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Carbohydrate Polymers 54 (2003) 143–147
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Carbamoylethylation of *Cassia tora* gum

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Received 11 October 2002; revised 18 March 2003; accepted 4 April 2003

Abstract

Carbamoylethylation of *Cassia tora* gum was carried out with acrylamide in presence of sodium hydroxide under different reaction conditions. Variables studied were concentration of sodium hydroxide, acrylamide, *Cassia tora* gum as well as reaction temperature and time. The nitrogen content, carboxyl content and total ether content were determined. The optimum condition for preparing carbamoylethyl *Cassia tora* gum (%N = 3.24) comprised concentration of acrylamide (1.12 mol), sodium hydroxide (1.25 mol), *Cassia tora* gum (0.197 mol) at 30 °C for 1 h. Rheological properties of carbamoylethyl *Cassia tora* gum solutions showed non-*Newtonian* pseudoplastic behavior regardless of the %N. At a constant rate of shear the apparent viscosity of carbamoylethyl *Cassia tora* gum solutions increase with the increase in %N of the product.

Keywords: *Cassia tora* gum; Carbamoylethylation

1. Introduction

Seed gums are important agrochemical used in various industries worldwide. The growing industrial utility of these gums or their modified derivatives in the field of paper, textile, petroleum recovery and pharmaceutical industries has resulted in an impetus in India for intensified research on new sources of gums and their modified products. *Cassia tora* gum (CTG) derived from the seeds of *Cassia tora* Linn. is a common herbaceous annual occurring weed throughout India. The pods are 15–22.5 cm long and up to 0.625 cm in diameter containing flattened dark seeds. The *Cassia tora* seed is composed of hull (27%), endosperm (32%) and germ (41%) (Soni & Pal, 1996). Methylation studies showed that backbone of the polysaccharide consists of $1 \rightarrow 4$ linked D-mannopyranose and D-glucopyranose units. In India, it is perhaps one of the cheapest gums available, however, because of few drawbacks such as very low solubility in water (cold water 22.8%, hot water (80 °C) 50.8% and water insolubles 27.93%) (Soni & Pal, 1996), dull color of gum solution and fast biodegradability, CTG is found wanting in several specialty end-use properties. Very few reports are there on the chemical modification of CTG to enhance and to improve the quality and acceptability of CTG products (Sharma, Kumar, & Soni, 2002; Sharma, Kumar, & Soni, 2003a,b; Sharma, Kumar, Soni, & Sharma, 2003c; Soni, Naithani, Singh, & Kapoor, 2001; Soni, Singh, & Naithani, 2000). With a view that carbamoylethyl-CTG (CB-CTG) may find better applications in comparison to native CTG, chemical modification of CTG via carbamoylethylation has been carried out to establish the optimum reaction conditions.

2. Materials and methods

2.1. Materials

CTG was isolated from seeds as per the method described by Soni and Pal (1996). 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 250 ml beaker containing distilled water (100 ml). CTG (0.098–0.246 mol) was added gradually to the beaker with stirring and heating at 60–70 °C until the formation of

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0144-8617/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0144-8617(03)00132-2

homogenous solution. The CTG solution was cooled to 30 °C and then sodium hydroxide (0.625–1.875 mol) dissolved in 25 ml distilled water was added to the CTG solution with continuous stirring. After 30 min, acrylamide (AA) (0.45–1.57 mol) was added with continuous stirring. The reaction mixture was stirred at 30 and 70 °C for a certain period of time (0.5–4 h). The reaction mixture was cooled and neutralized with dilute acetic acid and precipitated by pouring the reaction contents in the ethanol with vigorous 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-CTG was determined by Kjeldhal method.
- The carboxyl content of the CB-CTG was determined according to a reported method (Anonymous, 1999).
- The infrared spectra of CB-CTG was run on JASCO FT/IR-5300 using KBr pellets in the range 700–4000 cm^{-1}.
- The rheological properties of the CB-CTG solutions were determined at 25 °C using a Brookefield Digital Viscometer 'RVTD' Soughton, USA.
- The molecular weight was determined based on intrinsic viscosity (η) using Mark–Houwink–Sakurada (MHS) equation $\eta = kM^a$ where both k and a are constants for a given polysaccharide–solvent system (Lapasin & Pricl, 1995).
- 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 CTG was carried out by reacting it with AA in presence of sodium hydroxide under a variety of conditions. The variables studied were concentration of CTG, 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 CTG brought about by carbamoylethylation were assessed by the change in its physical properties such as solubility and rheology of CB-CTG. In a system containing CTG, sodium hydroxide, AA and water, the following reactions are expected to occur:

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

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

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

Furthermore Bruson and Reiner (1943) found that water adds to acrylamide in presence of alkali to give ethylene cyanohydrin which further reacts with acrylamide yielding bis-2-cyanoethyl ether as shown below:

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

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

Also, Mac Gregor (1951) has reported the fission of the ether linkage in alkaline medium as follows:

$$\text{CTG-O–CH}_2\text{–CH}_2\text{COONa} + \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{CTG-OH} + \text{OH–CH}_2\text{–CH}_2\text{COONa} \quad (6)$$

3.1. Effect of duration and temperature

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

Table 1
Dependence of %N of CB-CTG and carboxyl groups derived thereof on time of carbamoylethylation

Reaction time (h)	Reaction temperature					
	30 °C			70 °C		
	Yield (%)	%N	%Carboxyl content	Yield (%)	%N	%Carboxyl content
0.5	95.0	1.91	0.9495	87.6	0.97	1.1081
1	97.5	2.25	1.6413	89.5	1.16	1.8765
2	96.2	2.16	2.0385	88.4	1.11	2.3973
3	94.3	1.85	2.2893	85.8	0.90	2.7765
4	93.8	1.76	2.7472	83.2	0.77	3.0892

Reaction conditions: [CTG] = 0.246 mol; [NaOH] = 1.25 mol; [AA] = 0.67 mol; Total reaction volume = 125 ml.

3.1.1. Nitrogen content

Table 1 shows the variation of %N of the CB-CTG with reaction time at different temperatures. As is evident, the %N is temperature and time dependent. For instance, at 30 °C the %N increases from 1.91 to 2.25% by increasing the reaction time from 0.5 to 1 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 %N owing to conversion of some of the amide groups of the CB-CTG to carboxyl groups Eqs. (2)–(6) via hydrolysis (El-Molla, Abdel Rahman, & El-Thalouth, 1998; Hebeish, El-Thalouth, & Kashouti, 1981; Hebeish & Khalil, 1988; Khalil, Beliakova, & Aly, 2001;). Thus, 1 h is the optimum duration for the carbamoylethylation of CTG. At 70 °C, the increase in %N was also optimized in 1 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-CTG samples prepared at 30 and 70 °C for different periods of time (0.5–4 h) is shown in Table 1. It reveals that the carboxyl content increases by increasing the duration of reaction as well as temperature. This is rather a proof 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). 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, El-Thalouth, & Kashouti, 1981; Hebeish & Khalil, 1988; Khalil, Beliakova, & Aly, 2001).

3.1.3. Total extent of reaction

Table 2 shows the total extent of the reaction occurring between CTG and AA, expressed as the sum of nitrogen content and carboxyl content (in mmol/100 g sample). Calculation of nitrogen content and carboxyl content are based on the data of Table 1. Total extent of etherification is higher at 30 °C in comparison to 70 °C on increasing the reaction time from 0.5 to 4 h. It also shows that despite maximum carbamoylethylation at 1 h, 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 hydrolysis of the ether linkage Eq. (6).

Table 2
Sum of amide and carboxyl contents of the CB-CTG samples prepared at different reaction temperature and time

Reaction time (h)	Reaction temperature					
	30 °C			70 °C		
	−CONH2	−COOH	Total	−CONH2	−COOH	Total
0.5	136.42	21.10	157.52	69.28	24.62	93.90
1	160.71	36.47	197.18	82.85	41.70	124.55
2	154.28	45.30	199.58	79.28	53.27	132.55
3	132.14	50.87	183.01	64.28	61.70	125.98
4	125.71	61.05	186.76	55.00	68.65	123.65

Nitrogen content, carboxyl content and total ether content in mmol/100 g sample.

3.2. Effect of sodium hydroxide concentration

Table 3 shows the nitrogen content of the CB-CTG prepared in presence of different concentrations of sodium hydroxide (0.625–1.875 mol) at 30 °C for 1 h. It is seen that the extent of the carbamoylethylation reaction of CTG increases significantly by increasing sodium hydroxide concentration up to 1.25 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 CTG, and (c) hydrolyzing the amide groups in acrylamide and CB-CTG. Current data suggest that factors (a) and (b) are favored upon using sodium hydroxide concentration 1.25 mol thereby giving rise to higher extents of reaction. Above 1.25 mol sodium hydroxide, factor (c) prevails over (a) and (b) and, as a result, extent of reaction decreases (Khalil, Bayazeed, Farag, & Hebeish, 1987).

3.2.1. Alkaline degradation

Polysaccharides are degraded in the presence of alkali. The main reaction that takes place is peeling off the polysaccharide chain from the reducing end, the cleaved products appearing as saccharinic acids (Prabhanjan, Gharia, & Srivastava, 1989; Whistler & BeMiller, 1958; Whistler & BeMiller, 1961).

The extent of degradation was determined based on molecular weight determination of native CTG and alkali treated CTG using intrinsic viscosity method. The molecular weight of the CTG was determined as 3.605×10^5 amu whereas the molecular weight of alkali treated CTG under the experimental conditions was found to

Table 3
Effect of sodium hydroxide concentration on %N of the CB-CTG samples

Concentration of NaOH (mol)	%N
0.625	2.02
1.250	2.25
1.875	1.92

Reaction conditions: [CTG] = 0.246 mol; [AA] = 0.67 mol; Time = 1 h; Temperature = 30 °C; Total reaction volume = 125 ml.

Table 4
Effect of acrylamide concentration on %N of CB-CTG samples

Concentration of AA (mol)	%N
0.45	1.79
0.67	2.25
0.90	2.65
1.12	3.19
1.35	3.20
1.57	3.21

Reaction conditions: [CTG] = 0.246 mol; [NaOH] = 1.25 mol; Time = 1 h; Temperature = 30 °C; Total reaction volume = 125 ml.

Table 5
Effect of CTG concentration on %N of CB-CTG samples

Concentration of CTG (mol)	%N
0.098	2.14
0.148	2.66
0.197	3.24
0.246	3.19

Reaction conditions: [AA] = 1.12 mol; [NaOH] = 1.25 mol; Time = 1 h; Temperature = 30 °C; Total reaction volume = 125 ml.

be 2.386×10^5 amu. This shows degradation of CTG to the extent of 34%.

3.3. Effect of acrylamide concentration

Table 4 shows the effect of AA concentration on %N of CB-CTG samples taking optimum concentration of sodium hydroxide (1.25 mol). Results show the distinct pattern of %N increase on increasing the concentration of AA (0.45–1.57 mol), which gets optimized at 1.12 mol. No significant increase in %N occurs on further increase in the concentration of AA beyond 1.12 mol by using the optimum dose of sodium hydroxide concentration. It shows that enough CTG-alkoxide was not available for reaction with excess AA and may have been subjected to side reactions as shown in Eqs. (4)–(6). Similar type of observation has also been reported in the literature (Hebeish & Khalil, 1988). Thus, optimum concentration of AA for carbamoylethylation of CTG was found as 1.12 mol.

3.4. Effect of CTG concentration

Table 5 shows the dependence of the extent of the reaction (%N increased) of CB-CTG samples on CTG concentration. It is clear that the %N increases as we increase the concentration of CTG up to 0.197 mol and thereafter decreases. The increase in %N may be due to increase in number of CTG-alkoxides with increase in concentration of CTG, but after optimum concentration, there is a decrease in %N which may be due to insufficient diffusion of other reactants in the reaction mixture because of high viscosity of the reaction mixture beyond 0.197 mol concentration of CTG.

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-CTG were prepared in 3% concentration and their rheological properties were studied (Tables 6 and 7). It shows that regardless of the carbamoylethyl content, the aqueous CB-CTG 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 72 h are given in Tables 6 and 7. 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 increases as the %N of the product increases. At a rate of shear 3.4 s^{-1} the apparent viscosity increases from 2950 cps (1.79 %N) to 3500 cps (3.19 %N). The increase in apparent viscosity due to increase in the %N may be attributed to increase in the hydrodynamic volume (Maier, Anderson, Karl, Magnuson, & Whistler, 1993). Results also show that increase in concentration of alkali has a detrimental effect on the extent of reaction as well as on

Table 6
Apparent viscosity of CB-CTG solution of different nitrogen content at various rates of shear

Shear rate (s^{-1})	Apparent viscosity (cps) of CB-CTG samples at 25 °C (3% solution), Sodium hydroxide (1.25 mol)											
	0.45 mol AA, 1.79% N		0.67 mol AA, 2.25% N		0.90 mol AA, 2.65% N		1.12 mol AA, 3.19% N		1.35 mol AA, 3.20% N		1.57 mol AA, 3.21% N	
	I	II	I	II	I	II	I	II	I	II	I	II
3.4	2950	3625	3025	3825	3300	4050	3500	4375	3510	4415	3565	4475
6.8	2675	3300	2825	3565	3135	3850	3350	4075	3365	4135	3385	4215
17	2335	2925	2610	3060	2865	3610	3080	3375	3090	3745	3115	3755

I: Viscosity after 3 h; II: Viscosity after 72 h; Spindle SC-27.

Table 7
Effect of sodium hydroxide concentration on apparent viscosity of CB-CTG solution of different nitrogen content at various rates of shear

Shear rate (s^{-1})	Concentration of sodium hydroxide					
	0.625 mol, 2.02% N		1.25 mol, 2.25% N		1.875 mol, 1.92% N	
	I	II	I	II	I	II
3.4	2375	3025	3025	3825	1975	2450
6.8	2200	2775	2825	3565	1740	2135
17	2070	2510	2610	3060	1590	1995
34	1845	2145	–	–	1345	1695

I: viscosity after 3 h; II: viscosity after 72 h; Spindle SC-27. Reaction conditions: [CTG] = 0.246 mol; [AA] = 0.67 mol; Time = 1 h; Temperature = 30 °C; Total reaction volume = 125 ml. (–) Instrument shows error.

apparent viscosity; for example, by keeping the same rate of shear (3.4 s^{-1}) and concentration of AA (0.67 mol) the apparent viscosity drops from 3025 to 1975 cps by increasing the alkali concentration from 1.25 to 1.875 mol. Results show that the apparent viscosity remains stable up to 72 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 CTG are: [CTG] = 0.197 mol; [NaOH] = 1.25 mol; [AA] = 1.12 mol; Temperature = 30 °C, Time = 1 h; Total reaction volume = 125 ml. CB-CTG shows good cold water solubility, solution stability, solution clarity and increased viscosity. With all these properties the CB-CTG can be exploited in a much better way for its industrial applications.

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