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Carbohydrate Polymers 69 (2007) 251–255

Carbohydrate Polymers

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Carboxymethylation of Tamarind kernel powder

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Received 19 July 2006; received in revised form 29 September 2006; accepted 2 October 2006
Available online 27 November 2006

Abstract

Tamarind kernel powder is a rich source of xyloglucan gum. The gum can be utilized in a number of industries. With a view to utilize the gum for broader applications, carboxymethylation of tamarind kernel powder was carried out. The reaction conditions were optimized with respect to concentration of sodium hydroxide, monochloroacetic acid, solvent ratio, reaction time, and reaction temperature. Carboxymethylation of tamarind kernel powder increased its solubility in cold water and the stability of its paste to microorganisms.
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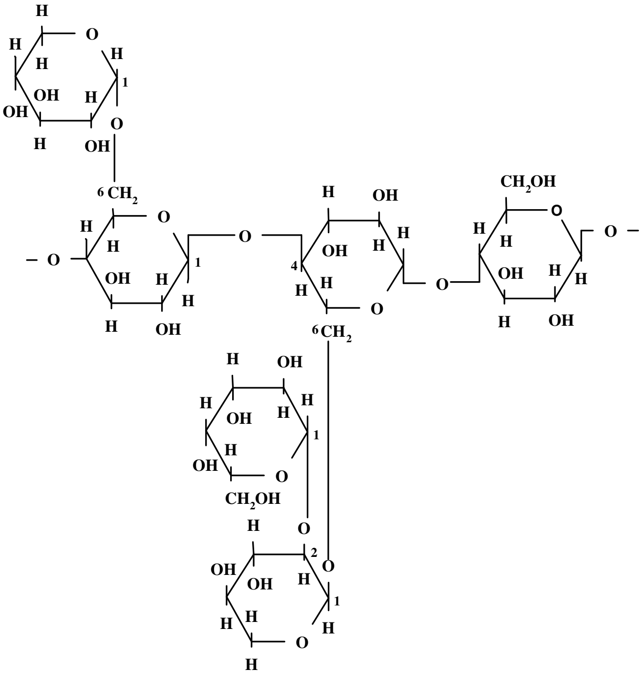
Keywords: Tamarind kernel powder; Carboxymethylation; Polysaccharides; Modification; Viscosity

1. Introduction

Tamarind kernel powder (TKP) is derived from the seeds of *Tamarindus indica* Linn., a common and most important tree of India and South East Asia (Anonymous, 1976). TKP, a crude extract of tamarind seeds, has been used as a replacement for starch in cotton sizing, and as a wet-end additive in the paper industry, where it replaces starch and galactomannans (Glicksman, 1986). Refined tamarind seed polysaccharide is used as a thickening, stabilizing and gelling agent in the food industry, particularly in Japan where it is a permitted food additive (Gidley et al., 1991; Glicksman, 1986). The polysaccharide is composed of (1 → 4)-β-D-glucan backbone substituted with side chains of α-D-xylopyranose and β-D-galactopyranosyl (1 → 2)-α-D-xylopyranose linked (1 → 6) to glucose residues. The glucose, xylose and galactose units are present in the ratio of 2.8:2.25:1.0 (Gidley et al., 1991; Glicksman, 1986). In India, TKP is one of the cheapest gums available. However, because of several drawbacks, such as unpleasant odor, dull color, presence of water insolubles, low solubility in cold water, and fast biodegradability, it is wanting in several speciality end-use properties. The present work was undertaken to overcome these drawbacks and make it more useful/industrially exploitable.



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0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.10.001

In our laboratory seed gums (*Cassia occidentalis*/*Cassia tora*/*Cyamopsis tetragonoloba*) were modified via carboxymethylation (Gupta, Sharma, & Soni, 2004; Sharma, Kumar, Soni, & Sharma, 2003e; Soni & Sharma, 2000), carbamoylethylation (Gupta, Sharma, & Soni, 2005; Sharma, Kumar, & Soni, 2003a, Sharma, Kumar, & Soni, 2004), cyanoethylation (Sharma, Kumar, & Soni, 2003b) and grafting (Sharma, Kumar, & Soni, 2002, 2003c, 2003d). A number of chemical modifications of tamarind seed polysaccharide have been described including acetyl (Rao & Beri, 1955), hydroxyalkyl (Schiavio & Maderno, 1958; Shimohiro, Ogawa, & Ohnishi, 1983) and carboxymethyl (Omya & Tabuchi, 1985; Prabhanjan, 1989; Shimohiro et al., 1983) derivatives. However, optimization of the reaction conditions to prepare carboxymethyl tamarind gum (CM-TKP) has not been studied so far. The present work attempts to study the optimization of the process for the preparation of carboxymethyl derivative of Tamarind kernel powder (CM-TKP). Carboxymethylation can be performed in water as a solvent (Hebeish & Khalil, 1988; Hebeish, Khalil, & Hashem, 1990; Kamel, Abd El-Thalouth, Abou Amer, Ragheb, & Nassar, 1992; Khalil, Hashem, & Hebeish, 1990) or in water-miscible organic solvents containing small amounts of water (Bhattacharyya, Singhal, & Kulkarni, 1995; Kwon et al., 1997; Ragheb, El-Sayiad, & Hebeish, 1997; Ragheb, Kamel, Abd El-Thalouth, & Nassar, 1994; Sharma et al., 2003e; Tijsen, Scherpenkate, Stamhuis, & Beenackers, 1999). The main reaction parameters, which influence the carboxymethylation process, are the solvent system, solvent composition, concentration of sodium hydroxide and monochloroacetic acid (MCA), reaction time, and reaction temperature (Bhattacharyya et al., 1995; Hebeish & Khalil, 1988; Hebeish et al., 1990; Khalil et al., 1990; Ragheb et al., 1997; Sharma et al., 2003e).

In the present work, carboxymethylation was performed in a methanol/water system, and the reaction parameters with respect to degree of substitution were studied.

2. Materials and methods

2.1. Materials

Tamarind kernel powder was obtained from M/s Sooraj Trading Co., KGF, Karnataka, India. Monochloroacetic acid (MCA), sodium hydroxide, methanol, and hydrochloric acid were of laboratory grade (SD Fine-Chem. Ltd, Mumbai, India).

2.2. Methods

2.2.1. Carboxymethylation

The synthesis of CM-TKP was carried out as follows (Table 1): TKP (0.050 mol) was dispersed in alkaline (0.090–0.180 mol, NaOH) aqueous methanol (100 ml). To the above solution MCA (0.079–0.101 mol) was added in solid form with continuous stirring for 15 min. At this end, the flask was immersed in a thermostatic water bath keeping a specific temperature (40–85 °C) at which the reaction was allowed to proceed for the desired duration (30–90 min). The flask contents were occasionally shaken during the course of the reaction. The reaction product was filtered on a G-3 sintered glass crucible, dissolved in water, and neutralized with dilute HCl (1:1, vol/vol). The reaction product was precipitated in ethyl alcohol and washed twice with aqueous methanol (methanol:H_2O, 80:20) followed by pure methanol. The products were initially dried at room temperature and then in vacuum oven at 40 °C for 4 h.

2.2.2. Analysis and measurements

Determination of the degree of substitution (DS). The DS of CM-TKP was determined by a method described elsewhere (Whistler, 1963).

Determination of rheological properties of CM-TKP. The rheological properties were determined using a Brookfield Digital Viscometer model 'RVTD', Stoughton, USA by adopting the following experimental conditions: Range of shear rate between 3.4 and 34.0 s^{-1}, temperature 25 ± 1°C.

3. Results and discussion

The carboxymethylation of TKP proceeds by a two-step consecutive reaction and is accompanied by an undesired side reaction. In the main reaction the sodium hydroxide reacts first with the hydroxyl groups of the gum to give alkoxides groups. The carboxymethyl groups are then formed in a S_N2 reaction between the gum alkoxide and MCA. The main reaction is given by

$$\mathrm{TKP{-}OH + NaOH \rightarrow TKP{-}ONa + H_2O} \quad (1)$$

$$\mathrm{TKP{-}ONa + ClCH_2COOH} \\ \mathrm{\rightarrow TKP{-}OCH_2COONa + NaCl} \quad (2)$$

The side reaction takes place in both the liquid bulk and the gum phase (Tijsen et al., 1999), and results in the formation of sodium glycolate from MCA and sodium hydroxide.

$$\mathrm{NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl} \quad (3)$$

The optimization of the process of carboxymethylation was performed by varying the process parameters such as concentration of sodium hydroxide and monochloroacetic acid, methanol–water ratio, temperature, and duration of the reaction. Each parameter was varied keeping the others constant as shown in Table 1.

3.1. Effect of sodium hydroxide concentration

The effect of variation of sodium hydroxide concentration from 0.090 to 0.180 mol at 70 °C on DS was studied and the results are shown in Fig. 1. It was observed that, as sodium hydroxide concentration increases up to 0.158 mol, the DS also increases and then level off. The

Table 1
Reaction parameters used in the carboxymethylation of TKP

Figure	Experiment number	Methanol (%) in solvent medium[a]	Time (min)	Temperature (°C)	NaOH:MCA:TKP[b], (mol)	DS
1	a	80	60	70	1.8:1.8:1	0.190
	b				2.26:1.8:1	0.209
	c				2.7:1.8:1	0.397
	d				3.16:1.8:1	0.649
	e				3.6:1.8:1	0.309
2	a	80	60	70	3.16:1.58:1	0.501
	b				3.16:1.68:1	0.592
	c				3.16:1.8:1	0.649
	d				3.16:1.92:1	0.470
	e				3.16:2.02:1	0.422
3	a	80	30	70	3.16:1.8:1	0.352
	b		45			0.479
	c		60			0.649
	d		75			0.418
	e		90			0.394
4	a	80	60	40	3.16:1.8:1	0.371
	b			55		0.496
	c			70		0.649
	d			85		0.326
5	a	0	60	70	3.16:1.8:1	0.178
	b	20				0.200
	c	40				0.235
	d	60				0.297
	e	80				0.649
	f	90				0.336
	g	100				0.301

[a] Solvent medium: methanol:water (vol/vol).

[b] In all experiments 0.050 mol of TKP was used.

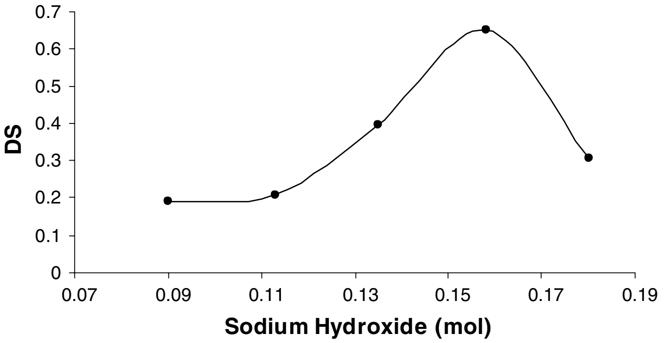

Fig. 1. Dependence of DS on sodium hydroxide concentration. Reaction conditions as shown in Table 1.

increase in DS with increase in NaOH concentration up to 0.158 mol suggests that the carboxymethylation reaction shown by Eq. (2) prevails over its competitive reaction shown by Eq. (3). Above 0.158 mol concentration of NaOH, the glycolate formation increases (Bhattacharyya et al., 1995; Gupta et al., 2004; Hebeish & Khalil, 1988; Khalil et al., 1990; Sharma et al., 2003e; Stojanovic, Jeremic, & Jovanovic, 2000; Verraest, Peters, Batelaan, & Bekkum, 1995) and, consequently, a lower value of the DS of the CM-TKP sample was obtained. Therefore, the 0.158 mol concentration of NaOH constitutes the optimum concentration for carboxymethylation of TKP.

3.2. *Effect of monochloroacetic acid concentration*

The MCA concentration was varied from 0.079 to 0.101 mol at 70 °C and the results are shown in Fig. 2. Results showed the distinct pattern of the increase in DS on increasing the concentration of MCA, which gets optimized at 0.090 mol. However, a further increase in concentration of MCA beyond 0.090 mol on using the optimum dose of NaOH concentration (0.158 mol) favors the side reaction Eq. (3). Similar observations are reported for *Cassia tora* gum, starch, *Leucaena glauca* seed gum and *Cassia*

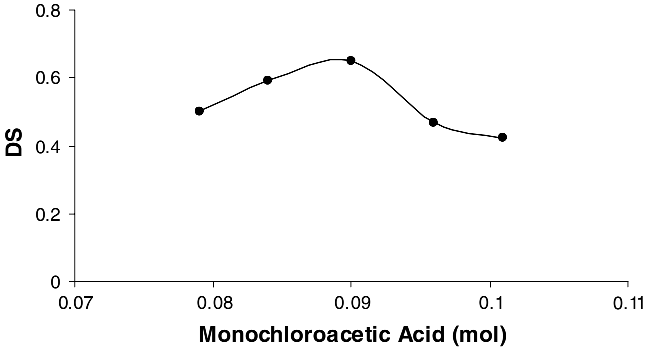

Fig. 2. Dependence of DS on monochloroacetic acid concentration. Reaction conditions as shown in Table 1.

occidentalis seed gum (Gupta et al., 2004; Hebeish & Khalil, 1988; Sharma et al., 2003e).

3.3. Effect of reaction time

Fig. 3. shows the effect of reaction time on DS at 70 °C. The DS increases with the increase in reaction time and reaches a maximum in 60 min and a significant decrease was observed on increasing the time thereafter. The enhancement of DS by prolonging the duration of reaction from 30 to 60 min is a direct consequence of the favorable effect of time on swelling of TKP as well as the diffusion and adsorption of the reactants with the ultimate effect of better contacts between the etherifying agents and TKP. Similar observations were made earlier by different workers (Bhattacharyya et al., 1995; Gupta et al., 2004; Hebeish & Khalil, 1988; Khalil et al., 1990; Sharma et al., 2003e; Stojanovic et al., 2000).

3.4. Effect of reaction temperature

Carboxymethylation of TKP was performed at different temperatures (i.e., 40–85 °C). The dependence of DS on reaction temperature is shown in Fig. 4. It is observed that DS increases from 0.371 to 0.649 prominently as the reaction temperature increases from 40 to 70 °C and decreases thereafter. It is due to the favorable effect of temperature on the swellability of TKP as well as the diffusion and adsorption of reactants with the ultimate effect of inducing better contacts between the etherifying agents and TKP. The value of DS decreases at 85 °C, due to the higher glycolate formation Eq. (3) (Gupta et al., 2004; Sharma et al., 2003e) prevailing over the carboxymethylation Eq. (2).

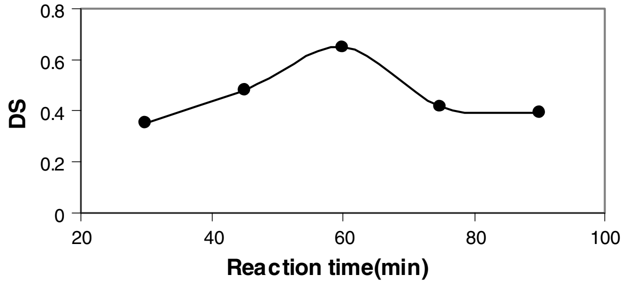

Fig. 3. Dependence of DS on reaction time. Reaction conditions as shown in Table 1.

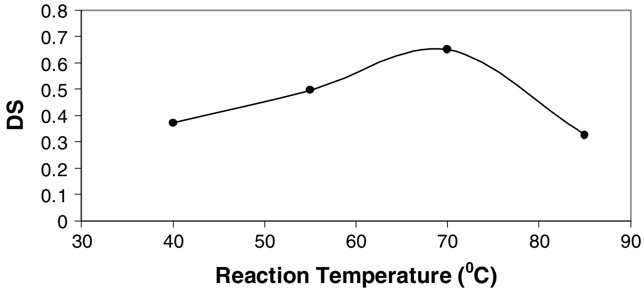

Fig. 4. Dependence of DS on reaction temperature. Reaction conditions as shown in Table 1.

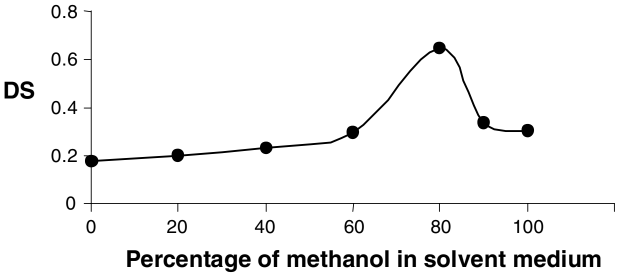

Fig. 5. Dependence of DS on percentage of methanol in solvent medium. Reaction conditions as shown in Table 1.

3.5. Effect of solvent medium

The effect of solvent medium on the extent of reaction is related to the miscibility, the ability to solubilize the etherifying agents and to swell the biopolymer and create an environment that favors carboxymethylation rather than glycolate formation Eq. (3). The results (Fig. 5) reveal that increasing the percentage of methanol in the mixture (CH_3OH–H_2O, vol/vol) enhances DS up to a maximum, after which it decreases, reflecting the negative effect of pure methanol on the carboxymethylation reaction. The maximum DS is obtained at a methanol:water ratio of 80:20. It may be attributed to the lower swelling of the tamarind kernel powder in higher organic solvent concentration. The above implies that solvent medium determines the extent of reaction (Bhattacharyya et al., 1995; Gupta et al., 2004; Khalil et al., 1990; Sharma et al., 2003e).

4. Rheological properties

To assess the importance and feasibility of any gum or hydrocolloid in food and other industries, the viscosity profile is generally considered as one of the parameters. The solutions of TKP and CM-TKP were prepared in 2% concentration, and their rheological properties were studied. It is clear from (Table 2) that CM-TKP solutions are more viscous compared to TKP solution and are characterized by a non-Newtonian pseudoplastic behavior. The compact structural organization is responsible for the low viscosity of TKP solution. Derivatization of TKP i.e. CM-TKP disrupt the organization and expose the polysaccharide network for hydration which results in higher viscosity. The apparent viscosity increases significantly up to DS (0.418) and decreases thereafter. The increase in the apparent viscosity with increase in DS (upto 0.418) is due to increase in hydrodynamic volume and higher intermolecular forces between the xyloglucan chains due to carboxymethyl groups introduced. However, with further increase in DS, there is a decrease in viscosity, which may be due to the steric hindrance developed by the carboxymethyl groups introduced at higher DS, leading to decrease in intermolecular forces. Results also indicate

Table 2
Rheological studies of tamarind kernel powder (apparent viscosity (cps) 25 ± 1 °C; 2% solution)

Unmodified gum			Modified gum (CM-TKP)												
Shear rate (s^{-1})	3 h	24 h	DS(0.178)		DS(0.297)		DS(0.394)		DS(0.418)		DS(0.592)		DS(0.649)	
			I	II	I	II	I	II	I	II	I	II	I	II
3.4	525	Degradation	1000	1050	1025	1113	1088	1138	1425	2913	1063	1175	638	800
6.8	500		900	944	938	1006	994	1019	1219	2281	925	1013	613	744
17.0	450		745	793	788	840	833	855	953	1595	780	830	558	655
34.0	413		600	658	651	700	678	709	754	1178	646	673	494	584

I = apparent viscosity of freshly prepared solution; II = apparent viscosity after 72 h.

the effect of storing the CM-TKP solutions up to 72 h at various rates of shear. The apparent viscosity increases on storing up to 72 h, whereas unmodified gum degraded completely within 24 h. This indicates the stability of CM-TKP paste towards microorganisms, since the presence of carboxymethyl groups makes the molecule resistant toward enzymatic attack. The increase in the viscosity through storage may have been due to the increase in swellability on account of hydrogen bonding and hydrodynamic volume (Gupta et al., 2004; Sharma et al., 2003e).

5. Conclusion

Carboxymethylation of tamarind kernel powder was carried out with monochloroacetic acid in the presence of alkali as a catalyst under heterogeneous conditions. The optimum DS (0.649) was obtained by using [TKP], 0.050 mol; [NaOH], 0.158 mol; [MCA], 0.090 mol; methanol–water ratio, 4:1; temperature 70 °C; and duration 60 min. The paste quality and microbial resistance of CM-TKP was much better than that of native gum. The viscosity of CM-TKP in 2% solutions was higher compared to native gum. Rheological studies showed the non-Newtonian pseudoplastic nature of CM-TKP solutions.

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