ELSEVIER

Carbohydrate Polymers 46 (2001) 217–226

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Preparation of some starch ethers using the semi-dry state process

M.I. Khalil*, M.K. Beliakova, A.A. Aly

National Research Center, Textile Division, Dokki, Cairo, Egypt

Accepted 14 September 2000

Abstract

Two types of starch ethers have been prepared using a semi-dry process. These starch ethers are cyanoethylated and carbamoylethylated starch. The different factors affecting the preparation of these ethers have been studied. These factors include mode of adding the different ingredients, reaction medium, sodium hydroxide/anhydroglucose unit molar ratio, monomer concentration, reaction temperature and duration. The extent of etherification and the etherification reaction efficiency (ERE) were traced by estimating nitrogen content, carboxyl and total ether contents. Comparison of the ERE on using the semi-dry state and the wet state processes indicates the privilege of the former. The highest degrees of substitution (DS) values obtained were 0.66 and 0.52 of carbamoylethylated and cyanoethylated starch samples, respectively, within the studied range. Conditions are described giving high DS at reaction times short enough to keep hydrolysis of polymer bound nitrile and amide groups low. At longer reaction times, the major side reaction during carbamoylethylation is hydrolysis and during cyanoethylation deetherification. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Cyanoethylation; Carbamoylethylation; Starch ether

1. Introduction

Chemical modifications of starch have been extensively studied and the subject has been reviewed (Whistler, BeMiller & Paschall, 1984). Physical and chemical modification of starch via oxidation (Abdel-Thalouth, Hanna & Hebeish, 1977; Kamel, Hebeish, & Abdel-Thalouth, 1971), gelatinisation (Peter, 1967), reaction with urea (Abdel-Thalouth, El-Kashoute & Hebeish, 1981; Khalil, Farag, Mostaff & Hebeish, 1994), cyanoethylation (Hebeish, Abdel-Thalouth, & El-Kashoute 1981; Hebeish & Khalil, 1988), carbamoylethylation (Khalil, Bayazeed, Farag & Hebeish, 1987), vinyl graft copolymerisation (Bayazeed, Farag & Hebeish, 1968; Hebeish, Bayazeed, El-Alfy & Khalil, 1988; Khalil, Mostaffa, & Hebeish, 1993), and vinyl polymer starch composite (Hebeish, El-Alfy & Bayazeed, 1988) have been reported. Furthermore, carboxymethylation (Hebeish & Khalil, 1988; Hebeish, Khalil & Hashem, 1990; Khalil, Hashem & Hebeish, 1990; Bhattacharyya, Singhal & Kulkarni, 1995), anionic starch bearing carboxyl (Khalil, Farag & Abdel-Fattah, 1996, Khalil, Farag & Hebeish, 1991) or phosphate (Khalil, Waly, Farag & Hebeish, 1991a) or sulphite, phosphate and/or carboxyl groups (Khalil, Abdel-Rahman, Farag & Abdel-Fattah, 1995) have been also reported. Different cationic starches were prepared via reacting poly(glycidyl methacrylate)- starch graft copolymer (Khalil, Waly, Farag & Hebeish, 1991b), or methylolated poly(acrylamide)-starch graft copolymer (Khalil & Farag, 1994) with different amines. Cationic starches bearing primary, tertiary or quaternary amino groups were prepared via reacting starch with aminated chlorohydrine compounds or amines containing epoxy groups (Khalil, Farag & Hashem, 1993; Khalil & Farag, 1998). The majority of mentioned methods of preparation were carried out in aqueous medium which accelerate some side reactions. These side reactions lower the etherification reaction efficiency (ERE) and lead to gelatinisation of prepared starch derivatives.

On reacting starch with acrylonitrile or acrylamide in the presence of sodium hydroxide using the wet process the following reactions occur (Hebeish et al., 1981; Hebeish & Khalil, 1988; Khalil et al., 1987; MacGregor, 1951, MacGregor & Pug, 1951; Bruson & Reimer, 1943):

(1) Etherification reaction

$$\text{St.OH} + \text{CH}_2\text{=CH–X} \xrightarrow{\text{NaOH}} \text{St.O–CH}_2\text{–CH}_2\text{X}$$

where X = $-\text{C}\equiv\text{N}$ or CONH_2

---

* Corresponding author. Fax: +20-2-337-0931.
E-mail address: mgouda@hotmail.com (M.I. Khalil).

PII: S0144-8617(00)00304-0

(2) The side reactions

$$\mathrm{CH_2{=}CH{-}X + H_2O \xrightarrow{NaOH} HO{-}CH_2{-}CH_2X}$$

$$\mathrm{CH_2{=}CH{-}X}$$
$$\mathrm{+HOCH_2{-}CH_2{-}X \xrightarrow{NaOH} X{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}X}$$

$$\mathrm{CH_2{=}CH{-}CN + H_2O \xrightarrow{NaOH} CH_2{=}CH{-}CO{-}NH_2}$$

$$\mathrm{CH_2{=}CH{-}CO{-}NH_2}$$
$$\mathrm{+H_2O \xrightarrow{NaOH} CH_2{=}CH{-}COONa + NH_3\uparrow}$$

$$\mathrm{St.O{-}CH_2{-}CH_2{-}CN}$$
$$\mathrm{+H_2O \xrightarrow{NaOH} St.O{-}CH_2{-}CH_2{-}CO{-}NH_2}$$

$$\mathrm{St.O{-}CH_2{-}CH_2{-}CO{-}NH_2}$$
$$\mathrm{+H_2O \xrightarrow{NaOH} St.O{-}CH_2{-}CH_2{-}COONa + NH_3\uparrow}$$

$$\mathrm{St.O{-}CH_2{-}CH_2{-}X}$$
$$\mathrm{+H_2O \xrightarrow{NaOH} St.OH + HO{-}CH_2{-}CH_2{-}X}$$

The present study aims to the preparation of two starch ethers namely cyanoethylated and carbamoylethylated starches using a semi-dry process to minimise both side reactions and energy consumption. The different factors affecting these reactions were studied. These factors include, the mode of reaction, the reaction medium, sodium hydroxide concentration, monomer concentration, reaction temperature and duration.

2. Experimental

2.1. Materials

Maize starch was supplied by Cairo Company for Starch and Glucose, acrylonitrile, acrylamide, sodium hydroxide, and isopropanol were of laboratory grade.

2.2. Etherification reaction (semi-dry process)

Ten grams of maize starch (11.36 g maize starch containing 12% humidity) and powdered sodium hydroxide (0.5–2.5 g) were mixed thoroughly for 5 min in a stainless steel cup using mechanical stirrer at room temperature and left to cool to 20°C. The monomer (5 ml acrylonitrile or 5 g acrylamide) was added to the previous mixture followed by solvent (water, isopropanol or water/isopropanol mixture) and mixed thoroughly for 5 min. The mixture was transferred into a stoppered bottle and kept for the specified time in a thermostated water bath at the desired temperature. At the end of reaction time, the reaction product was neutralised with an acetic acid/ethanol mixture (1/20 (v/v) ratio) and then Soxhlet extracted with ethanol/water mixture (80:20) for 10 h and dried at 60°C.

2.3. Cyanoethylation of starch (wet process) (Hebeish & Khalil, 1988)

The cyanoethylation reaction of starch was carried out in 100 ml stoppered bottle containing 75 ml sodium hydroxide (0.5 N). Starch (10 g) was added gradually to the reaction bottle while stirring. Stirring was continued until formation of a homogenous paste. To this acrylonitrile was added. The reaction bottle was stoppered and placed in a thermostated water bath at 40°C for 4 h. At this end, the reaction product was neutralised and precipitated with ethanol/acetic acid mixture, Soxhlet extracted with ethanol/water mixture (80:20) for 10 h and dried at 60°C.

2.4. Carbamoylethylation of starch (wet process) (Khalil et al., 1987)

Reaction of starch with acrylamide was carried out in a 150 ml stoppered bottle containing 80 ml of cyclohexane and 20 ml sodium hydroxide solution (1 N). Starch (2 g) and acrylamide were then added. The reaction mixture was kept in a thermostated water bath for 2 h at 30°C. At the end of reaction time the reaction product was neutralised and precipitated with ethanol/acetic acid mixture (1/20 (v/v) ratio). The precipitated reaction product was Soxhlet extracted using ethanol/water mixture (80:20) for 10 h and finally dried at 60°C.

2.5. Analysis

The amide and cyanide contents (m.eq./100 g sample) were calculated from the nitrogen content of the samples as determined using the micro Kjeldahl method (Vogel, 1975).

The carboxyl content (m.eq./100 g sample) of the prepared samples was determined using the alkalimetric method (Daul, Reinhardt, & Reid, 1953).

The total ether content (m.eq./100 sample) = the amide or cyanide content + carboxyl content.

The degree of substitution (DS) was calculated as follows:

(a) Cyanoethylated starch samples

$$\mathrm{DS} = \frac{(0.162)(\text{ether content})}{100 - (0.053)(\text{ether content})}$$

(b) Carbamoylethylated starch samples

$$\mathrm{DS} = \frac{(0.162)(\text{ether content})}{100 - (0.071)(\text{ether content})}$$

Table 1
The nitrogen, carboxyl and total ether contents (expressed as m.eq./100 g sample) of cyanoethylated starch samples prepared by different procedures (starch, 10 g; acrylonitrile, 5 ml, sodium hydroxide, 2.5 g; isopropanol, 3 ml; water, 3 ml; temperature, 25°C)

Reaction time (min)	Procedure 1			Procedure 2		
	Nitrogen content	Carboxyl content	Total ether content	Nitrogen content	Carboxyl content	Total ether content
10	238	6	244	169	8	177
30	247	7	254	182	9	191
60	229	7	236	168	12	180
90	206	8	214	153	17	170

Table 2
Amide, carboxyl and total ether contents (expressed as m.eq./100 g sample) of carbamoylethylated starches prepared in presence of different solvents (starch, 10 g; acrylamide, 5 g; sodium hydroxide, 2 g; temperature, 40°C; reaction time, 2 h)

Solvent volume	Water			Isopropanol		
	Amide content	Carboxyl content	Total ether content	Amide content	Carboxyl content	Total ether content
0	84	7	91	84	7	91
1	94	13	107	80	13	93
2	123	19	136	74	19	93
3	147	26	173	57	25	75
4	154	42	196	44	24	68
5	144	63	212	33	21	48
6	130	87	217	26	20	46

Table 3
Nitrogen, carboxyl contents (m.eq./100 g sample) and etherification reaction efficiency of cyanoethylated and carbamoylethylated starch samples prepared in various reaction media

Solvent volume (ml) water–isopropanol	Cyanoethylated starch[a]			Carbamoylethylated starch[b]		
	Nitrogen content	Carboxyl content	ERE (%)	Nitrogen content	Carboxyl content	ERE (%)
0:0	52	4	7.0	84	7	13.8
6:0	127	9	19.3	130	87	36.5
5:1	202	12	31.8	252	87	63.3
4:2	284	16	47.0	261	88	65.5
3:3	320	15	53.9	270	53	59.0
2:4	282	14	46.2	250	45	52.6
1:5	202	12	31.8	169	33	33.3
0:6	59	7	9.0	27	21	7.00

[a] Cyanoethylation conditions: starch, 10 g; acrylonitrile, 5 ml; NaOH, 2.5 g; temp., 40°C; time 30 min.
[b] Carbamoylethylation conditions: starch, 10 g; acrylamide, 5 g; NaOH, 2 g, temp., 40°C; time, 2 h.

Table 4
Effect of sodium hydroxide concentration (moles/mole of anhydroglucose unit) on nitrogen, carboxyl, and total ether contents (m.eq./100 g sample) of starch switched to reaction with acrylonitrile and acrylamide at the given conditions (starch, 10 g; monomer, acrylonitrile 5 ml or acrylamide, 5 g; water, 3 ml; isopropanol, 3 ml; temp., 40°C; time 30 min)

Sodium hydroxide/ anhydroglucose unit molar ratio	Cyanoethylated starch			Carbamoylethylated starch		
	Nitrogen content	Carboxyl content	Total ether content	Nitrogen content	Carboxyl content	Total ether content
0.2	154	7	161	72	7	79
0.4	229	8	237	92	9	101
0.6	280	12	292	112	19	131
0.8	310	12	322	136	24	160
1.0	321	13	334	164	27	191

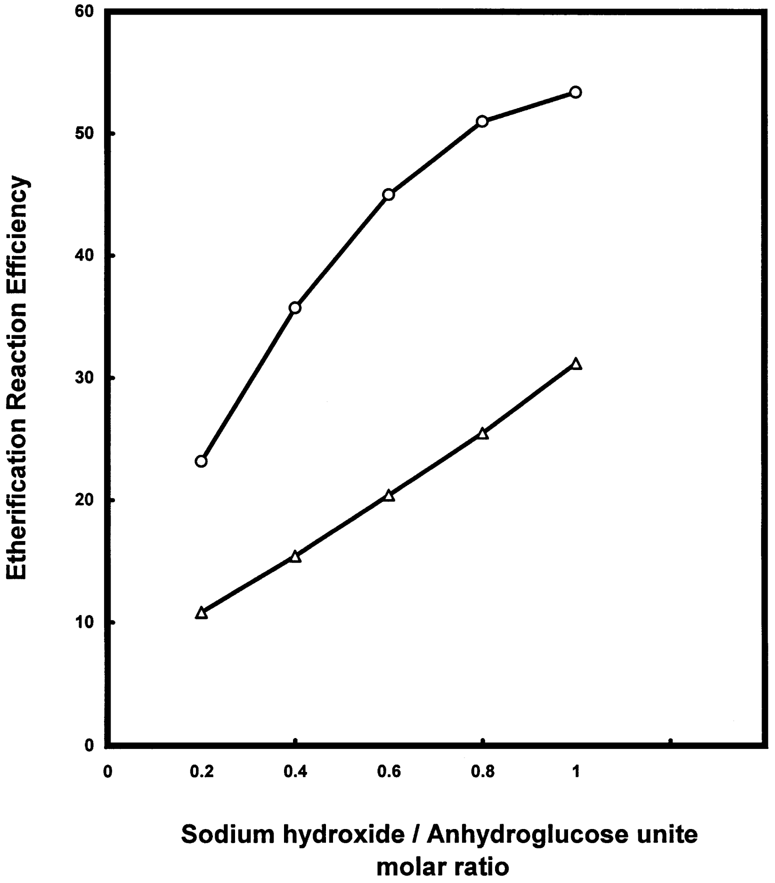

Fig. 1. Effect of sodium hydroxide concentration on etherification reaction efficiency % of prepared samples on using acrylonitrile and acrylamide. -○-, cyanoethylation; -△-, carbamoylethylation. Starch, 10 g; water, 3 ml; isopropanol, 3 ml; temp., 40°C; time, 30 min. Cyanoethylation: acrylonitrile, 5 ml. Carbamoylethylation: acrylamide, 5 g.

ERE was calculated as follows:

$$\mathrm{ERE} = \frac{\mathrm{DS}}{\text{monomer/anhydroglucose unit (molar ratio)}} \times 100.$$

3. Results and discussion

3.1. Effect of addition sequence

Maize starch (10 g) was reacted with acrylonitrile (5 ml) in the presence of sodium hydroxide (2.5 g), isopropanol (3 ml) and water (3 ml) using two procedures as follows.

Procedure 1. Starch and sodium hydroxide were mixed thoroughly for 5 min and left to cool up to 20°C then acrylonitrile and the solvent mixtures were added and thoroughly mixed.

Procedure 2. Starch and acrylonitrile were mixed first, followed by addition of sodium hydroxide and solvent mixture and thoroughly mixed.

Table 1 shows the nitrogen, carboxyl and total ether contents of the cyanoethylated samples prepared according to the two procedures. The data show that the nitrogen and total ether contents of the prepared samples using procedure 1 are higher than that of the prepared samples using procedure 2 while carboxyl content of the prepared samples using procedure 2 is higher than that of procedure 1. This may be explained as follows:

- procedure 1 accelerates the formation of alkali-starch before adding the acrylonitrile which leads to higher rate of cyanoethylation;
- procedure 2, on the other hand, increases the side reactions with both acrylonitrile and cyanoethylated starch samples.

3.2. Effect of reaction medium

The etherification reactions of starch were carried out in the absence or presence of water and/or isopropanol. Tables 2 and 3 show the nitrogen, carboxyl and total ether contents of the etherified starch samples as well as the ERE. The data show that:

1. Starch ether samples prepared in the presence of water

acquired higher ether contents than those prepared in the absence of water or in the presence of isopropanol, indicating that water enhances the etherification reaction (cf. Table 2).

2. On adding increasing amounts of water, the nitrogen content increased and reached a maximum value at 4 ml water/10 g starch, and then decreased. This indicates that, the presence of higher amounts of water enhances the hydrolysis of amide groups to carboxyl groups, leading to the decrement of nitrogen content (cf. Table 2).
3. Carboxyl and total ether contents increased with increasing amount of water (cf. Table 2). This may be explained as follows: increasing amount of water up to 4 ml/10 g starch increases sodium hydroxide solubilisation and alkali-starch formation which leads to higher etherification extent.
4. The samples prepared in the presence of isopropanol acquired lower ether contents than those prepared in its absence. The ether content also decreased on increasing the isopropanol amount. This may be due to competition between starch, sodium hydroxide and isopropanol to absorb water in the reaction medium which is essential for the etherification reaction (cf. Table 2).
5. Samples prepared in the presence of water–isopropanol mixtures acquired higher nitrogen, carboxyl and total ether contents than those prepared in the presence of water or in its absence (cf. Table 3).
6. The nitrogen, carboxyl and total ether contents first increased as the water content in the solvent mixture was increased. Maximum values were reached at a water/isopropanol volume ratio of 1:1 (cf. Table 3).

3.3. *Effect of sodium hydroxide concentration*

Cyanoethylation and carbamoylethylation of starch were carried out using different sodium hydroxide/anhydroglucose unit molar ratios (0.2–1) at 40°C for 30 min. Table 4 shows the nitrogen, carboxyl and total ether contents of the samples and Fig. 1 shows the ERE. The data show that:

1. Nitrogen and carboxyl contents as well as the ERE increased with increasing sodium hydroxide/anhydroglucose unit molar ratio. This is due to the increment of alkali-starch formation which accelerates the etherification reaction.
2. The products formed were mainly cyanoethylated or carbamoylethylated starch containing minute amounts of ether bond carboxyethyl groups.
3. The number of carboxyethyl groups formed on reacting starch with acrylamide was higher than that formed with acrylonitrile. The amount of carboxyethyl groups amounted to equal to 9–14.5% and 4% of the total ether contents of the carbamoylethylated and cyanoethylated starches, respectively. This is due to the fact that amide

Table 5

Nitrogen and carboxyl contents (m.eq./100 g sample) and etherification reaction efficiency (%) of cyanoethylated starch samples prepared at different reaction temperatures and durations (starch, 10 g; acrylonitrile, 5 ml; NaOH, 2.5 g; isopropanol, 3 ml; water, 3 ml)

Reaction time (min)	25°C			40°C			50°C		
	Nitrogen content	Carboxyl content	ERE (%)	Nitrogen content	Carboxyl content	ERE (%)	Nitrogen content	Carboxyl content	ERE (%)
10	239	7	37.2	293	7	47.0	251	11	40.0
30	247	7	38.6	321	11	53.0	229	14	36.5
60	229	8	35.4	296	12	48.4	216	15	34.7
90	206	9	32.0	229	13	36.6	181	16	29.0

Table 6
The amide, carboxyl contents (expressed as m.eq./100 g sample) and etherification reaction efficiency (%) of carbamoylethylated starch samples prepared at different reaction temperatures and durations (starch, 10 g; NaOH, 2 g; acrylamide, 5 g; isopropanol, 3 ml; water, 3 ml)

Reaction	20°C			30°C			40°C			50°C			60°C		
Time (min)	Amide content	COOH content	ERE (%)	Amide content	COOH content	ERE (%)	Amide content	COOH content	ERE (%)	Amide content	COOH content	ERE (%)	Amide content	COOH content	ERE (%)
15	29	7	5.3	46	7	7.80	121	23	22.6	215	23	40.1	235	24	44.8
30	34	9	6.0	64	11	11.2	171	28	32.8	240	31	47.4	239	32	47.4
45	49	11	8.8	87	20	16.4	217	34	43.2	245	43	51.1	234	48	49.8
60	72	14	12.9	105	28	20.8	250	39	51.3	233	55	51.1	220	62	49.8
120	125	20	23.3	173	32	33.9	270	53	59.2	230	58	51.1	218	65	49.8
180	184	24	34.5	225	39	45.9	262	61	59.2	224	64	51.1	201	81	49.8

groups are more easily saponified than nitrile groups, which need two steps of saponification to carboxyl groups.

4. The maximum etherification reaction efficiencies were 53.4 and 31.2% for cyanoethylated and carbamoylethylated starch samples, respectively, which indicates that acrylonitrile has a higher reactivity than acrylamide towards reaction with starch (cf. Fig. 1).

3.4. Effect of reaction temperature and duration

Cyanoethylation and carbamoylethylation of starch were carried out at various reaction temperatures (20–60°C) and durations. Tables 5 and 6 show data for the nitrogen and carboxyl contents of the samples as well as for the etherification reaction efficiencies. The data show that the rate of reaction depends on reaction temperature and duration beside monomer reactivity as follows:

1. At 20–30°C, the nitrogen content of carbamoylethylated starch increases with increasing reaction duration while at 40–60°C it first increases to a maximum value and then slightly decreases. At 40, 50 and 60°C the maxima occur after 120, 45, 30 min, respectively (cf. Table 6).
2. The nitrogen content of cyanoethylated starch increases with increasing reaction duration to reach a maximum and then decreases. The maxima occur after 30 and 10 min at 25–40 and 50°C, respectively. The extent of cyanoethylation was very high already after 10 min and then amounted to 96.7, 93.9 and 100% of the highest values observed during reaction at 25, 40, and 50°C, respectively (cf. Table 5). This illustrates the high reactivity of acrylonitrile in reaction with starch under alkaline conditions.
3. The carboxyl content of the samples increased with increasing reaction temperature and/or duration. The carboxyl content of the carbamoylethylated samples was higher than that of the cyanoethylated ones due to higher sensitivity of amide groups to hydrolysis than cyanide groups.
4. During the carbamoylethylation reaction, the ERE (Table 6) increased with reaction time. At 20–30°C ERE continued to increase during the entire time period studied, while at higher temperatures plateau values were reached after 120 min (40°C) or 45 min (50 and 60°C). For carbamoylethylation of starch under the set conditions, the highest ERE value (59.2%) were obtained by carrying out the reaction at 40°C for 120 min (cf. Fig. 2).
5. During preparation of cyanoethylated starch, ERE first increases with time up to a maximum value, and then decreases. The maxima occur after 30 and 10 min at 25–40 and 50°C, respectively. The highest reaction efficiency, 53% was observed at reaction temperature 40°C and a reaction time of 30 min (cf. Table 5 and Fig. 2).

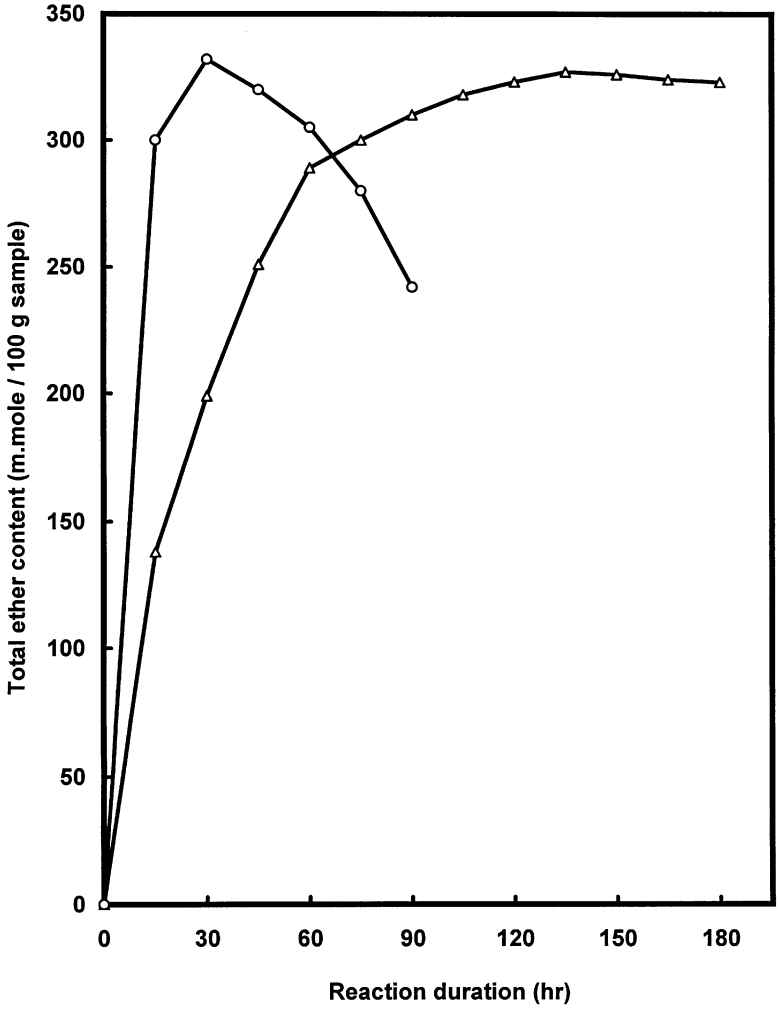

Fig. 2. The total ether content of cyanoethylated and carbamoylethylated starch samples prepared at 40°C versus reaction durations. -O-, cyanoethylation; -△-, carbamoylethylation. Starch, 10 g; water, 3 ml; isopropanol, 3 ml; temp. Cyanoethylation: acrylonitrile, 5 ml; sodium hydroxide, 2.5 g. Carbamoylethylation: acrylamide, 5 g; sodium hydroxide, 2 g.

Table 7
The amide, carboxyl and total ether contents (expressed as m.eq./100 g sample) of carbamoylethylated starch samples prepared at room temperature using different reaction times (starch, 10 g; acrylamide, 5 g; NaOH, 2 g; isopropanol, 3 ml; water, 3 ml; reaction temperature ~20°C)

Reaction time (h)	Amide content	Carboxyl content	Total ether content	DS	ERE (%)
6	242	39	281	0.570	49.6
9	255	41	296	0.600	53.0
12	272	46	319	0.663	58.1
15	309	49	358	0.773	67.8
18	301	58	359	0.773	67.8
24	298	65	363	0.796	69.0
48	289	77	366	0.796	69.0
72	289	78	367	0.800	69.0
96	265	111	376	0.823	72.2
120	237	138	375	0.823	72.2
144	237	138	375	0.823	72.2
168	237	138	375	0.823	72.2

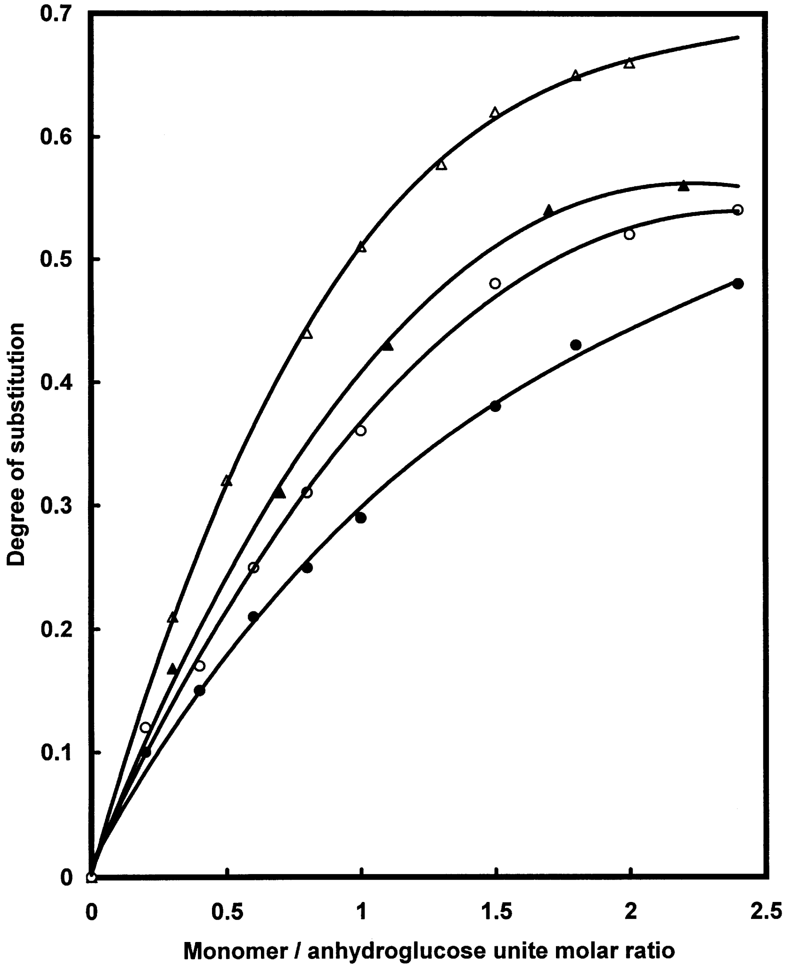

Fig. 3. The degree of substitution of cyanoethylated and carbamoylethylated starch samples prepared by the wet and by the semi-dry techniques versus monomer/anhydroglucose unit molar ratio. Cyanoethylation: -●-, wet technique; -○-, semi-dry technique. Carbamoylethylation: -▲-, wet technique; -△-, semi-dry technique. Cyanoethylation (semi-dry): starch, 10 g; sodium hydroxide, 2.5 g; water, 3 ml; isopropanol, 3 ml; temp., 40°C; time, 30 min. Cyanoethylation (wet): starch, 10 g; sodium hydroxide (0.5 N), 75 ml; temp, 40°C, time, 4 h. Carbamoylethylation (semi-dry): starch, 10 g; sodium hydroxide, 2 g; water, 3 ml; isopropanol, 3 ml; temp. 40°C; time, 120 min. Carbamoylethylation (wet): starch, 2 g; sodium hydroxide, 0.8 g; water/cyclohexane (20:80), 100 ml; temp, 30°C; time, 2 h.

6. A comparison of the total ether content of carbamoylethylated and cyanoethylated starch samples prepared at 40°C for different reaction durations is shown in Fig. 2. This diagram shows

   (a) After 30 min the extent of cyanoethylation reaction is higher than that of the carbamoylethylated (332 and 199 m.eq./100 g, respectively).

   (b) The highest reaction efficiency observed were 59.2 and 53% for carbamoylethylated and cyanoethylated starch samples, respectively (cf. Tables 5 and 6).

   (c) After 120 min the total ether content of carbamoylethylated starch samples remains constant, whereas amide groups are slowly converted to carboxyl groups (cf. Table 6). On the other hand, the total ether content of cyanoethylated samples decreases on increasing the reaction duration above 30 min, indicating that the major side reaction in this case is deetherification (cf. Table 5 and Fig. 2).

In a trial to minimise the side reactions and energy consumption, carbamoyl-ethylation of starch was carried out at room temperature (~20°C) for different reaction durations (6–168 h). Table 7 shows the full data of the samples obtained. The data show that:

1. The amide content increases with increasing reaction duration up to 15 h, then decreases at higher durations up to 120 h and then levels off.
2. The carboxyl content increases with time up to a reaction duration of 120 h and then levels off.
3. Within the reaction duration range of 18–96 h the increase of carboxyl content is higher than the decrement in amide content, meaning that etherification

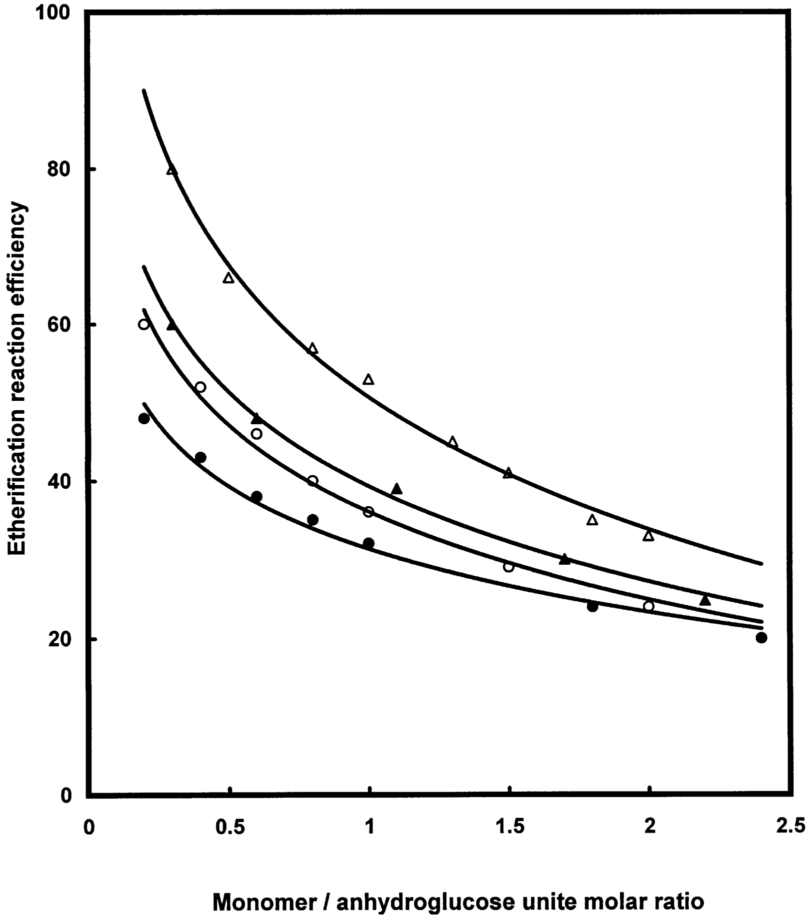

Fig. 4. The etherification reaction efficiency of cyanoethylated and carbamoylethylated starch samples prepared by the wet and semi-dry techniques versus monomer/anhydroglucose unit molar ratio. Conditions as given in the legends to Fig. 3.

and hydrolysis reactions occur simultaneously, while in the range of 96–120 h the increment in carboxyl content is equal to the decrement in the amide content, meaning that in this duration range, the hydrolysis reaction is the lonely reaction.

4. The total ether content increases sharply to reach 281 m.eq./100 g sample within 6 h after which it increases slightly to reach a constant level of 375 m.eq./100 g sample at about 96 h.
5. Under the conditions studied the optimal reaction time at 20°C seems to be 15 h. This gives a starch containing 309 m.eq. amide group/100 g sample and 49 m.eq. carboxyl group/100 g sample corresponding to the ERE of 67.8%. The corresponding value for the wet process (Khalil et al., 1987) was only 36.5%, which shows the privilege of the semi-dry process technique on the wet process technique.

In general it can be concluded that, using the best conditions under investigations lead to the highest etherification values the major reaction is etherification with minor hydrolysis, while at longer reaction durations the major reactions are hydrolysis and deetherification of the carbamoylethylated and cyanoethylated starch samples, respectively.

3.5. Effect of monomer concentration

Carbamoylethylation and cyanoethylation of maize starch were carried out at different monomer/anhydroglucose unit molar ratios (0.2–2.24) at conditions giving the highest reaction efficiency using both dry and wet techniques. The wet techniques were carried out according to the reported methods (Hebeish & Khalil, 1988; Khalil et al., 1987). For experimental details, see legend to Fig. 3. This figure shows DS values for the samples and Fig. 4 the corresponding etherification reaction efficiencies.

The data shows that:

1. With both monomers the DS of samples increased as the monomer/anhydro-glucose unit molar ratio was increased. This is due to the greater availability of the monomer in the vicinity of the starch molecules at higher monomer concentrations.

2. At equal monomer concentration the DS of the carbamoylethylated samples is higher than those of the cyanoethylated ones. This may be due to the lower extent of the side reactions in the case of the former.
3. The DS of the starch ethers prepared by the semi-dry technique is higher than those prepared by the wet technique. This is partly due to the fact that side reactions are minimised in the semi-dry process.
4. The ERE decreases with an increase in the monomer concentration. The highest ERE obtained, 82%, for the carbamoylethylated and 60% for the cyanoethylated samples prepared by the semi-dry technique at a monomer/anhydroglucose unit molar ratio 0.2. These figures can be compared with the corresponding highest ERE values obtained by the wet technique, 60 and 48%, respectively.

The above may be explained as follows: (a) at low monomer concentrations, the excess of starch hydroxyl groups over monomer favours etherification at the expense of side reactions; (b) at higher monomer concentration, the etherification reaction leads to consumption of the available starch hydroxyl groups. Once these groups are blocked by etherification, the side reactions tend to dominate. Also the greater availability of monomer in the reaction medium favours the hydrolysis of the monomer itself.

4. Conclusions

The semi-dry process carried out in the presence of sodium hydroxide and a 50/50 mixture of water and isopropanol can give starch ethers of high DS by reaction with either acrylamide or acrylonitrile. Acrylamide is by for the most reactive of these monomers. By suitable choice of temperature and reaction time, side reactions can be minimised. In the reaction with acrylamide, the major side reaction is hydrolysis, whereas deetherification is the dominating side reaction during etherification by acrylonitrile.

References

Abdel-Thalouth, I., Hanna, H. L., & Hebeish, A. (1977). *Textile Research Journal*, *47*, 209.

Abdel-Thalouth, I., El-Kashoute, M. A., & Hebeish, A. (1981). *Starch*, *33*, 306.

Bayazeed, A., Farag, S., & Hebeish, A. (1968). *Starch*, *38*, 268.

Bhattacharyya, D., Singhal, R. S., & Kulkarni, P. R. (1995). *Carbohydrate Polymers*, *27*, 247.

Bruson, H. A., & Reimer, T. W. (1943). *Journal of the American Chemical Society*, *65*, 23.

Daul, G. R., Reinhardt, M., & Reid, J. D. (1953). *Textile Research Journal*, *23*, 719.

Hebeish, A., & Khalil, M. I. (1988). *Starch*, *40*, 104.

Hebeish, A., & Khalil, M. I. (1988). *Starch*, *40*, 147.

Hebeish, A., Abdel-Thalouth, I., & El-Kashoute, M. A. (1981). *Journal of Applied Polymer Science*, *26*, 171.

Hebeish, A., Bayazeed, A., El-Alfy, E., & Khalil, M. I. (1988). *Starch*, *40*, 223.

Hebeish, A., El-Alfy, E., & Bayazeed, A. (1988). *Starch*, *40*, 191.

Hebeish, A., Khalil, M. I., & Hashem, A. (1990). *Starch*, *42*, 185.

Kamel, M., Hebeish, A., & Abdel-Thalouth, I. (1971). *Textile Research Journal*, *41*, 450.

Khalil, M. I., Farag, S., Mostaff, Kh. M., & Hebeish, A. (1994). *Starch*, *46*, 312.

Khalil, M. I., Bayazeed, A., Farag, S., & Hebeish, A. (1987). *Starch*, *39*, 311.

Khalil, M. I., Mostaffa, Kh. M., & Hebeish, A. (1993). *Die Angewandte Makromolekulare Chemie*, *213*, 43.

Khalil, M. I., & Farag, S. (1994). *Starch*, *46*, 17.

Khalil, M. I., & Farag, S. (1998). *Starch*, *50*, 267.

Khalil, M. I., Hashem, A., & Hebeish, A. (1990). *Starch*, *42*, 60.

Khalil, M. I., Farag, S., & Hebeish, A. (1991). *Starch*, *43*, 254.

Khalil, M. I., Waly, A., Farag, S., & Hebeish, A. (1991a). *Journal of Applied Polymer Science*, *43*, 2303.

Khalil, M. I., Waly, A., Farag, S., & Hebeish, A. (1991b). *Starch*, *43*, 349.

Khalil, M. I., Farag, S., & Hashem, A. (1993). *Starch*, *45*, 226.

Khalil, M. I., Abdel-Rahman, S., Farag, S., & Abdel-Fattah, S. (1995). *Egyptian Journal of Applied Science*, *10*, 900.

Khalil, M. I., Farag, S., & Abdel-Fattah, S. (1996). *Starch*, *48*, 270.

MacGregor, J. H. (1951). *Journal Society Dyer & Colourist*, *67*, 66.

MacGregor, J. H., & Pug, C. (1951). *Journal Society Dyer & Colourist*, *67*, 75.

Peter, R. H. (1967). *Textile chemistry*, vol. II. Amsterdam: Elsevier (chap. 2).

Vogel, A. I. (1975). *Quantitative organic analysis Elementary practical organic chemistry, part 3* (p. 652). London: Longman.

Whistler, R. L., BeMiller, J. N., & Paschall, E. F. (1984). *Starch chemistry and technology*, . (2nd ed.)Orlando, FL: Academic Press.