ELSEVIER

0144-8617(95)00083-6

Carbohydrate Polymers 27 (1995) 247–253
Elsevier Science Limited.
Printed in Great Britain.
0144-8617/95/$09.50+.00

A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch

Debasis Bhattacharyya, Rekha S. Singhal & Pushpa R. Kulkarni*

Food and Fermentation Technology Division, Department of Chemical Technology, Matunga, Bombay 400 019, India

(Received 26 May 1995; revised version received 13 July 1995; accepted 20 July 1995)

Conditions for the preparation of carboxymethyl derivatives of corn and amaranth starch were compared. The two starches differed considerably with respect to the optimum conditions such as temperature, pH, time, concentration of sodium monochloroacetate, and starch:liquor ratio. In both cases, isopropyl alcohol was the solvent of choice. Multistage carboxylation was also carried out. Amaranth starch differs from corn starch in two respects. It is waxy in nature and also has a small granule size of 1–2 μm. However, comparison with rice starch, having a granule size of 1–2 μm and potato starch, having a similar amylose content as corn starch showed no correlation between any of these parameters.

INTRODUCTION

The physical properties of native unmodified starches and the colloidal solutions produced on heating their suspensions limit commercial applications. Specific shortcomings include failure of the granules to swell and develop viscosity in cold water, excess or uncontrolled viscosity after cooking, cohesive or rubbery texture of the cooked starch, the sensitivity of the cooked starch to breakdown during extended cooking or shear or low pH. Starches are, therefore, modified suitably to overcome some or all of these problems. Starch ether derivatives of low degrees of substitution (DS) are probably the most important starch derivatives of commercial value (Whistler & Paschall, 1967), due to their increased solubility and high viscosity as compared to native starch. The most commonly prepared carboxyalkyl ether derivative of starch is carboxymethyl starch (CMS). The sodium salt of CMS has applications in both food as well as non-food industries, and the term CMS is loosely used to mean its sodium salt.

CMS can be prepared from a variety of starches like corn (Kataoka, 1985; Khalil *et al.*, 1990), wheat (Thewlis, 1969), potato (Kuniak *et al.*, 1985; Guns *et al.*, 1989; Bella *et al.*, 1969; Shirhizu & Araki, 1970; Szathmary *et al.*, 1970), high-amylose corn (Solan *et al.*, 1962; Senti & Russal, 1960) and related sources such as cellulose–starch mixture (Sanir & Bochow, 1983), corn starch waste (Yamauchi & Sasaki, 1991) and potato flour waste (Sasaki *et al.*, 1991). CMS is generally made by the action of an etherifying agent, monochloroacetic acid, in the presence of alkali. This is more popular than other methods using hydrolysis of the corresponding cyanoalkyl derivatives (Radley, 1968). The method is essentially based on Williamson's ether synthesis (Radley, 1976), and consists of treatment of starch with monochloroacetic acid or sodium monochloroacetate in an alkaline medium with a water-miscible solvent containing small amounts of water. Different types of solvents have been used including methanol and ethanol, but isopropanol is the solvent of choice (Suuki *et al.*, 1961). Since CMS becomes soluble above a DS of 0.1 (Whistler & Paschall, 1967), organic solvents are used to obtain granular product.

The efficiency of the carboxymethylation process is greatly influenced by the reagents used. The reaction efficiency is defined as the percentage of the reagent reacted with or substituted for starch. The remaining reagent is consumed in forming by-products. The efficiency of etherification depends upon the diffusion or penetration of the swelling agent and etherification reagent into the starch granular structure. The swelling agent, sodium hydroxide, must help by allowing uniform swelling of the starch and provides an alkaline environment throughout the reaction to ease the process. The elevated temperature of the reaction and

*Author to whom correspondence should be addressed.

solvent help by allowing diffusion of the etherifying reagent more readily to the reaction point and this may result in a reduction in consumption of the reagents.

The degree of substitution, molecular weight and distribution of the substituent determine the properties of CMS (Cch *et al.*, 1976). The main reaction parameters which influence the carboxymethylation process are the solvent system, solvent composition, material: liquor ratio, concentration of sodium hydroxide, temperature and duration of the reaction.

Since each starch type differs in its size/shape, amylose/amylopectin and other associated structural parameters, the processes of carboxymethylation for each starch type will differ. In this context, this work was planned to compare the optimisation of carboxymethylation of corn starch and waxy small size granule (1–2 μm) *Amaranthus paniculatas* starch. For comparison, rice starch, having a granule size similar to amaranth starch but an amylose:amylopectin ratio similar to corn; and potato starch, having a granule size larger than both corn and amaranth starch but an amylose: amylopectin ratio nearer to corn starch were also used.

MATERIALS AND METHODS

Corn starch was obtained from M/S Laxmi Starch Pvt. Ltd., Bombay, India. Amaranth and rice starch was isolated in the laboratory by the alkali steeping method (Yanez & Walker, 1986) and ground to 200 mesh. Potato starch was purchased from a local market in Bombay, India.

The procedure used to study the effect of process parameters on carboxymethylation was similar to that of Khalil *et al.* (1990) with the following modification. Sodium hydroxide, used as an alkylating reagent of the reaction media, was added dropwise over a fixed time interval and not once at the beginning of the reaction in order to retain the granular structure of the starch. This made subsequent steps such as the recovery of the product and drying easier. The process parameters, for example, the solvent used, starch:liquor ratio, solvent composition, alkali concentration, temperature and duration of the reaction were studied with respect to its DS. Determination of DS was based on the principles given by Sawicki *et al.* (1962) using J acid (6-amino-1-naphthol-3-sulfonic acid), the colorimetric method (Roushdi *et al.*, 1982) and as detailed previously (Khalil *et al.*, 1990).

Multistage carboxymethylation was carried out with both starches. The second and third stages of carboxymethylation were performed on CMS obtained from the first stage as raw material under the same optimised conditions. Carboxymethylation of rice and potato starch was carried out using the optimised set of conditions obtained for corn and amaranth starch.

RESULTS AND DISCUSSION

The optimisation of the process of carboxymethylation was performed by varying the process parameters. Initially, the parameters were selected on the basis of literature data (Khalil *et al.*, 1990; Habeish *et al.*, 1990). During this variation, the object of the process was a desirable DS. Each parameter was varied keeping other parameters constant as shown in different sets of trials A–G in Appendix A and A′–G′ in Appendix B.

The first effect of temperature on the reaction system was observed, the results of which are shown in Fig. 1. For corn starch, the optimum temperature was found to be 65°C, wherein a DS of 0.065 was obtained. At temperatures beyond 65°C, starch gelatinisation began with the formation of a semitransparent mass. Therefore, during carboxymethylation, the maintenance of the granular structure of starch was attempted, as well as avoiding gelatinisation which decreased the recovery of the product and made drying difficult. In the reaction media, the presence of a solvent with high electron polarisability and ions, especially anions such as chloride, were found to reduce the gelatinisation temperature as reported earlier (Oosten, 1984). At temperatures above 30°C, a similar trend was observed for amaranth starch. Amaranth starch has a lower gelatinisation temperature of 69°C as compared to corn starch (85°C). This may be responsible for the greater susceptibility of amaranth starch to gelatinisation at low temperature under the reaction conditions. Amaranth starch swells rapidly when sodium hydroxide is added and its hydroxyl group is substituted by chloroacetic acid in comparably less extreme conditions than for corn starch. Amaranth starch is waxy in nature, containing almost 100% amylopectin, and, therefore, swells more easily on addition of sodium hydroxide and water; subsequently etherification at high temperature causes a loss of granular structure and gelatinisation.

The second parameter that was selected for optimisation was the effect of addition of water to the reaction

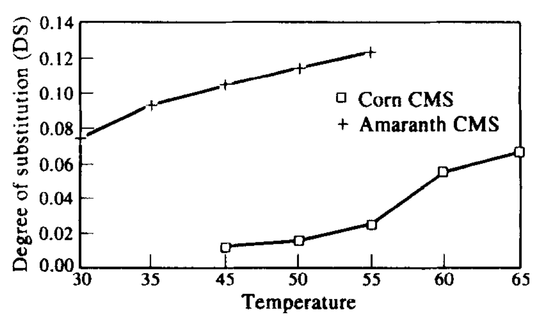

Fig. 1. Effect of temperature on the DS of CMS from corn and amaranth starch. Other conditions as shown in Appendices A and B.

mixture. Water aids the swelling of starch granules, thus facilitating the entry of etherifying agent into the starch granules. It also helps by dissolving sodium hydroxide and thus provides the alkaline environment without which carboxymethylation is not possible. The results of varying water levels in the isopropyl alcohol solvent are shown given in Table 1. In the case of corn starch, 20 ml water compared with 80 ml isopropyl alcohol was the optimum medium to give a maximum DS of 0.07, whereas for amaranth starch, this was 6 ml water with 54 ml of the solvent. The water requirement of amaranth starch was lower, probably because it is more soluble in water, swells very rapidly and has a lower gelatinisation temperature. It was also observed that addition of more than 12 ml water caused the gelatinisation of amaranth starch.

As shown in Tables 2 and 3, the effect of sodium hydroxide concentration was also studied by varying the concentration of sodium hydroxide solution, added dropwise to the reaction medium over the first hour. It was observed that the DS of CMS increased with sodium hydroxide concentration and attained a maximum at an alkali concentration equivalent to 20 ml of 4.5 N corn starch. Since the optimisation of starch: liquor (total solvent) ratio had suggested 12 ml to be the optimum volume of water at a water:starch ratio of 1:4, the concentration of sodium hydroxide was raised to 7.5 N. Applying the same argument, for amaranth starch carboxymethylation, the sodium hydroxide concentration was raised to 18.3 N. The volume of water after starch:liquor optimisation was not altered, since it was impossible to solubilise sodium hydroxide with less than 6 ml of water. Sodium hydroxide is not totally soluble in isopropyl alcohol.

At a particular alkali strength, the DS was maximum after which it started declining. This observation can be explained by considering the carboxymethylation process, where two competitive reactions take place simultaneously. The first involves reaction of the starch hydroxyl with sodium monochloroacetate in the presence of sodium hydroxide to give CMS as shown in equation (1):

Table 1. Effect of volume of water added to the reaction media on the DS of CMS

Sample No.	Volume of water (ml)	DS
Corn starch		
1	10	0.025
2	20	0.07
3	30	0.017
4	40	0.007
5	50	0.007
Amaranth starch:		
1	6	0.085
2	9	0.072
3	12	0.070
4	15	0.068

Table 2. Effect of sodium hydroxide concentration on DS of CMS from corn starch[a]

Sample No.	Sodium hydroxide concentration (N)	DS
1	2.5	0.026
2	3.0	0.027
3	3.5	0.040
4	4.0	0.064
5	4.5	0.134
6	5.0	0.120

[a] Other conditions are as described in Appendix A.

Table 3. Effect of sodium hydroxide concentration on DS of CMS from amaranth starch[a]

Sample No.	Sodium hydroxide concentration (N)	DS
1	13.3	0.083
2	15.0	0.090
3	16.6	0.099
4	18.3	0.240
5	20.0	0.210

[a] Other conditions are as described in Appendix B.

$$\text{St}-\text{OH}+\text{Cl–CH}_2\text{COONa} \rightarrow$$
Sodium monochloroacetate
$$\text{St}-\text{O}-\text{CH}_2\text{COONa}+\text{NaCl}+\text{H}_2\text{O} \quad (1)$$
Sodium carboxymethyl starch

The second reaction is that of sodium hydroxide with sodium monochloroacetate to form sodium glycolate as in equation (2):

$$\text{NaOH}+\text{Cl}-\text{CH}_2\text{COONa} \rightarrow \text{HO}-\text{CH}_2\text{COONa}+\text{NaC} \quad (2)$$

It appears that the first reaction prevails over the second up to an alkali concentration of 4.5 N for corn and 18.3 N for amaranth starch. Above these levels, glycolate formation predominates which means inactivation of monochloroacetic acid and its consumption by a side reaction. Similar observations have been reported for corn starch (Khalil *et al.*, 1990).

Figure 2 shows the effect of the concentration of monochloroacetic acid on the DS. With an increase in concentration of monochloroacetic acid up to 1.5 mol/mol starch, the DS increased in both cases, probably due to the greater availability of the acid molecules at higher concentrations in the proximity of starch molecules. At a concentration higher than 1.5 M monochloroacetic acid per mol of starch, glycolate formation seems to be favoured and the reaction efficiency decreases. The findings are supported by reports in the literature (Khalil *et al.*, 1990; Habeish & Khalil, 1988).

The enhancement in DS by prolonging the duration of the reaction is a direct consequence of the favourable

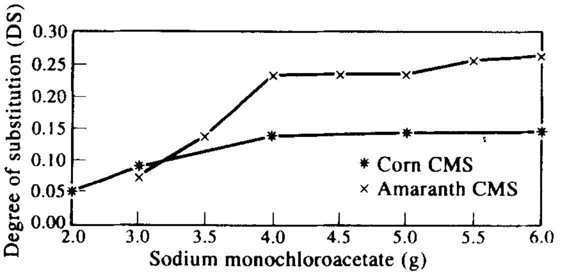

Fig. 2. Effect of concentration of sodium monochloroacetate on the DS of CMS from corn and amaranth starch. Other conditions as shown in Appendices A and B.

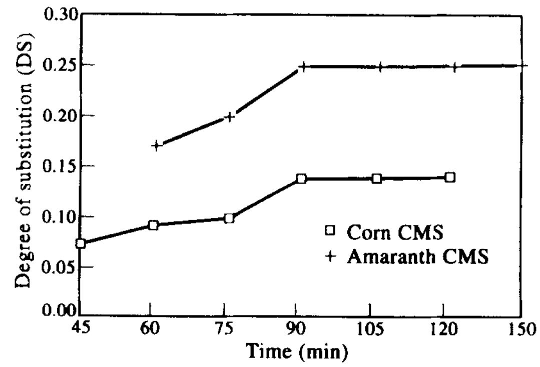

Fig. 3. Effect of time on the DS of CMS from corn and amaranth starch. Other conditions as shown in Appendices A and B.

effect of time on the swelling of starch as well as the diffusion and adsorption of the reactants with the ultimate effect of inducing better contacts between the etherifying agent and starch. Beyond 90 min of reaction time, however, no significant increase in DS was observed in both cases (Fig. 3).

The starch:liquor ratio (total solvent volume) had a significant effect on the DS of CMS. Here, liquor was considered as the total volume of solvent including water. This gave a sharp increase in the DS at a ratio of 1:7.5 for CMS from amaranth and 1:15 for CMS from corn starch (Fig. 4). The notable enhancement in the DS by a particular starch:liquor ratio signifies the role of volume of solvent medium on the carboxymethylation process. A critical amount of liquor helps the starch to swell and aids the diffusion and adsorption of etherifying agents on starch molecules. A decrease in the DS at higher liquor volume was observed which can be attributed to the reduced probability of collision of the reactants or a decrease in collision due to dilution. In the case of amaranth starch, a starch:liquor ratio lower than 1:7.5 was not possible since it was impossible to stir the reaction mixture during the reaction.

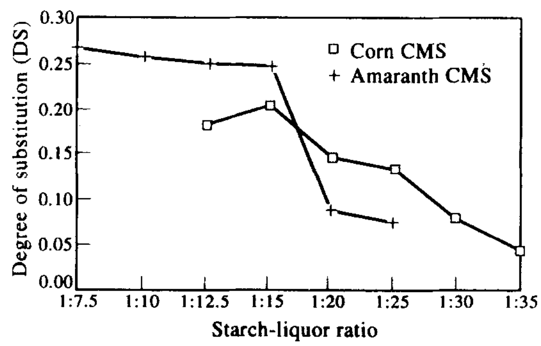

Fig. 4. Effect of starch:liquor ratio on the DS of CMS. Other conditions as shown in Appendices A and B.

Figure 5 shows the extent of carboxymethylation, expressed as DS when the reaction was carried out in different organic solvent medium. Seven different mediums were used. Among these, cyclohexane gave the best result followed by isopropyl alcohol. Cyclohexane has some toxic effects and was, therefore, not used for further work. Isopropyl alcohol was naturally the best choice which is in agreement with other reports (Khalil *et al.*, 1990; Suuki *et al.*, 1961). The effect of the solvent system on the extent of the reaction is related to miscibility, the ability to solubilise the etherifying agents and to swell the starch and creation of environment which favours carboxymethylation reaction rather than glycolate formation. The data obtained suggest that isopropyl alcohol:water in 4:1 ratio is most appropriate for both starches under study.

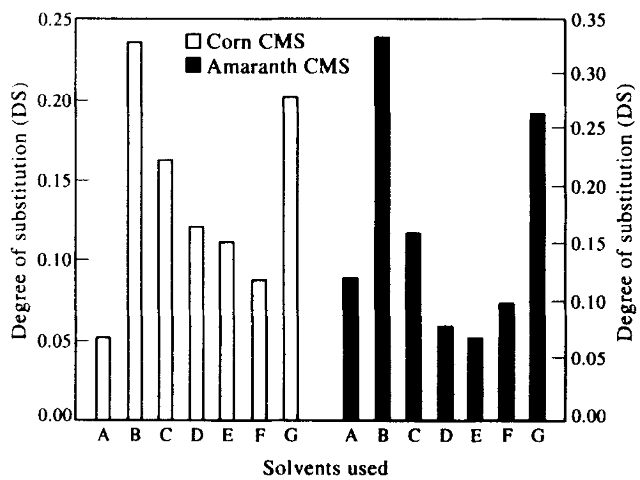

Fig. 5. Effect of various solvents on the DS of CMS from corn and amaranth starch. A, dimethyl formamide; B, cyclohexane; C, ethanol; D, acetone; E, butanol; F, methanol; G, isopropanol.

Multistage carboxymethylation (up to the third stage) was studied with both starch types and an increase in the DS was observed in both cases. In the multistage process, only an optimised set of conditions was used for both starch types. The results are as shown in Table 4. Though an increment in the DS was observed after each stage for both corn and amaranth starch, in the third stage the starches were gelatinised.

The effect on the DS of CMS prepared from rice

Table 4. Effect of multistage carboxymethylation on the DS of corn and amaranth starch

Sample	Degree of substitution		
	Stage 1	Stage 2	Stage 3
CMS from corn	0.200	0.305[a]	0.510[a]
CMS from amaranth	0.260	0.430	0.460[a]

[a] Starches were gelatinised.

Table 5. Comparison of the DS values of corn, amaranth, rice and potato starch

Conditions	Degree of substitution			
	Corn	Amaranth	Rice	Potato
Under optimised conditions of corn	0.205	—	0.206	0.194
Under optimised conditions of amaranth	—	0.265	0.117	0.266

and potato under both optimised sets of conditions of corn and amaranth starch was studied. The logic behind using such conditions was that rice starch has a similar granule size to amaranth starch, but a different amylose: amylopectin ratio. Potato starch, however, has an amylose:amylopectin ratio similar to corn starch, but a size granule greater than either corn or amaranth starch. Table 5 shows the DS measured for all the cases.

As can be seen, it is not possible to conclude a relationship between the DS of CMS and the size of the starch granule or the amylose:amylopectin ratio.

REFERENCES

Bella, J., Kodet, J., Pahl, Z. & Soukal, J. (1969). *Czech*, **130**, 554.

Cch, M., Stropnik, C. & Leskovar, S. (1976). *Starke*, **28**(4), 122.

Guns, J., Blecker, I.P. & Gielen, J.W. (1989). *EP* **332**, 292.

Habeish, A. & Khalil, M.I. (1988). *Starke*, **40**, 147.

Habeish, A., Khalil, M.I. & Hashem, A. (1990). *Starke*, **42**, 185.

Kataoka, H. (1985). *JP* **60**, 186, 504.

Khalil, M.I., Hasem, A. & Habeish, A. (1990). *Starke*, **42**, 60.

Kuniak, L., Kodet, J., Nevydal, J., Frimm, R. & Zemek, J. (1985). *Czech CS*, **219**, 107.

Oosten, B.J. (1984). *Starke*, **36**, 18.

Roushdi, M., Abdel Akher, M., Ismail, F.A. & Atia, E. (1982). *Starke*, **34**, 410.

Sanir, J.D. & Bochow, K. (1983). *Ger. (east)*, DD 158, 403 (cited in *Chemical Abstracts* **98**, 200104 x).

Sasaki, M., Watanabe, H. & Masuda, M. (1991). *JP*, **3**, 146, 502.

Sawicki, E., Hauser, T.R. & McPherson, S. (1962). *Analyt. Chem.*, **34**, 1463.

Senti, F.R. & Russal, C.R. (1960). *Tappi*, **43**, 343.

Shirhizu, T. & Araki, M. (1970). *Nippon Nogei Kagaku Kaishi*, **44**, 107.

Solan, J.W., Mehltretter, C.L. & Senti, F. R. (1962). *J. Chem. Engng Data*, **7**, 156.

Suuki, H., Tadokoro, Y. & Taketomi, N. (1961). *Denpun Kogyo Gakkaishi*, **9**, 33 (cited in *Chemical Abstract* **57**, 8784).

Szathmary, E., Petery, I. & Land, B. (1970). *Hung Teljes*, 7-08, (cited in *Chemical Abstract* **74**, 234800 c).

Thewlis, B.H. (1969). *Starke*, **21**, 21.

Whistler, R.L. & Paschall, E.F. (1967). In *Starch Chemistry and Technology*, Vol. 2. Academic Press, New York, pp. 317, 322.

Yamauchi, T. & Sasaki, M. (1991). *JP*, **3**, 146, 503.

Yanez, G.A. & Walker, C.E. (1986). *Cereal Chem.*, **63**, 164.

APPENDICES A & B FOLLOW OVERLEAF.

Appendix A. Reaction parameters used in trials of carboxymethylation of corn starch

Trial No.		Starch (g)	Solvent	Water: solvent in reaction liquor	Starch: liquor ratio	NaOH concentration (N)	Monochloroacetic acid added (g)	Temperature (°C)	Time (min)
A	1	4	Isopropyl alcohol	20:80	1:25	4	4	45	
	2	4						50	
	3	4						55	90
	4	4						60	
	5	4						65	
B	1		Isopropyl alcohol	20:80		5			
	2			10:90		10		65	
	3	4		30:70	1:25	3.33	4	65	90
	4			40:60		2.5			
	5			50:50		2.0			
C	1		Isopropyl alcohol			2.5			
	2					3.0			
	3	4		20:80	1:25	3.5	4	65	90
	4					4.0			
	5					4.5			
	6					5.0			
D	1		Isopropyl alcohol				2		
	2						3		
	3	4		20:80	1:25	4.5[a]	4	65	90
	4						5		
	5						6		
E	1		Isopropyl alcohol						45
	2								60
	3	4		1:4	1:25	4.5[a]	4	65	75
	4								90
	5								105
	6								120
F	1		Isopropyl alcohol		1:20				
	2				1:15				
	3	4		1:4	1:25	4.5[a]	4	65	90
	4				1:30				
	5				1:12.5				
	6				1:35				
G	1		Dimethylformamide						
	2		Cyclohexane						
	3	4	Ethanol	1:4	1:15	4.5[a]	4	65	90
	4		Acetone						
	5		Butanol						
	6		Methanol						
	7		Isopropyl alcohol						

[a] 4.5 N NaOH = 3.6 g NaOH.

Appendix B. Reaction parameters used in trials of carboxymethylation of amaranth starch

Trial No.	Starch (g)	Solvent	Water: solvent in reaction liquor	Starch: liquor ratio	NaOH concentration (N)	Monochloroacetic acid added (g)	Temperature (°C)	Time (min)
A′ 1	4	Isopropyl	1:4	1:15	7.5	4	30	
2	4	alcohol					35	
3	4						40	90
4	4						45	
5	4						55	
B′ 1		Isopropyl	6:54		15			
2		alcohol	9:51		10			
3	4		12:48	1:15	7.5	4	30	90
4			15:45		6.0			
C′ 1		Isopropyl			13.3			
2		alcohol			15.0			
3	4		1:9	1:15	16.6	4	30	90
4					18.3			
5					20.0			
D′ 1		Isopropyl				3		
2		alcohol				3.5		
3	4		1:9	1:15	18.3	4	30	90
4						4.5		
5						5		
7						6.0		
E′ 1		Isopropyl						60
2		alcohol						75
3	4		1:9	1:15	18.3	6.0	30	90
4								105
5								120
6								150
F′ 1		Isopropyl		1:10				
2		alcohol		1:7.5				
3	4		1:9	1:15	18.3	6.0	30	90
4				1:12.5				
5				1:20				
6				1:25				
G′ 1		Dimethylformamide						
2		Cyclohexane						
3	4	Ethanol	1:9	1:7.5	18.3	6.0	30	90
4		Acetone						
5		Butanol						
6		Methanol						
7		Isopropyl alcohol						