Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbohydrate Polymers 58 (2004) 449–453

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Carbamoylethylation of guar gum

Brij Raj Sharma, Vineet Kumar*, P.L. Soni*

Chemistry Department, Center of Advance Studies in Chemistry of Forest Products, Forest Research Institute, P.O. New Forest, Dehradun 248006, India

Received 14 July 2003; revised 5 July 2004; accepted 9 August 2004
Available online 11 September 2004

Abstract

Carbamoylethylation of guar gum was carried out with acrylamide in presence of sodium hydroxide under different reaction conditions. Variables studied were concentration of sodium hydroxide, acrylamide, guar gum as well as reaction temperature and time. The nitrogen content, carboxyl content and total ether content were determined. Rheological properties of carbamoylethyl guar gum solutions showed non-*Newtonian* pseudoplastic behavior regardless of the %N. At a constant rate of shear, the apparent viscosity of carbamoylethyl guar gum solutions decreases with the increase in %N of the product.

Keywords: Guar gum; Carbamoylethylation

1. Introduction

The worldwide industrial importance of galactomannans from plant seeds hardly needs to be emphasized. The traditional role of seed galactomannans in industries has been as viscosity builder and water behavior modifier in aqueous systems. The functions of a seed gum useful for its commercial utilization depends mainly on its physical properties rather than its chemical structure or biological properties. In more sophisticated applications, it is generally possible to improve the physical properties by suitable chemical modifications.

As a part of our major research and development activities we have paid a great deal of attention to chemical modification and characterization of galactomannans especially *Cassia tora* and guar gum (Sharma, Kumar, & Soni, 2002; Sharma, Kumar, & Soni, 2003a–e; Soni, Naithani, Singh, & Kapoor, 2001; Soni, Singh, & Naithani, 2000) with a view to promote industrial utilization of galactomannan based products.

Incomplete hydration of guar gum (GG) at ambient temperatures, poor solution clarity and the desire for products with modified or special properties led to the development of a variety of commercial ether derivatives (DeGuia, Stackman, & Conciatori, 1978; Kamel, El-Thalouth, Amer, Ragheb, & Nassar, 1992; Lapasin, Pricl, & Tracanelli, 1991; Moe, Miller, & Buckley, 1952; Nordgren, 1968; Prabhanjan, Gharia, & Srivatsava, 1989; Prabhanjan, Gharia, & Srivatsava, 1990; Ragheb, Kamel, El-Thalouth, & Nassar, 1994; Tessler, 1981). Significant changes in properties occur when the GG molecule is substituted with the new functional groups. With a view that carbamoylethyl guar gum (CB-GG) may find better applications in comparison to native GG, chemical modification of GG via carbamoylethylation has been carried out to establish the optimum reaction conditions.

2. Materials and methods

2.1. Materials

Guar gum was obtained from the Hindustan Gums and Chemical Ltd, Bhiwani, Haryana, India. Acrylamide, sodium hydroxide, ethanol and acetic acid were of laboratory grade.

2.2. Methods

2.2.1. Carbamoylethylation

The carbamoylethylation reaction was performed in a 1L beaker containing distilled water (500 ml).

---

* Corresponding authors. Tel.: +911352752671; fax: +911352756865.
E-mail addresses: vineetkmadaan@yahoo.com (V. Kumar), soniplin@yahoo.co.in (P.L. Soni).

0144-8617/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2004.08.013

GG (0.030–0.092 mol) was added gradually to the beaker with constant stirring and heating at 60–70 °C till the formation of homogenous solution. The resulting solution was cooled to 30 °C followed by addition of sodium hydroxide (0.25–1.0 mol). After 30 min, acrylamide (AA) (0.03125–1.25 mol) was added. Continuous stirring was done during addition of both sodium hydroxide and acrylamide and the stirring was continued at 30 and 70 °C for desired period of time (1–4 h). The reaction mixture was cooled, neutralized with dilute acetic acid and precipitated by pouring the reaction contents in ethanol (1500 ml) with stirring. The precipitated product was centrifuged, filtered, washed with acetone and dried over calcium chloride under vacuum.

2.2.2. Analysis and measurements

- The nitrogen content of the CB-GG was determined by Kjeldhal method.
- The carboxyl content of the CB-GG was determined according to a reported method (Anonymous, 1999).
- The infrared spectra of CB-GG was run on JASCO FT-IR-5300 using KBr pellets in the range 700–4000 cm^{-1}.
- The rheological properties of the CB-GG solutions were determined at 25 °C using a Brookefield Digital Viscometer ‘RVTD’ Soughton, USA.
- The apparent viscosity was calculated using the following equation

$$\eta = \frac{\tau}{D}$$

where

η the apparent viscosity in centipoise (cps)
τ the shearing stress (dyne/cm^2)
D the rate of shear (s^{-1})

3. Results and discussion

Carbamoylethylation of GG was carried out by reacting it with AA in presence of sodium hydroxide under a variety of conditions. The variables studied were concentration of GG, sodium hydroxide, AA as well as temperature and duration of reaction. The reaction was confirmed by FTIR, which showed the appearance of amide group at 1635 cm^{-1}. The changes in the chemical structure of GG brought about by carbamoylethylation were assessed by the change in its physical properties such as solubility and rheology of CB-GG. In a system containing GG, sodium hydroxide, AA and water, the following reactions are expected to occur:

$$\text{GG–OH} + \text{CH}_2 = \text{CH–CONH}_2 \xrightarrow{\text{NaOH}} \text{GG–O–CH}_2\text{–CH}_2\text{–CONH}_2 \quad (1)$$

$$\text{GG–O–CH}_2\text{–CH}_2\text{CONH}_2 + \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{GG–O–CH}_2\text{–CH}_2\text{–COONa} + \text{NH}_3 \quad (2)$$

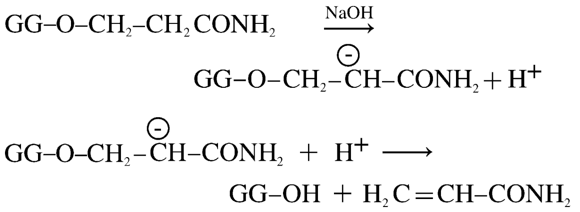
$$\text{CH}_2 = \text{CH–CONH}_2 + \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{CH}_2 = \text{CH–COONa} + \text{NH}_3 \quad (3)$$

Furthermore Bruson and Riener (1943) found that aqueous solution of acrylonitrile in presence of alkali give ethylene cyanohydrin, which further reacts with acrylonitrile yielding bis-2-cyanoethyl ether. In a similar way acrylamide in presence of alkali gives β-hydroxypropionamide, which further reacts with acrylamide to give bis-2-carbamoylethyl ether (Eqs. (4) and (5)) (Khalil, Bayazeed, Farag, & Hebeish, 1987).

$$\text{CH}_2 = \text{CH–CONH}_2 + \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{HO–CH}_2\text{–CH}_2\text{–CONH}_2 + \text{H}_2\text{O} \quad (4)$$

$$\text{CH}_2 = \text{CH–CONH}_2 + \text{HO–CH}_2\text{–CH}_2\text{–CONH}_2 \rightarrow \text{CONH}_2\text{–CH}_2\text{–CH}_2\text{–O–CH}_2\text{–CH}_2\text{–CONH}_2 \quad (5)$$

Also, fission of the ether linkage (Moe et al., 1952) takes place in CB-GG by β-elimination as shown in Eq. (6)



$$\text{GG–O–CH}_2\text{–CH}_2\text{CONH}_2 \xrightarrow{\text{NaOH}} \text{GG–O–CH}_2\text{–}\overset{\ominus}{\text{C}}\text{H–CONH}_2 + \text{H}^+$$

$$\text{GG–O–CH}_2\text{–}\overset{\ominus}{\text{C}}\text{H–CONH}_2 + \text{H}^+ \longrightarrow \text{GG–OH} + \text{H}_2\text{C=CH–CONH}_2 \quad (6)$$

3.1. Effect of duration and temperature

The effect of duration and temperature on increase in percent nitrogen (%N) and the carboxyl groups derived thereof on the CB-GG samples is shown in Table 1. The dependence of carbamoylethylation of GG on temperature and duration can be monitored in terms of nitrogen content, carboxyl content and total extent of etherification of the CB-GG samples.

3.1.1. Nitrogen content

Table 1 shows the variation of nitrogen content of the CB-GG with reaction time at different temperatures. As is evident, the nitrogen content is temperature and time dependent. For instance, at 30 °C the %N increases from 1.87 to 2.36 by increasing the reaction time from 1 to 2 h indicating that reaction suggested by Eq. (1) prevails over the other reactions as shown above. Further increase in reaction time resulted in decrease in nitrogen content and increase in –COOH content owing to conversion of some of the amide groups of the CB-GG to carboxyl groups (Eqs. (2) and (3)) via hydrolysis (El-Molla, Abdel Rahman, & El-Thalouth, 1998; Hebeish, El-Thalouth, & Kashouti, 1981; Hebeish & Khalil, 1988; Khalil, Beliakova, & Aly, 2001) and GG–OH via β-elimination (Eq. (6)). Thus optimum duration for the carbamoylethylation of GG was

Table 1
Dependence of %N of CB-GG and carboxyl groups derived thereof on time of carbamoylethylation and sum of amide and carboxyl contents of the CB-GG samples prepared at different reaction temperature and time

Reaction time (h)	Reaction temperature (°C)					
	30			70		
	–CONH$_2$ (%N)	–COOH (%COOH)	Total ether	–CONH$_2$ (%N)	–COOH (%COOH)	Total ether
1	133.57 (1.87)	31.90 (1.44)	165.47	69.28 (0.97)	38.95 (1.75)	108.23
2	168.57 (2.36)	38.12 (1.72)	206.69	92.14 (1.29)	48.80 (2.20)	140.94
3	140.0 (1.96)	48.42 (2.18)	188.42	50.00 (0.70)	61.52 (2.77)	111.52
4	115.71 (1.62)	54.57 (2.46)	170.28	44.28 (0.62)	71.15 (3.20)	115.43

Reaction conditions: [GG] = 0.061 mol; [NaOH] = 0.75 mol; [AA] = 0.50 mol; total reaction volume = 500 ml; amide content, carboxyl content and total ether content in mmol; values in parentheses show %N and %COOH.

found to be 2 h. At 70 °C, the increase in nitrogen content was also optimized in 2 h. However, on comparing the data of the extent of reaction at 30 and 70 °C, it was found that at higher temperature reaction is adversely affected. This shows that carbamoylethylation is favored at 30 °C.

3.1.2. Carboxyl content

The carboxyl content of the CB-GG samples prepared at 30 and 70 °C for different periods of time (1–4 h) is shown in Table 1. It reveals that the carboxyl content increases by increasing the duration of reaction as well as reaction temperature (Table 1). It proves that hydrolysis of amide groups to carboxyl groups takes place. This is evident that the amide groups are converted to carboxyl groups (Eq. (2)). Such conversions seem to occur early from the beginning of the reaction and concurrently with the carbamoylethylation reaction (Eq. (1)). Increase in reaction temperature acts in favor of these conversions since the carboxyl content is higher at higher temperature with the concomitant decrease in %N at higher temperature. This is in accordance with the results reported in the literature (Hebeish et al., 1981; Hebeish & Khalil, 1988; Khalil et al., 2001).

3.1.3. Total extent of reaction

Total extent of the reaction occurring between GG and AA, expressed as the sum of amide content and carboxyl content is given in Table 1. Calculation of amide content and carboxyl content are based on %N and %COOH. Total extent of etherification is higher at 30 °C in comparison to 70 °C on increasing the reaction time from 1 to 4 h. Maximum carbamoylethylation and total extent of etherification is highest at 2 h at both the temperatures. The decrease in total extent of etherification after 2 h may be attributed to fission of the ether linkage by β-elimination (Eq. (6)).

Table 2
Effect of sodium hydroxide concentration on %N of the CB-GG samples

Concentration of NaOH (mol)	%N
0.25	1.88
0.5	2.72
0.75	3.18
1.0	2.58

Reaction conditions: [GG] = 0.061 mol; [AA] = 1.0 mol; time = 2 h; temperature = 30 °C; total reaction volume = 500 ml.

3.2. Effect of sodium hydroxide concentration

Table 2 shows the nitrogen content of the CB-GG prepared in presence of different concentrations of sodium hydroxide (0.25–1.0 mol) at 30 °C for 2 h. It is seen that the extent of the carbamoylethylation reaction of GG increases significantly by increasing sodium hydroxide concentration upto 0.75 mol. Further increase in sodium hydroxide concentration is accompanied by a decrease in the nitrogen content. Sodium hydroxide seems to perform following functions: (a) catalyzing the reaction, (b) swelling the GG, and (c) hydrolyzing the amide groups and fission of the ether linkage. Current data suggest that factors (a) and (b) are favored upon using sodium hydroxide concentration 0.75 mol thereby giving rise to higher extents of reaction. Above 0.75 mol sodium hydroxide, factor (c) prevails over (a) and (b) and, as a result, extent of reaction decreases

Table 3
Effect of acrylamide concentration on %N of CB-GG samples

Concentration of AA (mol)	%N
0.03125	0.69
0.0625	0.95
0.125	1.17
0.25	1.72
0.50	2.36
0.75	2.97
1.0	3.18
1.25	2.20

Reaction conditions: [GG] = 0.0.061 mol; [NaOH] = 0.75 mol; time = 2 h; temperature = 30 °C; total reaction volume = 500 ml.

Table 4
Effect of GG concentration on %N of CB-GG samples

Concentration of GG (mol)	%N
0.030	2.59
0.061	3.18
0.092	3.07

Reaction conditions: [AA] = 1.0 mol; [NaOH] = 0.75 mol; time = 2 h; temperature = 30 °C; total reaction volume = 500 ml.

Table 5
Apparent viscosity of CB-GG solution of different nitrogen content at various rates of shear

Shear rate (s^{-1})	Apparent viscosity (cps) of CB-GG samples after 3 and 120 h at 25 °C (3% solution)							
	0.69%N	0.95%N	1.17%N	1.72%N	2.36%N	2.97%N	3.18%N	3.2%N
2.5	134160* (139510*)	55890 (56160)	39160 (39870)	26860 (27220)	19665 (20100)	16810 (17080)	11790 (12000)	8650 (8790)
5	90550* (91670*)	31460 (31990)	25560 (26120)	15610 (15975)	11290 (11760)	10420 (10750)	9570 (9810)	4660 (4800)
12.5	41600* (42120*)	–	11250 (11785)	9220 (9890)	7510 (7950)	5210 (5910)	4460 (4620)	2210 (2450)
25	20725 (21000*)	–	–	–	–	–	–	–

Spindle SC-29; (*) Spindle-RV-7; (–) Instrument shows error; values in parentheses show viscosity after 120 h.

(Khalil et al., 1987). Also at higher concentration of sodium hydroxide, the fission of the ether linkage by β-elimination (Eq. (6)) is enhanced finally decreasing the carbamoylethylation reaction.

3.3. *Effect of acrylamide concentration*

Table 3 shows the effect of AA concentration (0.03125–1.25 mol) on %N of CB-GG samples taking optimum concentration of sodium hydroxide (0.75 mol). It was observed that by increasing the AA concentration upto 1.0 mol, the %N increases and decreases afterwards. The decrease in %N on using 1.25 mol of acrylamide occurs due to side reactions (Eqs. (3)–(5), which are favored at higher concentration of AA. Similar type of observation has also been reported in the literature (Hebeish & Khalil, 1988). Thus, optimum concentration of AA for carbamoylethylation of GG was found as 1.0 mol.

3.4. *Effect of GG concentration*

Table 4 shows the dependence of the extent of the reaction (%N) of CB-GG samples on GG concentration. It is clear that the %N increases with the increase in concentration of GG upto 0.061 mol and thereafter decreases. The increase in %N may be due to increase in number of GG-alkoxides with increase in concentration of GG, but after optimum concentration, there is a decrease in %N which may be due to insufficient diffusion of other reactants in the reaction mixture (Bhattacharya, Singhal, & Kulkarni, 1995; Sharma et al., 2003c; Stojanovic, Jeremic, & Jovanovic, 2000) because of high viscosity of the reaction mixture beyond 0.061 mol concentration of GG.

4. Rheological properties

Hydrocolloids and their derivatives are generally used as viscosifier and thickener in the form of solutions; therefore, it is of interest to study the rheological properties of their solutions. The solutions of CB-GG were prepared in 3% concentration and their rheological properties were studied (Table 5). It shows that regardless of the carbamoylethyl content, the aqueous CB-GG solutions are characterized by non-*Newtonian* pseudoplastic behavior (Yamakawa, 1971).

Apparent viscosity of the aforementioned solutions at various rates of shear before and after storing for 120 h is given in Table 5. Data show that the %N plays a dominant role on the apparent viscosity of the product at any specific rate of shear. At a constant rate of shear, the apparent viscosity decreases as the %N of the product increases. Results show that the apparent viscosity remains stable upto 120 h for all the samples examined. The slight increase in the apparent viscosity of these derivatives by storing reflects its stability, which may be due to the increase in the swellability of molecules by the presence of carboxyethyl groups.

5. Conclusion

The optimum reaction conditions for carbamoylethylation of GG are: [GG] = 0.061 mol; [NaOH] = 0.75 mol; [AA] = 1.0 mol; temperature = 30 °C, time = 2 h; total reaction volume = 500 ml. CB-GG shows good cold-water solubility, solution stability, solution clarity and increased viscosity. With all these properties the CB-GG can be exploited in a much better way for its industrial applications.

References

Anonymous (1999). *Determination of carboxyl groups in starch. ISI-10-2e*. Denmark: International Starch Institute, Science Park Aarhus.

Bhattacharya, D., Singhal, R. S., & Kulkarni, P. R. (1995). A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch. *Carbohydrate Polymers*, *27*, 247–253.

Bruson, H. A., & Riener, T. W. (1943). The chemistry of acrylonitrile. IV. Cyanoethylation of active hydrogen groups. *Journal of American Chemical Society*, *65*, 23.

Deguia, A. A., Stackman, R. W., & Conciatori, A.B. US Patent, 4, 169, 945. De Guia, A. A., & Stackman, R. W. (1979). *Chemistry Abstracts*, *91*, 194929g.

El-Molla, M. M., Abdel Rahman, A. A., & El-Thalouth, I. A. (1998). Chemical modification of Fenugreek gum: Part I-carbamoylethylation. *American Dyestuff Reporter*, *87*(9), 56–62.

Hebeish, A., El-Thalouth, I. A., & Kashouti, E. M. A. (1981). Chemical modification of starch. II. Cyanoethylation. *Journal of Applied Polymer Science*, *26*, 171–176.

Hebeish, A., & Khalil, M. I. (1988). Characterization for the reaction products for starch and acrylonitrile. *Starch/Stärke*, *40*(3), 104–107.

Kamel, M., El-Thalouth, I. A., Amer, M. A., Ragheb, A., & Nassar, S. H. (1992). Chemical modification of guaran gum. Part I: Carboxymethylation in aqueous medium. *Starch/Stärke*, *44*(11), 433–437.

Khalil, M. I., Bayazeed, A., Farag, S., & Hebeish, A. (1987). Chemical modification of starch via reaction with acrylamide. *Starch/Stärke*, *39*(9), 311–318.

Khalil, M. I., Beliakova, M. K., & Aly, A. A. (2001). Preparation of some starch ethers using the semi-dry state process. *Carbohydrate Polymers*, *46*, 217–226.

Lapasin, R., Pricl, S., & Tracanelli, P. (1991). Rheology of hydroxyethyl guar gum derivatives. *Carbohydrate Polymers*, *14*, 411–427.

Moe, O. A., Miller, E. S., & Buckley, M. I. (1952). Investigation of the reserve carbohydrates of leguminous seeds. II. Derivatives. *Journal of American Chemical Society*, *74*, 1325–1327.

Nordgren, R. US Patent, 3,346,555. Nordgren, R. (1968). *Chemical Abstracts*, *68*, 90222e.

Prabhanjan, H., Gharia, M. M., & Srivastava, H. C. (1989). Guar gum derivatives. Part I: preparation and properties. *Carbohydrate Polymers*, *11*, 279–292.

Prabhanjan, H., Gharia, M. M., & Srivastava, H. C. (1990). Guar gum derivatives. II. Foaming properties of hydroxyalkyl derivatives. *Carbohydrate Polymers*, *12*, 1–7.

Ragheb, A. A., Kamel, M., El-Thalouth, I. A., & Nassar, S. H. (1994). Chemical modification of guaran gum. Part 3: carboxymethylation in non-aqueous medium. *Starch/Stärke*, *46*(11), 443–446.

Sharma, B. R., Kumar, V, & Soni, P. L. (2002). Graft copolymerization of acrylamide onto *Cassia tora* gum. *Journal of Applied Polymer Science*, *86*(13), 3250–3255.

Sharma, B. R., Kumar, V., & Soni, P. L. (2003a). Ce(IV)-ion initiated graft copolymerization of methyl methacrylate onto guar gum. *Journal of the Macromolecular Science, Part A. Pure and Applied Chemistry*, *40*(1), 49–60.

Sharma, B. R., Kumar, V., & Soni, P. L. (2003b). Cyanoethylation of *Cassia tora* gum. *Starch/Stärke*, *55*(1), 38–42.

Sharma, B. R., Kumar, V., & Soni, P. L. (2003c). Carbamoylethylation of *Cassia tora* gum. *Carbohydrate Polymers*, *54*(2), 143–147.

Sharma, B. R., Kumar, V., & Soni, P. L. (2003d). Graft copolymerization of acrylonitrile onto *Cassia tora* gum using ceric ammonium nitrate-nitric acid as redox initiator. *Journal of Applied Polymer Science*, *90*(1), 129–136.

Sharma, B. R., Kumar, V., Soni, P. L., & Sharma, P. (2003e). Carboxymethylation of *Cassia tora* gum. *Journal of Applied Polymer Science*, *89*(12), 3216–3219.

Soni, P. L., Naithani, S., Singh, S. V., & Kapoor, S. K. (2001). Natural and modified guar and *Cassia tora* seed gum as wet end additive vis-à-vis flocculant. *IPPTA Convention Issue* , 97–107.

Soni, P. L., Singh, S. V., & Naithani, S. (2000). Modification of *Cassia tora* seed gum and its application as beater additive in paper making. *Inpaper International*, *5*(1), 14–17.

Stojanovic, Z., Jeremic, K., & Jovanovic, S. (2000). Synthesis of carboxymethyl starch. *Starch/Stärke*, *52*, 413–419.

Tessler, M. M. US Patent, 4,276,414. Tessler, M. M. (1981). *Chemical Abstracts*, *95*, 134697c.

Yamakawa, H. (1971). *Modern theory of polymer solutions*. New York: Harper and Row.