Carboxymethylation of *Cassia tora* Gum

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

Center for Advanced Studies in Chemistry of Forest Products, Forest Research Institute, Dehra Dun 248 006, India

ABSTRACT: The preparation of carboxymethyl (CM)–*Cassia tora* gum (CTG) with monochloroacetic acid and sodium hydroxide was investigated under different reaction conditions. The carboxymethylation reaction was studied with respect to the degree of substitution of CM–CTG. The variables studied were the concentration of reactants, methanol–water ratio (solvent), reaction time, and reaction temperature. Carboxymethylation of CTG increased its solubility in cold water and the stability of its paste to microorganisms. Regardless of the degree of substitution of these products, their aqueous solutions were characterized by non-Newtonian pseudoplastic behavior. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3216–3219, 2003

Key words: polysaccharides; rheology; modification; viscosity

INTRODUCTION

Cassia tora gum (CTG) is derived from the seeds of *C. tora* Linn, a common herbaceous annual weed occurring throughout India. The pods are 15–22.5 cm long and up to 0.625 cm in diameter and contain flattened dark seeds. The *C. tora* seed is composed of hull (27%), endosperm (32%), and germ (41%). Methylation studies have shown that backbone of the polysaccharide consists of 1→4 linked D-mannopyranose and D-glucopyranose units.[1] In India, it is perhaps one of the cheapest gums available; however, because of a few drawbacks, such as a very low solubility in water [cold water 22.8%, hot water (80°C) 50.8%, and water insolubles 27.93%],[1] dull color of the gum solution, and fast biodegradability, CTG is wanting in several specialty end-use properties. There are very few reports on the chemical modification of CTG[2–6] to enhance and improve the quality and acceptability of its products. With the opinion that carboxymethyl (CM)–CTG may find better applications in comparison to native CTG, we undertook a systematic study concerning the chemical modification of CTG via carboxymethylation to establish the optimum reaction conditions for the preparation of CM–CTG in our laboratory.

EXPERIMENTAL

Materials

Gum from the *C. tora* seed was isolated according to the method described by Soni.[7] Monochloroacetic acid (MCA), sodium hydroxide, methanol, and hydrochloric acid were laboratory reagent grade (S. D. Fine-Chem, Ltd., Mumbai, India).

Method

The synthesis of CM–CTG was carried out as follows: CTG (0.03 mol) was dispersed in aqueous methanol (30 : 70 to 10 : 90; 166.65 mL) containing 0.100−0.175 mol of alkali at 30°C with continuous stirring for 15 min followed by the addition of MCA (0.042−0.095 mol). It was allowed to react at 30°C, 50°C, and reflux temperature for 30−180 min in a constant-temperature water bath. The reaction mixture was occasionally shaken during the course of the reaction. After the completion of the reaction, the product was filtered on a G-3 sintered glass crucible, dissolved in water, and neutralized with dilute HCl (1 : 1 v/v). The resultant solution was precipitated with methanol. The precipitated mass (CM–CTG) was centrifuged at 2500 rpm for 30 min; the centrifugate was decanted out, and the product was washed twice with aqueous methanol followed by pure methanol on a G-3 sintered glass crucible *in vacuo*. It was dried overnight at 45°C in a vacuum oven.

Analysis and measurements

Determination of the degree of substitution (DS)

The DS of CM–CTG was determined by a method described elsewhere.[8]

Determination of the rheological properties of CM–CTG

The rheological properties were determined with a Brookfield digital viscometer (model RVTD, Stough-

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TABLE I
Effect of Sodium Hydroxide Concentration

Concentration of NaOH (mol/L)	DS
0.100	0.050
0.125	0.069
0.150	0.058
0.175	0.039

Reaction conditions: [CTG] = 0.03 mol/L, [MCA] = 0.052 mol/L, duration = 60 min, temperature at reflux, and solvent medium = 80 : 20 methanol–water.

ton) at the following experimental conditions: (1) a range of shear rate between 3.4 and 17 s^{-1}, (2) a temperature of 25 ± 1°C, and (3) the apparent viscosity of 1 and 2% solution of CM-CTG was calculated using the following formula:[9]

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

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

RESULTS AND DISCUSSION

CTG in the presence of sodium hydroxide reacts with MCA to yield CM–CTG as shown:

$$CTG\text{—}OH + Cl\text{—}CH_2\text{—}COOH \xrightarrow{NaOH}$$

$$CTG\text{—}O\text{—}CH_2COONa + NaCl + H_2O \quad (1)$$
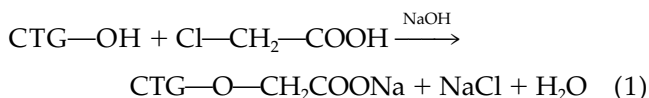
The effect of influencing factors on the reaction, such as the concentration of sodium hydroxide, the concentration of MCA, the duration and temperature of reaction, and the ratio of reaction medium (methanol–water), were optimized with respect to DS.

TABLE II
Effect of MCA Concentration

Concentration of MCA (mol/L)	DS
0.042	0.040
0.052	0.069
0.063	0.071
0.074	0.090
0.084	0.099
0.095	0.079

Reaction conditions: [CTG] = 0.03 mol/L, [NaOH] = 0.125 mol/L, duration = 60 min, temperature at reflux, and solvent medium = 80 : 20 methanol–water.

TABLE III
Effect of the Duration of the Reaction

Duration of reaction (min)	DS
30	0.065
60	0.099
120	0.096
180	0.094

Reaction conditions: [CTG] = 0.03 mol/L, [NaOH] = 0.125 mol/L, [MCA] = 0.084 mol/L, temperature at reflux, solvent medium = 80 : 20 methanol–water.

Effect of sodium hydroxide concentration

The concentration of NaOH in the reaction mixture was varied from 0.100 to 0.175 mol/L as shown in Table I. With increasing NaOH concentration up to 0.125 mol/L, DS increased significantly and decreased thereafter. The significant enhancement in DS by the increase of the concentration of NaOH up to 0.125 mol/L suggested that the carboxymethylation reaction shown in eq. (1) prevailed over its competitive reaction:

$$NaOH + ClCH_2COONa \rightarrow$$

$$HO\text{—}CH_2\text{—}COONa + NaCl \quad (2)$$
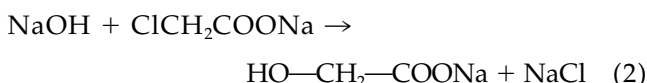
Above 0.125 mol/L NaOH, the glycolate formation[10–14] increased, and consequently, a lower value of the DS of the CM–CTG sample was obtained. This was confirmed by the estimation[15] of glycolate formed in the products obtained with a maximum DS (0.099) and the lowest DS (0.039). For the maximum and lowest DSs, the sodium glycolate formations were 0.030 and 0.048 mol, respectively. Therefore, 0.125 mol/L NaOH constituted the optimum concentration for the carboxymethylation of CTG.

Effect of MCA concentration

Table II shows the effect of MCA concentration on the DS of CM–CTG with the optimum concentration (0.125 mol/L) of NaOH. Results showed a distinct pattern of increase in DS with increasing MCA concentration (0.042–0.095 mol/L), which was optimized at 0.084 mol/L. However, a further increase in the

TABLE IV
Effect of Reaction Temperature

Reaction temperature	DS
30°C	0.030
50°C	0.060
Reflux temperature	0.099

Reaction conditions: [CTG] = 0.03 mol/L, [NaOH] = 0.125 mol/L, [MCA] = 0.084 mol/L, duration = 60 min, and solvent medium = 80 : 20 methanol–water.

TABLE V
Effect of Solvent Medium

Methanol–water ratio	DS
70 : 30	0.070
80 : 20	0.099
90 : 10	0.046

Reaction conditions: [CTG] = 0.03 mol/L, [NaOH] = 0.125 mol/L, [MCA] = 0.084 mol/L, duration = 60 min, and temperature at reflux.

concentration of MCA beyond 0.084 mol/L on using the optimum dose of NaOH decreased the DS, which showed that enough CTG–alkoxide was not available for reaction with MCA.

Effect of reaction time

We varied the duration of the carboxymethylation reaction of CTG by performing the reaction for 30–180 min. The values of DS for the obtained CM–CTG are given in Table III, which shows that DS increased from 0.065 to 0.099 when the reaction time was increased from 30 to 60 min, and after 60 min, the change in DS was almost constant. The enhancement of DS by prolonging the duration of reaction from 30 to 60 min was a direct consequence of the favorable effect of time on the swellability of CTG as well as the diffusion and adsorption of reactants with the ultimate effect of inducing better contacts between the etherifying agents and CTG. These results were in agreement with the results reported in the carboxymethylation of starch.[13,14]

Effect of reaction temperature

The carboxymethylation of CTG was performed at different temperatures (i.e., 30°C, 50°C, and reflux temperature). The reaction conditions and DSs are shown in Table IV. DS increased from 0.030 to 0.099 as the reaction temperature increased from 30°C to reflux temperature because of the favorable effect of temperature on the swellability of CTG as well as the diffusion and adsorption of reactants with the ultimate

effect of inducing better contacts between the etherifying agents and CTG. As these effects were less pronounced at lower temperatures, the chances of glycolate formation was higher in comparison to that at reflux temperature, and hence, a low DS was observed. Thus, reflux temperature was the optimum reaction temperature for the carboxymethylation of CTG.

Effect of solvent medium

The effect of solvent on the carboxymethylation of CTG (extent of reaction) depends on its ability to solubilize the etherifying agents and swelling of the gum. It is well known that water is a not an appropriate solvent for etherification; therefore, a mixture of water and organic polar solvents was employed. Our results showed that when the concentration of methanol in water was increased from 7 : 3 to 8 : 2 (optimum) the DS increased from 0.070 to 0.099. However, the DS decreased further (0.046) if methanol water ratio was increased to 9 : 1, which could be attributed to the lower swelling of CTG in the higher organic solvent concentration. A methanol–water ratio of 7 : 3 resulted in higher glycolate formation and a lower DS despite the higher swelling of the gum. Our results were in agreement with results reported earlier.[14,16]

Rheological studies

Hydrocolloids and their derivatives are generally used in the form of solutions; therefore, it is of interest to study the rheological properties of their solutions. The solutions of CM–CTG were prepared in 1 and 2% concentrations, and their rheological properties were studied. It is clear from Table VI that regardless of the carboxymethyl content, the aqueous CM–CTG solutions were characterized by non-Newtonian pseudoplastic behavior.[17]

The apparent viscosities of the 1 and 2% CM–CTG solutions at various rates of shear showed that the DS played a dominant role on the apparent viscosity of the product at any specific rate of shear. At a constant

TABLE VI
Effect of Shear Rate and Storage on the Solution of CM–CTG Samples of Various DSS at 25°C

Shear rate (s^{-1})	Apparent viscosity (cps)[a]											
	1% solution						2% solution					
	DS (0.030)		DS (0.060)		DS (0.099)		DS (0.030)		DS (0.060)		DS (0.099)	
	I	II	I	II	I	II	I	II	I	II	I	II
3.4	590	675	890	965	3050	3150	5150	5210	7510	7575	9625	9850
6.8	510	595	785	805	2350	2387	3965	3995	5325	5395	7537	7725
17	395	465	605	665	1595	1615	3080	3110	4105	4165	5950	6115

I = apparent viscosity of freshly prepared solution; II = apparent viscosity after 120 h.
[a] Spindle-SC-27.

rate of shear, the apparent viscosity increased as the DS of the product increased. At a rate of shear of 3.4 s^{-1}, the apparent viscosity increased from 590 cps (DS = 0.030) to 3050 cps (DS = 0.099). The increase in apparent viscosity with increasing DS may have been due to the increase in the hydrodynamic volume[18] because of the carboxyl groups introduced.

It was also clear from the data that at any specific rate of shear, the apparent viscosity increased when the solutions were stored up to 120 h. The increase in viscosity through storage may have been due the increase in swellability on account of hydrogen bonding and hydrodynamic volume.

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