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Physicochemical properties of carboxymethyl starch prepared from corn and waxy amaranth starch

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

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

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Modification of corn and amaranth starch to their carboxymethyl derivatives in the degree of substitution (DS) range of 0.1–0.2 enhances their viscosity characteristics as determined on a Brabender amylograph and also improves the freeze–thaw stability. The changes in amaranth starch were more pronounced than in corn starch. All the derivatives, however, had poor flow characteristics.

INTRODUCTION

Carboxymethyl starch (CMS) is an ether derivative, having food as well as non-food applications. The applications are based on the properties of CMS, which in turn are dependent on various factors such as degree of substitution, average molecular weight, distribution of the substituents and purity (Khalil *et al.*, 1990). The reaction conditions influence these parameters and are responsible for properties such as viscosity, solubility, freeze–thaw stability etc. Although many reports are available on the manufacturing aspects of CMS, not much literature is available on the comparative properties of CMS derived from corn starch containing amylose and waxy starch devoid of amylose. Since each starch type is unique and since starches cannot be used interchangeably, this aspect is worth looking into. This communication reports on the comparative physicochemical properties of CMS derived from corn starch and waxy amaranth starch differing not only with respect to amylose content but also having an extremely tiny granule size of 1–2 μ (Singhal & Kulkarni, 1988). The degrees of substitution (DS) chosen for this study were 0.10, 0.15 and 0.20, since it is reported that CMS with a degree of substitution $\geqslant 0.4$ causes diarrhoea (Wang *et al.*, 1950).

MATERIALS AND METHODS

Corn starch was procured from M/S Laxmi Starch Pvt. Ltd, Bombay, India. Amaranth starch was extracted in the laboratory by the alkali steeping method (Yanez & Walker, 1986). The preparation of sodium carboxymethyl starch from corn and waxy amaranth starch was carried out under alkaline conditions using sodium hydroxide (dissolved in water) in isopropyl alcohol as the solvent medium and sodium monochloroacetate as the carboxymethylating agent. The reaction was carried out for a definite time period at a previously optimised temperature after which time the carboxymethyl starch was isolated by pricipitating in 95% alcohol. It was subsequently filtered and washed with 80% ethanol to make it alkali-free, reprecipitated with 95% ethanol and then dried at 85°C for a suitable time period to obtain a dry powdered product. All the parameters of this preparation were optimised (Bhattacharyya *et al.*, unpublished). In particular, sodium carboxymethyl starch (CMS) from corn and amaranth starch of DS 0.10, 0.15 and 0.20 were prepared in the laboratory as shown in Table 1 and then analysed as follows.

Moisture was estimated by the AOAC method (AOAC, 1984) and the pH values on 5% dispersions of CMS were measured using a glass calomel electrode digital pH meter. Per cent compressibility was calculated by estimating aerated bulk density (A) and packed bulk density (P) using the formula $[(P-A)/P] \times 100$ by a standard method (Lachman *et al.*, 1987).

Flow rate and angle of repose were also determined by methods documented in the literature (Craik & Miller, 1958; Danish & Parott, 1971). CMS obtained from corn and amaranth starch and having a DS of 0.1, 0.15 and 0.2 were studied in a Brabender amylograph using 5% concentration, heating at a rate of 1.5°C per

*Author to whom correspondence should be addressed.

Table 1. Conditions used for the preparation of CMS from corn and amaranth starch having DS 0.10, 0.15 and 0.20

DS of CMS	0.10	0.15	0.20
Corn starch			
Amount of starch (g)	10	10	15
Amount of NaOH (g)	9	9	13.5
Amount of sodium monochloroacetate (g)	10	10	15
Volume of isopropanol medium (ml)	200	150	180
Volume of water added to the medium through NaOH solution (ml)	50	30	35
Time of reaction (min)	90	90	90
Temperature of the reaction (°C)	50	55	65
Amaranth starch			
Amount of starch (g)	12	12	15
Amount of NaOH (g)	9.6	10.8	16.5
Amount of sodium monochloroacetate (g)	12	12	22.5
Volume of isopropanol medium (ml)	72	72	90
Volume of water added to the medium through NaOH solution (ml)	18	18	22.5
Time of reaction (min)	90	90	90
Temperature of the reaction (°C)	Room temp. (30 ± 2°C)	Room temp. (30 ± 2°C)	Room temp. (30 ± 2°C)

Table 2. Moisture content and pH of 5% CMS prepared from corn and amaranth starch[a]

Sample	Moisture (%)	pH of 5% solution
Corn CMS		
DS 0.10	5.72 ± 0.10	8.92 ± 0.32
DS 0.15	6.10 ± 0.21	9.50 ± 0.20
DS 0.20	6.50 ± 0.16	9.70 ± 0.20
Amaranth CMS		
DS 0.10	6.48 ± 0.06	9.20 ± 0.41
DS 0.15	6.63 ± 0.12	9.80 ± 0.36
DS 0.20	7.10 ± 0.10	9.90 ± 0.11

[a]Values are mean ± S.D. of three individual determinations.

Table 3. Flow characteristics of CMS from corn and amaranth starch[a]

Flow characteristics	Angle of repose (°)	Flow rate (g/s)	% Compressibility
Corn CMS			
DS 0.10	44.3 ± 1.5	1.46 ± 0.18	6.9 ± 1.7
DS 0.15	45.0 ± 2.5	0.95 ± 0.22	7.9 ± 0.9
DS 0.20	45.7 ± 2.5	0.67 ± 0.18	8.48 ± 1.3
Amaranth CMS			
DS 0.10	44.2 ± 2.5	1.60 ± 0.19	7.6 ± 1.0
DS 0.15	45.7 ± 2.1	0.76 ± 0.13	7.8 ± 1.3
DS 0.20	46.4 ± 1.7	0.63 ± 0.10	8.48 ± 1.9

[a]Values are mean ± S.D. of three individual determinations.

min from room temperature to 95°C, holding at 95°C for 10 min and then cooling back to 25°C at the same rate of 1.5°C per min.

5% pastes of CMS were also evaluated for freeze–thaw stability by alternate freezing and thawing for 18 h at −18°C and 6 h at room temperature, respectively, followed by centrifuging at 4000 r.p.m. for 10 min. The percentage of water separated after each freeze–thaw cycle was measured and this was continued up to six freeze–thaw cycles (Kite *et al.*, 1963).

RESULTS AND DISCUSSION

Table 2 gives the moisture content and pH of different 5% CMS solutions. The moisture content of CMS samples ranged from 5.7 to 7.1% for all DS, similar to carboxymethyl cellulose (Thewlis, 1969). The pH values of all the 5% CMS solutions were very close to each other, being in the alkaline range. This could be due to the presence of a small quantity of alkali which could have been trapped in the swollen granules.

Per cent compressibility was calculated from aerated bulk and packed bulk density for CMS samples. As shown in Table 3, it was observed that at lower DS, CMS prepared from amaranth starch had higher per cent compressibility which indicates lower flowability of the material (Lachman *et al.*, 1987; Carr, 1965). Results from Table 3 indicate better flowability characteristics for the commercial sample. The angle of repose and the flow rate are given in Table 3. From both these values, it can be concluded that CMS samples made from corn and amaranth starch at lower DS have better flowability than that of CMS at higher DS. The better flowability of a commercial sample of CMS was also evident from these values. From the values of angle of repose and flow rate measured for various CMS samples, it can be said that since the angle of repose was more than 40° for all cases, carboxymethyl starch is a poorly flowing material (Lachman *et al.*, 1987). This could be attributed to slight hygroscopicity of CMS, because of which it absorbs moisture from the air which is retained on the surface.

The Brabender characteristics of CMS with DS 0.10, 0.15 and 0.2 and also those of the native starch from which these derivatives have been obtained are given in Table 4. It can be seen that CMS paste with low DS had higher peak viscosity as compared to that of higher DS. This was found to be true for both corn and amaranth CMS. CMS from amaranth starch had

Table 4. Brabender viscosity characteristics of CMS samples from corn and amaranth starch[a]

Sample	Corn CMS of DS			Amaranth CMS of DS		
	0.10	0.15	0.20	0.10	0.15	0.20
Gelatinization temp (°C)	28 (85)	25	25	30 (68)	30	27
Peak viscosity (BU)	270 (105)	230	200	1900 (295)	1360	1080
Viscosity at 95°C (BU)	140 (105)	115	110	1080 (260)	940	680
Viscosity after holding at 95°C for 10 min (BU)	95 (85)	110	200	1100 (255)	980	640
Viscosity after cooling to 30°C (BU)	200 (220)	210	200	1820 (320)	1820	740

[a]Values in parentheses are those for native unmodified corn and amaranth starch.

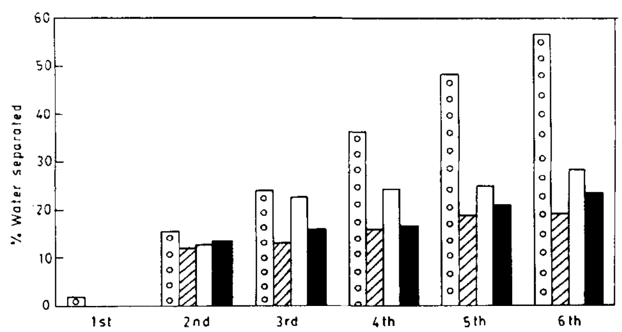

Fig. 1. Freeze–thaw stability of carboxymethyl corn starch: ⊡, native corn starch; ▨, corn CMS at 0.1 DS; □, corn CMS at 0.15 DS; ■, corn CMS at 0.2 DS.

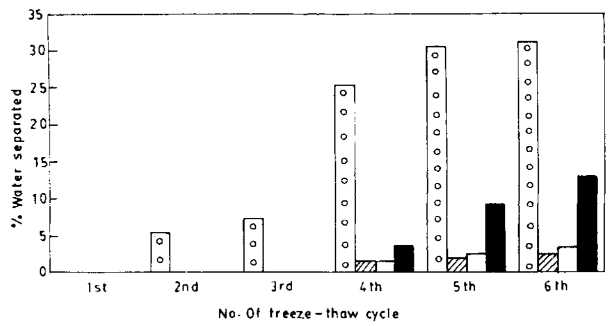

Fig. 2. Freeze–thaw stability of carboxymethyl amaranth starch: ⊡, native amaranth starch; ▨, amaranth CMS at 0.1 DS; □, amaranth CMS at 0.15 DS; ■, amaranth CMS at 0.2 DS.

a much higher viscosity. This could be because the native starch itself had a high viscosity and carboxymethylation enhanced this characteristic. Amaranth starch is waxy and, therefore, has a more branched structure than corn starch. This could be responsible for amaranth starch's greater hydrogen bonding with water molecules, and its greater absorption of water as compared with corn starch. This interaction with water is probably enhanced by carboxymethylation. These findings are also supported by an earlier finding (Solan *et al.*, 1962).

The freeze–thaw stability of carboxymethyl starch pastes are shown in Figs 1 and 2. Amaranth starch is known to have a better freeze–thaw stability than corn starch (Singhal & Kulkarni, 1990) which seems to be true also of its carboxymethyl derivative. The CMS with lower DS had better freeze–thaw stability than that at higher DS, supporting the fact that CMS at lower DS can entrap water more effectively than CMS at higher DS.

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