

# Physicochemical Properties of Corn Starch Selectively Oxidized with 2,2,6,6-Tetramethyl-1-Piperidinyl Oxoammonium Ion

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## ABSTRACT

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This study was conducted to examine the characteristics of oxidation reaction on the primary alcohol groups in corn starch, when 2,2,6,6-tetramethyl-1-piperidinyl oxoammonium ion (TEMPO) was used, and to determine the optimum conditions for the preparation of oxidized corn starch (OCS). Applicability of the OCS in the food system was also investigated. The effects of TEMPO, sodium bromide (NaBr), and temperature on oxidation reaction time, yield, and selectivity for primary alcohol groups were examined by response surface methodology. As the temperature and the levels of TEMPO and NaBr increased, reaction time and selectivity decreased. Yield decreased with increased NaBr and

selectivity decreased with the increased temperature and NaBr. Selectivity increased with higher TEMPO levels up to a certain point and then decreased. Optimum levels of TEMPO, NaBr, and temperature for the preparation of OCS were determined as 0.6 mM/100 mM of anhydroglucose unit (AGU), 45 mM/100 mM AGU, and 7°C, respectively. Water binding capacity, emulsion stability, and viscosity of starch increased significantly by oxidation. Corn starch containing OCS had decreased initial pasting temperature, setback, and gelatinization and retrogradation enthalpy ( $\Delta H$ ). Corn starch gel containing OCS showed delayed staling during storage.

Sodium hypochlorite (NaOCl) is the most frequently used oxidizing agent for oxidation of starch, while sodium bromide (NaBr), gaseous chlorine, calcium hypochlorite, hydroperoxide, potassium permanganate, and ammonium persulfate are used less frequently (Wing 1994). These agents randomly attack the secondary alcohol groups at C2, C3, and C4 as well as the primary alcohol groups at C6 in glucose units (Brouch 1985; Floor 1989). Oxidation of secondary alcohol groups is accompanied by the hydrolysis of glycosidic bond and opening and cleavage of monomeric rings. Consequently, there is a loss of polymer properties and decreased viscosity (Chang and Cho 1997). It is hard to control this oxidation reaction and to obtain the desired degree of oxidation.

Selective oxidation of the primary alcohol groups in the presence of secondary group has gained interest during the last few years since a novel method using a stable organic nitroxyl radical, 2,2,6,6-tetramethyl-1-piperidinyl oxoammonium ion (TEMPO), NaBr, and NaOCl was presented by De Nooy et al (1994, 1995). In TEMPO-mediated oxidation, NaOCl and NaBr were used as regenerating oxidants, and water was used as a solvent. Recently, TEMPO-mediated oxidation has been applied to the oxidation of various polysaccharides including water-soluble potato starch, inulin (De Nooy 1994), potato starch, methyl  $\alpha$ -D-glucopyranoside (De Nooy 1995), microcrystalline cellulose, corn, rice, and sweet potato starch (Chang and Cho 1997), wheat starch, cellulose, pullulan, chitin and chitosan, and others (Chang and Robyt 1996). The implications of these studies were optimum pH level for the reaction was pH 10.5–11.0; oxidation was first order in TEMPO and Br<sup>-</sup>; selectivity was >95%; and side products such as starting material were not detected. De Nooy et al (1995) predicted that selectivity would be decreased at higher levels of NaBr and reaction temperature; however, that remains to be studied. Also, the details of the reaction mechanism are poorly elucidated; in particular, optimum conditions for the oxidation of starch are not clear.

Because most of the primary alcohol groups in starch are converted into carboxyl groups (polyglucuronic acid) and the oxidized starch has a similar structure to gums, it was thought that the oxidized starch could be used as a new hydrocolloid. It already has been shown that oxidation resulted in increased water solubility

and viscosity of starch, and gave gelling properties with calcium ion added (Chang and Robyt 1996).

This study was conducted to examine the influence of levels of TEMPO and NaBr and reaction temperature on the oxidation of corn starch, and to determine the optimum conditions for the oxidation. Applicability of oxidized corn starch (OCS) in food system was also investigated.

## MATERIALS AND METHODS

### Materials

Corn starch was obtained from Daesang Co. (Seoul, Korea). TEMPO (2,2,6,6-tetramethyl-1-piperidinyl oxoammonium ion), NaBr, and NaOCl were purchased from Aldrich Chemical Co. (Milwaukee, WI), Yakuri Pure Chemicals Co. (Osaka, Japan), and Junsei Chemical Co. (Tokyo, Japan), respectively. All other chemicals were analytical-grade commercial products.

### Experimental Design and Preparation of OCS

Because an excess of NaOCl led to breakage of the glycosidic bond in the starch, concentration of NaOCl was fixed at 2.2 mM/1 mM anhydroglucose unit (AGU) as 10% excess of a limit (De Nooy et al 1995). The treatment variables examined were concentrations of TEMPO (0.3, 1.0, and 1.7 mM/100 mM AGU) and NaBr (20, 60, and 100 mM/100 mM AGU) and the reaction temperature (2, 6, and 10°C). Fifteen samples including three centerpoints were selected according to the second-order response surface design (Box and Oaper 1987).

Starch was oxidized by the method of Suh et al (2001). Corn starch (50 mM) was suspended in 500 mL of water and stirred at the desired temperature. TEMPO, NaBr, and NaOCl solution (110 mM) were added simultaneously to the suspension according to the experimental design. The pH level was adjusted to optimum at pH 10.8 (De Nooy et al 1995; Chang and Cho 1997) by adding 4N HCl and maintained at pH 10.8 with 1M NaOH during reaction. When 50 mM of NaOH was consumed, the reaction was quenched by adding 10 mL of ethanol. It was then neutralized to pH 7.0 with 4N HCl. The oxidized starch thus prepared was precipitated by the addition of 2 L of ethanol and filtered (Whatman No. 41). The residue was washed three times with 2 L of ethanol, dried in a vacuum oven (45°C) for 24 hr, and passed through a 60-mesh screen.

The reaction time was determined as the time taken for the consumption of 50 mM NaOH to maintain at pH 10.8. The yield was determined by the weight of the dried OCS corrected by the molecular weight of the sodium salt of polyglucuronic acids. Selectivity was described in terms of the percentage of anhydroglucose units converted to anhydroglucuronic acid units and this was deter-

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**TABLE I**  
Reaction Time, Yield, and Selectivity of Corn Starch Oxidized with Different Levels of TEMPO, NaBr, and Temperature

Treatment No.	TEMPO <sup>a</sup>	NaBr <sup>a</sup>	Temperature (°C)	Reaction Time (min)	Yield (%)	Selectivity (%)
1	0.3	20	6	220	91.60	98.17
2	1.7	20	6	129	92.82	98.01
3	0.3	100	6	102	90.26	97.53
4	1.7	100	6	65	90.16	97.15
5	0.3	60	2	230	90.93	98.29
6	1.7	60	2	137	91.12	98.28
7	0.3	60	10	77	91.03	97.39
8	1.7	60	10	48	91.35	92.05
9	1.0	20	2	254	91.21	98.79
10	1.0	100	2	128	90.53	98.50
11	1.0	20	10	99	92.78	97.86
12	1.0	100	10	43	90.29	91.37
13	1.0	60	6	88	90.79	98.16
14	1.0	60	6	93	90.60	98.77
15	1.0	60	6	92	90.74	98.67

<sup>a</sup> Expressed as mM/100 mM anhydroglucose unit.

**TABLE II**  
Analysis of Variance Showing Significance of Effects of TEMPO, NaBr, and Temperature on Reaction Time, Yield, and Selectivity

Source	Sum of Squares ( <i>F</i> values <sup>a</sup> )		
	Reaction Time	Yield	Selectivity
TEMPO	10,388 (468.3***)	0.93 (4.2)	17.68 (17.0**)
NaBr	21,210 (956.3***)	6.78 (30.9***)	25.14 (24.2**)
Temperature	32,329 (1,457.6***)	1.28 (5.8*)	50.01 (48.2***)

<sup>a</sup> \*, \*\*, \*\*\* = Significant at  $P < 0.05$ ,  $0.01$ , and  $0.001$ , respectively.

mined by the modified method of the carbazole procedure (Knutson and Janes 1968).

Response surface methodology was used to evaluate the oxidation reaction characteristics and to optimize the levels of experimental variables. Data were analyzed using the Statistical Analysis System (SAS Institute, Cary, NC).

### Properties of OCS

The structure of OCS was confirmed by <sup>13</sup>C-nuclear magnetic resonance (NMR) spectroscopy. <sup>13</sup>C-NMR spectrum of OCS dissolved in D<sub>2</sub>O was obtained at 400 MHz using an NMR instrument (JMN LA 400 FT-NMR, Jeol Co., Tokyo, Japan). Dimethyl sulfoxide (DMSO) was used as an internal standard.

Water binding capacity (WBC) was measured by the methods of Collins and Post (1981) with some modification. Aliquots (0.5 g, db) of oxidized or native starch were added to conical graduated centrifuge tubes containing 50 mL of water. The contents were shaken for 3 min and allowed to stand at 20, 40, 60, and 80°C for 1 hr. They were then centrifuged (1,500 × *g*, 30 min), and the pellet was weighed after the supernatant was decanted. The difference in weight between the wet pellet and the starch was defined as WBC (g of water/g of starch).

To measure rheological properties of OCS using a Haake rotational rheometer (model RS150, Haake Co., Karlsruhe, Germany) with a Z 20 DIN sensor, OCS solutions of 1 and 3% were prepared and a designated amount was put into a measuring cup (Z 20/D 48 Din). Shear stress ( $\tau$ , Pa) and apparent viscosity ( $\eta$ , Pa·s) were measured at 20 and 60 ± 0.1°C, while the shear rate ( $\dot{\gamma}$ , sec<sup>-1</sup>) was varied from 0 to 1,000 during a 2-min period. The viscosity-shear rate relationships were generated using a software (Haake RheoWin Pro 2650).

Emulsion stabilizing capacity (ESC) of OCS was determined according to the procedure of Inklaar and Fortuin (1970). The total volume of an emulsion was set at 60 mL. Soybean oil was added to distilled water dispersed with OCS in a 100-mL beaker and mixed at 9,500 rpm for 2 min in a homogenizer (Ultra-Turrax T25,

**TABLE III**  
Regression Coefficients<sup>a</sup> of the Second-Degree Polynomials<sup>b</sup> for Reaction Time, Yield, and Selectivity of Corn Starch Oxidized with Different Levels of Variables

Coefficients	Reaction Time (min)	Yield (%)	Selectivity (%)
$\beta_0$	518.7112***	91.3647***	90.1441***
$\beta_1$	-170.9810***	0.0031	8.0194**
$\beta_2$	-3.9951***	-0.0179	0.1215**
$\beta_3$	-40.3326***	0.0766	1.4332**
$\beta_{11}$	31.4873***	-0.4408	-2.2846
$\beta_{22}$	0.0142***	-0.0002	-0.0005*
$\beta_{33}$	1.0828***	-0.0111	-0.0709**
$\beta_{12}$	0.4859***	-0.0107	-0.0402*
$\beta_{13}$	5.7143***	0.0116	-0.4759**
$\beta_{23}$	0.1094***	-0.0028	-0.0097**
% Variability Explained ( $R^2$ )	99.95	97.01	98.26

<sup>a</sup> \*, \*\*, \*\*\* = Significant at  $P < 0.05$ ,  $0.01$ , and  $0.001$ , respectively.

<sup>b</sup>  $Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3$ , where  $X_1$ ,  $X_2$ , and  $X_3$  are levels of TEMPO, NaBr, and temperature, respectively.

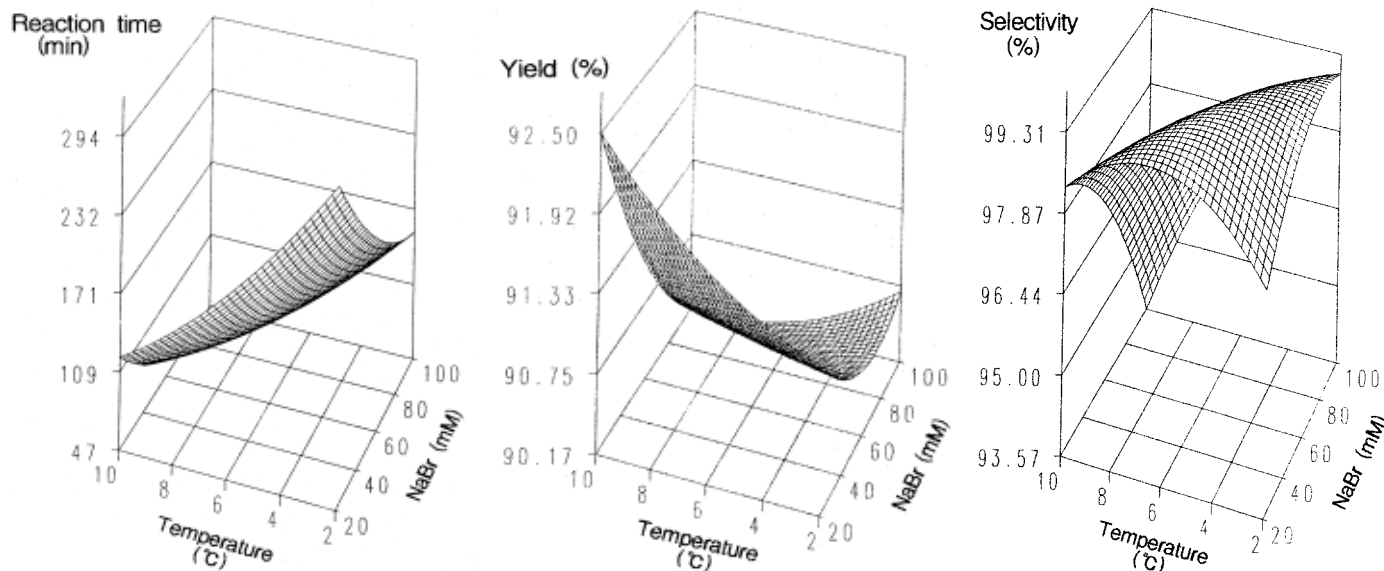
IKA-Labortechnik, Staufen, Germany). Immediately after emulsification, the emulsion was poured into a 50-mL mess cylinder. The cylinder was put in a water bath (25°C) for 2 hr. The volume of water and oil separated from the emulsion were measured every 10 min. ESC was expressed as % volume of the emulsion layer remaining after the holding. ESC was evaluated in various emulsion systems (7:3, 5:5, and 3:7 oil-to-water) containing 1% (w/v, db) OCS.

The pasting properties were measured with a Viscograph-E (model No. 8-025-25, Brabender, Duisburg, Germany) at 700-g·cm and 75 rpm. The suspensions containing 6% corn starch replaced with OCS at 0, 1, and 3% of corn starch (w/w, db) were heated at a rate of 1.5°C/min from 30 to 95°C, held at 95°C for 30 min, and then cooled to 50°C (Medcalf and Gilles 1965).

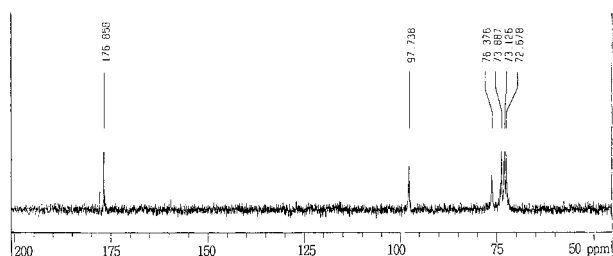
### Gelatinization and Retrogradation Properties

Corn starch was replaced with OCS at 0, 1, and 3% of corn starch (db), and gelatinization and retrogradation properties were examined with differential scanning calorimetry (DSC, model SSC/120, Seiko, Chiba, Japan). Corn starch and OCS were directly weighed into aluminum pan (total starch weight of 3 mg), and 6  $\mu$ L of water was added. The pans were sealed hermetically, and allowed to stand for 2 hr before heating. The pans were heated using DSC at 5°C/min from 30 to 135°C, cooled immediately to 10°C, and stored at 4°C for seven days. To examine the retrogradation properties, the pans were reheated with the same procedure as above. A pan containing 9  $\mu$ L of water was used as a reference.

The effects of partial replacement of OCS for corn starch on the textural characteristics of starch gel were evaluated. To prepare the



**Fig. 1.** Spline interpolation of response surface for reaction time, yield, and selectivity of corn starch oxidized with different levels of NaBr and temperature with TEMPO level fixed at 0.6 mM/100 mM anhydroglucose unit.



**Fig. 2.**  $^{13}\text{C}$ -NMR spectrum of oxidized corn starch.

**TABLE IV**  
Water Binding Capacity of Corn Starch and Oxidized Corn Starch (OCS)

Temperature ( $^{\circ}\text{C}$ )	Corn Starch	OCS
20	1.95e <sup>a</sup>	43.12c
40	1.94e	45.49b
60	2.69e	49.52a
80	10.06d	nd <sup>b</sup>

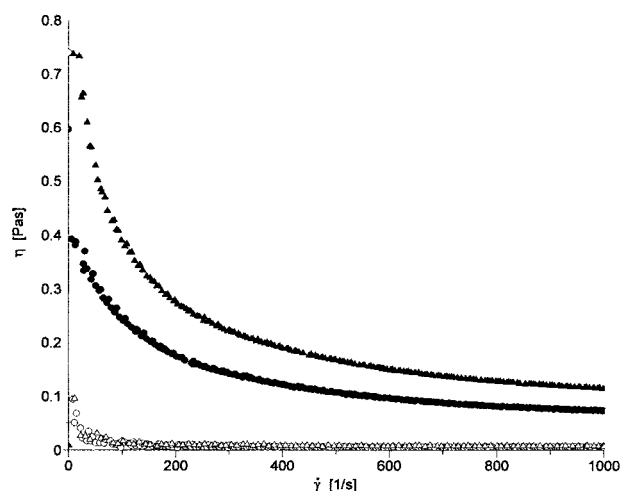
<sup>a</sup> Values not followed by the same letter are significantly different ( $P < 0.05$ );  $n = 3$ .

<sup>b</sup> Not determined.

gels, 6% corn starch suspension replaced with OCS at 0, 1, and 3% (db) was heated in a double boiler for 15 min and stirred constantly. The hot paste was then poured into shallow petri dishes (85 × 15 mm), covered, and sealed with parafilm to prevent loss of water. After cooling the paste for 3 hr at room temperature ( $20 \pm 2^{\circ}\text{C}$ ), the gel was stored for one, three, and five days at  $4^{\circ}\text{C}$  for texture analysis. After the film was removed, the gel was cut to  $2.5 \times 2.5 \times 1.5 \text{ cm}^3$ . Textural properties of the gel were examined (TA-XT2i, Stable Microsystems LTD, Godalming, England). The operating conditions of the texture analyzer were probe type, SMS-P/5 (stainless cylinder type; 5 mm, diameter); distance, 40% strain; load cell force, 25 kg; pretest speed, 2.0 mm/sec; test speed, 0.5 mm/sec; and posttest speed, 2.0 mm/sec).

### Statistical Analysis

All the physicochemical measurements were repeated three times. Analysis of variance (ANOVA) and Tukey's studentized range test were performed to determine significant effects and differences among treatment means using statistical software (SAS Institute, Cary, NC).



**Fig. 3.** Apparent viscosity as a function of shear rate for 1 and 3% oxidized corn starch (OCS) solutions at 20 and  $60^{\circ}\text{C}$ . 1% OCS at  $20^{\circ}\text{C}$  ( $\Delta$ ), 1% OCS at  $60^{\circ}\text{C}$  ( $\circ$ ), 3% OCS at  $20^{\circ}\text{C}$  ( $\blacktriangle$ ), 3% OCS at  $60^{\circ}\text{C}$  ( $\bullet$ ).

## RESULTS AND DISCUSSION

### Optimizing Oxidation Conditions of Corn Starch

Reaction time, yield, and selectivity obtained with different levels of TEMPO, NaBr, and temperature for the starch oxidation are shown in Table I. The effects of treatment variables on the oxidation determined by ANOVA are shown in Table II. TEMPO, NaBr, and temperature showed marked effects on reaction time and selectivity. Reaction time and selectivity were more affected by temperature than by NaBr under the conditions of this study. NaBr and temperature showed significant effects on yield, and the effect of NaBr concentration was greater than that of the temperature.

The regression equations and percent of variability explained ( $R^2$ ) are shown in Table III. The  $R^2$  values were all greater than 97%, showing adequacy of the models. Expected values (data not shown) calculated with the models (Table III) were considered to examine the effect of TEMPO, NaBr, and temperature on reaction time, yield, and selectivity. The expected values of the reaction time were 38–330 min, decreasing with the increased levels of TEMPO, NaBr, and temperature. The reaction time decreased more sharply up to certain point of TEMPO and NaBr level, and then gradually decreased. It was thought that use of TEMPO or NaBr at higher

**TABLE V**  
**Pasting and Gelatinization Properties<sup>a</sup> of Corn Starch Partially Replaced with Different Levels of Oxidized Corn Starch (OCS)**

Levels of OCS (%)	Temperature (°C)		Viscosity (BU)						$T_o$	$T_p$	$T_c$	$\Delta H$ (J/g)
	Initial Pasting	Peak	Peak	Hold for 30 min	Cool to 50°C	Breakdown	Setback					
0	80.0a <sup>b</sup>	91.0a	275c	197a	482a	78a	285a	61.6a	66.1c	72.2c	4.50a	
1	75.3b	91.5a	304b	164b	393b	140b	229b	61.7a	66.4b	72.8b	4.37a	
3	71.3c	89.6b	376a	146c	356c	230c	210c	61.9a	66.9a	74.1a	4.21a	

<sup>a</sup>  $T_o$ ,  $T_p$ , and  $T_c$  = onset, peak, and completion temperatures (°C) of endotherm.  $\Delta H$  = enthalpy change.

<sup>b</sup> Values not followed by the same letter are significantly different ( $P < 0.05$ );  $n = 3$ .

**TABLE VI**  
**Retrogradation Properties<sup>a</sup> of Corn Starch Partially Replaced with Different Levels of Oxidized Corn Starch (OCS) During Storage at 4°C**

Storage Period (days)	$T_o$			$T_c$			$\Delta H$ (J/g)		
	Levels of OCS								
	0	1	3	0	1	3	0	1	3
1	35.6b <sup>b</sup>	37.3ab	41.3a	61.2a–d	60.5d	59.9d	0.47b	0.33b	0.20b
2	35.8b	36.6ab	36.2b	60.5d	59.9d	60.1d	0.57b	0.50b	0.40b
3	34.0bc	35.1bc	34.5bc	60.5d	61.0b–d	60.8cd	0.70b	0.77b	0.57b
7	29.0e	30.7cde	29.6de	63.0ab	62.1a	62.7ab	2.10a	1.80a	1.65a

<sup>a</sup>  $T_o$  and  $T_c$  = onset and completion temperatures (°C) of endotherm.  $\Delta H$  = enthalpy change.

<sup>b</sup> Values not followed by the same letter are significantly different ( $P < 0.05$ );  $n = 3$ .

**TABLE VII**  
**Textural Characteristics<sup>a</sup> of Corn Starch Gel Partially Replaced with Different Levels of Oxidized Corn Starch (OCS) During Storage at 4°C**

Textural Characteristics	Storage (days)	Levels of OCS (%)		
		0	1	3
Hardness (g)	0	5.13d	4.81d	5.60d
	1	17.25b	15.97bc	14.44c
	3	18.07ab	16.96b	14.57c
	5	19.07a	18.07ab	16.25c
	0	0.21d	0.22cd	0.21d
Cohesiveness	1	0.30a–c	0.26b–d	0.31ab
	3	0.28b–d	0.33ab	0.34ab
	5	0.37a	0.37a	0.38a
	0	0.53ef	0.62d–f	0.50f
	1	0.67cd	0.64c–f	0.70b–d
Springiness	3	0.71a–d	0.76a–c	0.75a–d
	5	0.83a	0.81ab	0.82ab
	0	1.00f	1.16f	1.19f
	1	5.45b–d	4.20e	4.43de
	3	5.20c–e	5.39b–d	4.95c–e
Gumminess (g)	5	7.28a	6.38ab	5.98bc
	0	0.54f	0.62f	0.53f
	1	3.78c–e	2.85e	3.11de
	3	3.68c–e	4.22b–d	3.74c–e
	5	6.02a	5.09ab	4.87a–c

<sup>a</sup> Values not followed by the same letter in the same textural characteristic are significantly different ( $P < 0.05$ ) ( $n = 4$ ).

level was inefficient. The decreased reaction time with the increased temperature could be due to the increased rate of decomposition of NaOCl (El-Thalouth et al 1977) and increased exposure rate of functional group coming from the destruction of crystalline structure because of the alkalinity of the reaction mixture.

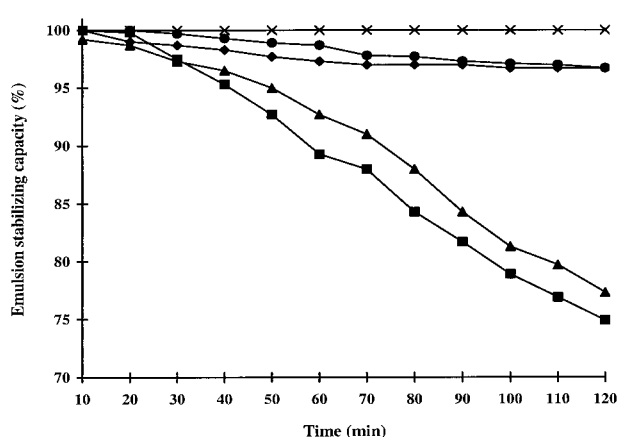
The expected values of yield were 90.07–92.74%, showing decreased yield with the increased NaBr and temperature. The effect was more obvious at the higher levels of NaBr and temperature.

The expected values of selectivity were 86.95–99.48%. NaBr and temperature showed a negative effect on selectivity, indicating greatly decreased selectivity at the higher levels of NaBr and temperature. This result confirmed the studies of Anelli et al (1987) and De Nooy et al (1995), which indicated an increased reaction rate of nonselective oxidation by NaBr at a higher temperature.

It is more desirable that the oxidation reaction time is shorter, and yield and selectivity are higher. However, these requirements could not coincide in the three-dimensional variable spaces. Therefore,

the values of <120 min in reaction time, >92% in yield, and >99% in selectivity were set for the limits of the optimization, considering the expected values. Under such limits, the optimum conditions were to use less TEMPO and NaBr concentration, and higher temperature. With these constraints, the optimum levels of TEMPO and NaBr were determined as 0.6 and 45 mM/100 mM AGU, respectively, and temperature as 7°C.

The reaction characteristics of corn starch, selectively oxidized under the various levels of TEMPO, NaBr, and temperature, are shown in spline plots (Fig. 1) of the response surface for the reaction time, yield, and selectivity, respectively, with the levels of TEMPO fixed at 0.6 mM/100 mM AGU. Under the conditions determined, the predicted values obtained using the model equations were 119.0 min for reaction time, 91.07% for yield, and 99.01% for selectivity. They were very close to the experimental values ( $113.7 \pm 2.5$  min,  $90.85 \pm 0.21\%$ , and  $98.68 \pm 0.20\%$ , respectively), indicating the appropriateness of the models.



**Fig. 4.** Emulsion stabilizing capacity of oxidized corn starch (OCS) in soybean oil and water system containing OCS for 2 hr. Oil-to-water ratio of 3:7 system containing 1.0% OCS (●); 7:3 system containing 1.0% OCS (▲); 5:5 system containing 1.0% OCS (◆); 5:5 system containing 0.5% OCS (■); 5:5 system containing 1.5% OCS (×).

### NMR Spectrum of OCS

$^{13}\text{C}$ -NMR spectrum of OCS (Fig. 2) shows new resonance in 176.9 ppm resulted from the formation of carboxylic acid at C6. No resonance in the region of 198–205 ppm was observed, indicating no ketone group formation from the oxidation of secondary alcohol group during the oxidation reaction. Therefore,  $^{13}\text{C}$ -NMR spectrum of OCS, prepared under the optimum conditions determined above, provided good evidence that only the primary alcohol groups of corn starch were oxidized to carboxylate during TEMPO-mediated oxidation.

### Water Binding Capacity of OCS

Water binding capacity (WBC) of OCS and native starch is shown in Table IV. WBC for OCS was significantly higher than that of native starch, confirming the study of Chang and Robyt (1996). WBC for OCS and native starch at 20°C were 43.12 and 1.95 g of water/g of sample, respectively, giving 20-fold increase over native starch. This result could be explained by the hydrophilic and bulky carboxyl groups induced from the oxidation of corn starch (Wurzburg and Szymanski 1970; Wurzburg 1986). WBC of OCS was significantly increased with increased temperature.

### Rheological Properties of OCS

The viscosity-shear rate relationships for 1 and 3% solution of OCS at 20 and 60°C, respectively, are shown in Fig 3. The viscosity of the solution decreased as the rate of shear increased. The viscosity decreased greatly at the lower shear rate and decreased slightly at the higher shear rate, indicating pseudoplastic flow properties, as seen in various gums. The apparent viscosity of OCS increased with higher OCS concentration and with a lower temperature. The apparent viscosity of 3% OCS solution at 20°C when shear rate was 1,000  $\text{sec}^{-1}$  was 116 cps. This is much greater than the apparent viscosity (60 cps) of the 4% corn starch slurry gelatinized in 0.5*N* KOH solution (Kim et al 1992). The high viscosity of OCS might have come from the high molecular weight polymer maintaining  $\alpha$ -1,4 glycosidic bonds. This result shows the potential of OCS for use as a thickening agent.

### Emulsion Stabilizing Capacity of OCS

Changes in emulsion stabilizing capacity (ESC) with time in the various emulsion systems containing different concentration of OCS are shown in Fig. 4. OCS showed good emulsion stability, especially in the 3:7 oil-to-water emulsion system. Emulsion stability, however, decreased as the oil-to-water ratio increased. Also, ESC increased with increased OCS concentration in the system. This indicates that OCS has the possibility to be used as a stabilizer in emulsion systems

containing a high proportion of water. ESC of OCS can be due to the high viscosity of OCS and to electrical repulsion of carboxyl group formed in the OCS during oxidation. In a related study, Konoo et al (1996) reported that oxidized tapioca starch with NaOCl had higher ESC. The mechanism should be further investigated however.

### Pasting Properties of Corn Starch Containing OCS

The pasting profile of corn starch illustrates the modification induced by the partial replacement of corn starch with OCS (Table V). The initial pasting temperature of corn starch was the highest, and it decreased with the increased levels of OCS in the system. This effect of OCS could be explained by inherent viscosity of OCS contributing to increased viscosity of the mixture, thus showing an earlier viscosity change in the amylograph (Crossland and Favor 1948; Christianson et al 1981). The peak viscosity increased with increased levels of replacement with OCS for corn starch. This result was probably due to the network formation between soluble amylose and OCS as the report of Christianson et al (1981), who suggested an interaction of amylose with gums, and the inherent viscosity of OCS. The network formation may be observed from the  $^{13}\text{C}$ -NMR spectrum of amylose-OCS paste. Correlation analysis on the peak viscosity and the levels of amylose in the OCS-water system with varying levels of soluble amylose can be a further proof for the network formation between amylose and OCS.

The breakdown of corn starch paste was increased by the replacement of starch with OCS. Christianson et al (1981) noted that the addition of thickening-agent gums would make the forces exerted on the granules in the shear field much greater than those encountered in starch-water suspension. These increased forces should affect granule breakdown and the amount of material exuded into the medium. OCS could interact with starch in a manner similar to gums, thus increasing breakdown of corn starch paste.

The setback, which indirectly indicates the degree of retrogradation in starch paste, decreased with increased replacement of starch with OCS. Carboxyl groups induced in OCS could have decreased association of starch molecules (Autio et al 1992), and thus retarded starch retrogradation.

### Gelatinization and Retrogradation Properties

Gelatinization and retrogradation properties of the corn starch partially replaced with OCS observed by DSC are shown in Tables V and VI, respectively. Onset temperature ( $T_o$ ) was not significantly affected by OCS replacement. However peak ( $T_p$ ) and completion temperature ( $T_c$ ) increased incrementally with OCS in the systems. Because WBC of OCS was higher than that of native starch, it might have limited the water available for starch to be gelatinized, therefore the crystalline area of starch did not melt until it reached a higher temperature (Donavan 1980; Evans and Haisman 1982). Changes in enthalpy ( $\Delta H$ ) for gelatinization tended to decrease with the increased levels of OCS replacement, but there was no significant difference.

The result of retrogradation characteristics of corn starch evaluated during storage at 4°C showed that  $T_o$  tended to increase while  $\Delta H$  tended to decrease incrementally with OCS content in corn starch. As the storage period was extended,  $T_o$  decreased while  $\Delta H$  increased, as expected.  $T_c$  did not show any changes with the OCS content in the system but gradually increased with longer periods of storage, reaching the highest temperature at the final stage of storage. Decreased  $\Delta H$  due to OCS might be related to the report of Ferro et al (1993), who observed the effect of xanthan gum on starch retrogradation. They suggested that the association of amylose with xanthan gum competes with amylose-amylose interaction, so retrogradation of starch could be depressed. Carboxyl group in OCS is bulky and has a negative charge, so if OCS interacts with soluble amylose, the resulting material would also have negative charges and be very bulky, thus retarding amylose-amylose interaction by electrostatic repulsion and steric hinderance. Differences in  $\Delta H$

with and without shielding negative charges of OCS by positive charges would provide an evidence of decreased amylose-amylose interaction due to negative charges.

### Textural Properties

Parameters obtained from TPA of corn starch gel with 0, 1, and 3% OCS are summarized in Table VII. The positive effects of OCS on the textural characteristics of starch gel were noted. Hardness and gumminess values of gel containing OCS were not significantly different from that of fresh starch gel, but values of gel with OCS were smaller than that of starch gel after storage. Cohesiveness and chewiness values were not significantly different among the samples.

Increase in hardness is related to starch retrogradation and indicates deterioration in quality of starch gel. OCS added in starch paste resulted in slower retrogradation process during storage. This result, as mentioned earlier, could be due to bulky and negatively charged carboxyl group induced in OCS, which could inhibit amylose association. This result supports the study by Sajjan and Rao (1987), who mentioned that starch gels containing hydrocolloids were depressed in syneresis and improved in the textural properties.

### CONCLUSIONS

Reaction characteristics and optimum preparation conditions of selectively oxidized corn starch using TEMPO, NaBr, and NaOCl were elucidated. From the results of physicochemical measurements on OCS, we concluded that OCS could be used as a food ingredient to improve water binding properties, emulsion stability, viscosity, and textural properties of starch gel.

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