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# Carboxymethylation of maize starch at mild conditions

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ABSTRACT

A process for carboxymethylation of maize starch (St.) at 30 °C was adopted. Although mild reaction conditions were employed, 100% reaction efficiency and a completely cold water soluble product with a clear and transparent solution were obtained. A multifunctional catalyst was used to accelerate the carboxymethylation reaction at 30 °C. An increase in the catalyst concentration was found to increase the reaction rate, thus the reaction time was reduced from 168 to 24 h. Factors affecting the carboxymethylation reaction such as material:liquor ratio, using different solvents in the reaction medium, the ratio between solvent and water, the sequence of addition of the reactants and cooling during addition of the reactants were studied. 100% reaction efficiency was obtained using equivalent molar ratios of etherifying agents (0.2 mol/mole St.), 0.3 mol/mole St. of catalyst; isopropanol:water ratio of 90:10 and a material:liquor ratio of 1:1.5 at 30 °C for 24 h. The carboxymethylation reaction was tested for its reproducibility and suitability for other types of starch (rice and potato) while the carboxymethyl starch (CMS) prepared was further characterized for its viscosity, transparency and suitability as a sizing agent for cotton yarns. The CMS prepared was found suitable as a sizing agent. The tensile strength of the sized samples increased by 38.6% compared with the blank samples and the desizing efficiency of the sized samples was 98% at 30 °C.

## 1. Introduction

Since its first synthesis in (1924), CMS has become one of the most important modified starch products to be widely applied in the textile, petroleum, paper, food and pharmaceutical industries as stated by Zhang and Wu (1992).

In the textile industry, CMS has been used as a sizing agent as mentioned by Hebeish, Khalil, and Hashem (1990) and Mostafa and El-Sannabary (1997). It has also been used as a thickening agent in printing pastes using disperse, reactive, direct, vat and naphthol dyes as reported by Ragheb, El-Sayiad, and Hebeish (1997) and Kumbasar and Bide (2000). CMS has also been used as a finishing agent as noted by Mostafa and Morsy (2004).

Although many research papers and patents according to Sen and Pal (2009), Bi, Liu, Wu, and Cui (2008), Lawal, Lechner, Hartmann, and Kulicke (2007), Volkert, Loth, Lazik, and Engelhardt (2004), Kwon, Cho, Park, and Ko (1998, 1997), Kwon et al. (1997), Bhattacharyya, Singhal, and Kulkarni (1996, 1995a, 1995b), Yang, Hattori, and Takahashi (1995), Hattori, Yang, and Takahashi (1995), Yamauchi and Sasaki (1992), Portnoy and Eastman (1991), Kako and Tokunage (1990a, 1990b), Khalil, Hashem, and Hebeish (1990) have been published on the preparation, manufacturing and application of CMS, the relation between the quality and the costs still plays an important role in the manufacture of CMS. So, CMS still finds a great interest.

The textile industry is one of the most important industries in Egypt. Unfortunately, the CMS used in the Egyptian textile industry is not a local product. The need to produce a local high quality CMS with lower costs for use in the textile industry, as a substitute of imported CMS, was the motive behind the current work.

The challenge in this work is to make equilibrium between the quality and the costs. This could be done via reducing the costs by using mild reaction conditions, lowering the concentrations of the reactants and using simple equipment. Quality could be achieved by uniform distribution of the carboxymethyl groups along the starch molecule and full utilization of the etherifying agents thus high (*E*%) could be obtained.

In this work, a carboxymethylation method has been adopted and used to produce a high quality CMS product at mild reaction conditions. All the reactions took place at room temperature (30 °C) without stirring during the reaction course and simple reactor was used (a sealable bottle).

## 2. Experimental

### 2.1. Materials

Native maize starch (NS) was kindly supplied by the Egyptian Company for Starch and Glucose Manufacture, Cairo, Egypt.

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Sodium hydroxide, sodium carbonate monohydrate, ethanol, isopropanol, methanol were of commercial grade. Monochloroacetic acid, hydrochloric acid, acetic acid, tertiary butanol and propylene glycol were of laboratory grade.

Light cotton fabric was kindly supplied by Misr Company for spinning and weaving, El-Mahala El-Kobra, Egypt.

### 2.2. Methods and procedures

#### 2.2.1. Carboxymethylation

A certain amount of maize starch was placed in a sealable bottle and mixed together with a known volume of the solvent. An aqueous solution of sodium hydroxide was added drop wise to the starch–solvent mixture under stirring until the whole amount of sodium hydroxide were added. The sodium salt solution of monochloroacetic acid, prepared by the reaction of monochloroacetic acid with sodium carbonate monohydrate, was added drop wise to the starch–solvent–sodium hydroxide mixture under continuous stirring until complete addition of the sodium monochloroacetate solution. Stirring was then stopped and the bottle was closed and kept at 30 °C for certain reaction time. After carboxymethylation, the CMS samples were washed with ethanol:water solution (80:20) while excess alkali was neutralized using acetic acid. After washing, the CMS samples were filtered, oven dried at 100 °C.

#### 2.2.2. Cooking

A solution containing 10 g of the prepared CMS in 100 $cm^3$ of water was kept under stirring in a thermostatic water bath. The temperature of the water bath was raised gradually until it reached to 85 °C and left, at this temperature, for 30 min.

#### 2.2.3. Sizing and desizing

*Sizing*: The light cotton fabric samples were padded in the cooked CMS solution and squeezed to a wet pick up of ca 100% and dried in an electric oven at 100 °C for 3 min.

*Desizing*: The sized light cotton fabric samples were washed with water at 30 °C for 1 h using a thermostatic water bath then rinsed with water and dried in an electric oven at 100 °C.

### 2.3. Characterizations and analyses

#### 2.3.1. Degree of substitution

The DS of the carboxymethylated starch samples was determined via determination of the carboxyl content according to Daul, Reinhardt, and Reid (1953).

#### 2.3.2. Solubility

The solubility of the carboxymethylated starch was determined according to Seydel (1972, chap. VI).

#### 2.3.3. Reaction efficiency

The percent of reaction efficiency ($E\%$) was calculated as follows:

$$E\% = (\text{practical DS}/\text{theoretical DS}) \times 100$$

#### 2.3.4. Apparent viscosity

The apparent viscosity of the cooked starch and CMS samples was determined using a co-axial rotary viscometer (Haake RV 20) at 85 °C using a range of shear rates between 129 and 1161 $s^{-1}$. The viscosities at 516 $s^{-1}$ of the down curves of both NS and CMS were recorded for sake of comparison.

The apparent viscosity was calculated as follows:

$$\eta = T/D \ (\text{Pa s})$$

$$\eta = (T/D) \times 1000 \ (\text{mPa s})$$

where: $\eta$ is the apparent viscosity (mPa s), $T$ is the shear stress (Pa) and $D$ is the shear rate ($s^{-1}$).

#### 2.3.5. Tensile strength and elongation at break

Tensile strength and elongation at break of the light cotton fabric (control) samples and the sized light cotton fabric samples were determined according to ASTM procedure D-2296-66T.

#### 2.3.6. Transparency

Transparency of the CMS solution was measured using UV–vis spectrophotometer, Shimadzu Scientific Instrument by measuring the transparency of 0.1% aqueous solution at 623 nm according to Kwon et al. (1998).

## 3. Results and discussion

### 3.1. Mechanism of the reaction

The carboxymethylation process could be considered by the following three reactions:

$$2ClCH_2COOH + Na_2CO_3 \cdot H_2O \rightarrow 2ClCH_2COONa + CO_2 + 2H_2O \quad (1)$$

$$\text{St-OH} + ClCH_2COONa \xrightarrow{NAOH} \text{St-OCH}_2COONa + NaCl + H_2O \quad (2)$$

$$NaOH + ClCH_2COONa \rightarrow \text{HO-CH}_2COONa + NaCl \quad (3)$$

Eq. (1) represents the reaction between $ClCH_2COOH$ and $Na_2CO_3{\cdot}H_2O$ to form $ClCH_2COONa$. In Eq. (2), sodium hydroxide is required for the carboxymethylation process, in an amount equivalent to the $ClCH_2COONa$. If the concentration of NaOH is too high, formation of sodium glycolate takes place according to Eq. (3) as reported by El-Sheikh (1999, chap. 2).

A multifunctional catalyst (alkali metal hydroxide) acting as: (i) swelling agent, and (ii) etherifying agent was used. Thus, breaking the H-bonds, consequently opening up the starch structure, decreasing the crystallinity, making the starch molecule more accessible to carboxymethylation, and guaranteeing the penetration of the etherifying agents. Thus, utilizing the etherifying agents to a great extent as stated by El-Sheikh (1999, chap. 2).

### 3.2. Rate of carboxymethylation reaction

#### 3.2.1. DS, reaction efficiency and rate constant after 50 h

Native maize starch was carboxymethylated at 30 °C for 50 h using 0.2 mol of both sodium monochloroacetate and sodium hydroxide/mole St. in absence of catalyst. Ethanol was the solvent and was used with water in a ratio of 70:30 (ethanol:water). The material:liquor ratio was 1:2.5. No cooling during the addition of the etherifying agents to starch took place and the sequence of addition of the reactants was: ethanol followed by starch followed by sodium hydroxide followed by sodium monochloroacetate (sequence I). Samples were picked from the reaction bottle at different lengths of time for measuring the DS and ($E\%$). Fig. 1(a and b) shows the carboxymethylation rate and rate constant during 50 h of the reaction.

Fig. 1(a) shows the effect of the carboxymethylation time on the DS and ($E\%$). It can be seen from this figure that increasing the reaction time increases the DS and ($E\%$). The rate of increase in the DS and the ($E\%$) is fast from the beginning of the reaction till the end of the 50 h. Maximum DS obtained was 0.068 with a maximum ($E\%$) of 34.2% after 50 h.

The enhancement in DS and ($E\%$) by prolonging the duration of carboxymethylation is a direct consequence of the favorable effect of time on swellability of starch as well as diffusion of reactants with the ultimate effect of inducing better contact between etherifying agents and starch as stated by Khalil et al. (1990).

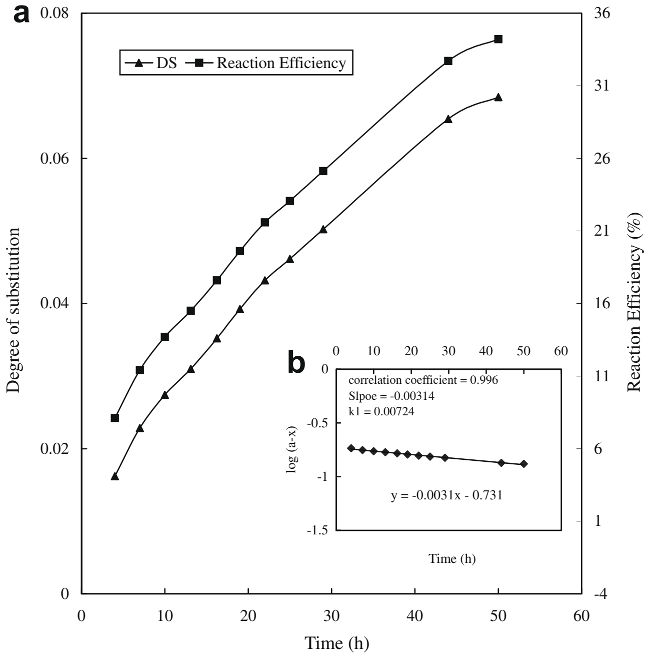

**Fig. 1.** (a) Rate of carboxymethylation reaction within the first 50 h. (b) Carboxymethylation rate constant within the first 50 h. (a and b): [$ClCH_2COONa$] and [NaOH]: 0.2 mol/mole St.; temp.: 30 °C; time: 0–50 h; M:L ratio: 1:2.5; EtOH:$H_2O$ ratio: 70:30; sequence: I; no cooling.

Fig. 1(b) represents the relation between time and $\log(a-x)$ where: “$a$” is the initial concentration of the reactants and “$x$” is the concentration of the reactants at any time “$t$”. If the relation between time and $\log(a-x)$ is a straight line, the reaction is said to be first order and the rate constant can be calculated from the slope of the line according to Sharma and Sharma (1997, chap. 17) according to the following equation:

$$\text{Log}\,(a-x) = (-k1/2.303)t + \log a$$

This equation is similar to an equation of a straight line with a slope = $(-k1/2.303)$ and an intercept on the $y$-axis equal to log “$a$”. The rate constant “$k1$” can then be calculated from the slope as follow:

$$k1 = -2.303 \text{ (slope)}$$

As clear from Fig. 1(b) the relation between time and $\log(a-x)$ is a straight line (correlation coefficient = 0.996) with an equation $y = -0.0031x - 0.731$ and a slope equals to $-0.0031$. So, $k1 = 0.00724$.

### 3.2.2. DS, reaction efficiency and rate constant after 168 h

Using the same reaction conditions as in Fig. 1(a), a new trial for getting higher DS and ($E$%) was made by prolonging the reaction time to 168 h. Samples were picked every 24 h for analysis. Fig. 2(a) shows the effect of increasing reaction time up to 168 h on both DS and ($E$%).

Fig. 2(b) gives the rate constant of the reaction after 168 h. The rate constant was calculated similarly as in Fig. 1(b).

Fig. 2(a) shows that the DS and ($E$%) increase by increasing the reaction time. The rate of increasing the DS and ($E$%) is fast during the first 48 h. After 48 h the reaction rate tended to be slower. However, the DS and ($E$%) still increase dramatically till the end of the 168 h. Maximum DS (0.1375) and ($E$%) (68.75%) were obtained after 168 h of carboxymethylation.

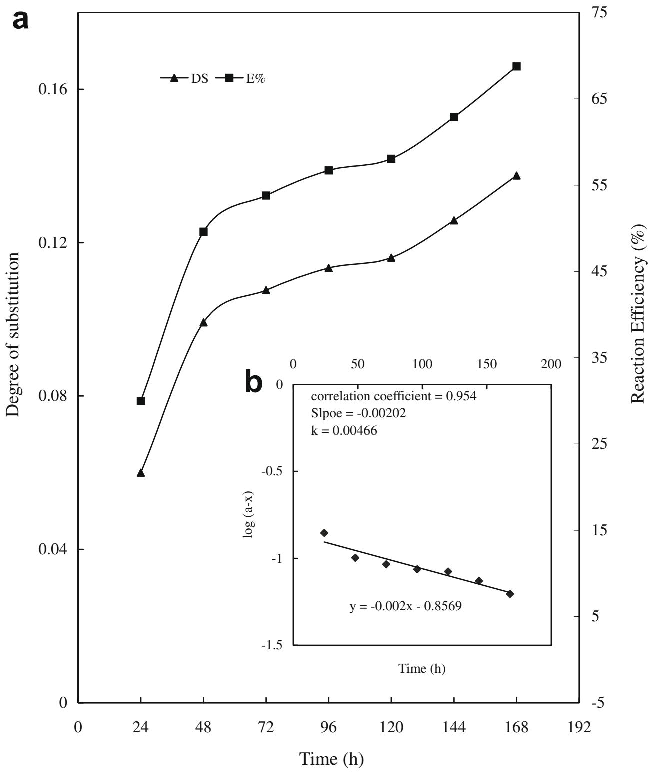

**Fig. 2.** (a) Rate of carboxymethylation within 7 days. (b) Carboxymethylation rate constant within 7 days. (a and b): [$ClCH_2COONa$] and [NaOH]: 0.2 mol/mole St.; temp.: 30 °C; time: 0–168 h; M:L ratio: 1:1.5; EtOH:$H_2O$ ratio: 70:30; sequence: I; no cooling.

The increase in DS and ($E$%) by prolonging the duration of carboxymethylation up to 168 h is, again, a direct consequence of the favorable effect of time on swellability of starch as well as diffusion of reactants. The more the reaction time the more the effect of inducing better contact and the higher extent of the reaction between etherifying agents and starch.

Fig. 2(b) shows the relation between time and $\log(a-x)$. It can be seen from this figure that a straight line was obtained (correlation coefficient = 0.954). On the same basis as in Fig. 1(b), the rate constant $k1$ was calculated. The overall reaction rate was found to be $k1 = 0.00466$. As compared with $k1$ of Fig. 1(b) (0.00724), the decrease in the rate constant of Fig. 2(b) is due to the slowdown of the rate of carboxymethylation starting from 49 h to the end of the 168 h as compared with a faster rate within the first 48 h.

## 3.3. Effect of catalyst concentration

As seen in Fig. 2(a), although too much time was given to the carboxymethylation reaction, the DS and ($E$%) were not high enough to meet the aims of this work. Consequently, a multifunctional catalyst (alkali metal hydroxide) acting as: (i) swelling agent and (ii) etherifying agent was used. The catalyst was applied to the carboxymethylation reaction in different concentrations (0.1–0.6 mol/mole St.) keeping the reaction conditions same as in Fig. 2(a).

Fig. 3 shows the effect of catalyst concentration on both the DS and ($E$%). It is clear that both the DS and ($E$%) increase significantly by increasing the catalyst concentration up to 0.3 mol/mole St. and increasing reaction time up to 96 h. Further increase in the catalyst concentration and reaction time is accompanied by a sharp decrement in both the DS and ($E$%).

According to Fig. 3, it is also seen that a DS of 0.172 and ($E$%) of 86% were obtained after 24 h of carboxymethylation using 0.3 (mol/mole St.) of catalyst. When compared with the previous results (Fig. 2(a)), maximum DS (0.1375) and ($E$%) (68.75%) were

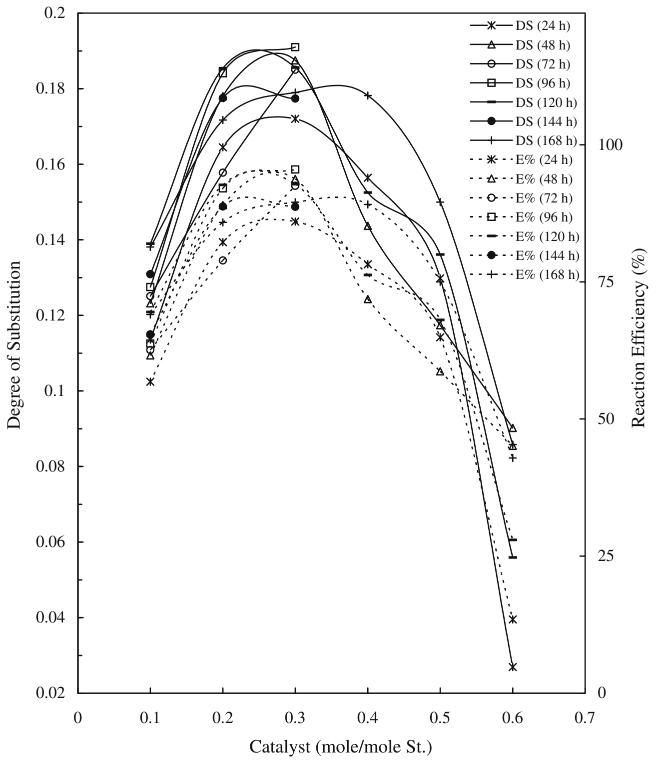

**Fig. 3.** Effect of catalyst concentration on the degree of substitution and the reaction efficiency. [$ClCH_2COONa$] and [NaOH]: 0.2 mol/mole St.; [catalyst]: 0.1–0.6 mol/mole St.; temp.: 30 °C; time: 0–168 h; M:L ratio: 1:1.5; EtOH:$H_2O$ ratio: 70:30; sequence: I; no cooling.

obtained after 168 h of carboxymethylation, under identical reaction conditions, one can say that the catalyst (0.3 mol/mole St.) reduced the reaction time from 168 h to 24 h with even higher DS and (*E*%).

These findings could be explained in terms of the effect of the catalyst as a swelling agent. As an alkali metal hydroxide, the catalyst has the ability of breaking the H-bonds, consequently opening up the starch structure, decreasing the crystallinity, guaranteeing the penetration of the etherifying agents and making the starch molecule more accessible to carboxymethylation, thus, utilizing the etherifying agents to a great extent according to El-Sheikh (1999, chap. 2). On the other hand, higher concentrations of the catalyst have an adverse effect on the sodium salt of monochloroacetic acid where the formation sodium glycolate is favored. The formation of glycolate means inactivation of the sodium salt of monochloroacetic acid and its consumption in side reactions rather than the carboxymethylation.

These good achievements make it possible to obtain 100% reaction efficiency by adjusting the remaining factors.

### 3.4. Effect of cooling and sequence of addition

Three sequences of mixing the reactants with starch were studied. The three sequences were: sequence I (solvent then starch then sodium hydroxide then catalyst then $ClCH_2COONa$), sequence II (solvent then sodium hydroxide then catalyst then starch then $ClCH_2COONa$) and sequence III (solvent then sodium hydroxide then catalyst then $ClCH_2COONa$ then starch). Carboxymethylation took place for 24 h at 30 °C using ethanol:water ratio of 70:30 and material:liquor ratio of 1:1.5. Cooling took place during the initial stages of the reaction, i.e., during the addition of the etherifying agents and mixing with starch.

It can be seen in Fig. 4 that regardless of the sequence of addition, the DS and (*E*%) were about 0.185 and 93%, respectively. This means that any of the three sequences can be used in the carboxymethylation. The increase in the DS and (*E*%) compared with the last values (0.172 and 86%, Fig. 3) under the same carboxymethylation conditions, is certainly due to the cooling effect.

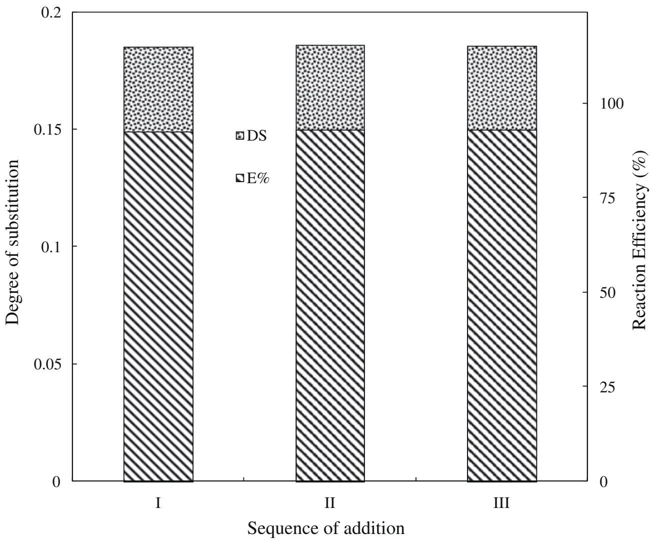

**Fig. 4.** Effect of cooling and sequence of addition on the degree of substitution and the reaction efficiency. [$ClCH_2COONa$] and [NaOH]: 0.2 mol/mole St.; [catalyst]: 0.3 mol/mole St.; temp.: 30 °C; time: 24 h; M:L ratio: 1:1.5; EtOH:$H_2O$ ratio: 70:30; sequence: I, II and III; cooling.

It is believed that cooling decreases the chance of forming glycolate as a result of the reaction between $ClCH_2COONa$ and NaOH (Eq. (3)) which is favored by high temperature. Cooling during addition prevents any increase in the temperature due to addition or dilution. Consequently, carboxymethyl starch formation (Eq. (2)) prevails over glycolate formation (Eq. (3)).

### 3.5. Effect of material:liquor ratio

The effect of the material:liquor ratio on both DS and (*E*%) was studied using a material:liquor ratios range from 1:1 to 1:3.

As seen in Fig. 5, both DS and (*E*%) increase with increasing the material:liquor ratio from 1:1 to 1:1.5 then decrease sharply by further increment in the material:liquor ratio. This indicates that 1:1.5 constitutes the optimal material:liquor ratio. Maximum DS and (*E*%) obtained at this point were 0.185 and 93%, respectively.

The use of low material:liquor ratio makes the mixture very concentrated and, hence, decreases the mobility of reactants and subsequently minimize the extent of carboxymethylation. Consequently, both DS and (*E*%) decrease. By increasing the material:liquor ratio, the mobility of the reactants increases and causes an increase in both DS and (*E*%). Further increase in the material:liquor ratio dilutes the $ClCH_2COONa$ and sodium hydroxide and, hence, the number of $ClCH_2COONa$ and sodium hydroxide molecules in the vicinity of the starch decreases so that the DS and (*E*%) decrease according to El-Sheikh (1999, chap. 2).

### 3.6. Effect of ethanol:water ratio

The effect of ethanol:water ratio (50:50–90:10) on both DS and (*E*%) was also studied (Fig. 6).

As clear from this figure, both the DS and (*E*%) increase with decreasing the amount of water. Maximum DS and (*E*%) were obtained at an ethanol:water ratio of 90:10 (0.1989 and 99.36%, respectively).

The outstanding enhancement in the DS and (*E*%) as a result of decreasing the amount of water in the ethanol:water mixture sig-

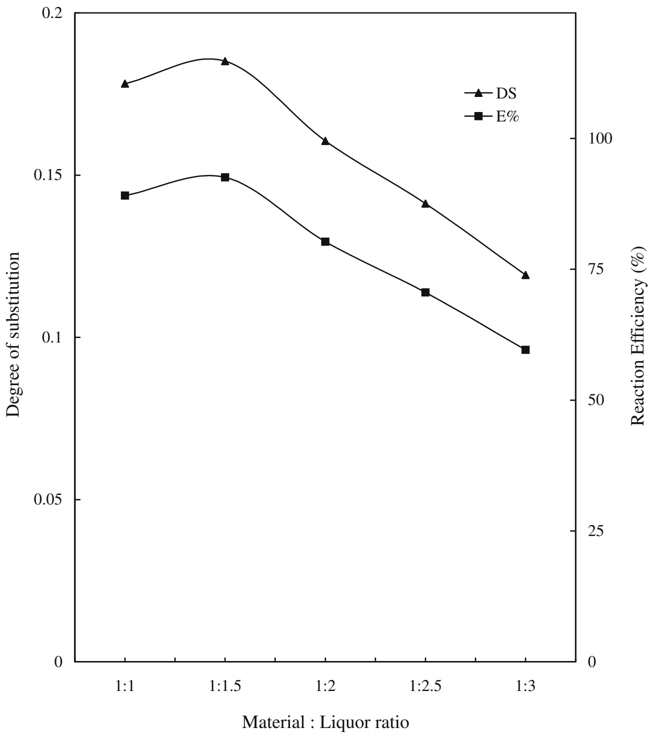

**Fig. 5.** Effect of material:liquor ratio on the degree of substitution and the reaction efficiency. [$ClCH_2COONa$] and [NaOH]: 0.2 [mol/mole St.]; [catalyst]: 0.3 mol/mole St.; temp.: 30 °C; time: 24 h; M:L ratio: 1:1–1:3; EtOH:$H_2O$ ratio: 70:30; sequence: I; cooling.

nifies the role of water in the carboxymethylation process. It is logical that there is a critical amount of water which is required for swelling of starch granules and dissolving the reactants, as well as facilitating dissociation, adsorption and diffusion of the etherifying agents on starch molecule according to Khalil et al. (1990). The current results suggest that the ratio 90:10 presents this critical amount of water under the carboxymethylation conditions used.

The study is now coming closer to a 100% reaction efficiency.

### *3.7. Effect type of solvent*

Fig. 7 shows the values of DS and (*E*%) when the carboxymethylation took place using different organic solvents. Organic solvents used were: Methanol (MeOH), Ethanol (EtOH), Isopropanol, Tertiary butanol (Tert. butanol) and Propylene glycol. Solvent:water ratio used was 90:10 keeping the rest of reaction conditions as same as in Fig. 5.

It is observed (Fig. 7) that the highest DS and (*E*%) were achieved by using isopropanol and the lowest by using propylene glycol. It is also observed that the DS and (*E*%) using the aforementioned solvents follow the descending order:

$$\text{Isopropanol} > \text{Ethanol} > \text{Tertiary butanol} > \text{Methanol} > \text{Propylene glycol}$$

The above results imply that the reaction medium determines the extent of the carboxymethylation reaction. Reasons for this are the differences among the solvents examined and the onset of such differences among the carboxymethylation process with respect to miscibility, ability to swell the starch and to solubilize the etherifying agents and creation of an environment which favors the carboxymethylation reaction than the glycolate formation.

A DS of 0.2 and a (*E*%) of 100% were finally obtained using isopropanol as the solvent. The use of isopropanol led to a 100% reaction efficiency while the use of ethanol led to a 99.36% which is an excellent result for both. This means that both isopropanol and ethanol can be used efficiently for the carboxymethylation of starch.

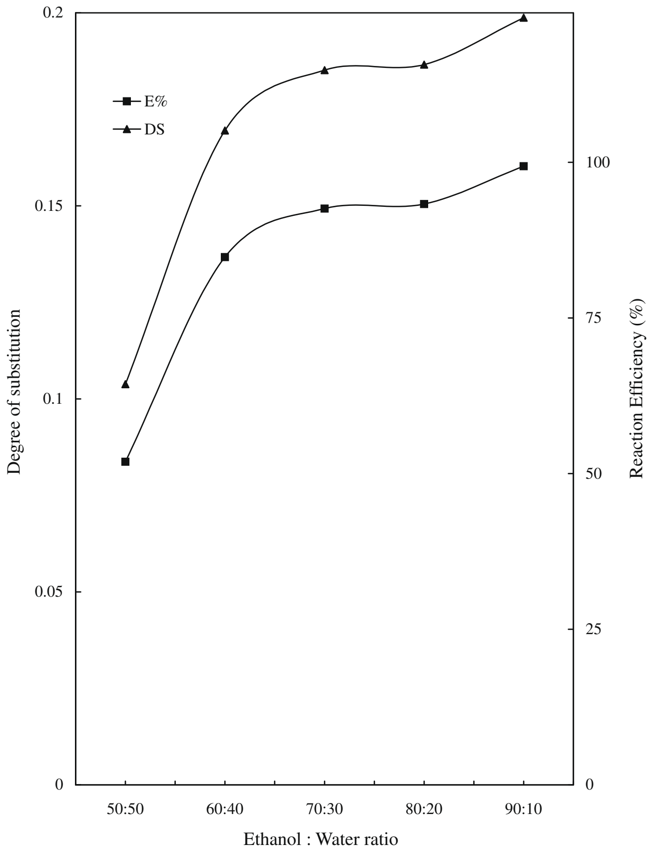

**Fig. 6.** Effect of ethanol:water ratio on the degree of substitution and the reaction efficiency. [$ClCH_2COONa$] and [NaOH]: 0.2 mol/mole St.; [catalyst]: 0.3 mol/mole St.; temp.: 30 °C; time: 24 h; M:L ratio: 1:1.5; EtOH:$H_2O$ ratio: 50:50–90:10; sequence: I; cooling.

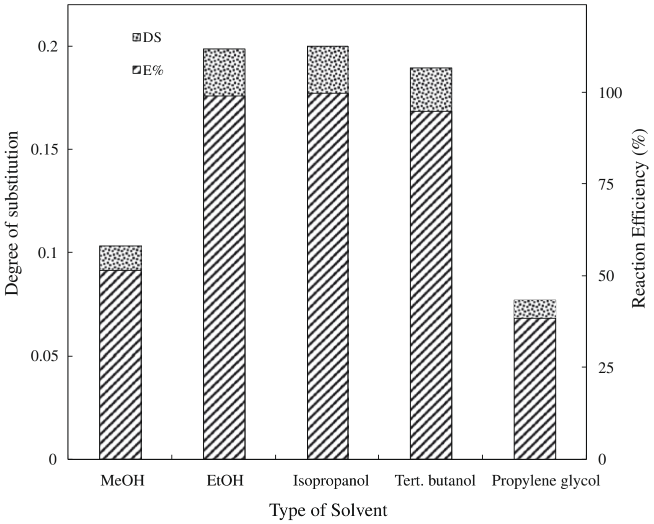

**Fig. 7.** Effect of type of solvent on the degree of substitution and the reaction efficiency. [$ClCH_2COONa$] and [NaOH]: 0.2 mol/mole St.; [catalyst]: 0.3 mol/mole St.; temp.: 30 °C; time: 24 h; M:L ratio: 1:1.5; solvent:$H_2O$ ratio: 90:10; sequence: I; cooling.

### *3.8. Optimum conditions*

Optimum conditions for attaining a DS of 0.2 and a (*E*%) of 100% were:

- concentration of $ClCH_2COONa$: 0.2 mol/mole St.,
- concentration of NaOH: 0.2 mol/mole St.,
- concentration of Catalyst: 0.3 mol/mole St.,
- carboxymethylation temperature: 30 °C,
- carboxymethylation time: 24 h,
- material:liquor ratio: 1:1.5,
- solvent:water ratio: 90:10,
- solvent: isopropanol,
- sequence of addition: Solvent then sodium hydroxide then catalyst then starch then $ClCH_2COONa$,
- cooling during addition of the reactants.

### *3.9. Reproducibility*

After studying the factors affecting the carboxymethylation, the optimum conditions were applied to prepare CMS three times under the same reaction conditions to determine the reproducibility and the consistency of the carboxymethylation using the current process. Table 1 shows the reproducibility of CMS derived from NS using the current method. The DS and (*E*%) for each experiment were given.

The results in Table 1 indicate that the carboxymethylation process is reproducible and consistent under the set of reaction conditions used.

### *3.10. Type of starch*

The optimum conditions obtained were applied to prepare carboxymethyl rice and potato starch to determine the suitability of using the optimum conditions of the modified method for other types of starch. Table 2 shows the DS and the (*E*%) of CMS produced from maize, rice and potato starch.

As seen in Table 2, high DS and reaction efficiencies were obtained using maize, rice and potato starch. The high values of DS and (*E*%) reveal that the carboxymethylation process is suitable for different kinds of starch under the set of reaction conditions used.

The variation in DS and (*E*%) of CMS produced from the three types of starch reflects the differences among different types of starch in: (1) size and shape of granule, (b) association of the starch molecules within the granule, (c) available active sites, (d) crystalline: amorphous ratio in the starch structure, (e) ratio of amylose and amylopectin and their degree of association and (f) molecular size of amylose and amylopectin according to Hebeish et al. (1990).

### *3.11. Characterization of CMS produced*

Optimum conditions were applied to maize starch to produce a bulk sample for more characterizations. In addition to DS and (*E*%), the produced CMS was further characterized for its solubility in cold water, transparency (expressed as % transmittance), viscosity and its suitability as a sizing agent for light cotton fabric. Table 3 summarizes the major properties of the CMS produced.

**Table 1**
Reproducibility of CMS.

| Exp. No. | Theoretical DS | Practical DS | Reaction efficiency (%) |
|---|---|---|---|
| 1 | 0.2 | 0.21 | 100 |
| 2 | 0.2 | 0.21 | 100 |
| 3 | 0.2 | 0.2 | 100 |

[$ClCH_2COONa$] 0.2 mol/mole St., [NaOH], 0.2 mol/mole St.; [catalyst]: 0.3 mol/mole St.; temp.: 30 °C; time: 24 h; M:L ratio: 1:1.5; isopropanol:$H_2O$ ratio: 90:10; sequence: I; cooling.

**Table 2**
Suitability of the carboxymethylation method and carboxymethylation conditions for different types of starch.

| Type of starch | Theoretical DS | Practical DS | Reaction efficiency (%) |
|---|---|---|---|
| Maize | 0.2 | 0.2 | 100 |
| Rice | 0.2 | 0.1938 | 96.9 |
| Potato | 0.2 | 0.1984 | 99.2 |

[$ClCH_2COONa$] 0.2 mol/mole St., [NaOH], 0.2 mol/mole St.; [catalyst]: 0.3 mol/mole St.; temp.: 30 °C; time: 24 h; M:L ratio: 1:1.5; isopropanol:$H_2O$ ratio: 90:10; sequence: I; cooling.

Coming down are the interpretations on the results shown in Table 3.

#### *3.11.1. Solubility*

It was found that CMS with DS 0.2 is completely soluble in cold water. The solution of the cold water soluble CMS is clear and its pH is 7. It is well known that introducing the carboxymethyl group, in its sodium form ($-CH_2COONa$), to the starch molecule increases its solubility. The higher the DS the higher the solubility of the CMS. In the present study, CMS with DS of about 0.2 is completely soluble in cold water although this DS is not high. This might be an indication of the superior even distribution of the etherifying agents along the starch molecule in the initial stages of the carboxymethylation. Consequently, a uniform distribution of the carboxymethyl groups along the starch molecule arises.

#### *3.11.2. Transparency*

As indicated in Table 3, the transparency (expressed as% transmittance) of 0.1% aqueous solution of CMS with DS of 0.2 is 97%. This high value reveals the clarity of the aqueous solution of CMS prepared using the adopted method. The clarity of the aqueous solution in spite of the low DS could be an indication of a uniform distribution of the carboxymethyl groups along the starch molecule, as mention earlier.

#### *3.11.3. Viscosity*

The viscosity of cooked NS and CMS has been measured at shear rate range from 129 to 1161 $s^{-1}$. The curves obtained using the coaxial rotary viscometer, with a uniformly increasing rate shear, were used to calculate the viscosity as mentioned in Section 2.3.4. The viscosities at 516 $s^{-1}$ of the down curves of both NS and CMS were recorded for sake of comparison. Fig. 8 shows the viscosity curves of NS and CMS.

**Table 3**
Major properties of CMS produced.

| | | | |
|---|---|---|---|
| Practical DS | | | 0.2 |
| Reaction efficiency | | | 100% |
| Solubility in cold water (pH 7) | | | Soluble |
| % transmittance (0.1% aqueous solution) | | | 97% |
| Viscosity at 516 $s^{-1}$ (mPa s) | | | |
| NS | | | 350 |
| CMS | | | 198.3 |
| Sizing | Tensile strength (kg) | Elongation at break (%) | |
| Control sample | 30.8 | 7 | |
| Sample sized with cooked CMS | 42.7 | 5.9 | |
| Desizing efficiency | | | |
| % of size removal at 30 °C | 98% | | |

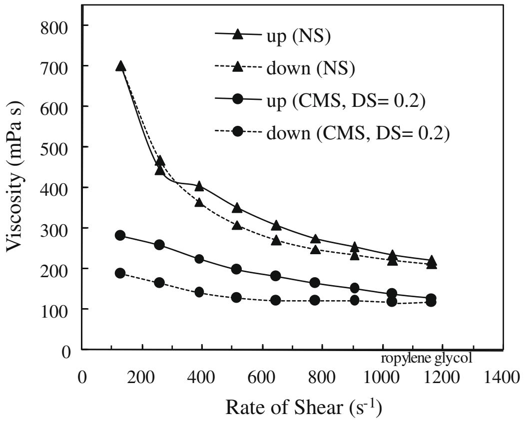

**Fig. 8.** Viscosity curves of NS and CMS. CMS was prepared according to the optimum condition obtained. Cooking: [NS] and [CMS]: 10%; pH 7; temperature: 85 °C, time: 20 min.

Fig. 8 shows that carboxymethylation sharply decreases the viscosity of the starch used. The viscosity at 516 $s^{-1}$ of NS was 350 mPa s while that of CMS was 198.3 mPa s. The decrease in the viscosity of the carboxymethylated starch, relative to that of NS is due to introduction of the solubilizing carboxymethyl group in its sodium form. The viscosity decreases when the solubility increases. It is also possible that oxidative degradation might have taken place due to the presence of sodium hydroxide and carrying out the carboxymethylation in presence of air. Thus the molar mass of the starch has been decreased according to El-Sheikh (1999, chap. 2).

### *3.12. Sizing and desizing*

Results obtained (Table 3) showed that the tensile strength of the light cotton fabric increases as a result of sizing with the CMS under testing. As seen in Table 3, the tensile strength of the sized light cotton fabric and the tensile strength of the control light cotton fabric were 42.7 and 30.8 kg, respectively. In another meaning, the percent of the increase in the tensile strength was 38.6%.

On the other hand, the elongation at break of the sized light cotton fabric and the elongation at break of the control light cotton fabric were 5.9% and 7%, respectively. The drop in the elongation at break as a result of sizing is rather expected as stated by Hebeish (1987, chap. I). However, the drop in the elongation at break still in the accepted ranges (not less than 4–5% for cotton fabric) according to Hebeish (1987, chap. I).

The results obtained from the tensile strength and elongation at break of the light cotton fabric sized with CMS under test reveals the suitability of this CMS as a sizing agent.

Desizing efficiency is 98% at 30 °C (Table 3) is another evidence of the suitability of CMS under test as a sizing agent where the size is removed efficiently using mild conditions.

## 4. Conclusions

The current carboxymethylation method produced CMS with DS of 0.2 and reaction efficiency of 100% using 0.2 mol of both $ClCH_2COONa$ and NaOH/mole St., 0.3 mol catalyst/mole St., M:L ratio: 1:1.5, isopropanol:$H_2O$ ratio: 90:10, cooling took place during addition of the reactants, for 24 h at 30 °C. The carboxymethylation process was found reproducible and suitable for different types of starch. The CMS produced was cold water soluble giving a transparent solution with viscosity of 198.3 mPa s at shear rate of 516 $s^{-1}$. The CMS produced was suitable for use as sizing agent.

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