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Carboxymethylation of cellulose using reactive extrusion

Pratik N. Bhandari[a], David D. Jones[b], Milford A. Hanna[c,*]

[a] University of Nebraska-Lincoln, Department of Biological Systems Engineering, 156 L.W. Chase Hall, Lincoln, NE 68583-0730, United States
[b] University of Nebraska-Lincoln, Department of Biological Systems Engineering, 215 L.W. Chase Hall, Lincoln, NE 68583-0730, United States
[c] University of Nebraska-Lincoln, Industrial Agriculture Product Center, 211 L.W. Chase Hall, Lincoln, NE 68583-0730, United States

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ABSTRACT

Carboxymethyl cellulose was prepared using a continuous, reduced solvent, reactive extrusion process with a short reaction time. The effects of the amounts of NaOH (30 g, 40 g and 50 g), water:ethanol ratio (100%, 70%, 50%, 30% and 10% H_2O) and their interactions on the physical, chemical and morphological properties of carboxymethyl cellulose were studied. Experiments were conducted using to a 5 × 3 blocked factorial design. X-ray diffraction analyses revealed higher degrees of crystallinity and fractions of cellulose-II crystalline structure when 100% H_2O was used as compared to that for 70%, 50%, 30% and 10% H_2O and a commercially available brand of carboxymethyl cellulose, AQUASORB A500. Statistical analysis revealed a significant interaction between the effects of NaOH and H_2O on the degrees of substitutions. The degrees of substitutions decreased with increasing amounts of NaOH and tended to increase with increasing alcohol concentrations. Liquid uptake measurements revealed that the extent of saline uptake, measured at intervals of 1 min, 5 min and 10 min, by carboxymethyl cellulose prepared with 100% H_2O, especially when 40 g and 50 g NaOH was used, was higher than that for 70%, 50%, 30% and 10% H_2O and AQUASORB A500. This may have been because of the higher crystallinity in carboxymethyl cellulose prepared with 100% H_2O. Carboxymethyl cellulose prepared with 70% H_2O and 30 g and 50 g NaOH had the highest saline absorption, using the soak method, before and after centrifugation, respectively. Scanning electron microscopy for carboxymethyl cellulose prepared with 100% and 10% H_2O, through images at 120X magnification, revealed fibers 100 μ to >800 μ in length and 0.8–3.3 μ in breadth. Some non fibrous particles, 0.8–6.7 μ in dimensions, also were observed for 100% H_2O. Images at 900× magnification revealed partially damaged fiber surfaces.

1. Introduction

Cellulose ethers were described theoretically, first, in the year 1905 and their preparation was first studied and published by Chowdhury in 1924 (Chowdhury, 1924; Savage, Young, & Maasberg, 1954). The sodium salt of carboxymethyl cellulose is a water soluble cellulose ether also known as cellulose gum, sodium cellulose glycolate or only carboxymethyl cellulose (Savage et al., 1954). Carboxymethyl cellulose has colloidal, binding, thickening, absorbing, stabilizing and film-forming properties, because of which it finds applications in the food, personal care, detergent, cosmetics, pharmaceutical, oilfield, printing and dyeing, and paper industries (Savage et al., 1954; Yang & Zhu, 2007). Carboxymethyl cellulose is used in the biomedical field for applications such as preventing postoperative adherences and epidural scarring (Barbucci, Magnani, & Consumi, 2000). Tomanová et al. (2008) recently found partially esterified carboxymethyl cellulose an environmentally friendly alternative to surfactants.

Carboxymethyl cellulose is obtained by reacting cellulose with sodium mono chloro acetate (SMCA) in the presence of NaOH. Sodium chloride and water are the by-products. Although, generally, alkali cellulose is formed separately by treating cellulose with a NaOH solution and this alkali cellulose is then reacted with SMCA.

$$\text{Cell-(OH)}_3 + \text{ClCH}_2\text{COONa} + \text{NaOH} \rightarrow \text{Cell-(OH)}_2\text{OCH}_2\text{COONa} + \text{NaCl} + \text{H}_2\text{O}$$

Also, sodium glycolate is formed by a side reaction.

$$\text{ClCH}_2\text{COONa} + \text{NaOH} \rightarrow \text{HOCH}_2\text{COONa} + \text{NaCl}$$

Production of carboxymethyl cellulose is carried out commercially on a large scale, exclusively, by the slurry process (Heinze & Koschella, 2005). In the slurry method, cellulose is suspended in an alcohol–water–NaOH system, which has an excess of alcohol (Mann, Kunze, Loth, & Fink, 1998). In this process the liquid phase acts as a solvating agent which dissolves the NaOH and distributes it uniformly to the cellulose hydroxyl groups. The aqueous NaOH

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[*] Corresponding author. Tel.: +1 402 472 1634; fax: +1 402 472 6338.
E-mail addresses: pbhandari2@unl.edu (P.N. Bhandari), djones1@unl.edu (D.D. Jones), mhanna@unlnotes.unl.edu, mhanna1@unl.edu (M.A. Hanna).

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penetrates the crystalline structure of cellulose, solvates the hydroxyl groups in this region and makes them available for etherification by breaking the hydrogen bonds (Savage et al., 1954). This process of treating cellulose with NaOH is termed mercerization. Further, this alkali cellulose is then reacted with SMCA to form carboxymethyl cellulose ethers.

Several factors affect the carboxymethylation of cellulose and the resultant properties, such as the type of solvent (Barai, Singhal, & Kulkarni, 1997; Olaru, Olaru, Stoleriu, & Ţîmpu, 1998; Pushpamalar, Langford, Ahmad, & Lim, 2006), concentration of solvent (Pushpamalar et al., 2006; Zhang, Li, Zhang, & Shi, 1993), amount of H_2O, amount of SMCA(Mann et al., 1998), concentration of NaOH (Heinze & Pfeiffer, 1999), reaction time(Hedlund & Germgård, 2007), temperature (Xiquan, Tingzhu, & Shaoqui, 1990) and additional ingredients like borax (Majewicz, 1981)and cobalt (Stigsson, Kloow, Germgård, & Andersson, 2005) used during the reaction.

Researchers have experimented with several methods for preparing cellulose ethers, such as homogeneous carboxymethylation (Heinze, Liebert, Klufers, & Meister, 1999), rotating drum technique (Swinehart & Allen, 1950), fluidized bed technique (Durso, 1981), sheet carboxymethylation (Collings, Freeman, & Anthonisen, 1942), Werner-Pfleiderer type mixers (Tokimatsu & Yamashita, 1969) and also a solvent-less method using a double screw press (Edelman & Lindroos, 1990; Eichenseer & Kletschke, 1971) and a paddle reactor (Holst, Lask, & Kostrzewa, 1978).

Reactive extrusion is a popular technique for chemical modification of starches (Moad, 2011). However, extruders also have been used as chemical reactors for non-thermoplastic polysaccharides, such as in the acid hydrolysis of cellulose to glucose (Green, Kimchie, Malester, Rugg, & Shelef, 1988; Rugg & Stanton, 1982), partial hydrolysis of cellulose to microcrystalline cellulose using mineral acids (Hanna et al., 2001) and hydrogen peroxide (Kopesky & Ruszkay, 2006) and alkaline extraction of alginates from seaweeds (Vauchel, Kaas, Arhaliass, Baron, & Legrand, 2008). Carlborn and Matuana (2002) used reactive extrusion for the surface esterification of wood particles with maleated polyethylene and maleated polypropylene. In this case, although, the esterification agents used were thermoplastic and formed a melt phase in the extruder, their amounts, used along with wood particles were small (5–20 wt%).

The objective of this project was to prepare carboxymethyl cellulose using reactive extrusion and study the effects of the water:ethanol ratio, amounts of NaOH and their interactions on the properties of carboxymethyl cellulose. NaOH and ethanol concentrations were found to be important factors in the slurry process of preparation of carboxymethyl cellulose, affecting the reaction rate and hence DS (Barai et al., 1997; Heinze & Pfeiffer, 1999), degree of polymerization and viscosity (Zhang et al., 1993) and crystalline structure (Zhang et al., 1993).

2. Experimental

2.1. Extrusion

Cotton linter pulp sheets (Grade UVE ($DP_w = 7077$ and viscosity = 14,000 s), Buckeye Technologies Inc., Memphis, TN) were cut, using a sheet cutter, into 15 mm × 15 mm pieces and then shredded to a fluff using a blender (Model 31BL92, Waring Products Limited, New Hartford, CT). NaOH (Thermo Fisher Scientific, Hampton, NH) solution in aqueous ethanol (USP grade, Decon Labs, King of Prussia, PA) or distilled water, cooled to 15 °C, was added to the cellulose fluff under a nitrogen atmosphere and then shredded in the blender for 5 min. For high ethanol concentrations, NaOH was not completely soluble and the suspension was used as is. Powdered SMCA (Alfa Aesar, Ward Hill, MA) was then added to the alkali cellulose and the formulation was again shredded in the blender, under a nitrogen atmosphere. The formulation was then mixed in a planetary mixer (model C-100, Hobart Corp., OH) and sealed in plastic bags, with nitrogen maintaining an inert atmosphere, and stored at 25 °C for 7 h, for mercerization.

Table 1
Elaboration of screw profile.

No. of screw elements (from die end)	Screw type	Length of each element (mm)
9	Compression	20
3	Conveying	30
1	Conveying	15
1	Kneading	20
2	Conveying	30
1	Kneading	20
1	Conveying	30
1	Kneading	20
6	Conveying	30

A co-rotating twin-screw extruder (model TSE-20, Branender Technologies Inc., South Hackensack, NJ), with four heating zones and an injection port in the barrel, was used as a reactor for carboxymethylation of cellulose. The extruder was operated without a nozzle and die because of the fibrous and non-thermoplastic nature of cellulose. The screw configuration used consisted of four kneading blocks and nine compression screws and is detailed in Table 1. The formulation was force fed into the second zone of the extruder screw using a plastic plunger. Nitrogen was injected in the extruder barrel through the injection port. The barrel temperature for the feed zone was set at 100 °C and the temperatures for both the subsequent zones were set at 150 °C. On the die end of the extruder, an 80 mm × 80 mm × 900 mm steel tube was placed perpendicular to the extruder barrel. The extrudates leaving the extruder, dropped through the steel tube in which a nitrogen atmosphere was maintained, and were collected in a plastic bag attached to the lower end of the steel tube. The extrudates were sealed in the plastic bags and stored under inert conditions until further processing.

2.2. Extrudate purification

The extrudates were ground using a blender (model F203, Krups USA) and separated from the by-products by centrifuging an 80% aqueous ethanol suspensions using a Baxter MEGAFUGE (model 2.0R, Heraeus Instruments Inc., South Plainfield, NJ) at 4000 rpm. The aqueous ethanol was periodically replaced. The pHs of the extrudates were neutralized by adding glacial acetic acid to the ethanol. The extrudates were centrifuged until the NaCl content was found to have been reduced below 0.1 wt%. The NaCl content was measured by potentiometric titration with 0.1 M silver nitrate and has been described elsewhere (Bhandari & Hanna, 2011). Finally, the extrudates were washed with anhydrous ethanol and dried overnight in a vacuum oven. The purified extrudates were ground to pass through a 70 mesh Tyler Standard Series sieve.

2.3. Fourier-transform infrared spectroscopy

The Fourier-transform infrared (FTIR) spectrum for carboxymethyl cellulose was obtained using an Avatar 360 FT-IR E.S.P. spectrometer (Thermo Nicolet, Madison, WI). Sixteen scans were acquired per image at a resolution of 4 cm^{-1}.

2.4. X-ray diffraction

X-ray diffraction studies were conducted using a Rigaku D/Max-B diffractometer (Rigaku Americas, TheWoodlands, TX). X-rays, produced using a 2 kW copper target, were converged into a monochromator which removed all radiations except the Cu Ka wavelength (~1.544 Å). The samples were sprinkled uniformly on glass slides covered with vacuum grease (Dow Corning, Midland, MI) which were then inserted in the diffractometer. The sample and the detector were rotated at angles θ and 2θ with respect to the incident beam. Diffractograms were registered for the angular range (2θ) of 5° to 35°, with a scanning speed of 5° (2θ)/min and a step size of 0.02° (2θ). The degree of crystallinity was determined using the equation $X = n \times I_k/I_o$, $n = 0.75$. Here, I_o is the intensity of the maximum diffraction from the baseline and I_k is intensity obtained by subtracting the base level from I_o (Zhang et al., 1993). The fraction of cellulose-II crystalline form present in the carboxymethyl cellulose was calculated using the equation $X_{II} = X(1 - C_{II})$, where C_{II} is the fraction of cellulose-II in the crystalline aggregation and is calculated as $C_{II} = I_{12}/[I_{12} + 0.5(I_{14.7} + I_{16.1})]$. Here, I_{12}, $I_{14.7}$ and $I_{16.1}$ are the intensities at 2θ angles of 12°, 14.7° and 16.1°, respectively, in the diffractogram, and they were determined as indicated by Zhang et al. (1993).

2.5. Degree of substitution

The degrees of substitutions were determined using the method described by US Pharmacopoeia NF24. In a crucible, which was previously ignited at 600 °C for 30 min, then cooled in a desiccator and weighed, 1 g of carboxymethyl cellulose was added. The sample was moistened with 1 mL of dilute sulfuric acid (50 wt%) and then the crucible was heated on a flame until the cellulose was completely charred. After the sample had cooled down, it was again moistened using 1 mL sulfuric acid and ignited in a muffle furnace at 600 °C for 3 h. The crucible was cooled in a desiccator, weighed and the percentage of residue was calculated. The moistening with sulfuric acid and igniting was repeated until constant percentage of residue was obtained. The Na in sodium carboxymethyl cellulose was assayed using the equation $\%\text{Na} = 0.3238A$, where A is the percentage of sulfated ash residue obtained on ignition. The %Na assay was converted to DS using the equation:

$$\text{DS} = \frac{[(\%\text{Na}/2300) \times 162]}{[1 - ((\%\text{Na}/2300) \times 80)]}$$

The measurements were replicated once.

2.6. Capillary liquid uptake

The set-up for capillary liquid uptake measurements consisted of a graduated glass burette that was connected, through a tube, to a Millipore (Billerica, MA) 47 mm filter setup consisting of a fritted glass filter plate. The position of the fritted filter plate was adjusted so that the test liquid (1 wt% NaCl solution) in the graduated burette was level with it and the liquid barely touched the fritted plate. Any kinks present in the tube and any air bubbles present in the tube or under the fritted plate were removed. The powdered extrudate (0.2 g) was spread uniformly on the sintered glass plate. The test liquid passed through the tube and fritted plate by capillary action and was absorbed by the extrudates. The liquid level in the burette was noted periodically and the rate of water uptake by the extrudates was determined. The measurements were replicated once. Similarly, water uptakes were also determined for AQUASORB A500 (carboxymethyl cellulose, Ashland Aqualon Functional Ingredients, Wilmington, DE) and cross-linked sodium polyacrylate (The Ark Enterprises, Inc., MO).

2.7. Water absorption

2.7.1. Flood method

Carboxymethyl cellulose (0.2 g) was immersed in 20 mL of 1% NaCl solution, in a beaker. After soaking for 30 min, the suspension was filtered using a 60 mesh (Tyler standard series) sieve and the filtrate was collected in a measuring cylinder. The unabsorbed liquid was measured and the absorbency (mL of liquid absorbed) was calculated. The measurements were replicated once. Water absorptions also were determined for AQUASORB A500 and sodium polyacrylate.

2.7.2. Centrifuge method

Carboxymethyl cellulose (0.2 g) was immersed in 20 mL of 1% NaCl solution for 30 min and then centrifuged using a Baxter MEGAFUGE 2.0R (Heraeus Instruments Inc., South Plainfield, NJ) for 2 min at 1800 g. The suspension then was filtered using a 60 mesh sieve and the absorbency was determined. Using the absorbency before and after centrifugation, the % retention after centrifugation also was calculated. The measurements were replicated once. Water absorptions, using this method, also were determined for AQUASORB A500 and sodium polyacrylate.

2.8. Scanning electron microscope

A variable pressure scanning electron microscope (model S-3000 N, Hitachi High Technologies America Inc., San Jose, CA) was used to determine the product microstructures as described by Bhandari and Hanna (2011). Images were obtained at 1280 × 960 pixel resolution and 120× and 900× magnifications.

2.9. Experimental design and data analyses

There were fifteen treatment combinations (5 levels of water:ethanol ratio × 3 levels of NaOH). These fifteen treatment combinations were blocked and replicated twice. The data on the degrees of substitutions, capillary water uptakes and water absorptions using flood and centrifuge methods were analyzed using 'Proc Mixed' procedure of SAS version 9.1 (SAS Institute Inc., Cary, NC) with a significance level of $\alpha \leq 0.05$.

3. Results and discussions

3.1. FTIR spectroscopy

The FTIR spectra for purified carboxymethyl celluloses for the wave-numbers 850–3500 cm^{-1} are summarized in Fig. 1. The peaks corresponding to the backbone of the cellulose molecule were observed at 3432 cm^{-1} (broad absorption band due to stretching of –OH groups and intermolecular and intramolecular hydrogen bonds), 2920 cm^{-1} (C–H stretching), 1420 cm^{-1} ($-CH_2$ scissoring), 1320 cm^{-1} (–OH bending) and 1060 cm^{-1} ($CH-O-CH_2$ stretching) (Pushpamalar et al., 2006). The peak at 1600 cm^{-1} confirmed the carboxymethylation of cellulose.

3.2. X-ray diffraction

The X-ray diffractogram for cotton linter pulp and carboxymethyl cellulose are presented in Figs. 2 and 3, respectively. The X-ray diffractogram of cotton linter pulp, illustrated in Fig. 2, shows the characteristic peaks of cellulose-I crystalline structure at 14.7°, 16.1°, 22.4° and 34.2°. While, in the X-ray diffractograms of carboxymethyl cellulose and AQUASORB A500, illustrated in Fig. 3, the peaks at 14.7°, 16.1° and 22.4° disappeared and peaks at 12°, 20° and 21.5°, characteristic of cellulose-II crystalline structure, appeared (Zhang et al., 1993). That indicated that during mercerization, prior to the carboxymethylation process, destruction of cellulose-I crystalline structure and formation of cellulose-II crystalline structure took place. During such metamorphosis, the NaOH solution penetrates the amorphous regions interspaced between the crystalline regions which results in the formation of Na

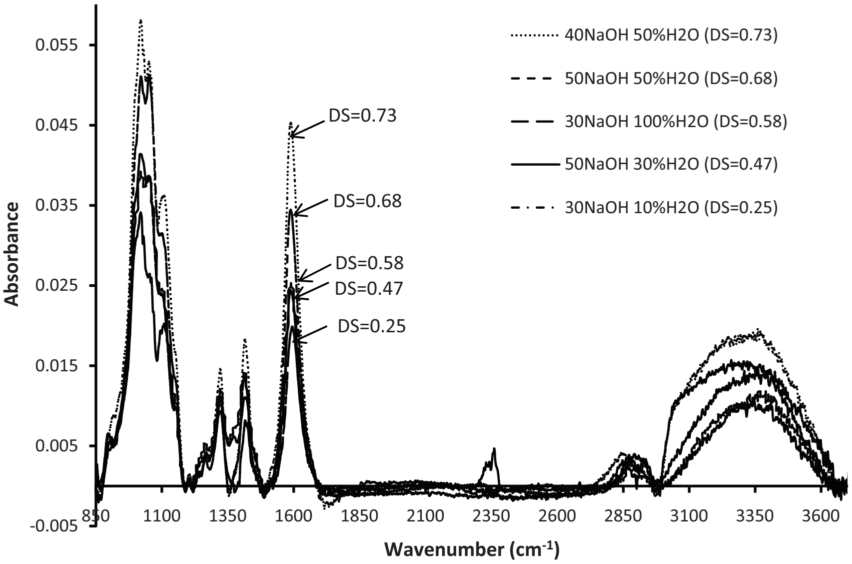

Fig. 1. FTIR spectra of carboxymethyl celluloses.

cellulose-I with anti-parallel chains, effecting a gradual reduction of cellulose-I crystallinity which then leads to the formation of Na cellulose-I crystallites. Then, Na cellulose-I is able to absorb more alkali and is converted to Na cellulose-II which, after washing and drying, is converted to cellulose-II (Oudiani, Chaabouni, Msahli, & Sakli, 2010). Thus, cellulose-II crystalline form is regenerated from amorphous cellulose. During this regeneration, small amounts of cellulose-I also is regenerated (Yokota, 1985).

Table 2 summarizes the degrees of crystallinity (X) and the cellulose-II crystalline fraction in the sample (X_{II}) for carboxymethyl cellulose, AQUASORB A500 and cotton linter pulp. Cotton linter pulp has a high degree of crystallinity (0.7), which also was apparent from the high intensity of the peak at 22.4° in the diffractogram (Fig. 2), and no cellulose-II crystalline aggregation. AQUASORB A500 has a degree of crystallinity and fraction of cellulose-II crystalline aggregate of 0.37 and 0.12, respectively. Carboxymethyl cellulose prepared using reactive extrusion had degrees of crystallinity ranging from 0.18 to 0.51 and cellulose-II crystalline fraction ranging from 0.14 to 0.36. Carboxymethyl cellulose prepared with 100% H_2O seemed to have the highest degree of crystallinity and cellulose-II crystalline fraction, ranging from 0.43 to 0.51, and 0.27 to 0.36, respectively. Kumar, Luz Reus-Medina, and Yang (2002), in the process of modification of the crystalline structure of micro crystalline cellulose using NaOH concentrations (5 N, 7.5 N and 10 N) similar to those used for 100% H_2O in this study, obtained products with similar degrees of crystallinity (46.99%, 49.3% and 47.58%) after 4 h of treatment.

The average degrees of crystallinity and cellulose-II fraction at 70% H_2O (0.36 and 0.18), 50% H_2O (0.25 and 0.19), 30% H_2O (0.26 and 0.21) and 10% H_2O (0.38 and 0.21) were less than that for 100% H_2O (0.47 and 0.31). Mansikkamäki, Lahtinen, and Rissanen (2007)

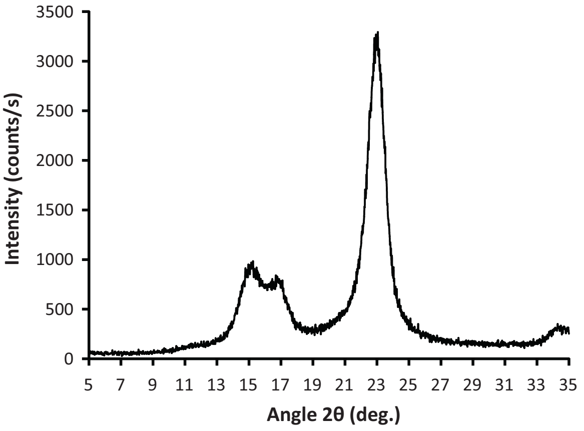

Fig. 2. X-ray diffraction pattern for cotton linter pulp.

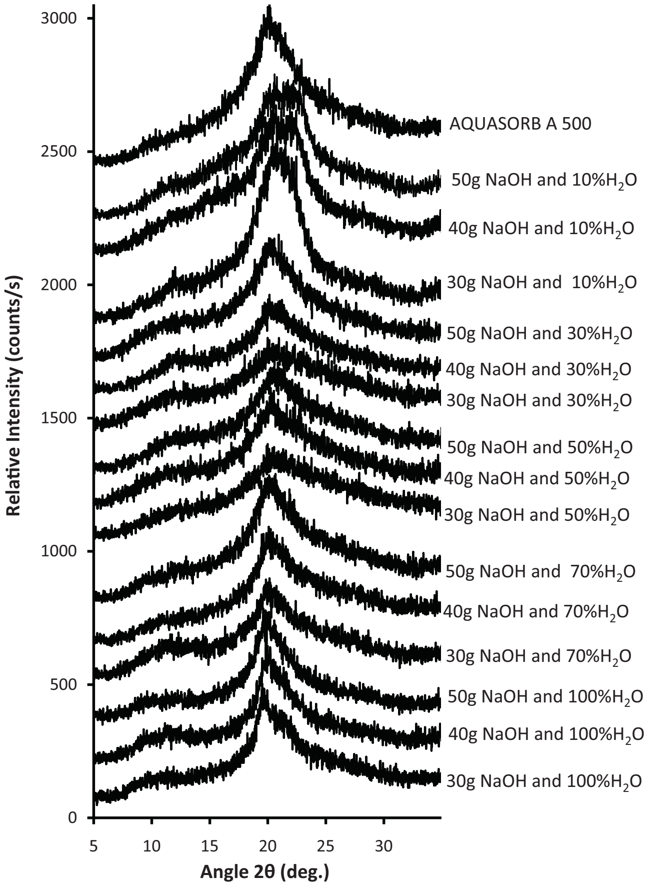

Fig. 3. X-ray diffraction patterns for carboxymethyl celluloses prepared with reactive extrusion and AQUASORB A500.

Table 2
Degree of substitutions, reaction efficiencies, degree of crystallinity and cellulose-II crystalline fraction for carboxymethyl cellulose, AQUASORB A500 and cotton linter pulp.

Sample	DS	RE (%)	X	X_{II}
30 g NaOH and 100%H_2O	0.56	20.12	0.43	0.27
40 g NaOH and 100%H_2O	0.43	15.61	0.48	0.36
50 g NaOH and 100%H_2O	0.46	16.37	0.51	0.30
30 g NaOH and 70%H_2O	0.60	21.69	0.36	0.15
40 g NaOH and 70%H_2O	0.60	21.57	0.36	0.18
50 g NaOH and 70%H_2O	0.55	19.94	0.35	0.20
30 g NaOH and 50%H_2O	0.70	25.29	0.20	0.15
40 g NaOH and 50%H_2O	0.73	26.27	0.29	0.23
50 g NaOH and 50%H_2O	0.56	20.31	0.27	0.19
30 g NaOH and 30%H_2O	0.72	25.77	0.18	0.14
40 g NaOH and 30%H_2O	0.55	19.93	0.26	0.23
50 g NaOH and 30%H_2O	0.48	17.29	0.33	0.26
30 g NaOH and 10%H_2O	0.30	10.64	0.43	0.34
40 g NaOH and 10%H_2O	0.22	7.84	0.36	0.21
50 g NaOH and 10%H_2O	0.10	3.46	0.34	0.22
AQUASORB A500	0.70	–	0.37	0.12
Cotton Linter Pulp	–	–	0.70	0.0

Reaction conditions: 30 g cellulose, 60 g SMCA and 130 g aqueous ethanol/H_2O.

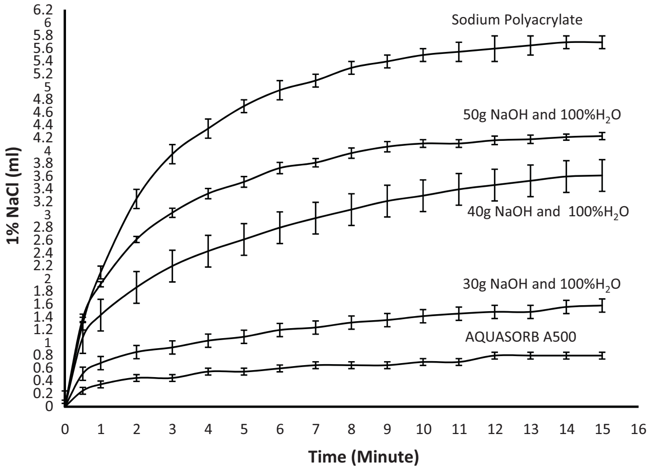

Fig. 4. Water uptake measurements for carboxymethyl celluloses prepared using 100%H_2O, AQUASORB A500 and sodium polyacrylate.

found that for wet mass mercerization (aqueous ethanol:cellulose ratio = 6, v/w basis), the degree of mercerization (C-II % in crystalline fraction) decreased as the concentration of ethanol increased because of the reduced solubility of NaOH at the high alcohol concentrations. In this study too, at high alcohol concentrations, 2-phase solutions and insoluble NaOH were observed which may have resulted in lower crystallinity at higher alcohol concentrations.

Mansikkamäki et al. (2007) also found that the degree of mercerization increased with increasing NaOH concentrations. In this study too, the average degree of crystallinity increased slightly with increasing amounts of NaOH from 30 g NaOH (0.32) to 40 g NaOH (0.35) and 50 g NaOH (0.36).

3.3. Degree of substitution

The degrees of substitutions of carboxymethyl cellulose are summarized in Table 3. Statistical analysis of the degree of substitution revealed a significant interaction between NaOH and H_2O ($P = 0.0308$), suggesting that the effect of one experimental variable was dependent on the level of the other. The effect of the amount of H_2O used was significant at all levels of NaOH ($P < 0.0001$). The effect of NaOH was not significant when 70% H_2O was used ($P = 0.4725$) but was significant for all other levels of H_2O.

Table 3
Water Absorption using flood and centrifuge methods for carboxymethyl cellulose, AQUASORB A500 and sodium polyacrylate.

Sample	Absorption (mL)	Absorption after centrifugation (mL)	Retention (%)
30 g NAOH and 100%H_2O	9.3	8.3	89.3
40 g NAOH and 100%H_2O	9.8	8.7	88.1
50 g NAOH and 100%H_2O	9.8	8.8	89.0
30 g NAOH and 70%H_2O	15.5	9.0	58.1
40 g NAOH and 70%H_2O	13.8	8.5	61.8
50 g NAOH and 70%H_2O	13.7	12.3	90.2
30 g NAOH and 50%H_2O	8.8	7.0	79.2
40 g NAOH and 50%H_2O	7.7	6.2	80.4
50 g NAOH and 50%H_2O	8.3	8.2	98.0
30 g NAOH and 30%H_2O	9.3	7.3	78.4
40 g NAOH and 30%H_2O	6.7	5.7	85.0
50 g NAOH and 30%H_2O	7.0	6.5	92.9
30 g NAOH and 10%H_2O	3.5	2.3	66.7
40 g NAOH and 10%H_2O	4.2	2.0	48.0
50 g NAOH and 10%H_2O	2.7	1.0	37.5
AQUASORB A500	13.0	8.0	61.5
Sodium polyacrylate	10.0	9.8	97.5

When the amount of NaOH was increased from 30 g to 40 g there was a significant decrease in the DS at 100% and 30% H_2O, and when the NaOH was further increased from 40 g to 50 g there was a significant decrease in DS at 50% and 10% H_2O. At all other levels of H_2O there were no significant differences. The decrease in DS with an increase in NaOH concentration, above a critical NaOH concentration, was reported by Barai et al. (1997) and Heinze and Pfeiffer (1999). The effect of NaOH concentration on the DS may have been due to the predomination of the side reaction which results in the formation of sodium glycolate, over the carboxymethylation reaction, at high NaOH concentrations (Barai et al., 1997).

The H_2O/ethanol compositions also affected the DS. When the H_2O content decreased from 100% to 70%, the increase in DS was found to be significant when 40 g ($P = 0.0014$) and 50 g ($P = 0.0484$) of NaOH were used but not when 30 g NaOH were used ($P = 0.3276$). With a further decrease in H_2O content from 70% to 50%, the DS again increased which was found to be significant when 30 g ($P = 0.0484$) and 40 g ($P = 0.0097$) of NaOH were used but not when 50 g of NaOH were used ($P = 0.7780$). With further decrease in H_2O content from 50% H_2O to 30% H_2O, the DS decreased at 40 g NaOH ($P = 0.0008$) but no difference was found at 30 g ($P = 0.7780$) and 50 g ($P = 0.0748$) NaOH. Finally, when H_2O content was decreased from 30% H_2O to 10% H_2O, the DS decreased for all values of NaOH ($P < 0.0001$). The DS at 30% H_2O was higher than that at 100% H_2O and was significant at 30 g (0.0024) and 40 g (0.0161) NaOH. The DS at 10% H_2O was lower than that at 100% H_2O at all levels of NaOH ($P < 0.0001$).

The DS at 70%, 50% and 30% H_2O, in general, was found to be higher than that at 100% H_2O. This may have been a result of the lower degrees of crystallinities and fractions of cellulose-II crystalline forms at 70% (0.36 and 0.18), 50% (0.25 and 0.19) and 30% (0.26 and 0.21) H_2O as compared to 100% H_2O (0.47 and 0.31). Cellulose-II crystalline form, especially, is compact and difficult for the reactants to penetrate, resulting in a lower rate of carboxymethylation (Zhang et al., 1993). However, despite the lower degree of crystallinity and cellulose-II crystalline fraction at 10% H_2O (0.38 and 0.26), its DS was not higher than that at 100% H_2O. The presence of ethanol also may have contributed to the higher DS by reducing the water binding tendency of carboxymethyl cellulose and hence facilitating better reactant penetration. The highest DS (0.73) was obtained at a 50% H_2O concentration when 40 g of NaOH was used, at reaction efficiency (RE) of 26.3%.

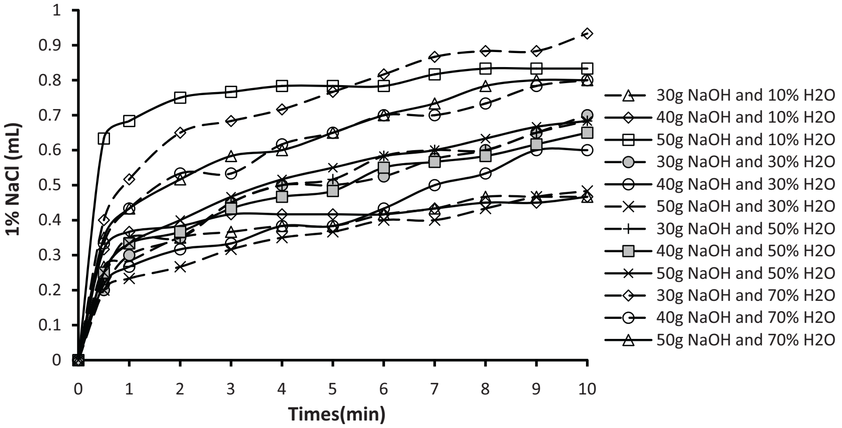

Fig. 5. Water uptake measurements for carboxymethyl celluloses prepared using 10%, 30%, 50% and 70% H_2O.

3.4. Liquid uptake

The rates of liquid uptake for carboxymethyl cellulose, AQUASORB A500 and sodium polyacrylate are illustrated in Figs. 4 and 5. The liquid uptake for carboxymethyl cellulose prepared with 100% H_2O seemed to be higher in rate and extent than those prepared with 70, 50, 30 and 10% H_2O and AQUASORB A500. However, statistical analysis revealed that there were no significant difference

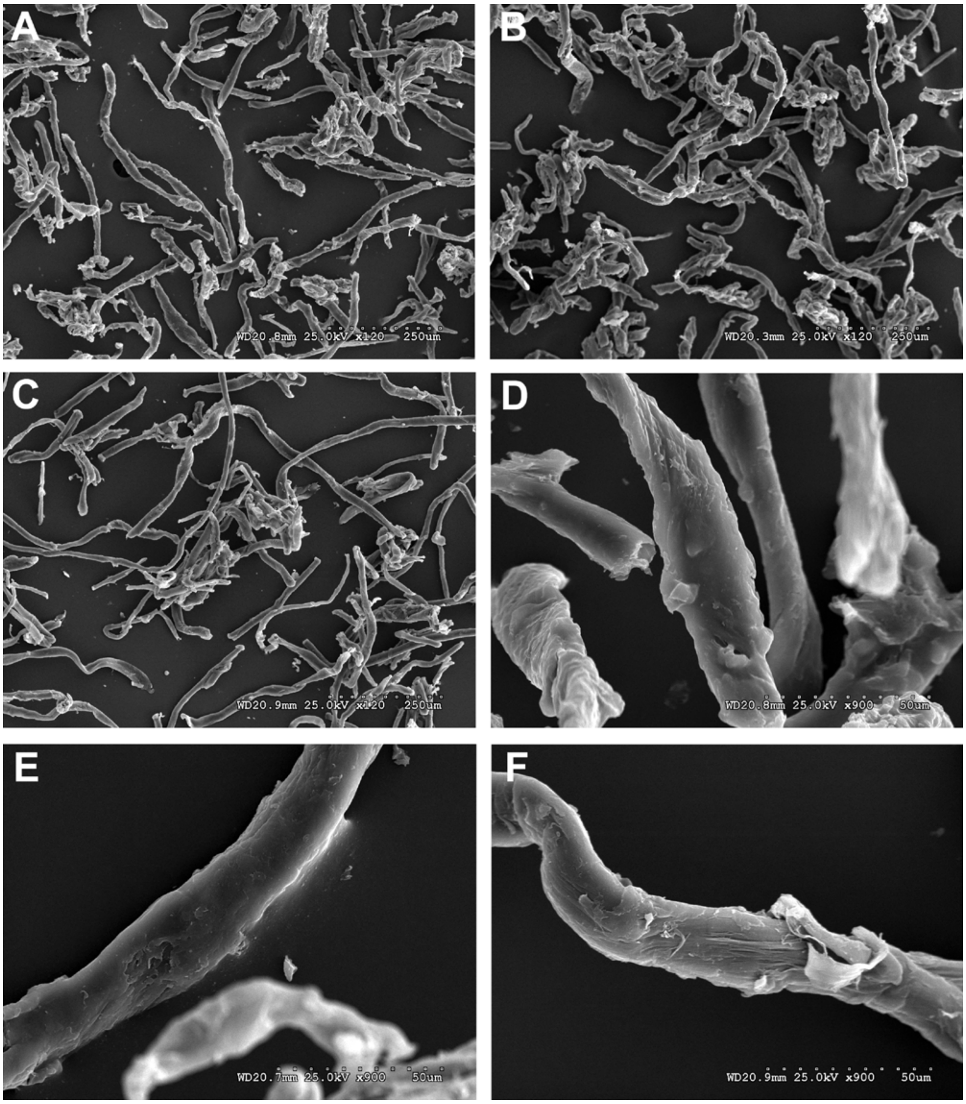

Fig. 6. Scanning electron micrograph images (120× and 900× magnification) of carboxymethyl celluloses prepared using 10% H_2O and 30 g NaOH (A & D), 40 g NaOH (B & E) and 50 g NaOH (C & F).

between the extents of liquid uptake for carboxymethyl cellulose prepared with 30 g of NaOH + 100%H_2O and 50 g of NaOH + 10% H_2O and 30 g of NaOH + 70%H_2O at intervals of 1 min ($P = 0.9358$, $P = 0.4696$) and 5 min ($P = 0.1599$, $P = 0.1378$) and also between 30 g of NaOH +100%H_2O and 40 g of NaOH + 70%H_2O, 50 g of NaOH + 70%H_2O and AQUASORB A500 at a time period of 1 min ($P = 0.2621$, $P = 0.2621$, $P = 0.1083$). However, the extents of liquid uptake of carboxymethyl cellulose prepared with 40 g and 50 g NaOH + 100% H_2O was found to be statistically higher than those prepared with 70, 50, 30 and 10% H_2O and AQUASORB A500 at all time periods.

The liquid uptakes for 50 g of NaOH + 100%H_2O, at intervals of 1, 5 and 10 min, were statistically higher than those for 40 g of NaOH + 100%H_2O ($P = 0.0224$, $P < 0.0001$, $P = 0.0002$), which in turn were higher than those for 30 g of NaOH + 100%H_2O ($P = 0.0004$, $P < 0.0001$, $P < 0.0001$). The highest rate and extent of liquid uptake, for carboxymethyl cellulose, was obtained at 50 g NaOH + 100%H_2O with absorption of 4.2 mL (21 mL/g) 1% NaCl solution after 15 min. However, that was found to be lower than the extent of water uptake of sodium polyacrylate, a synthetic superabsorbent, at 5 ($P < 0.0001$), 10 ($P < 0.0001$) and 15 min ($P < 0.0001$), while no differences were found at 1 min ($P = 0.3494$). Sodium polyacrylate had an impressive rate and extent of water absorption with an absorption capacity of 5.7 mL (28.5 mL/g) of 1% NaCl after 15 min.

During the early stages of liquid uptake, carboxymethyl cellulose, prepared with 70%, 50% and 30% H_2O, began to form a viscous mass after absorbing water which acted as a barrier between the filter plate and some of the still dry, powder mass. Even after large time intervals (~10 min), a significant amount of carboxymethyl cellulose powder remained dry because of this viscous barrier. This phenomenon, called gel blocking, significantly limited the liquid uptake for carboxymethyl cellulose prepared at these conditions. Carboxymethyl cellulose prepared using 10% H_2O did not exhibit gel blocking, but had low rates and extents of water absorptions due to low absorption power, likely to have resulted from the lower DS. The higher rate and extent of water uptake by carboxymethyl cellulose, prepared with 100% H_2O, may have been because of its higher degrees of crystallinity. Cellulose crystallites are rendered insoluble by the presence of hydrogen bonds. This may have contributed in preventing the formation of a viscous barrier, which permitted a rapid rate of water uptake.

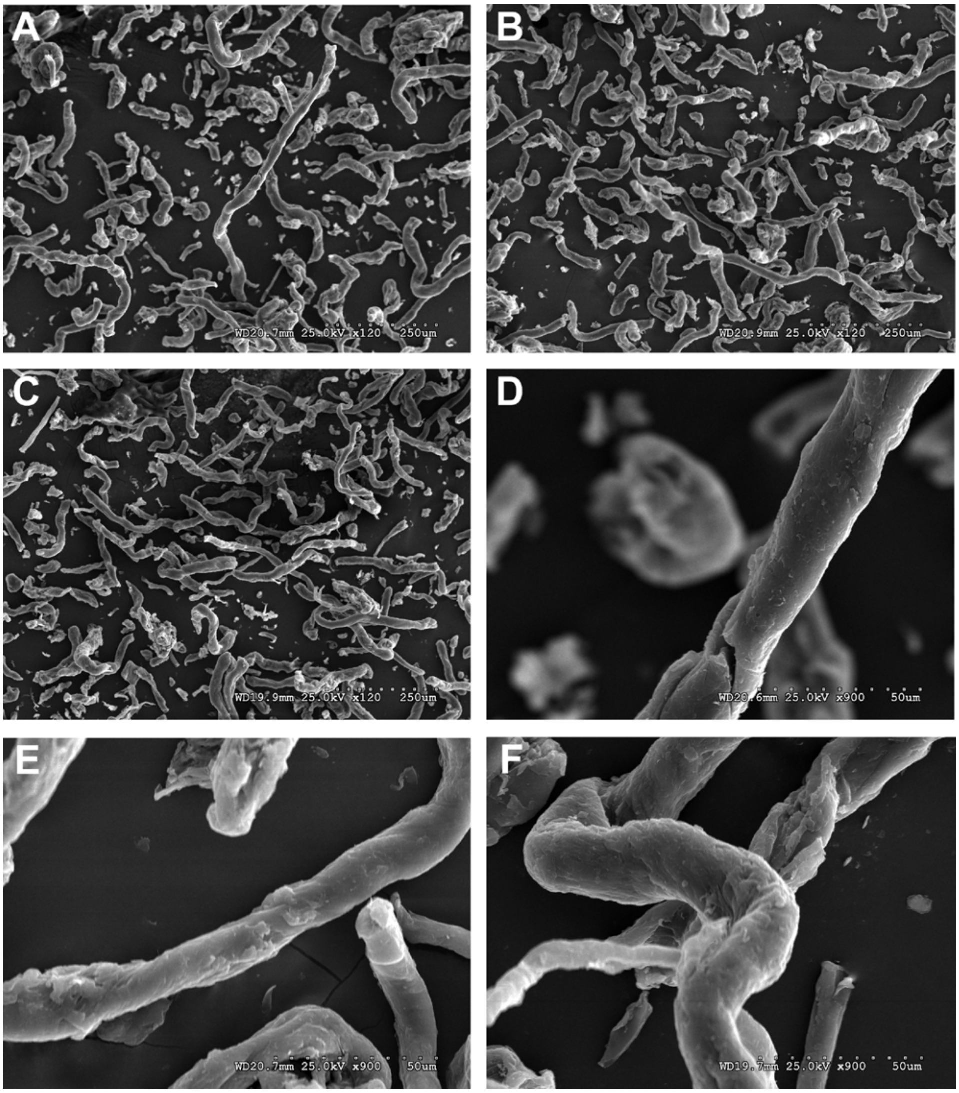

Fig. 7. Scanning electron micrograph images (120× and 900× magnification) of carboxymethyl celluloses prepared using 100% H_2O and 30 g NaOH (A & D), 40 g NaOH (B & E) and 50 g NaOH (C & F).

3.5. Water absorption

The water absorption capacities for carboxymethyl cellulose, AQUASORB A500 and sodium polyacrylate are presented in Table 3. Statistical analyses revealed significant effects of the H_2O/ethanol ratio on the water absorption before and after centrifugation ($P < 0.0001$). No difference were found in the absorption using 100% H_2O and 50% H_2O ($P = 0.0702$) and between 50% H_2O and 30% H_2O ($P = 0.3740$) before centrifugation and between the use of 100% H_2O and 70% H_2O ($P = 0.0904$) and again between 50% H_2O and 30% H_2O ($P = 0.3416$) after centrifugation. The highest absorption before centrifugation was obtained by carboxymethyl cellulose prepared with 30 g of NaOH + 70% H_2O (15.5 mL), however, after centrifugation, carboxymethyl cellulose prepared with 50 g of NaOH + 70% H_2O had the highest absorption (12.3 mL). The highest retention was obtained at 50 g NaOH + 50%H_2O (98%). AQUASORB and sodium polyacrylate had water absorption capacities of 8 mL and 9.8 mL after centrifugation with water retention capacities of 61.5% and 97.5%, respectively.

3.6. Carboxymethyl cellulose microstructures

Figs. 6 and 7 illustrate the microstructures of carboxymethyl cellulose, at magnifications of 120× and 900×, prepared with 10% H_2O and 100% H_2O respectively, at all levels of NaOH. From the microstructures of carboxymethyl cellulose prepared using 10% H_2O, at 120× magnification, fibers 100 μ to >800 μ in length and 0.8–2 μ in breadth are observed for 50 g NaOH (Fig. 6C), $\leq$375 μ in length and 1.7–3.3 μ in breadth for 40 g NaOH (Fig. 6B) and $\leq$440 μ in length and 1.75–3.75 μ in breadth for 30 g NaOH (Fig. 6A) were observed. For 30 g and 40 g of NaOH, after purification, extrudates were ground to pass through a 70 mesh screen, whereas for 50 g NaOH, because of the difficulty in size reduction, the fraction retained on 70 mesh also was used which explains the longer fiber length. On the other hand, the lower thickness of fibers at 50 g NaOH may have been because of its lower DS (0.1). The microstructure images at 900× magnification reveal some peeling and pitting of the carboxymethyl cellulose surfaces which may have occurred due to mechanical damage during extrusion or during grinding after product purification. No differences were observed found between the microstructures of carboxymethyl celluloses prepared using 30 g, 40 g and 50 g of NaOH.

Microstructure images of carboxymethyl cellulose, prepared with 100% H_2O (Fig. 7), at 120× magnification exhibited fibers with dimensions of $\leq$330 μ and 1.25–2.5 μ (Fig. 7C), $\leq$430 μ and 1.6–3.3 μ (Fig. 7B), and 670 μ and 1.6–3.3 μ (Fig. 7A) at 50 g, 40 g and 30 g of NaOH, respectively. These images also showed some non fibrous particles, 0.8–6.7 μ in dimensions, likely to have formed during extrudate grinding, after purification. Images at 900× magnification revealed fractured and rough fiber surfaces, similar to those observed in Fig. 6. No differences were observed between the microstructures of carboxymethyl cellulose prepared with 30, 40 and 50 g of NaOH at 100% H_2O.

4. Conclusion

Reactive extrusion presents a continuous, reduced solvent, convenient and fast process for carboxymethylation of cellulose. The reaction time for the reactive extrusion process was less than 2 min. The water:ethanol ratios and NaOH concentrations were found to have significant effects on the DS and crystallinity which effected the liquid uptake properties of carboxymethyl cellulose. Carboxymethyl cellulose prepared using 100% H_2O, as revealed by X-ray diffraction analysis, had higher degree of crystallinity and fraction of cellulose-II crystalline content than those at lower H_2O contents. The higher crystalline content may have been responsible for the lower DS when 100% H_2O was used as compared to those prepared with lower water contents. The higher rate of liquid-uptake, also, may have resulted from the higher degree of crystallinity. The rate of liquid uptake of carboxymethyl cellulose prepared using 100% H_2O was significantly higher than that of AQUASORB A500. The rapid liquid uptake properties of such carboxymethyl cellulose render them ideal for applications as a super absorbent.

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