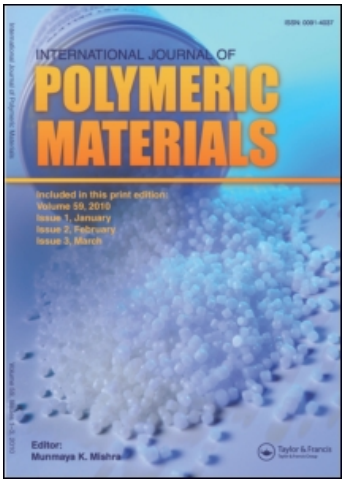


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# Synthesis and characterization of Sodium salt of partially carboxymethylated starch

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# SYNTHESIS AND CHARACTERIZATION OF SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED STARCH

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*Sodium salt of partially carboxymethylated starch (Na-PCMS) was prepared in a completely heterogeneous process in an isopropyl water slurry and the influence of the reaction conditions on the degree of substitution (DS) was checked. The concentration of aqueous sodium hydroxide solution, which was used to activate the starch, was varied in the range from 8 to 30% Wt, reaction time from 2 to 6 hr at 55°C. The reaction with sodium monochloroacetate leads to the highest degree of substitution of 1.24 at a NaOH concentration of 15% and 5 hr reaction time. Using a lye concentration of 30% no influence of the reaction time between 2 hr and 6 hr was found. From FTIR spectroscopical studies it was concluded that all the samples were Na-PCMS.*

*Keywords*: carboxymethylated starch, IR spectrum synthetic conditions

## INTRODUCTION

A process to produce carbohydrate esters and ethers was disclosed in 1927, wherein starch and cellulose were etherified. In the process, starch is first converted into alkali starch and subsequent treatment with monochloroacetate [1]. In 1952, starch was partially carboxymethylated having viscosity of 128 centipoises in 10% solution [2] Large scale production of Na-PCMS is carried out by slurry process *i.e.*, by conversion of alkali starch swollen in aqueous NaOH and a surplus of an organic liquid *e.g.*, ethanol or isopropanol with monochloroacetic acid or its sodium salt.

The carboxymethyl starch is one of the most important ether derivatives in which the hydroxyl groups are partially substituted with the ether group —O—$CH_2$—COOH. The term CMS is commercially applied for the water

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soluble starch ether which is actually the sodium salt of carboxymethyl starch. It is frequently called the sodium starch glycolate [3].

$$2XNaOH + XClCH_2COOH + C_6H_7O_2(OH) \rightarrow C_6H_7O_2(OH)_3{-}X(COONa)X + XNaCl + 2XH_2O$$

where X is the degree of substitution obtained [4]. With even a modest substituent content the products are largely water soluble polyelectrolytes with somewhat viscous dispersions. Various methods were also used for determining the degree of substitution in CMS derivatives. These are volumetric [5, 6] precipitation [7–9] and colorimetric [10] methods.

The aim of the paper is to furnish details about synthesis and characterization of sodium salt of partially carboxymethylated starch. The previous work attempts to show the infrared spectral analysis of the samples prepared with varying degrees of substitution, ranging from 0.66 to 1.24. In the process, a fixed quantity of starch is suspended in isopropanol. It is stirred for 15 minutes and sodium hydroxide solution 10–30% is added at room temp. The stirring is continued for 1 hr. In a later stage, a fixed quantity of sodium monochloroacetate is added and the reaction is continued for 2–6 hr. The product was isolated purified and D.S. was measured. All the samples were confirmed to be Na-PCMS by infrared spectral analysis showing key peaks at 3400 $cm^{-1}$ and 1635 and 1440 $cm^{-1}$.



## EXPERIMENTAL

Starch (L.R) from Qualigen fine Chemicals Mumbai, Sodium Hydroxide pellets from Chiti Chem, Baroda. Sodium monochloroacetate and isopropyl alcohol were of Laboratory Reagent Grade (L.R).

### Carboxymethylation of Starch

Carboxymethylation was carried out by a standard slurry method. 5 gm of starch in 150 ml isopropanol were stirred vigorously, while 15 ml of 8 to 30% (w/v) aqueous NaOH were added dropwise during 10 minutes at room temperature stirring was continued for 1 hr to activate the starch and 6 gm sodium monochloroacetate were then added. The mixture was then placed on a water bath at 55°C for 5 hr with stirring. The mixture was filtered, suspended in 300 ml of methanol and neutralized with acetic acid. The product was washed with ethanol and dried at 60°C. The DS was measured. The white colored product obtained was then ground into fine particles. The yield was 8–10 gm.

Infrared spectral analysis helps in confirming the preparation of Na-PCMS. The spectra of Na-PCMS samples were taken in KBr pellets using a FTIR inkjet nicolet 400D spectrophotometer. Figure 1 represents the IR

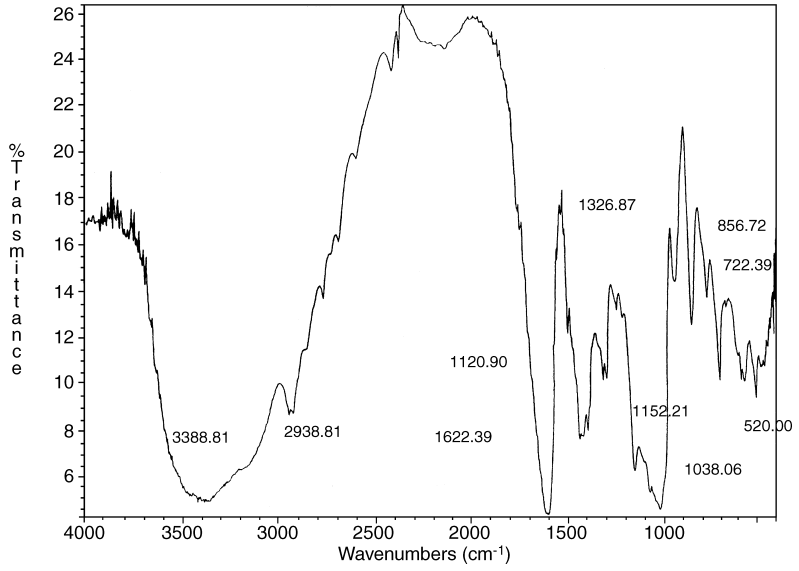


**FIGURE 1** IR spectrum of Na-PCMS.



spectra of Na-PCMS. The key peaks are shown at 3400 $cm^{-1}$ and 1635 and 1440 $cm^{-1}$.

## RESULTS AND DISCUSSION

To activate the starch and to initiate the carboxymethylation reaction, aqueous sodium hydroxide solution is commonly used. In dependence on the lye concentration, the polymer swells to various extent and yields a more or less amorphous polymer. Beyond a lye concentration of 12 to 15% a uniform activation of the whole material is reached. *i.e.*, a uniform accessibility of any reactive hydroxyl group is guaranteed. This is due to the so called intracrystalline swelling caused by an inclusion of NaOH and water in the crystallites.

### Reaction Conditions Versus Degree of Substitution

In our experiments, starch slurried in isopropanol was converted with sodium monochloroacetate after activation of the polymer with aqueous NaOH solution in the concentration range from 8 to 30% using different reaction times from 2 to 6 hr at 55°C.

Na-PCMS samples synthesized show the typical absorptions as indicated by the results Table 1 it has to be emphasized that under all reaction conditions applied Na-PCMS was obtained. The IR spectra of all samples

**TABLE 1** Effect of reaction parameters on degree of substitution

| *Sr. no.* | *Reaction time, hr* | *NaOH used, gm* | *Yield, gm* | *D.S* |
|---|---|---|---|---|
| 1 | 2 | 8 | 8.2 | 0.66 |
| 2 | 2 | 10 | 8.3 | 0.70 |
| 3 | 2 | 30 | 8.3 | 0.97 |
| 4 | 3 | 8 | 7.5 | 0.77 |
| 5 | 3 | 10 | 8.3 | 0.81 |
| 6 | 3 | 15 | 8.5 | 0.94 |
| 7 | 3 | 20 | 8.1 | 0.97 |
| 8 | 3 | 30 | 8.1 | 0.97 |
| 9 | 4 | 8 | 8.3 | 0.78 |
| 10 | 4 | 10 | 8.4 | 0.93 |
| 11 | 4 | 15 | 8.8 | 1.20 |
| 12 | 4 | 20 | 8.2 | 1.09 |
| 13 | 4 | 30 | 8.2 | 0.98 |
| 14 | 5 | 8 | 8.5 | 0.93 |
| 15 | 5 | 10 | 8.6 | 1.00 |
| 16 | 5 | 15 | 8.1 | 1.24 |
| 17 | 5 | 20 | 8.7 | 1.03 |
| 18 | 5 | 30 | 8.7 | 0.95 |
| 19 | 6 | 8 | 8.3 | 0.86 |
| 20 | 6 | 10 | 8.3 | 0.92 |
| 21 | 6 | 15 | 8.4 | 1.20 |
| 22 | 6 | 20 | 8.5 | 1.15 |
| 23 | 6 | 30 | 8.5 | 0.95 |



reveal the presence of starch backbone as well as peaks at 1610 and 1420 $cm^{-1}$, indicating the presence of the carboxy methyl group. Figure 1 shows representative spectrum of Na-PCMS.

The DS reached a maximum value of 1.24 at a concentration of 15% aqueous NaOH after a reaction time of 5 hr. Any other NaOH concentration and/or reaction time gave products of lower DS. It is worth mentioning that the extension of the reaction time to 6 hr does not result in products of higher DS.

From the results in Table 1 it is obvious that at low lye concentration of 8 and 10%, a strong influence exists of the reaction time on the achieved DS. For instance the DS is 0.66 after 2 hr and 0.93 after 5 hr reaction time at 8% NaOH concentration. It is surprising that the DS values are lower after a reaction time of 6 hr. This phenomenon was observed in some cases. A possible explanation may be the fact that the prolongation of reaction time leads to an increased degradation of the polymer especially at high NaOH concentration.

At concentration in the range from 15 to 30% of the aqueous NaOH solution the influence of the reaction time on the achieved DS is much less

pronounced. Using a 30% aqueous NaOH solution the DS values are in the range from 0.95 to 0.99.

It may be concluded about the carboxymethylation of starch in the system isopropanol/aqueous NaOH solution, that best results are reached with a 15% aqueous NaOH solution and after a reaction time of 5 hr at 55°C.

## CONCLUSION

From the results, it may be concluded that both the higher DS and conversion of sodium monochloroacetate are reached using a 15% aqueous sodium hydroxide solution for activating the polymer. FTIR spectral analysis confirmed that all the samples prepared are Na-PCMS. Carboxymethylation of starch in the presence of a 30% aqueous NaOH solution yields products with a DS of approximately 0.95–0.99, independent of the reaction time.



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