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MICROWAVE ASSISTED SYNTHESIS OF CARBOXYMETHYL STARCH

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ABSTRACT

A simple and efficient method is described for the synthesis of carboxymethyl starch (CMS) using insoluble wheat starch under microwave irradiation. The reaction of starch with monochloro acetic acid or its sodium salt in presence of sodium hydroxide in isopropanol or isopropanol : water (80 : 20 v/v) gives CMS. The degree of substitution (D.S.), active content (A.C.) and alkaline fluidity (A.F.) of the CMS were studied with respect to reaction time and concentration of reactants.

Key words: Carboxymethyl starch, Wheat starch, Microwave irradiation.

INTRODUCTION

Sodium alginates have become very important for print paste thickening because of their ready solubility, even after high temperature fixation treatments. They are especially important for pastes of reactive dyes, because the extent of interaction is very small. This is due to the absence of primary hydroxyl groups and to the repulsion of dye anions by the ionized carboxyl groups of the polymer under alkaline conditions. Sodium alginate is suitably used as thickener, however, because of its limited supply and relatively high cost and, considerable attention has been focused on the discovery of alternative to it[1].

In the rapidly increasing biopolymers industries, starch derivatives play an important role because of its low cost, non-toxic, renewable and compatibility with many other materials for industrial applications. They are used in diverse polymer applications directly or in combination with other synthetic polymers. Starch derivatives were extremely used in food[2,3], environmental management[4-6], agriculture[7], pharmacy[8], biomedical engineering[9] and textile[10].

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The term starch derivatives include those modifications, which change the chemical structure of some of the D-glucopyranosyl units in the molecule. These modifications usually involve etherification, oxidation, hydrolysis, esterification, cross-linking, grafting and dextrinization. Of particular importance among these, in textile printing, are starch ethers and grafted starch based thickeners. When starch is used in its native form, then there occur certain limitations because of its undesirable properties such as poor solubility, low mechanical properties, instability at high temperature, pH and shear during processing. Therefore, modifications of starch become important for the specific industrial processes.

Modification of starch properties by derivatization is an important factor in the continued and increased use of starch to provide thickening, gelling, binding, adhesive and film-forming functionality[11]. Chemical modification of starch involves the reaction of hydroxyl groups on the AGU based on oxidation[12], acetylation[13], hydroxypropylation[14] carboxylation[15] and cross-linking.[16] There are number of starch derivatives such as hydroxyl ethyl starch (HES), cyanoethyl starch (CES), carbamoylethylated starch, carboxymethyl starch (CMS) etc.

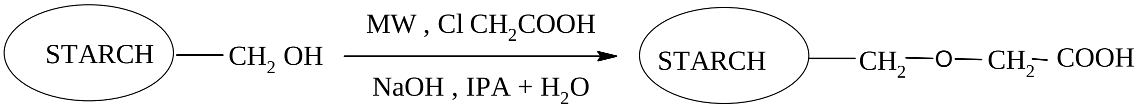
Among the derivatives of starch, carboxymethyl starch (CMS) is one of the most important starch derivatives, synthesized first in 1924. It is extensively used in textile, petroleum, food and pharmaceutical industries. It is also useful for the non-food applications like as paper additives, thickening agent and auxiliary agents in pharmaceuticals[17]. CMS are white or cream coloured granular starch ethers and esters. Being ethers, they are resistant to cleavage by acids, alkalis and mild oxidizing agents.

CMS is obtained by reacting starch with monochloro acetic acid or its sodium salt in presence of sodium hydroxide. The etherification of the OH group of the starch leads to significant change in the properties of starch. It prevents association of the starch molecules. At the same time, the solubility and washing off properties are considerably improved. CMS has been used as thickener in polyester printing and disperse dyes[18].

The present study deals with the synthesis of CMS at optimized conditions like high product yield, high reaction efficiency and high DS. Here DS indicates the amount of carboxymethyl group formed from starch molecules. It is defined as the average number of substituent per anhydro glucose unit (AGU). AGU is monomer of starch having three hydroxyl groups. Therefore DS is always in between 0 to 3. The functional properties of CMS depends on DS which includes the viscosity of the solution, film forming properties, interaction with cations, formation of supramolecular aggregates and rheological properties.

The important sources of starch, used for the synthesis of CMS, are potato starch[19], rice starch[20], corn starch, amaranth starch[21], wheat starch[22], cassava starch[23], mung bean starch[24], cocoyam starch[25], water yam starch[26] and pigeon pea[27]. Several methods were used for the synthesis of CMS[28-30], while traditional method was used for the synthesis of CMS, the degree of dissociation of CMS was quite low (0.01 to 0.1)[31]. In cold water, the product could not be dispersed, while in 80% methanol it was soluble and the DS increases above 0.5[32].

In the present study, modification or derivatization of wheat starch (insoluble) was carried out to develop the natural thickener for printing. Carboxymethyl starch was prepared by 'Williamson Etherification' by reacting wheat starch (insoluble) with monochloro acetic acid in presence of sodium hydroxide under variety of conditions using microwave irradiation (Scheme 1).



Scheme 1

EXPERIMENTAL

Procedures

Preparation of carboxymethyl starch (CMS)

20 g of the wheat starch (Insoluble) was introduced in a 250 mL beaker containing isopropanol or isopropanol : water (80 : 20 v/v) mixture. Then required amount of sodium hydroxide pellets based on the amount of monochloro acetic acid was added to the mixture. (Two moles of sodium hydroxide per one mole of monochloro acetic acid were used). The reaction mixture were mixed well and stirred at 30°C for 30 minutes. Monochloro acetic acid was then added gradually with agitation. Then the reaction mixture was subjected to microwave irradiation at 180 W for 10-30 minutes at an interval of 1 minute. At the end, the excess of caustic soda was neutralized with glacial acetic acid and filtered. Purification of CMS was carried out by washing with methanol (80-90%) to freed sodium glyconates, sodium chloride and sodium acetate, and dried under vaccum at 70°C for 5 hours.

The carboxymethylation was studied with respect to degree of substitution (DS), active content (A.C.) and alkaline fluidity (A.F.). The CMS of different degrees of substitution were prepared by changing either the reactants ratio or the reaction time.

Determination of Degree of Substitution (D.S.)

The residue (0.5 g) was ashed gently in a crucible. The ash was dissolved in water and titrated against H_2SO_4 (0.1 N) using methyl red indicator. To ascertain the presence of sodium chloride in the ash, it is titrated with 0.1 N silver nitrate and correction factor for CMS content is applied.

$$\text{Degree of substitution (D.S.)} = \frac{0.162\,B}{1 - 0.08\,B}$$

$$\text{Where, } B = \frac{0.1 \times b}{c}$$

b = volume of H_2SO_4 in mL.

c = mass of residue in g.

Determination of Active Content (A.C.)

1 g of CMS was taken in a 250 mL beaker. Then 10 mL HCl solution (1 N) was added and the content was stirred for 10 minutes. After adding 20 mL of water, the solution is neutralized with NaOH solution (1 N) using phenolphthalein. The solution was made alkaline by adding 0.2 mL NaOH solution (1 N) in excess. Sodium CMS was precipitated by adding 160 mL of alcohol (95%) with vigorous agitation. The beaker is placed in a steam bath. The residue is filtered through a G-3 sintered glass crucible and the beaker is washed with alcohol (80%). The precipitate is washed with alcohol (95%) followed by ether. The crucible is dried at 105°C for 1-2 hours. It is cooled in a desiccator and weighed.

Determination of Fluidity (A.F.)

First funnel is standardized in terms of time required for the flow of 100 mL distilled water through it. This time should be between 70-75 sec. A paste of dry starch (about 4.5 g) in 10 mL distilled water was made. Then 90 mL NaOH solution (1%) was added and stirred for 5 minutes and placed in a water bath for about 30 minutes at room temperature. The starch paste is then transferred to the funnel and the amount of starch paste in terms of mL flowed through the funnel within 70-75 sec is measured. This volume is designated as the fluidity.

RESULTS AND DISCUSSION

Carboxymethyl starch (CMS) was prepared by reacting starch with monochloro acetic acid or its sodium salt in presence of sodium hydroxide under microwave irradiation (Scheme 1). The carboxymethylation reaction was studied with respect to the D.S., A.C. and A.F. of the CMS. Variables studied include concentration of the reactants, reaction medium and reaction time. The results for the preparation of CMS were tabulated in the Table 1. D.S. was greatly enhanced by increasing the reaction time (entries 1-3 and 4-6). D.S. also increases with increasing both monochloroacetic acid and sodium hydroxide concentration. It was also observed that alkaline fluidity increases with decrease in active content both in either IPA or IPA : Water mixture. It was found that isopropanol : water [80 : 20] constitutes the most favorable medium for the carboxymethylation reaction to prepare CMS with required D.S. and fluidity. Resulting CMS could be very good thickener in printing, paste with environmentally renewable and partially or fully alternating material for sodium alginate.

Table 1: Characteristic properties of CMS

CMS	Starch (g)	CAA (g)	NaOH (g)	IPA-Water	Time (min.)	Wt. of crude CMS (g)	DS (%)	AC (%)	AF (mL)
CMS-1	20	14.17 (0.15 mol)	12 (0.3 mol)	IPA	10	28	0.6	77.5	05
CMS-2	20	16.53 (0.175 mol)	14 (0.35 mol)	IPA	20	30	0.7	70.0	10
CMS-3	20	18.90 (0.2 mol)	16 (0.4 mol)	IPA	30	31	1.0	55.2	58
CMS-4	20	14.17 (0.15 mol)	12 (0.3 mol)	IPA : Water 80 : 20	10	26	0.5	89.0	17
CMS-5	20	16.53 (0.175 mol)	14 (0.35 mol)	IPA : Water 80 : 20	20	28	0.6	80.0	22
CMS-6	20	18.90 (0.2 mol)	16 (0.4 mol)	IPA : Water 80 : 20	30	31	0.8	75.0	29

CONCLUSION

In conclusion, microwave irradiation technique is found to be efficient and rapid method for the preparation of carboxymethyl starch in IPA : Water mixture.

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