swelling [25]. After the required time, the samples were removed, blotted with filter paper to remove excess water and filtered by a commercial sieve of 681μm (30 mesh). The equilibrium degree of Swelling was measured by Eq. 3 and percentage of swelling by Eq. 4:

\[
\text{SR} = \frac{W_x - W_y}{W_y}
\]

where:

SR = Swelling ratio
Wx = Weight of sample after swelling
Wy = Dry weight of sample before swelling

\[
\text{PS} = \text{SR} \times 100
\]

Gelation Study

Modified samples of GG-1 and GG-2 (2-15% w/v) were prepared in DMSO (5 mL). Continuous stirring of the mixture was done at 80°C for 30 min in order to form a homogeneous mixture followed by quick cooling at 4°C for 2 h. Least gelation observed at that concentration when the sample did not fall down from the inverted test tube.

Results and Discussion

Modification of autochthonic guar (GG) occurred by reacting hydroxyl groups of mannose and galactose with a variety of fatty acid chlorides (Table 2) ranging from C5-C18. A series of fatty acid esters are obtained by this method with variable DS values and physical properties.

Acyl chlorides are useful as reactive intermediates and are used in numbers of organic transformation. The first step involves the preparatory methods for synthesis of acid chloride by refluxing fatty acids with slight excess of thionyl chloride (Fig. 2a). The product was analyzed by elemental analysis [26]. In the second step GG was dissolved in DMF, which ensured homogeneous substitution by enhancing accessibility of reactants then it was allowed to react with 2 moles equivalent of carboxylic acid chloride along with a catalytic amount of pyridine under inert atmosphere for different time intervals at 100-140°C [27].

A range of diverse guar esters was successfully prepared via this path. These guar derivatives possess different solubilities, viscosities, gelation abilities, water-holding capacities and viscosities as compared
Table 2. Spectroscopic data of modified guar derivatives.

| Fatty Acids Chloride | Elemental Analysis EA: | Product | FTIR (KBr): cm⁻¹ | NMR ¹HNMR (400MHz, DMSO6/DCI): ppm |
|----------------------|------------------------|---------|------------------|-----------------------------------|
| valeryl chloride     | C, 48.81; H, 7.05; Cl, 30.39; O, 13.75 | | 3430 (OH stretch), 2928, 2830 (C-H stretch), 1754 (C=O ester), 1238 (C-O-C ester) | 3.8-5.6 (sugar Protons), 1.34-2.54 (CH2-Valerate), 0.97 (CH3-Valerate); |
| Caproic Chloride     | C, 53.54; H, 8.34; Cl, 25.24; O, 12.88 | | 3445 (OH stretch), 2938, 2825 (C-H stretch), 1754 (C=O ester), 1240 (C-O-C ester) | 3.8-5.6 (sugar Protons), 1.24-2.30 (CH2-Caproate), 0.87 (CH3-Caproate); |
| Heptanoyl Chloride   | C, 55.47; H, 9.92; Cl, 23.65; O, 10.96 | | 3398 (OH stretch), 2930, 2876 (C-H stretch), 1743 (C=O ester), 1240(C-O-C ester) | 4.3-6.4 (sugar Protons), 1.35-2.33 (CH2-Heptanoate), 0.83 (CH3-Heptanoate); |
| caprylic chloride    | C, 60.07; H, 9.20; Cl, 20.69; O, 10.81 | | 3470 (OH stretch), 2930, 2858 (C-H stretch), 1760 (C=O ester), 1230 (C-O-C ester) | 3.6-5.4 (sugar Protons), 1.25-2.36 (CH2-Caprylate), 0.85 (CH3-Caprylate); |
| Pelargonic Chloride  | C, 61.20; H, 9.68; Cl, 21.07; O, 8.05 | | 3450 (OH stretch), 2930, 2845 (C-H stretch), 1753 (C=O ester), 1245(C-O-C ester) | 3.6-5.6 (sugar Protons), 1.26-2.82 (CH3-Pelargonate), 0.79 (CH3-Pelargonate); |
| Capric Chloride      | C, 61.88; H,11.14; Cl, 18.49; O, 8.49 | | 3478 (OH stretch), 2930, 2845 (C-H stretch), 1753 (C=O ester), 1240(C-O-C ester) | 3.5-5.4 (sugar Protons), 1.24-2.33 (CH3-Caprates), 0.88 (CH3-Caprates); |
to native gum. A remarkable change in physical properties was observed which depending upon chain length of carboxylic acid and substitution degree. It was demonstrated that the extent of reaction depends upon reactivity of acid chloride, which in turn increases with chain length of fatty acid [28, 29]. The greater the DS value, the greater the organo-soluble capacity. Surface changes were confirmed by SEM imaging, which showed more networking in derivatives as compared to the native one.

**FTIR Spectra Analysis**

The FTIR (KBr) spectra showed typical absorption for the guar gum backbone at 3630, 2940 and 1130 cm\(^{-1}\). A comparison of FTIR (KBr) spectrum of native gum and guar valerate (GG-A) prepared from a valeryl chloride solution with a DS of 0.87 confirmed completion of the reaction. Compound (GG-A) spectra displayed hydroxyl group stretching absorption at 3430 cm\(^{-1}\), which decrease in intensity and which reveal the success of the reaction. The difference showed that a large number of hydroxyl groups was replaced. The increase in bond absorption at 2928-2830 cm\(^{-1}\) is linked with C-H bond antisymmetric and symmetric stretching vibrations, which are additional proof of linkage of fatty long-chain moieties with gum. The appearance of new bands at 1754 cm\(^{-1}\) and 723 cm\(^{-1}\) corresponding to the carbonyl ester group and the second one due to the presence of at least four linearly connected CH\(_2\) groups are rocking vibrations. The disappearance of absorption bands around 1330-1150 cm\(^{-1}\) showed that no unreacted acyl chlorides are present. Guar esters showed two featured peaks in FTIR spectra typical for the ester moieties due to C-O-C\(_{_{\text{Ester}}}\) and C=O\(_{_{\text{Ester}}}\) vibrations. The absence of absorption bands around 1800 cm\(^{-1}\) and 1700 cm\(^{-1}\) in all spectra indicated the absence of any unreacted acyl chloride and carboxylic acid. Relative to O–H absorbance, the intensity of the C–H stretching bands enhanced with increasing acid chain
length in FTIR spectra. These results obtained are in good agreement with the values given in literature for cellulose and starch esters via fatty acids [30-36]. Similar results were obtained for other products (GG-A to GG-J) irrespective of carbon chain length as shown in Table 2.

H-NMR Characterization

H-NMR characterization was an interesting tool to investigate the existence of the fatty chains on the guar backbone. All the spectra showed almost similar peaks corresponding to chain lengths. Characteristic signals due to long-chain fatty acid protons appeared between 0.79 to 2.84 ppm. All spectra showed carbohydrate proton resonance within the range of 3.35-5.78 ppm. The H-NMR spectrum of GG-A was recorded in DMSO6 and DCl showed the characteristic signals due to sugar protons resonating at 3.8-5.6 ppm. The signals of the methylene groups of valeric acid appeared in the range 1.23-2.75 ppm. The methyl group resonates at 0.97 ppm. In the same way, compound GG-B showed three different types of signals at 3.8-5.6 ppm (due to sugar protons), 1.24-2.30 ppm (methylene protons) and 0.87 ppm (methyl protons). Compound GG-C showed multiple signals at 1.35-2.33 ppm, typical for methylene protons of 1.38 ppm and singlet at 0.83 ppm due to three protons of the methyl group. The signals of the methylene groups of the compound (GG-D to GG-J) appeared in the ranges 1.25-2.36, 1.26-2.82, 1.24-2.33, 1.26-2.32, 1.26-2.34 ppm and 1.23-2.75 ppm respectively. All methylene protons resonate almost at similar range irrespective of the chain length. All methyl protons of fatty acid moieties were detectable at 0.79-0.83 ppm. H-NMR confirmed the modification of GG-2 into value-added products.

Determining Degree of Substitution of Guar Gum Derivatives

Heinze et al. [23] and Klemm et al. [24] methods were used for determining DS of guar ester. The back titration methods discussed above give more accurate, reliable and fast determination of substitution degree. We can quantitatively measure the number of hydroxyl groups substituted per sugar unit of gum. Back titration was employed in 1947 to determine DS values of carboxymethyl cellulose. Later on, it was applied for other polysaccharides.

Modified samples were treated with acid (HCl or H2SO4) to finish acid hydrolysis of substituted groups, after which they are converted into sodium and potassium salts by treating with a known amount of alkali. Back titration of excess base was done to quantitatively determine the number of liberated groups. Other methods can be employed for determining the substitution of hydroxyl groups, but titration methods are considered more simple and accurate.

Surface Morphological Studies of Guar Gum Derivatives

A surface morphological study was done with the help of scanning electron microscopy [37-42]. SEM photomicrographs of autochthonic gum and modified gum showed remarkable differences in structure and morphology (Fig. 3), which is evidence of variations in gum structure. Significant changes in shape and size of native gum and derivatives indicated modification in guar backbone [43]. The appearance of native guar was portrayed under SEM with distinctive granules and with various shapes. Most guar granules possessed elliptical shapes with a few spherical ones with a wide range of granule sizes ranging from 8.7 to 30.2 mm. SEM microspheres of guar are non-porous and have uniform solidification as expected. Guar granules lacked their individuality and smoothness for derivatives GG-A to GG-J when observed using SEM.
They showed transition from granules to agglomerates upon gelatinization. Profound increment in networking were observed as DS value increased, because more hydroxyl groups were substituted by fatty acid groups. Compound GG-I and GG-J showed maximum deformation in structure.

Swelling Index and Gelation Study of Guar Gum Esters

Swelling index is an important factor that determines industrial applications of polysaccharides. Swelling ratios or water-holding capacity is the ability of hydrogels to hold water after the equilibrium attained under certain conditions resulting in gel formation and lose of granular morphology. Due to the hydrophilic nature of GG it showed greater water uptake capacity as compared to other galactomannans and as a result can be used to improve the texture of end products in different industrial formulations. It is a prerequisite to determining swelling index of guar derivatives in the viewpoint of its potential applications in foods, pharmaceuticals, cosmetics and many other commercial and industrial sectors [44]. Swelling power formulated a better product throughout processing and enhanced end-use performance.

Variation in swelling ratios among modified samples should be attributed to the type of functional group substituted. The relationship between swelling of GG and molecular structure is a complex phenomenon. Compound GG-A to GG-J showed a gradual decrease in water retention capacity. Sample GG-I and GG-J were not found to have good water-holding ability due to the long fatty acid chain. Fatty acids introduced hydrophobicity in guar backbone as a result of decreases in swelling ability (Table 3).

Gelation properties of autochthonic guar and its derivatives were studied. Gelation index was determined from least gelation concentration (LGC). After modification of gum there was a reduction in gelation properties due to the substitution of hydroxyl groups by different functional moieties that hamper inter-granular association between guar molecules [45]. The formation of gels depends upon intermolecular forces being stronger than swelling and hydration rates, which in turn appeared as stronger gels. Substitution limited the formation of stronger gels, thus resulting in weaker gel formation. Lowest LGC was observed for GG-I samples, which were attributed to high molecular weight [46-48].

Conclusions

Knowledge about these structural changes can be of great importance for understanding the changes in properties of guar esters. Even at lower DS, products showed marked difference in physical behavior as compared to native ones. A saturation limit of swelling properties was observed with increasing DS value of esters. The tendency may be investigated by studying other properties such as viscosity, rheology, thermal stability, etc. In future, studies may be performed to discover optimal reaction conditions that endorsed higher conversion rate, higher yield and degree of substitution.

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Conflict of Interest

The authors declare no conflict of interest.

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