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Carboxymethylation of *Cassia angustifolia* seed gum: Synthesis and rheological study

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ABSTRACT

The seeds of *Cassia angustifolia* are a rich source of galactomannan gum. The seed gums possess a wide variety of industrial applications. To utilize *C. angustifolia* seed gum for broader industrial applications, the carboxymethyl-*Cassia angustifolia* seed gum (CM-CAG) was synthesized. The gum was etherified with sodium monochloroacetate (SMCA) in a methanol-water system in presence of alkali (NaOH) at different reaction conditions. The variables studied includes alkali concentration, SMCA concentration, methanol:water ratio, liquor:gum ratio, reaction temperature and time. The extent of carboxymethylation was determined as degree of substitution (DS). The optimum conditions for preparing CM-CAG (DS = 0.474) comprised 0.100 mol of NaOH, 0.05 mol of SMCA, 80% of methanol:water ratio (as % methanol) and liquor:gum ratio (v/w) of 10:1 at 75 °C for 60 min using 0.03 mol (as AGU) of CAG. Rheological studies showed CM-CAG to exhibit non-Newtonian pseudoplastic behaviour, relatively high viscosity, cold water solubility and solution stability.

1. Introduction

Cassia angustifolia (family: *Leguminosae*; subfamily: *Caesalpiniaceae*) is an important medicinal, drought-resistant, fast growing and spreading Indian shrub of which seeds, pods and leaves are extensively used for pharmaceutical applications. The seeds of *C. angustifolia* have been reported by Chaubey and Kapoor (2001) to be an alternate source of commercial seed gums and that the *C. angustifolia* seed gum (CAG) is a water-soluble tri-dimensional polysaccharide containing β-D-mannose and α-D-galactose in the ratio 2.90:1. The main chain of the *C. angustifolia* seed gum consists of (1→4)-linked β-D-mannopyranosyl units to which single α-(1→6)-linked-D-galactopyranosyl units are attached as shown in Fig. 1 (Sanghi, Bhatttacharya, & Singh, 2002).

Galactomannans, important polysaccharides, finds utility in different industries such as food processing, paper & pulp, pharmaceutical, well drilling and so on. *C. angustifolia* seed gum has potential on account of its availability and can be developed to replace the conventional gums such as *Guar* gum and *Locust bean* gum. A survey of the literatures reveals that in order to synthesize value added products, Goyal, Kumar, and Sharma (2007) and Omya and Tabuchi (1985) have worked on the carboxymethylation of *Tarmind kernel* powder, Gupta, Sharma, and Soni (2004) investigated the carboxymethylation of *C. occidentalis* gum, Dodi, Hritcu, and Popa (2011); Gong et al. (2012) and Kamel, Ragheb, Haggag, and El-Thalout (1992) have worked on carboxymethylation of *Guar* gum in different solvent mediums. Other than these the carboxymethylation of *Cassia tora* gum (Sharma, Kumar, Soni, & Sharma, 2003), *Locust bean* gum (Dey, Sa, & Matti, 2011) and *Sesbania* galactomannan gum (Rekaby, Abd El-Thalouth, Rahman, & Abd El-Satar El-Khabery, 2010) have also been reported in literatures. However, no systematic work has been reported on the optimization of the process of carboxymethylation of *C. angustifolia* seed gum.

The study of the literature on carboxymethylation of different polysaccharides (including seed gums) reveals that carboxymethylation of the polysaccharides can be achieved either in water as a solvent (Hebeish & Khalil, 1988; Hebeish, Khalil, & Hashem, 1990; Khalil, Hashem, & Hebeish, 1990; Kamel, Abd El-Thalouth, Amer, Ragheb, & Nassar, 1992) or in water-miscible organic solvents containing small amounts of water (Bhattacharyya, Singhal, & Kulkarni, 1995; Kwon et al., 1997; Ragheb, El-Sayiad, & Hebeish, 1997; Sharma et al., 2003) or in non-aqueous systems (Parvathy, Susheelamma, Tharanathan, & Gaonkar, 2005; Ragheb, Kamel, El-Thalouth, & Nassar, 1994). Also, these literatures demonstrates that main reaction parameters influencing the carboxymethylation process includes the solvent system, solvent composition,

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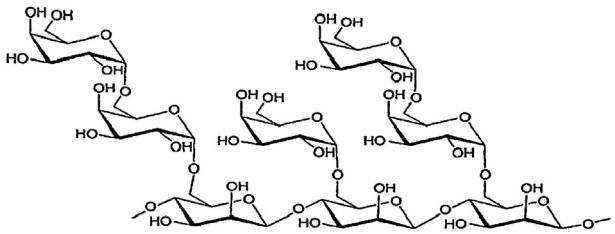

Fig. 1. Chemical structure of *Cassia angustifolia* seed gum.

concentration of sodium hydroxide and etherifying agent used, reaction time and reaction temperature.

The present work attempts to study the optimization of the process for the synthesis of carboxymethyl derivative of *C. angustifolia* seed gum. In this work carboxymethylation was performed in a methanol/water system, and effect of the reaction parameters on the DS of the product (CM-CAG) were studied.

2. Materials and methods

2.1. Materials

2.1.1. Plant seeds

C. angustifolia seeds were obtained from M/S Sindhi Seeds corp., Dehradun (UK).

2.1.2. Chemicals

Sodium monochloroacetate (SMCA), sodium hydroxide (NaOH), acetic acid and methanol were of laboratory grade and ethanol was of analytical grade (SD Fine-Chem. Ltd., Mumbai, India). Distilled water was utilized for all purposes.

2.2. Methods

2.2.1. Separation of the gum from the seeds

The gum was separated from the *C. angustifolia* seeds according to the method reported by Soni and Pal (1996) in which the seeds were heated for few minutes in a hot air oven and the endosperm was isolated by removing seed coat and germ by impact grinding using high speed domestic grinder. Germ and seed coat from the endosperm were separated by sifting. Endosperm was tempered to 37.5% moisture by steam and flaked by passage through smooth roller. The flaked endosperm was made to flour *C. angustifolia* gum (100 mesh) using millcent flour mill.

2.2.2. Carboxymethylation of the gum

Carboxymethylation of the *C. angustifolia* seed gum (CAG) was performed as follows-CAG 0.03 mol per AGU (Anhydrous Glucose Unit); was dispersed in aqueous methanol (0–100%, v/v) containing 0.075–0.175 mol NaOH at room temperature with continuous stirring for 25 min and varying liquor:gum ratio from 5:1 to 20:1 (v/w) by addition of 0.010–0.070 mol SMCA with continuous stirring for another 25 min. The reaction mixture was heated (30–75 °C) for duration of 30–120 min. The reaction mixture was occasionally shaken during the course of the reaction. The reaction product was filtered on a G-3 sintered glass crucible, dissolved in water and neutralised by acetic acid (1:1 v/v). The reaction product was precipitated in ethanol and washed twice with aqueous methanol followed by pure methanol. The product is first dried at room temperature and then in vacuum oven at 70 °C for 60 min.

3. Analysis and measurement

3.1. Determination of DS

The DS of CM-CAG was determined according to the acid-wash method reported by Eyler, Klug, and Diephuis (1947).

3.2. Determination of rheological properties of CM-CAG

The rheological properties were determined using Brookfield Digital Viscometer model "RVTD", Stoughton, USA by utilizing the following experimental conditions:

- Range of shear rate between 2.5–25.0 s^{-1}.
- Spindel-27.
- Temperature 25 ± 1 °C.
- The apparent viscosity (η) in centipoise (cps) was calculated by using formula.

$$\eta = \tau/S$$

Where, τ is shear stress (Dyne/cm^2) and S is shear rate (s^{-1}).

4. Evidence of carboxymethylation

IR spectra were recorded with a Bruker tensor 27 spectrophotometer using KBr pellets in the range 4000–450 cm^{-1}.

5. Result and discussion

The carboxymethylation of CAG is a two-step process and is accompanied by an undesired side reaction. The main reaction comprises of

I. Generation of alkoxide of CAG by the action of NaOH.

$$\text{CAG-OH} + \text{NaOH} \rightarrow \text{CAG-O}^-\text{Na}^+ + \text{H}_2\text{O} \quad (1)$$

II. SN2 reaction of the alkoxide formed with SMCA to form CM-CAG.

$$\text{CAG-O}^-\text{Na}^+ + \text{ClCH}_2\text{COO}^-\text{Na}^+ \rightarrow \text{CAG-O-CH}_2\text{COO}^-\text{Na}^+ + \text{NaCl} \quad (2)$$

The side reaction occurs in both the liquid bulk as well as the gum phase (Tijsen, Scherpenkate, Stamhuis, & Beenackers, 1999). The side reaction results in the formation of sodium glycolates from NaOH and SMCA.

$$\text{NaOH} + \text{ClCH}_2\text{COO}^-\text{Na}^+ \rightarrow \text{HO-CH}_2\text{COO}^-\text{Na}^+ + \text{NaCl} \quad (3)$$

The optimization of the process of carboxymethylation with reference to DS was performed by varying the reaction parameters such as concentration of NaOH and SMCA, reaction temperature, reaction time, methanol:water ratio and liquor:gum ratio. Each of the above parameter was varied keeping the other constant (as shown in Table 1).

5.1. Effect of NaOH concentration

The effect of NaOH concentration (0.075–0.175 mol) on the carboxymethylation of CAG was studied in terms of the effect on DS of the CM-CAG formed in the following experimental condition: CAG 0.030 mol (as AGU), SMCA concentration 0.050 mol, solvent medium 80% methanol, reaction time 60 min, liquor:gum ratio 10:1 and reaction temperature 75 °C (reflux temperature). The results are shown in Fig. 2.

It was observed that as NaOH concentration increases to 0.100 mol, the DS also increases and decreases thereafter. The

Table 1
Reaction parameters investigated in carboxymethylation of CAG.

Figure	Experiment no.	Solvent medium or methanol/water ratio (% methanol, v/v)	Liquor/gum ratio (mL/g)	Time (min)	Temperature (°C)	SMCA concentration (mol)	NaOH concentration (mol)	DS
2	A	80	10:1	60	Reflux temperature (75)	0.050	0.075	0.262
	B						**0.100**	**0.474**
	C						0.125	0.416
	D						0.150	0.358
	E						0.175	0.293
3	A	80	10:1	60	Reflux temperature (75)	0.010	0.100	0.096
	B					0.020		0.163
	C					0.030		0.296
	D					0.040		0.393
	E					**0.050**		**0.474**
	F					0.060		0.364
	G					0.070		0.312
4	A	80	10:1	60	30	0.050	0.100	0.033
	B				45			0.198
	C				60			0.396
	D				**75**			**0.474**
5	A	80	10:1	30	Reflux temperature (75)	0.050	0.100	0.313
	B			45				0.357
	C			**60**				**0.474**
	D			75				0.392
	E			90				0.385
	F			105				0.342
	G			120				0.327
6	A	100	10:1	60	Reflux temperature (75)	0.050	0.100	0.163
	B	**80**						**0.474**
	C	60						0.321
	D	40						0.273
	E	20						0.236
	F	100(water)						0.031
7	A	80	5:1	60	Reflux temperature (75)	0.050	0.100	0.328
	B		**10:1**					**0.474**
	C		15:1					0.368
	D		20:1					0.352

In all the experiments 0.030 mol (as AGU) of CAG was used.

increase in DS with the increase in the NaOH concentration up to 0.100 mol indicated that the carboxymethylation reaction shown by Eq. (3) prevails over its competitive side reaction shown by Eq. (3). Above 0.100 mol NaOH concentration, the glycolate formation increases thereby lowering the DS. These finding is in accordance to those reported in literature (Goyal et al., 2007; Gupta et al., 2004; Stojanović, Jeremić, & Jovanović, 2000). Therefore, the NaOH concentration of 0.100 mol constitute the optimum NaOH concentration for carboxymethylation of CAG.

5.2. Effect of SMCA concentration

The effect of SMCA concentration (0.010–0.070 mol) on the carboxymethylation of CAG was studied in terms of the effect on DS at the following experimental condition: CAG 0.030 mol (as AGU), optimum NaOH concentration 0.100 mol, solvent medium 80% methanol, reaction time 60 min, liquor:gum ratio 10:1 and reaction temperature 75 °C (reflux temperature). The results are shown in Fig. 3.

Results showed the distinct pattern of the increase in DS on increasing the SMCA concentration, which gets optimized at 0.050 mol. The increase in the DS on increasing SMCA concentration up to 0.050 mol is because the increase in the SMCA concentration appear to enhance the availability of the acid molecules in the vicinity of the CAG hydroxyls thereby facilitating the carboxymethylation. However, a further increasing the SMCA concentration beyond 0.050 mol, the side reaction Eq. (3) between NaOH and SMCA becomes more significant consuming NaOH to form sodium glycolate as result of which DS is lowered.

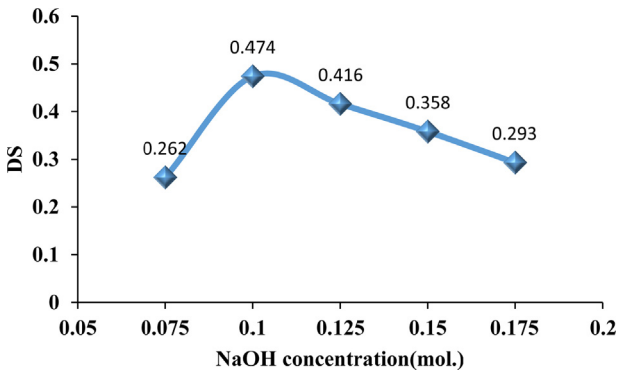

Fig. 2. Effect of NaOH concentration on carboxymethylation of CAG.

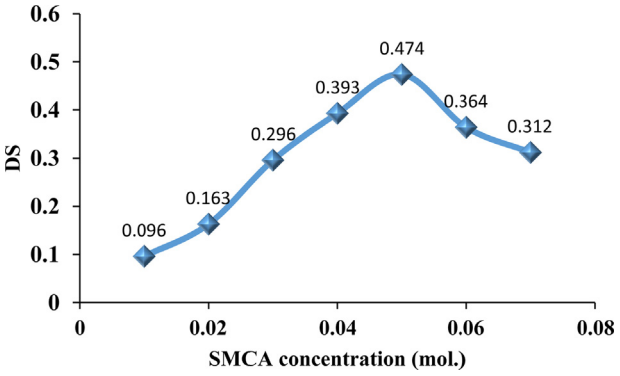

Fig. 3. Effect of SMCA concentration on carboxymethylation of CAG.

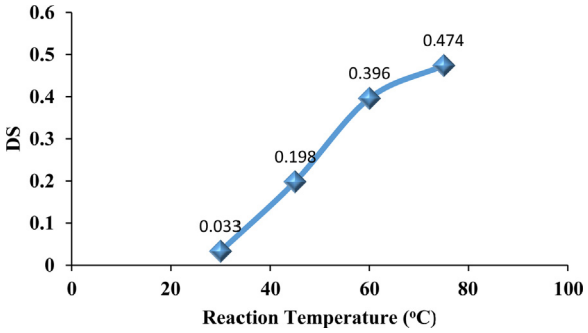

Fig. 4. Effect of reaction temperature on carboxymethylation of CAG.

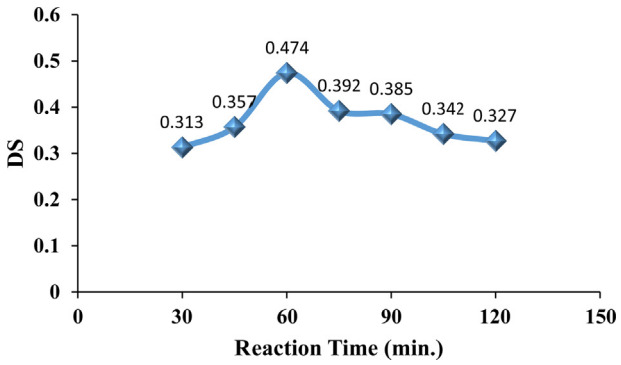

Fig. 5. Effect of reaction time on carboxymethylation of CAG.

In literatures, similar observations are reported for *C. tora* gum (Sharma et al., 2003), *Leucaena glauca* seed gum (Kamel, Ragheb et al., 1992), tarmind kernel powder (Goyal et al., 2007) and *Cassia occidentalis* seed gum also (Gupta et al., 2004) etc.

5.3. Effect of reaction temperature

The effect of reaction temperature in the range 30 °C to reflux temperature (75 °C) on the carboxymethylation of CAG was studied in terms of the effect on DS of the CM-CAG formed in the following experimental condition: CAG 0.030 mol (as AGU), optimum NaOH concentration 0.100 mol, optimum SMCA concentration 0.050 mol, solvent medium 80% methanol, reaction time 60 min, and liquor:gum ratio 10:1. The results are shown in Fig. 4.

It was observed that DS increases from 0.033 to 0.474 prominently as the reaction temperature increases from 30 °C to 75 °C (reflux temperature). At higher temperature, the ionic mobility of solutes in solution increases, faster diffusion and adsorption of reactants (etherifying agent and CAG) and thus maximum etherification occur probably due to the requirement of higher temperature for effective collision between reactants to form the reactive intermediate. This provides the favourable conditions to obtain the product of higher DS at reflux temperature (75 °C). The similar observations have reported during the optimisation of carboxymethylation of various seed gums such as *C. occidentalis* seed gum (Gupta et al., 2004) and *Guar*an gum (Kamel, Abd El-Thalout et al., 1992) etc.

5.4. Effect of reaction time

The effect of reaction time (30–120 min) on the carboxymethylation of CAG was studied in terms of the effect on DS of the CM-CAG formed in the following experimental condition: CAG 0.030 mol (as AGU), optimum NaOH concentration 0.100 mol, optimum SMCA concentration 0.050 mol, solvent medium 80% methanol, liquor:gum ratio 10:1 and optimum reaction temperature 75 °C (reflux temperature). The results are shown in Fig. 5.

It was observed that the DS is increased and reaches a maximum upto 0.474 on increasing the reaction time up to 60 min and decreases thereafter. The enhancement in DS by prolonging the duration of reaction from 30 to 60 min is a direct consequence of the favourable effect of time on swelling of CAG as well as the diffusion and adsorption of the reactants with the ultimate effect of inducing better contacts between the etherifying agent and CAG. The lowering of DS on further increasing the reaction time may be attributed to the oxidation (degradation) of CAG at reflux temperature (75 °C). Also, long period (more than 60 min) of heating at reflux temperature will degrade CM-CAG and permanently reduces its gelling or hydrocolloidal property. Similar observations were made earlier by different workers on the carboxymethylation of different seed gums (Bhattacharyya et al., 1995; Goyal et al., 2007; Gupta et al., 2004; Sharma et al., 2003; Stojanović et al., 2000).

5.5. Effect of solvent medium or methanol/water ratio

The effect of solvent medium or methanol/water ratio (as v/v%) in the range 100% methanol to 0% methanol (i.e. 100% water) on the carboxymethylation of CAG was studied in terms of the effect on DS of the CM-CAG formed in the following experimental condition: CAG 0.030 mol (as AGU), optimum NaOH concentration 0.100 mol, optimum SMCA concentration 0.050 mol, optimum reaction time 60 min, liquor:gum ratio 10:1 and optimum reaction temperature 75 °C (reflux temperature). The results are shown in Fig. 6.

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 favours carboxymethylation rather than glycolate formation. From the results, it is observed that increasing the percentage of methanol from 0% to 80% in the mixture enhances DS up to a maximum of 0.474, after which it decreases, reflecting the negative effect of pure methanol on the carboxymethylation reaction. The maximum DS of 0.474 is obtained at a methanol:water ratio of 80:20. It may be attributed to the lower swelling of the CAG in higher organic solvent concentration. Thus, it may be concluded that solvent medium determines the extent of reaction (Bhattacharyya et al., 1995; Goyal et al., 2007; Gupta et al., 2004; Khalil et al., 1990; Sharma et al., 2003).

5.6. Effect of liquor/gum ratio

The effect of liquor/gum ratio (5:1, 10:1, 15:1 and 20:1) on the carboxymethylation of CAG was studied in terms of the effect on DS of the CM-CAG formed in the following experimental condition:

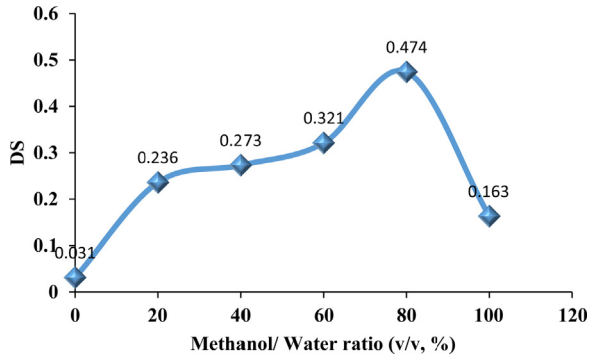

Fig. 6. Effect of solvent medium or methanol/water ratio on carboxymethylation of CAG.

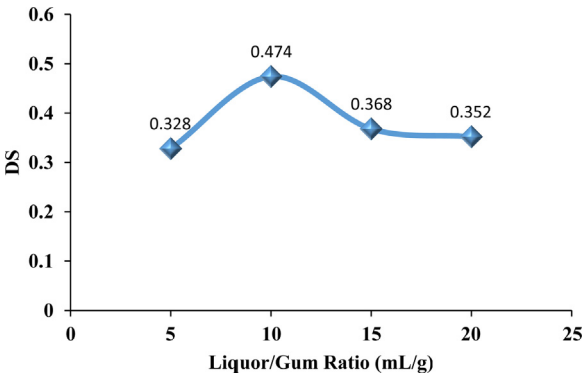

Fig. 7. Effect of liquor/gum ratio on carboxymethylation of CAG.

CAG 0.030 mol (as AGU), NaOH concentration 0.100 mol, SMCA concentration 0.050 mol, solvent medium 80% methanol, reaction time 60 min and reaction temperature 75 °C (reflux temperature). The results are shown in Fig. 7.

The amount of gum and reactants used during these experiments was constant, but the concentration of gum and reactants was decreased by increasing the amount of solvent. The optimum DS (0.474) at liquor:gum ratio of 10:1 signifies the role of volume of liquor medium. A critical amount of liquor helps the CA to swell and facilitates the diffusion and adsorption of etherifying agent on CAG molecules. A decrease in the DS at higher liquor volumes was observed which can be a consequence of the reduced probability of collision of the reactants or a decrease in collision due to dilution. At a lower liquor:gum ratio lower that 10:1, it was difficult to stir the reaction due to high viscosity which ultimately results in lower DS. Similar results were observed during the carboxymethylation of *C. occidentalis* gum, *C. tora* gum (Gupta et al., 2004; Sharma et al., 2003).

5.7. Rheological properties of CM-CAG

In order to weigh the importance and feasibility of any gum or hydrocolloid in food and other industries, the viscosity profile is usually considered as one of the parameter to decide the performance of said gum in a particular industry. The solution of CAG and CM-CAG (optimum DS = 0.474) were prepared in 1%, w/v and 2%, w/v concentrations at 25 ± 1 °C and their rheological properties were studied. The results are shown in Table 2.

From Table 2, it is clear that CM-CAG solutions are highly viscous as compared to CAG solutions and characterised by a non-Newtonian pseudoplastic behaviour. Results also give an insight into the effect of storing unmodified CAG and CM-CAG solutions for 3, 24, 48 and 120 h at various shear rates (2.5, 5.0, 12.5 and 25.0 s^{-1}). It was observed that 1%, w/v and 2%, w/v unmodified gum solutions degraded within 24 h of storage on the other hand, the 1%, w/v and 2%, w/v CM-CAG solutions were found to be stable even up to 120 h of storage. Further, it was seen that the apparent viscosities of 1%, w/v and 2%, w/v solution of CM-CAG decrease only about 35.15% and 35.58% respectively on storing them up to 120 hrs. This indi-

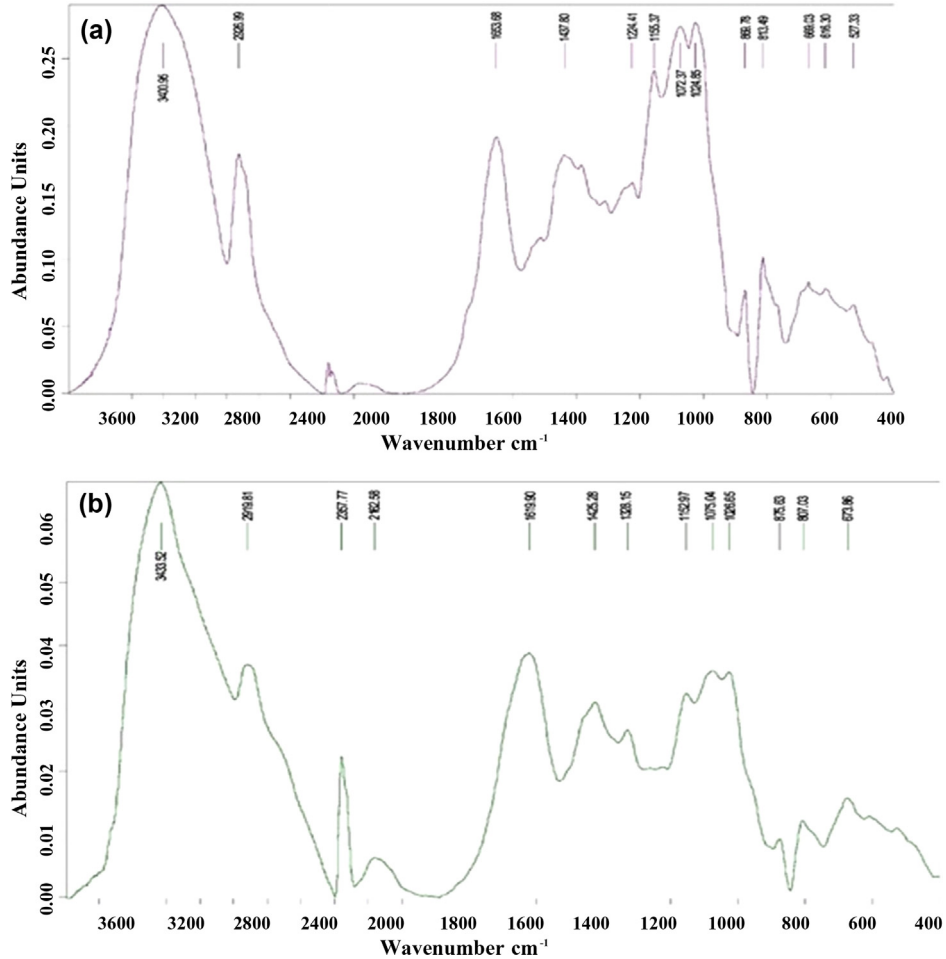

Fig. 8. IR spectra of – (a) CAG and (b) CM-CAG.

Table 2
Effect of shear rate and storage on 1% w/v and 2% w/v solutions of unmodified CAG sample and CM-CAG sample at room temperature (25 ± 1°C).

Shear rates	Apparent viscosity (η) in centipoise at room temperature Spindle-27											
	Unmodified CAG				CM-CAG (DS = 0.474)							
	3 h		24 h		3 h		24 h		48 h		120 h	
	1% solution	2% solution	1% solution	2% solution	1% solution	2% solution	1% solution	2% solution	1% solution	2% solution	1% solution	2% solution
2.5	240	270	Degradation	Degradation	7725	9625	7610	9480	6920	8650	5010	6200
5.0	210	220			6115	7525	6935	7230	5430	6825	4735	5200
12.5	165	170			5550	6220	5320	6030	5010	5850	4560	4550
25.0	150	155			4090	4980	3915	4135	3560	3910	2980	3815

cates the stability of CM-CAG pastes towards microorganism which may be attributed to the presence of the carboxymethyl groups provide the CM-CAG molecules an increased resistant towards enzymatic attack and less depolymerisation of CM-CAG molecules at room temperature. This is in comply with the observations reported in the literatures for the carboxymethyl derivatives of other gums such as *C. tora*, *C. occidentalis*, guar gum etc. (Gupta et al., 2004; Prabhanjan, Gharia & Srivastav, 1989; Sharma et al., 2003).

5.8. Evidence of carboxymethylation

FTIR analysis has been utilized as an evidence of carboxymethylation of CAG. For this purpose the IR spectra of CAG and CM-CAG were recorded in the range 4000–450 cm^{-1}.

In the IR spectra of unmodified CAG (Fig. 8(a)), the presence of a very strong and broad absorption band at 3400 cm^{-1} was due to OH stretching while the sharp absorption band at 2926 cm^{-1} attributed to CH stretching. The absorption band appearing at 1653 cm^{-1} was corresponding to the OH bond of water molecules (moisture). The absorption band at 1437 cm^{-1} belongs to CH_2 group bending while the presence of strong peak 1024 cm^{-1} was observed due to the bending $H_2C—O—CH_2$ bond. The peaks at 869 and 813 cm^{-1} were related with the presence of glycosidic linkages and anomeric configurations (α- and β-conformers), attributed to two sugar units, respectively (Figueiró, Góes, Moreira, & Sombra, 2004; Prado, Kim, Özen, & Mauer, 2005; Yuen, Choi, Phillips, & Ma, 2009).The IR spectrum of CM-CAG (Fig. 8(b)) shows the absorption band at 3433 cm^{-1} belongs to OH stretching while the CH stretching band appeared at 2926 cm^{-1}. The band due to OH of water molecule at 1653 cm^{-1} in the CAG sample was disappeared in the CM-CAG sample. The appearance of new and strong absorption bands at 1619 cm^{-1} and 1425 cm^{-1} was due to the asymmetrical and symmetrical vibrations of carboxylic group, respectively. The bands around 1425 and 1328 cm^{-1} are assigned to $—CH_2$ and —OH bending vibration, respectively. The band at 1075 cm^{-1} is due to $OCH—O—CH_2$ stretching (Biswal & Singh, 2004).

6. Conclusion

Carboxymethylation of *C. angustifolia* seed gum was carried out with sodium monochloro acetate (SMCA) in the presence of alkali (NaOH) as a catalyst under heterogeneous conditions. The optimum DS of 0.474 was obtained at reflux temperature using 80% methanol, 0.03 mol (as AGU) of *C. angustifolia* seed gum, 0.100 mol of NaOH, 0.05 mol of SMCA, 10:1 liquor/gum ratio and a reaction time of 60 min. The microbial resistance and paste quality of CM-CAG was found to be better than the unmodified CAG. The increase in the viscosity of 1% and 2% CM-CAG solutions is about 32.19 and 35.65 times respectively in comparison to 1% and 2% unmodified CAG solutions. Further, rheological studies revealed the non-Newtonian pseudoplastic behaviour of CM-CAG.

References

Bhattacharyya, 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*(4), 247–253.

Biswal, D. R., & Singh, R. P. (2004). Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers*, *57*(4), 379–387.

Chaubey, M., & Kapoor, V. P. (2001). Structure of a galactomannan from the seeds of *Cassia angustifolia* Vahl. *Carbohydrate Research*, *332*(4), 439–444.

Dey, P., Sa, B., & Maiti, S. (2011). Carboxymethyl ethers of locust bean gum-a review. *International Journal of Pharmacy & Pharmaceutical Sciences*, *3*(2), 4–7.

Dodi, G., Hritcu, D., & Popa, M. I. (2011). Carboxymethylation of guar gum: Synthesis and characterization. *Cellulose Chemistry and Technology*, *45*(3), 171.

Eyler, R. W., Klug, E. D., & Diephuis, F. (1947). Determination of degree of substitution of sodium carboxymethylcellulose. *Analytical Chemistry*, *19*(1), 24–27.

Figueiro, S. D., Góes, J. C., Moreira, R. A., & Sombra, A. S. B. (2004). On the physico-chemical and dielectric properties of glutaraldehyde crosslinked galactomannan–collagen films. *Carbohydrate Polymers*, *56*(3), 313–320.

Gong, H., Liu, M., Chen, J., Han, F., Gao, C., & Zhang, B. (2012). Synthesis and characterization of carboxymethyl guar gum and rheological properties of its solutions. *Carbohydrate Polymers*, *88*(3), 1015–1022.

Goyal, P., Kumar, V., & Sharma, P. (2007). Carboxymethylation of tamarind kernel powder. *Carbohydrate Polymers*, *69*(2), 251–255.

Gupta, S., Sharma, P., & Soni, P. L. (2004). Carboxymethylation of *Cassia occidentalis* seed gum. *Journal of Applied Polymer Science*, *94*(4), 1606–1611.

Hebeish, A., & Khalil, M. I. (1988). Chemical factors affecting preparation of carboxymethyl starch. *Starch-Stärke*, *40*(4), 147–150.

Hebeish, A., Khalil, M. I., & Hashem, A. (1990). Carboxymethylation of starch and oxidized starches. *Starch-Stärke*, *42*(5), 185–191.

Kamel, M., Abd El-Thalouth, I., 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.

Kamel, M., Ragheb, A., Haggag, K., & Abd El-Thalout, I. (1992). Isolation, chemical modification and rheological characterization of leucaena gum. Part I: Carboxymethylation. *Starch-Stärke*, *44*(10), 374–378.

Khalil, M. I., Hashem, A., & Hebeish, A. (1990). Carboxymethylation of maize starch. *Starch-Stärke*, *42*(2), 60–63.

Kwon, K., Auh, J. H., Kim, J. W., Park, K. H., Park, C. H., & Ko, C. J. (1997). Physicochemical properties and functionality of highly carboxymethylated starch. *Starch-Stärke*, *49*(12), 499–505.

Omya, T., & Tabuchi, K. (1985). Tamarind gum carboxymethyl ether alkali metal salts. *Japanese Patent*, *60*(166), 302.

Parvathy, K. S., Susheelamma, N. S., Tharanathan, R. N., & Gaonkar, A. K. (2005). A simple non-aqueous method for carboxymethylation of galactomannans. *Carbohydrate Polymers*, *62*(2), 137–141.

Prabhanjan, H., Gharia, M. M., & Srivastava, H. C. (1989). Guar gum derivatives. Part I: Preparation and properties. *Carbohydrate Polymers*, *11*(4), 279–292.

Prado, B. M., Kim, S., Özen, B. F., & Mauer, L. J. (2005). Differentiation of carbohydrate gums and mixtures using Fourier transform infrared spectroscopy and chemometrics. *Journal of Agricultural and Food Chemistry*, *53*(8), 2823–2829.

Ragheb, A. A., El-Sayiad, H. S., & Hebeish, A. (1997). Preparation and characterization of carboxymethyl starch (CMS) products and their utilization in textile printing. *Starch-Stärke*, *49*(6), 238–245.

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.

Rekaby, M. M., Abd El-Thalouth, I., Rahman, A. A., & Abd El-Satar El-Khabery, S. (2010). Technological evaluation of carboxymethyl sesbania galactomannan gum derivatives as thickeners in reactive priniting. *BioResources*, *5*(3), 1517–1529.

Sanghi, R., Bhatttacharya, B., & Singh, V. (2002). *Cassia angustifolia* seed gum as an effective natural coagulant for decolourisation of dye solutions. *Green Chemistry*, *4*(3), 252–254.

Sharma, B. R., Kumar, V., Soni, P. L., & Sharma, P. (2003). Carboxymethylation of *Cassia tora* gum. *Journal of Applied Polymer Science*, *89*(12), 3216–3219.
Soni, P. L., & Pal, R. (1996). Industrial gum from *Cassia tora* seeds. *Trends in Carbohydrate Chemistry*, *2*, 33–44.
Stojanović, Ž., Jeremić, K., & Jovanović, S. (2000). Synthesis of carboxymethyl starch. *Starch-Stärke*, *52*(11), 413–419.
Tijsen, C. J., Scherpenkate, H. J., Stamhuis, E. J., & Beenackers, A. A. C. M. (1999). Optimisation of the process conditions for the modification of starch. *Chemical Engineering Science*, *54*(13), 2765–2772.
Yuen, S. N., Choi, S. M., Phillips, D. L., & Ma, C. Y. (2009). Raman and FTIR spectroscopic study of carboxymethylated non-starch polysaccharides. *Food Chemistry*, *114*(3), 1091–1098.