Carboxymethyl Guar: Its Synthesis and Macromolecular Characterization

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ABSTRACT: Guar gum was partially carboxymethylated by the reaction of the base polysaccharide with the sodium salt of monochloroacetic acid in presence of sodium hydroxide. The resulting products (carboxymethyl guar with different degrees of substitution) were characterized by a variety of material characterization techniques, such as intrinsic viscosity measurement, determination of molecular weight, elemental analysis, thermal analysis, ^{13}C-NMR spectra, and Fourier transform infrared analysis. Various grades of carboxymethyl guar gum, which were synthesized in the laboratory, were studied for their suitability as flocculants and viscosifiers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2630–2636, 2009

Key words: FT-IR; light scattering; NMR; polysaccharides; rheology

INTRODUCTION

The world's population is increasing, whereas the availability of potable water is decreasing. Water is essential for the survival of human beings, not to mention modern industry. This necessitates the recycling of municipal wastewater and industrial effluents on a massive scale. To meet the requirements of potable, industrial, and agricultural water, the wastewater has to be treated, particularly, municipal sewage sludges and slimes and industrial effluents. These effluents are highly undesirable and unsafe to use. Wastewater contains solid particles with a wide variety of shapes, sizes, densities, and so on. The specific properties of these particles affect their behavior in liquid phases and, thus, the removal capabilities. Many chemical and microbiological contaminants found in wastewater are adsorbed on or incorporated into solid particles. Thus, the removal of solid particles is essential for the purification and recycling of both wastewater and industrial effluents.

Effluent disposal is a now major problem all over the world. The development of industries has created hazards and environmental problems. Hence, environmental concerns and depleting raw material resources have forced scientists and technologists to develop materials from renewable agricultural and plant resources to protect the environment from pollution.

Water-soluble polysaccharides have a myriad of industrial and agricultural applications, such as viscosity controllers,[1] drag reducers,[2] flocculants,[3] controlled delivery agents,[4] adsorbent polymers, responsive polymers, dispersants, stabilizers, crystal growth inhibitors, water borne polymers coatings, and adhesives.

As renewable raw materials, polysaccharides today play a major role as alternatives to fossil raw materials because of both their generally nontoxic nature and the constantly rising global demand for energy and raw materials. Polysaccharides are large organic molecules that occur in a variety of natural sources. Depending on the source, these polysaccharides have many impurities and molecular distributions. However, through purification and chemical modification, useful products can be made that can be used as flocculants,[5–10] drag reducers,[11,12] viscosifiers,[12] and matrices for controlled drug release.[13–15]

Among various water-soluble polysaccharides, guar gum (GG) is one of the most important polysaccharides. It has been extracted from the seeds of *Cyamopsis tetragonoloba*, which belongs to the Luguminosoe family.[16] It is a galactomannan and consists of a (1–4)-linked β-D-mannopyranose backbone with random branch points of α-D-galactose units[16] (Fig. 1). GG possesses a high level of galactose substitution along the mannan backbone. On average, there are between 1.5 and 2 mannose residues for every galactose residue, with few, if any, nonsubstituted regions. GG is widely used in various industrial applications, such as oil recovery, food, and
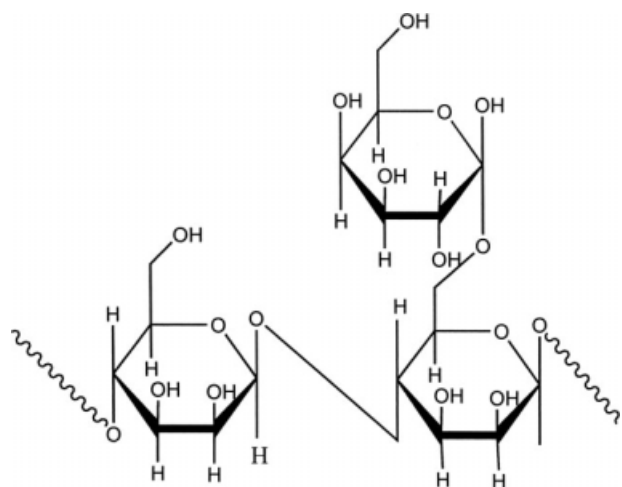
Figure 1 Structure of GG.

personal care, because of its ability to produce highly viscous, pseudoplastic aqueous solutions even at low concentrations.

In the laboratory, I have performed the partial carboxymethylation of GG, which resulted in a new material, carboxymethyl guar gum (CMG). The reaction was carried out in the homogeneous phase to obtain CMG with different degrees of substitution (DS). The attachment of carboxymethyl groups to the polymer moiety of starch is expected to result in modified properties such as higher viscosity in solution, lower biodegradability (and, hence, a longer shelf life), and so on. The developed materials (CMGs) and GG samples were characterized in a comparative fashion. The applicability of this derivative (CMG) as a flocculant and viscosifier is addressed in this article.

EXPERIMENTAL

Materials

Materials for synthesis

GG was a gift sample from Hindustan Gum & Chemicals, Ltd. (Bhiwani, Haryana, India). Analargrade sodium hydroxide (NaOH) and hydrochloric acid were obtained from E. Merck (India), Ltd.

TABLE I
Characteristics of the Kaolin Suspensions

Colloidal suspension	Specific gravity (g/cc)	Particle size (nm)	pH	ζ potential (mV)
Kaolin suspension	2.0	5.6	4.0	+1.20
			7.0	−2.40
			10.0	−5.00

(Mumbai, India). The sodium salt of monochloroacetic acid (SMCA) was procured from E. Merck (India). All chemicals were used without further modification.

Materials for flocculation

Kaolin was purchased from B. D. Pharmaceutical Works (Howrah, India). The detailed characteristics of the kaolin suspension, that is, the specific gravity, particle size, and suspension ζ potential, are reported in Table I.

Synthesis

The carboxymethylation reaction adopted was as follows. The GG powder (a required amount) was slowly dissolved in water in a round-bottom flask and maintained at room temperature (27°C) with constant stirring. The resulting mixture was heated to 50°C and purged with nitrogen for 1 h. The required amount of an aqueous solution of NaOH was added to the slurry, and the mixture was stirred for 15 min. Afterward, the carboxymethylation agent (SMCA) was added under constant stirring. The reaction was continued for 2 h. The reaction mixture was cooled gradually and dispersed in acetone, and I neutralized the excess alkali with diluted HCl by bringing the pH to 7. The product was finally washed with acetone, filtered, and then dried in a vacuum oven.

With the aforementioned technique, by changing the concentration of SMCA, I obtained CMGs with different DSs. The details of the synthesis parameters are listed in Table II.

TABLE II
Synthetic Details of the CMGs

Polymer	Amount of AGU (mol)[a]	Amount of SMCA (mol)	Amount of NaOH (mol)	DS	Intrinsic viscosity (g/dL)	Molecular weight (g/mol)
CMG 1	0.0062	0.0024	0.0026	0.4	10.4	2.9×10^5
CMG 2	0.0062	0.0030	0.0035	0.5	10.9	3.4×10^5
CMG 3	0.0062	0.0037	0.40	0.6	11.6	4.1×10^5
CMG 4	0.0062	0.0043	0.0047	0.7	11.3	3.8×10^5
GG	—	—	—	—	7.9	1.1×10^5

[a] Calculated on the basis of anhydroglucose units (AGU): 1 mol of AGU = 162 g.

TABLE III
Elemental Analysis Results

Polymer	C (%)	H (%)	N (%)	O (%)
GG	42.0	11.4	0.10	43.2
CMG 1	38.2	10.6	0.14	50.3
CMG 2	37.6	10.2	0.11	51.7
CMG 3	37.1	9.8	0.12	52.0
CMG 4	37.0	9.6	0.09	52.8

Characterization

Density measurement of kaolin

The density of the kaolin sample was measured with a specific gravity bottle by the standard method. The result is summarized in Table I.

Measurement of the particle size distribution and suspension ζ potential of the kaolin sample

The measurements of the particle size and suspension ζ potential of the kaolin sample were done with Nano ZS (Malvern, Worcestershire, United Kingdom). The results are reported in Table I.

Intrinsic viscosity measurement

The intrinsic viscosity measurements of GG and various grades of CMGs were carried out with an Ubbelohde viscometer (Borosil, Mumbai, India) (constant = 0.003899) at 25°C. The viscosities were measured in a $0.1M$ $NaNO_3$ solution. The pH of the solution was neutral. The time of flow for the solutions was measured at four different concentrations. From the time of flow of the polymer solutions (t) and that of the solvent (t_0; for distilled water), the relative viscosity ($\eta_{rel} = t/t_0$) was obtained. The specific viscosity (η_{sp}) was calculated as follows: $\eta_{sp} = \eta_{rel} - 1$. Then, the reduced viscosity [$\eta_{red} = \eta_{sp}/C$, where C is the polymer concentration (g/dL)] and the inherent viscosity ($\eta_{inh} = \ln \eta_{rel}/C$) have been calculated. The intrinsic viscosity has been obtained from the point of intersection after the extrapolation of two plots,[17] that is, η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C, to zero concentration. The viscosity values are summarized in Table II.

Determination of the weight-average molecular weight by static light-scattering (SLS) analysis

The weight-average molecular weights of GG and various grades of CMGs were determined by SLS analysis with a light-scattering spectrophotometer (Nano ZS, Malvern). The results are summarized in Table II.

Elemental analysis

The elemental analysis was undertaken with an elemental analyzer (model Vario EL III, Elementer, Hanau, Germany). The estimation of four elements, that is, carbon, hydrogen, nitrogen, and oxygen, was undertaken. The results are given in Table III.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectrums of GG and various grades of CMGs was carried out with an FTIR spectrophotometer (model IR-Prestige 21, Shimadzu Corp., Kyoto, Japan). The potassium bromide pellet method was used for FTIR study. The FTIR results are described in Table IV.

Thermal analysis

The thermal analysis of GG and CMG 3 was carried out with a DTG-60 (TGA Instrument, Shimadzu, Kyoto, Japan). Thermogravimetric analysis (TGA) and differential thermal analysis were performed up to a temperature of 600°C from a starting point of 25°C in an inert atmosphere. The heating rate was uniform in all cases at 5°C/min. The TGA curves are shown in Figure 2.

^{13}C-NMR spectroscopy

^{13}C-NMR spectroscopy of GG and CMG 3 was performed at 300 MHz with a Bruker 300 P spectrometer. The spectrums are shown in Figure 3(a,b), respectively, for GG and CMG 3.

Investigation of the flocculation efficacy

Flocculation studies of GG and various grades of CMGs were carried out in 5 wt % kaolin

TABLE IV
FTIR Results for GG and Various Grades of CMGs

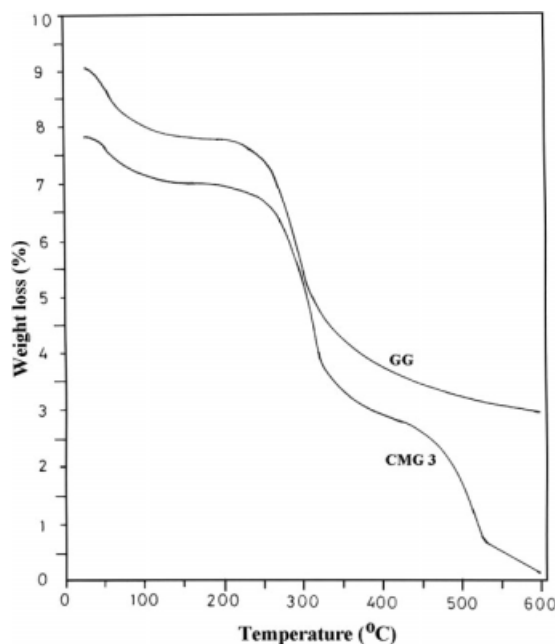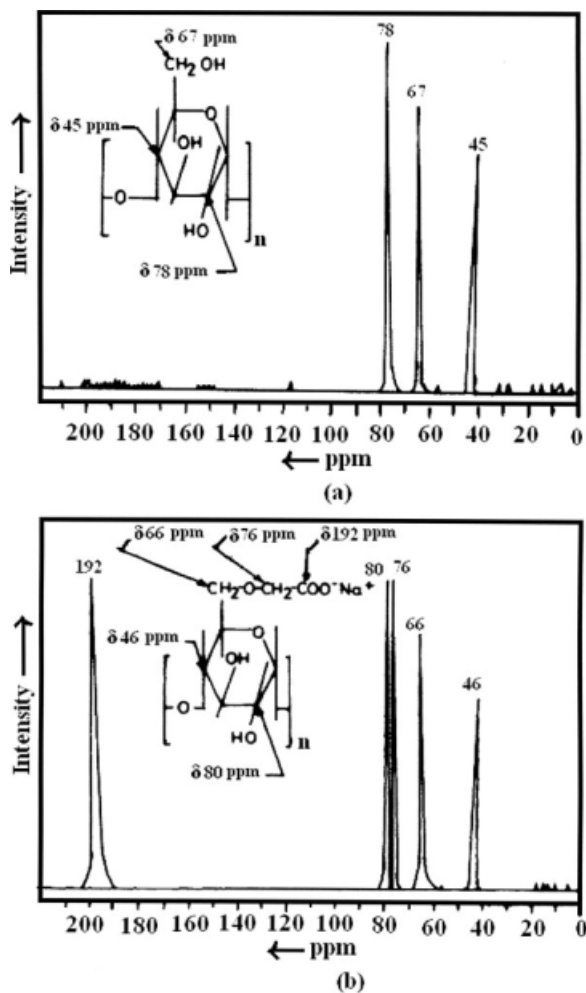| Polymer	—OH stretching (cm^{-1})	—CO stretching (cm^{-1})	—CH stretching (cm^{-1})	—COO$^-$ stretching (cm^{-1})	CH$_2$—O—CH$_2$ stretching (cm^{-1})
GG	3440	1156	2910	—	1005, 1026
CMG 1	3450	1150	2900	1650, 1440	1010, 1028
CMG 2	3445	1152	2945	1655, 1410	1000, 1025
CMG 3	3510	1140	3015	1640, 1395	1015, 1030
CMG 4	3440	1165	2980	1642, 1405	1010, 1032

Figure 2 TGA curves of GG and CMG 3.

Figure 3 ^{13}C-NMR spectra of (a) GG and (b) CMG 3.

suspensions by a column test in a 100-mL, stoppered graduated cylinder. The kaolin suspension carried a slight negative charge; hence, it was chosen for the flocculation studies with GG and the CMGs (because CMG is anionic in nature, so it should have shown better flocculation efficacies in a suspension containing a positive charge or slightly negative charge). The process was as follows: the 5 wt % slurry sample was placed in a cylinder, the flocculant was added, and the cylinder was inverted 10 times. After mixing, the cylinder was set upright, and the height of the interface between the water and the settling solid bed was measured over time. The results are shown in Figure 4.

Rheological investigations

The rheological investigations were conducted with a TA Instruments AR-1000 Advanced controlled-stress rheometer. The temperature of the system was maintained at 30°C throughout the experiments.

For rheological investigations, the preparation of the solution is very important. Aqueous solutions of GG and CMG 3 were prepared by the slow addition of the required quantity of the polymers to distilled water to avoid lumping and with continuous stirring by a magnetic stirrer at a temperature of 60°C. For GG and CMG 3, 0.5 wt % solutions were prepared. The results are shown in Figures 5 and 6, respectively.
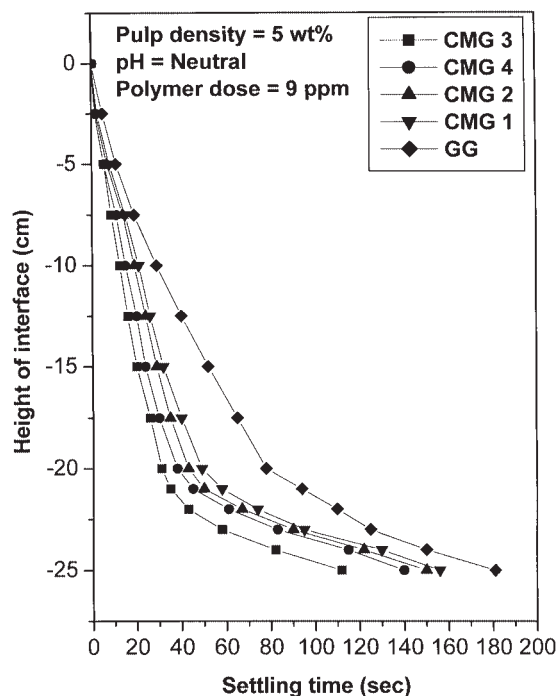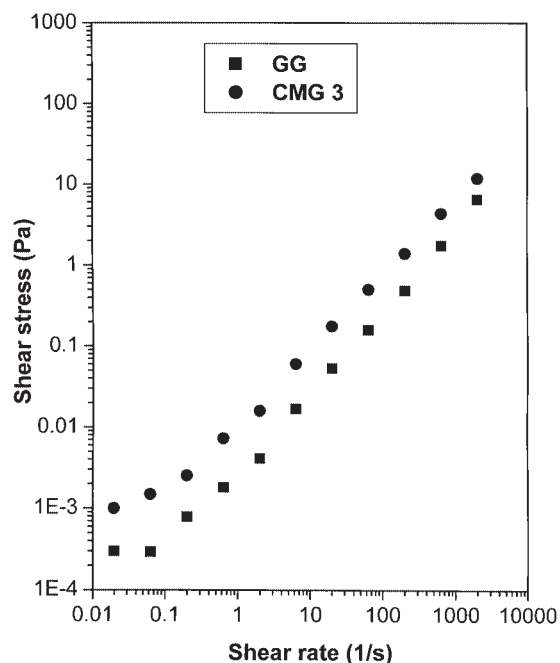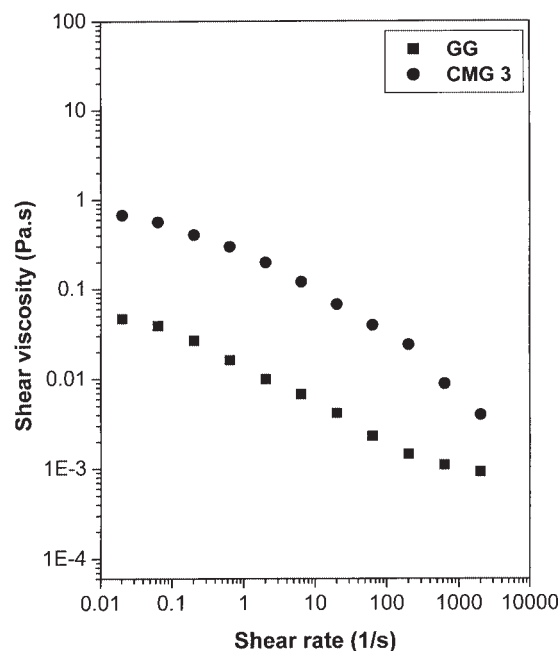

Figure 4 Settling characteristics of a 5 wt % kaolin suspension with GG and various grades of CMGs as flocculants.

Figure 5 Flow curves of 0.5 wt % GG and CMG 3 solutions.

**Figure 6** Viscosity curves of 0.5 wt % GG and CMG 3 solutions.

RESULTS AND DISCUSSION

Synthesis and measurement of the intrinsic viscosity

The carboxymethylation reaction used was designed to provide GG derivatives, in principle, to substitution at hydroxyl groups (particularly, the hydroxyl group of —CH$_2$OH, up to DS = 1 because a primary alcohol is more reactive than a secondary alcohol) of the anhydroglucose rings. The reaction proceeded through a two-step reaction, which is schematically shown in Scheme 1.

To diminish the oxidative degradation of polysaccharide chains, the reaction was carried out in an oxygen-free nitrogen atmosphere. The carboxymethylation reaction between GG and SMCA was conducted in the presence of a slight excess of NaOH concentration (preferably, 10% in excess), which performed both as a reactant and as a catalyst.[18] The NaOH and the GG interacted to form an alkoxide derivative, which reacted with the carboxymethylation agent through a substitution reaction, which led to carboxymethyl substitution along the polysaccharide backbone. The reaction temperature was maintained at 50°C. Although at relatively high temperature the reaction was faster, the chances of the formation of byproducts (hydroxyl acid) increased; the carboxymethylation reaction, therefore, was carried out at normal pressure and not at high temperature (50°C).

Through the variation of the concentration of the carboxymethylation agent (SMCA), four grades of
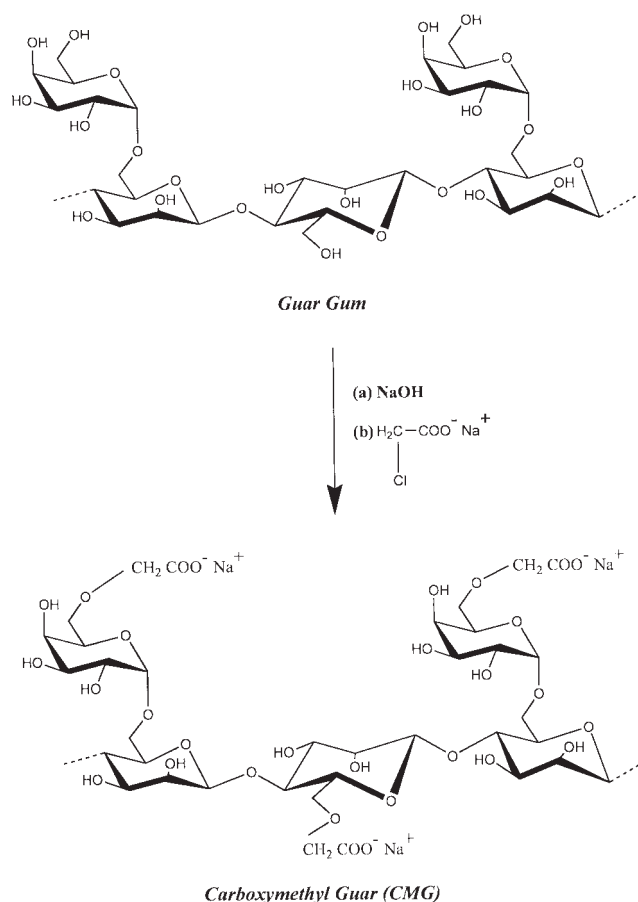
Scheme 1 Schematic representation of the formation of CMG from GG.

CMG with different DSs were developed. The details of the synthesis parameters are summarized in Table II.

Intrinsic viscosity is a measure of the hydrodynamic volume of the polymer in solution. From the η_{rel} values of various polymer solutions of known strength, η_{inh} and η_{red} were evaluated and plotted against concentration. The intrinsic viscosity was determined from the point of intersection of two extrapolated (to zero concentration) plots, that is, η_{inh} versus C and η_{red} versus C.

η_{red} and η_{inh} were calculated with the following equations:

$$\eta_{rel} = t/t_0 \tag{1}$$

$$\eta_{sp} = \eta_{rel} - 1 \tag{2}$$

$$\eta_{red} = \eta_{sp}/C \tag{3}$$

$$\eta_{inh} = (\ln \eta_{rel})/C \tag{4}$$

As was evident, the intrinsic viscosity of all of the grades of CMGs was greater than that of GG (Table II). This was because of the insertion of the carboxymethyl group onto the guar backbone. From CMG 1 to CMG 4, with increasing DS, the viscosity values increased up to CMG 3 [an optimized grade with respect to the intrinsic viscosity value, molecular weight (Table II), and flocculation characteristics (Fig. 4)]; afterward, it decreased, although the DS is higher. This may be because of the degradation of the polygalactomannan backbone as well as the greater byproduct formation.

Determination of the weight-average molecular weight by the SLS technique

The weight-average molecular weights of GG and the CMGs were determined from a Debye plot with SLS analysis. The results are given in Table II. From the results, it is obvious that the weight-average molecular weights of the CMGs increased drastically compared to GG, which accounted for the incorporation of the carboxymethyl group onto the guar backbone. Again, CMG 3, which was the optimized grade, had the highest molecular weight.

Elemental analysis

The results of elemental analysis for GG and the CMGs are given in Table III. From the results, it is clear that a higher percentage of oxygen in the case of the CMGs compared to GG could be explained by the fact that the carboxymethyl group was inserted onto the backbone of GG.

FTIR spectroscopy

The FTIR results for GG and the CMGs are listed in Table IV. From the results, it is apparent that there were two additional peaks for the stretching frequency of the COO^- groups, which are present in the CMGs, is a clear indication of the formation of CMG.

Thermal analysis

The TGA curves of GG (Fig. 2) essentially involved two distinct zones of weight loss. The initial weight loss was at 25–115°C. This was due to the traces of moisture present. The second zone of weight loss was at 200–366°C. This was due to the degradation of the polymer backbone.

CMG 3 (Fig. 2), in addition to these zones of weight loss, had a third zone of weight loss at 410–535°C. This was due to the degradation of the carboxymethyl groups incorporated in the polymer moiety. This third zone of weight loss, which was present only in CMG, provided more proof of the insertion of the carboxymethyl groups.

^{13}C-NMR spectroscopy

Evidence of the formation of CMG from GG was confirmed by the ^{13}C-NMR spectra. As shown in Figure 3(a) (i.e., ^{13}C-NMR for GG), GG had three distinct peaks in the ^{13}C-NMR spectrum. The absorption peak at $\delta = 46$ ppm was for the anomeric carbon atom, the peak at $\delta = 79$ ppm was for carbon atoms connected by $-OH$ groups (i.e., the carbon atoms in the six-membered ring except the anomeric carbon atom), and another peak at $\delta = 66$ ppm was attributed to the carbon atom of the $-CH_2OH$ group.

In the case of CMG 3 [Fig. 3(b)], apart from the peaks present at GG, there were additional peaks at $\delta = 74$ ppm, which was for the carbon atom of the $-O-CH_2-$ of the inserted carboxymethyl group, and at $\delta = 192$ ppm for the carboxyl carbon atom of $-COO^-Na^+$.

Hence, the presence of two additional peaks in the case of CMG was clear evidence of the insertion of the carboxymethyl group onto the GG backbone.

Flocculation characteristics

The flocculation efficacies of GG and various grades of CMGs were carried out with a settling test (Fig. 4).

A better measure of flocculation can be developed on the basis of settling times plotted against the height of the interface, which is known as a settling test. When the flocculant is introduced into the

container, an interface is formed between the suspended solid and the supernatant liquid. Under the action of the flocculating agent, that is, along with the progress of the flocculation process, that interface descends, until all of the contaminants are settled at the bottom. The fall of interface was linear for a considerable height before it became nonlinear (Fig. 4). This means that the rate of fall of the interface was constant initially, after which it gradually declined.

As shown in Figure 4, it is obvious that the flocculation efficacy of the CMGs are much better compared to that of GG, and out of four different grades of CMGs, CMG 3 showed the highest flocculation efficacy. From CMG 1 to CMG 4, with increase in DS, the flocculation efficacies increases up to CMG 3 [an optimized grade with respect to the intrinsic viscosity value and molecular weight (Table II)]; afterwards, it decrease, although the DS is higher for CMG 4. This may be because of the degradation of the polygalactomannan backbone with higher DS and the formation of more byproducts.

Rheological investigations

The rheological investigations of aqueous solutions of GG and CMG 3 were carried out in 0.5 wt % solutions. The shear rate, shear stress, and shear viscosity values of aqueous solutions of polymer samples were measured with an AR-1000 Advanced rheometer. In the steady-state shear flow state, two main relationships of double logarithmic scales illustrated the rheological fingerprints of the samples under study. These were the flow behavior curves (Fig. 5), which showed the relationship between the shear stress and shear rate and the viscosity curves (Fig. 6), which indicated the log–log plots of shear viscosity versus shear rate of aqueous solutions of the polysaccharides GG and CMG 3. All of the measurements were based on the assigned shear in controlled-rate mode ranging from 0.028 to 2800 s^{-1}. Both aqueous solutions of GG and CMG 3 showed strong pseudoplastic behavior. In this case, shear stress increased with increasing shear rate, and the polymer solutions showed non-Newtonian behavior. The viscosity curve (Fig. 6) illustrated the variation of viscosity of aqueous solutions of the polysaccharide (GG) and modified polysaccharide (CMG 3). It was obvious that the viscosity of the CMG 3 solution increased compared to the base polysaccharide solution because of the presence of the carboxymethyl

group on the guar backbone. As a mater of fact, the hydrodynamic volume of GG was less than that of CMG, so its solution viscosity was also lower over the extended shear rate.

CONCLUSIONS

The feasibility of inserting a carboxymethyl group onto GG with SMCA and NaOH was demonstrated in this study. Various grades were synthesized by the variation of the reaction parameters to obtain the optimized one. The macromolecular characterization (i.e., intrinsic viscosity measurement, elemental analysis, determination of molecular weight, FTIR spectroscopy, ^{13}C-NMR spectroscopy, and thermal analysis) proved that carboxymethylation did take place. Furthermore, this carboxymethylated guar will find potential application as a flocculant and viscosifier.

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