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Synthesis and characterization of sodium salt of partially carboxymethylated guar gum

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ABSTRACT

Sodium salt of partially carboxymethylated guar gum [Na-PCMGG] of different degrees of substitution (DS) were synthesized by heterogeneous and homogeneous solution methods. The DS was measured by Amberlite IRA 96 anion exchange resin. The reaction parameters viz. reaction time, reaction temperature, effect of NaOH, effect of mono chloro acetic acid was optimized. Na-PCMGG having optimized reaction condition was characterized by Fourier transforms infrared spectroscopy (FTIR).

KEYWORDS

Guar gum (GG);
Carboxymethylation;
FTIR.

INTRODUCTION

Guar gum (GG) is galactomannan, derived from guar (*cyamopsistetragonolobus*) seeds which belong to family *Leguminosae*. The guar plant is about 0.6 m high and pods are 5-12.5 cm long and contain average 5-6 light brown seeds[1].

The general structure of guar gum is as shown in Figure : 1, which consists of a linear backbone of β (1, 4) – linked D-mannose units with various amounts of α (1,6) – linked D- galactose side chains. The ratio of mannose to galactose is 2:1. The average molecular weight of guar gum is between 220,000 - 300,000[2, 3, 4, 5, 6]. Guar gum is soluble in water but insoluble in hydrocarbon, fats, alcohol, esters, and ketones[7]. The solution of guar gum in water has the highest viscosity amongst all the natural polysaccharide discovered till the date[8]. Further it has better biodegradability and bio-compatibility compare to other natural polysaccharides. Due to these properties guar gum finds applications in industries like mining, textiles, explosives,

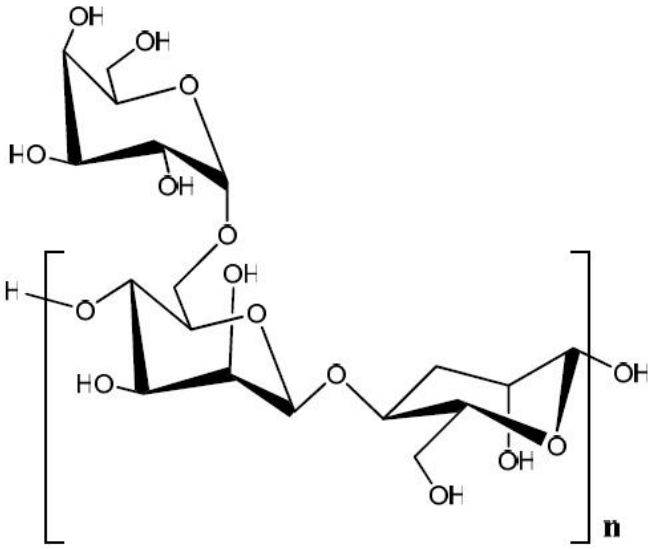

Figure 1 : Structure of guar gum

paper, petroleum, etc[9]. Further the biodegradability and bio-compatibility of guar gum encourage the researchers for its use in pharmaceutical industries. But due to the uncontrollable viscosity of the guar gum solution, uncontrollable rate of hydration, instability of its solutions for longer time and susceptibility to microbial contamination restricts its use in pharmaceutical industries[10,11, 12, 13].

To overcome these draw back guar gum should be chemically modified. Modified guar gum by one or more reactions like, depolymerization, oxidation, hydroxyalkylation, cyanoethylation, quarternization and sulphation was reported[14, 15, 16, 17, 18]. GG derivatives like O-(2-hydroxyethyl), O-(2-hydroxypropyl) were reported but this fails to more or less extent in getting used in pharmaceutical industries due to introduction of substituents groups to the galactomannan polymer which increased branching and entanglements and therefore higher viscosity[7]. Modified natural polysaccharides like carboxymethyl cellulose, carboxymethyl starch finds application in pharmaceutical industries[19,20].

There so, in the present work guar gum was carboxymethylated by homogenous andheterogenous methods. The reaction parameters were optimized and synthesized Na-PCMGG was characterized by FTIR.

EXPERIMENTAL

Materials and methods

Guar gum, sodium hydroxide, monochloro acetic acid was purchased from Sigma- Aldrich. Solvents likemethanol and iso propyl alcohol were of A.R. grade. All other reagents were of LR grade.

Carboxymethylation of guar gum

Guar gum was carboxymethylated by two methods viz. homogenous solution method and heterogeneoussolution method.

Heterogeneous method

Purified guar gum was dispersed in 150 ml of iso propyl alcohol, in 250 ml of three neck flask equipped with a mechanical stirrer and contact thermometer for control of temperature. After the gum was well dispersed, the appropriate volume of NaOH solution (30%) was added at a rate of 1 ml within 15 min. After that required amount of monochloro acetic acid was added to the reaction mixture over a period of 10 min. The reaction mixture was heated and maintained ata specific temperature with continuous stirring for constant time to drive the reaction process to completion. After completion of reaction carboxymethyl guar gum was precipitated with the help of methanol and the precipitated product was purified.

Homogenous solution method

In homogenous solution method iso propanol was replaced by water by keeping other parameters as same as heterogeneous method.

Crude carboxymethyl guar gum purified with the help of water. Product was dialyzed against distilled water for 48 hrs. and then carboxymethyl guar gum was precipitated with the help of methanol. Finally product was dried in an oven at temperature 40-45^{o}C.

Degree of substitution in modified guar gum

The degree of substitution (DS) is the average number of sodium carboxymethyl groups bound per anhydroglucose unit. This method is used to determine the number of substituent groups added to the guar gum backbone. From the DS one can find how many hydroxyl groups is converted into carboxymethyl group. Degree of substitution markedly affects the properties of the compound.

1 gm. of Na- CMGG was dissolved in known amount of water. Then this solution was passed through regenerated Amberlite IRA 96 anion exchange resinno. of times till it become acidic. Then solution was divided into two equal parts labeled as solution 1 and solution 2. The exhausted resin was regenerated by passing 1 N HCl solution (3-4 times) followed by washing with distilled water to remove any excess acid.

Solution1was taken into previously weighed beaker. The solution was heated until dryness on hot plate and then cooled and weighed Na-CMGG.

TABLE 1 : The effects of temperature on DS

Temperature (in °C)	NaOH (in ml)	Chloroacetic acid (in gms)	Time (in hours)	DS
40	10 (30%)	10	5	0.768
50				0.834
60				1.144
70				1.013

TABLE 2 : The amount of NaOH and its effect on DS

NaOH (in ml)	Temperature (in °C)	Chloroacetic acid (in gm)	Time (in hours)	DS
5 (30%)	60°C	10	5	0.212
10 (30%)				1.144
15 (30%)				1.012

Solution 2 was titrated against a standard solution of NaOH. Note down the burette reading andfind out the degree of substitution by following equation (1) & (2).

$$DS = \frac{0.162\,B}{1 - 0.58\,B} \quad (1)$$

Where,

$$B = \frac{\text{Volume of 1NNaOH used}}{\text{Weight of sample}} \quad (2)$$

Characterization of modified guar gum

The resulting products were characterized by FTIR spectroscopy using Perkin Elmerspectrum GX instrument, by the KBr pallet method.

RESULT AND DISCUSSION

Carboxymethyl guar gum (CMGG)

Carboxymethylation of guar gum is a consecutive two-step reaction proceeding with a strong-base- such as sodium hydroxide- that deprotonates the free hydroxyl groups (particularly, the hydroxyl group of (- CH_2OH) in guar gum) to form alkoxides, thereby increasing their nucleophilicity. Carboxymethyl groups are then formed in a reaction between guar alkoxides and chloro acetic acid.

Four parameters are selected to study their influence on the efficiency of the carboxymethylation process, and they are volume of NaOH, reaction time, weight of monochloro acetic acid and temperature. In this paper the dependent variables includes the degree of substitution (DS).

Effect of temperature on the degree of substitution

The carboxymethylation reaction is carried out in the range of 40°C-70°C keeping other parameters constant. It can be concluded from the TABLE-1 that DS increased with increase in temperature from 40°C-60°C but at 70°C DS obtained is almost same as obtained at 60°C. So we select 60°C as an optimum reaction temperature against 70°C because to maintain higher temperature, more energy consumption which leads to increase in production cost.

Effect of NaOH

The carboxymethylation reaction is carried out by varying the amount of NaOH from 5-15 ml is shown in TABLE 2. The DS is increase by increasing the amount of NaOH up to 10 ml, further increase in amount of NaOH results in to the decrease in DS. Increase in amount of NaOH leads to the degradation of polymer. If the amount of NaOH is decrease, number of free hydroxyl group deprotonates to form alkoxide is less which leads to lower value of DS.

Effect of chloroacetic acid

The carboxymethylation reaction is carried out in the range of 5-20 gm. keeping other parameters constant. It can be concluded from the table that DS increased with increase in amount of chloroacetic acid from 5-10 gm. Monochloro acetic acid reacts

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TABLE 3 : The amount of chloro acetic acid and its effect on DS

Chloroacetic acid (in gm)	NaOH (in ml)	Temperature (in ^{o}C)	Time (in hours)	DS
5	10 (30%)	60	5	0.368
10				1.144
15				0.836
20				0.768

TABLE 4 : The effect of time on DS

Time (in hours)	NaOH (in ml)	Temperature (in ^{o}C)	Chloroacetic acid (in gm)	DS
4	10 (30%)	60	10	0.401
5				0.598
6				1.144
7				1.006

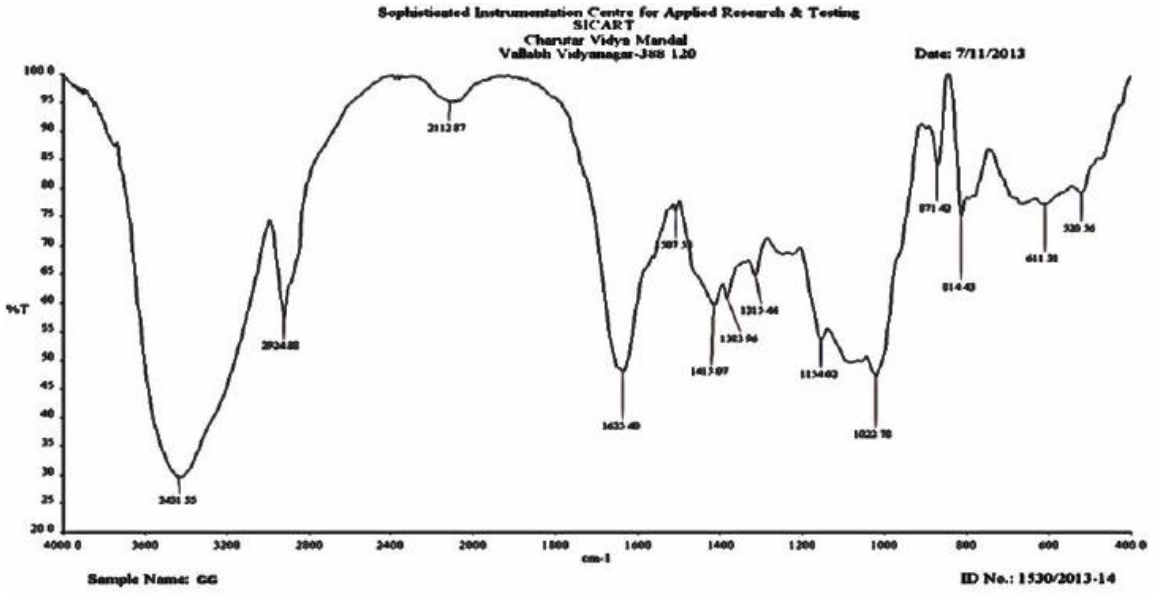

Figure : 2 IR spectra of GG

with alkoxides groups formed by reaction between guar gum and NaOH and converts them into caroxymethyl group. If the amount of monochloroacetic acid used is less than the less amount of carboxymethy groups formed which leads to low value of DS.

Effect of Time

The carboxymethylation reaction is carried out in the range of 4-7 hrs. keeping other parameters constant. It can be concluded from the table that DS increased with increase in time from 4-6 hrs. but DS decrease with further increase in temperature. It can be concluded that maximum DS is obtained by carrying reaction for 6 hrs. further increase in reaction time has no effect on the DS.

FTIR Analysis

The IR spectrum of guar gum and carboxymethyl guar gumwasshown in Figure: 2 and Figure: 3 respectively. The IR spectrum of carboxymethyl guar gum shown a reduced intensity of the absorption band located at 3439 cm^{-1}, as compared to guar gum IR spectrum due to -OH is stretching, indicating that some -OH group were carboxymethylated. The C-O symmetrical and asymetrical vibrations at a frequency of 1090.67 cm^{-1} and 1156.06 cm^{-1} confirms the incorporation of the carboxymethyl group on to the guar gum molecule, which is absent in the guar gum spectra.

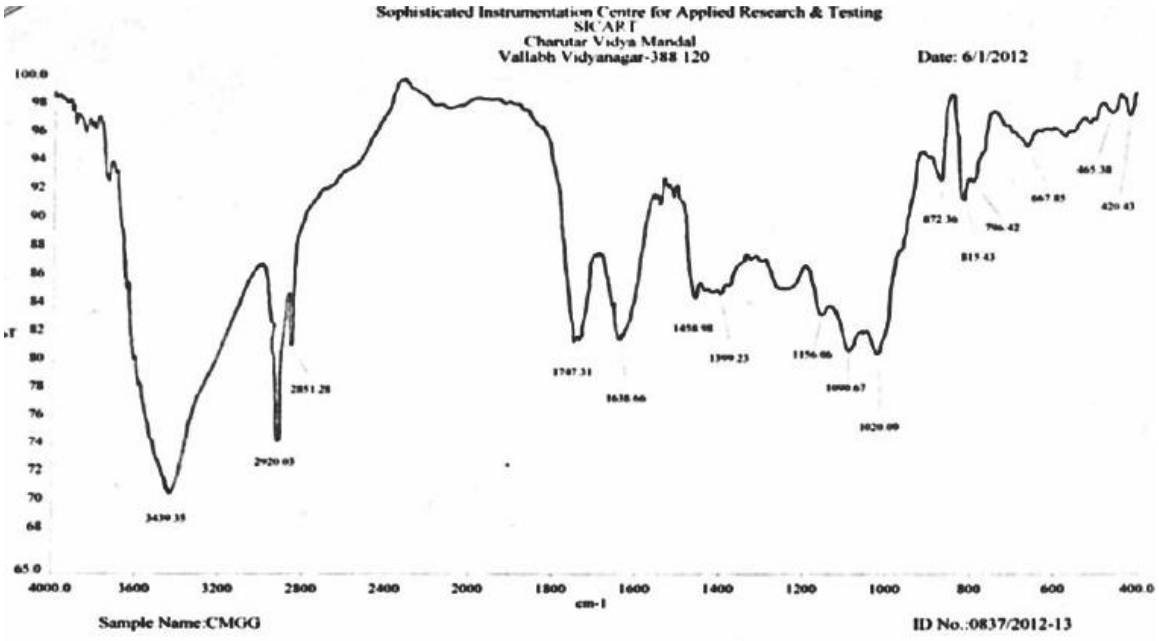

Figure 3 : IR spectra of Na-PCMGG

CONCLUSION

The carboxymethylation of guar gum carried out successfully. Carboxymethylationimproves the properties of guar gum especially, rate of hydration, viscosity and susceptibility to microbial contaminations. The best result for DS obtained by carrying reaction at 60°C for 5 hrs. by adding 10 ml.(30%) of NaOH and 10 gm. of chloro acetic acid. Modified guar gum has wide application in pharmaceutical industry as a drug carrier by grafting / crosslinking compound of interest.

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