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HNO_3/H_3PO_4–$NANO_2$ mediated oxidation of cellulose — preparation and characterization of bioabsorbable oxidized celluloses in high yields and with different levels of oxidation

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Abstract

The reaction of cellulose with a mixture of HNO_3/H_3PO_4–$NaNO_2$ (2:1:1.4, v/v/%w) at room temperature for different time intervals has been investigated to produce oxidized cellulose (OC), a biocompatible and bioresorbable polymer. The results revealed an increase in carboxyl content of OC with increasing reaction time, corresponding to about 8.0, 13.4, 17.4 and 18.4% carboxyl content after 12, 24, 36, and 48 h, respectively. The yield of OC ranged between 75 and 81%. The use of different ratios of HNO_3 and H_3PO_4, (11:1, 4:1, 2:1, 1:1, 1:2, and 1:4; v/v), in the reaction had no significant effect on the carboxyl content and yield of the OC products. All products, as produced, were low crystallinity (27–35%) fibrous materials. The length of fibers decreased with increasing reaction time. After ball milling for 24 h, the length of fibers further decreased and products converted into a fine powder consisting of small fibers and aggregated non-fibrous particles. The degrees of polymerization (DP) of the OC products produced after 12, 24, and 48 h of reaction duration were 81, 63, and 53, respectively. After ball milling for 24 h, the corresponding values changed to 57, 51 and 46. However, no significant change in the crystallinity of the products was noted after ball milling. The TGA results showed the OC products to be less thermally stable than cellulose. The degradation temperature appears to decrease with increasing carboxyl content. In conclusion, the results show that the low crystallinity OC products can be successfully prepared in high yields and with different levels of carboxyl content from cellulose by treatment with a mixture of HNO_3/H_3PO_4–$NaNO_2$. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oxidized cellulose; 6-Carboxycellulose; Oxycellulose; Modified cellulose

1. Introduction

Oxidized cellulose (OC) and oxidized regenerated cellulose (ORC) (Fig. 1) containing carboxyl groups represent an important class of biodegradable polymers. Currently, OC containing 16–24% carboxyl content is commercially available in a powder or knitted fabric (gauze) form for use in humans to stop bleeding during surgery and to prevent the formation and reformation of post-surgical adhesions (Johnson & Johnson Patient Care Inc., 1989; Sizerega, 1994). Ashton (1968) reported that OC containing as low as 3% carboxyl content is bioabsorbable, and the hemostatic properties and absorption of OC increase with increasing carboxyl levels or decreasing degree of polymerization (DP). Recently, OC has been shown to possess antibacterial (Abaev, Kaputskii, Adarchenko, & Sobeshchukh, 1986), antitumor (Tokunaga & Naruse, 1998), immunostimulant (Otterlei, Espvik, Skjak-Braek & Smidsrod, 1992), and wound healing properties (Finn, Schow & Schneiderman, 1992; Pollack, & Bouwsma, 1992). It has also been extensively investigated as an immobilizing matrix for a variety of amine drugs (Balakleevskii, Gubkina, Tkachev, Khaniia, Kalinaki & Kotsyurva, 1986; Dol'berg, Shuteeva, Yasnitskii, Obolentseva, Khadzhai & Furmanov, 1974; Firsov, Nazarov & Fomina, 1987; Kaputskii, Bychkovskii, Yurkshtovich, Burtin, Korolik & Buslov, 1995; Kosterova, Yurkshtovich, Zimatkin & Kaputsky, 1993; Sosnin, Balakleevskij & Dmitrieva, 1993; Yasnitskii & Dol'berg, 1973; Yasnitskii, Dol'berg, Shuteev & Kovalev, 1986; Zimatkina, Yurkshtovich, Zimatkin & Kaputsky, 1996), enzymes (Alinovskaya, Kaputskii, Yurkshtovich, Talapin & Stel'makh, 1988; Alinovskaya, Yurkshtovich & Kaputskii, 1989), and proteins (Kumar & Deshpande, 2001).

Commercially, OC is produced by reacting cellulose with

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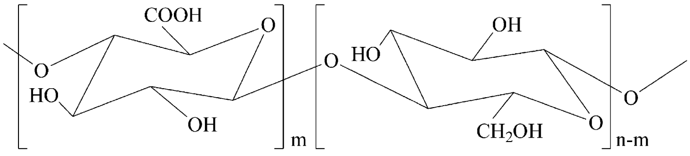


Fig. 1. Structure of oxidized cellulose.

nitrogen dioxide (NO_2) or dinitrogen tetraoxide (N_2O_4). NO_2 and N_2O_4 exist in equilibrium and can be used in the gaseous form or as a solution in an appropriate organic solvent (Ashton, 1968; Bertocchi, Konowicz, Signore, Zanetti, Flaibani, Paoletti, et al., 1995; Kenyon, 1941; Nevell, 1985). Other oxidants used to prepare OC include dichromate/N_2O_4 (Walimbe, Pandya & Lalla, 1978), HNO_3 (Gert, Shishonok, Zubets, Torgashov & Kaputskii, 1995), HNO_3–$NaNO_2$ (Gert et al., 1995; Statni, 1979a,b), HNO_3/H_2SO_4–$NaNO_2$ (Wanleg, 1956), H_3PO_4–$NaNO_2$ (Heinze, Klemm, Schnabelrauch & Nehls, 1993; Painter, 1977; Painter, Cesaro, Delben & Paoletti, 1985), H_3PO_4–$NaNO_2$–$NaNO_3$ (Besemer, Nooy & Bekkum, 1998), and H_3PO_4/NO_2 (Bertocchi et al., 1995). In the dichromate/N_2O_4 method, the cellulose source is first treated with a dichromate solution and then reacted with N_2O_4. This method is faster compared to that with N_2O_4 alone and produces OC with 6–18% carboxyl content. However, it introduces chromium in the product, which is objectionable. The reaction with nitric acid alone requires heating at 50–100°C. This causes extensive hydrolysis of cellulose. The use of HNO_3–$NaNO_2$ produces OC with 14–18% carboxyl content, but requires a long reaction time. The oxidation of cellulose with a mixture of HNO_3/H_2SO_4–$NaNO_2$ is faster compared to that with HNO_3–$NaNO_2$ alone and allows the production of OC with 16% carboxyl content. However, the yield of OC was found to be low (20–30%, vide infra). The preparation of OC using a mixture of H_3PO_4–$NaNO_2$ reportedly involves N_2O_3 as an oxidant. The starting cellulose is first dissolved in H_3PO_4 and then reacted with N_2O_3, generated in situ on addition of $NaNO_2$. This method produces OC in high yields (~80%) and with up to 21% carboxyl content. However, the initial dissolution step is slow at room temperature and heating the reaction mixture reportedly causes extensive hydrolysis of cellulose (Wei, Kumar & Banker, 1996). The H_3PO_4/NO_2 (gas) method involves soaking the cellulose in phosphoric acid for 1–5 h at 4°C and then reacting with NO_2 (gas) at -8 to 0°C. Owing to the lower reaction temperatures, the DP of the OC products was high (~140–400).

In this study, the use of a mixture of HNO_3/H_3PO_4–$NaNO_2$ as an oxidant for cellulose is investigated. The goal of the study was to prepare OC in high yields and with different levels of oxidation for potential applications as a biodegradable macromolecular prodrug carrier or as an aid in the design and development of biodegradable drug delivery systems.

2. Experimental

2.1. Materials

Cotton linter sheets (grade 10-270), used as the starting cellulose source, were obtained from Southern Cellulose Products, Inc. (Chattanooga, TN). $NaNO_2$, H_3PO_4 (85% w/v), HNO_3 (69.7% w/v), and acetone were purchased from Fisher Scientific (Pittsburgh, PA), and used as supplied. A commercial oxidized cellulose sample, labeled as OC-EM, was received as a gift from Eastman Chemical Co. (Eastman Chemical Co. (Kingsport, TN) and used as a standard in the study. This material contained about 16% (w/w) of carboxyl groups and about 5.6% (w/w) of ketone groups.

2.2. Preparation of oxidized cellulose

Nitric acid and phosphoric acid were mixed in 11:1, 4:1, 2:1, 1:1, 1:2, and 1:4 (v/v) ratios. To a 70 ml solution of the acid mixture, 5.0 g. of cotton linter sheet, cut into small pieces, was added. Once the cotton linter pieces were completely soaked, 1.0 g. of sodium nitrite was added all at once. An immediate formation of reddish brown fumes occurred. To prevent the release of these fumes to the air, the reaction container was covered with a petri dish. The reaction mixture was allowed to react at room temperature, with occasional stirring using a glass rod, for 12, 24, 36 or 48 h. The reaction mixture, which appeared green in color, was terminated by slowly adding an excess of water (about five times the volume of the reaction mixture). The diluted reaction mixture was filtered, and the white fluffy solid obtained was filtered and washed with water until the filtrate showed a pH of about 4. It was finally washed with acetone and then air-dried at room temperature. The dried OC was ball milled for 24 h and then sieved. The fraction that contained particles ranging between 74 and 105 μm was used for characterization.

2.3. Determination of carboxyl content

This was performed according to the method described in the United States Pharmacopoeia (USP, 1995). Approximately 0.5 g of the sample was accurately weighed and suspended in 50 ml of a 2% (w/w) calcium acetate solution for 30 min. The mixture was titrated with 0.1N NaOH (standardized) using phenolphthalein as an indicator. The volume of NaOH solution consumed was corrected for the blank. The carboxyl content in the sample was calculated using the following relationship:

$$\text{Carboxyl groups (\% w/w)} = \frac{N \times V \times \text{MW}_{\text{COOH}}}{\text{Weight of sample (mg)}} \times 100$$

where N is the normality of NaOH, and V is the volume of NaOH in ml consumed in titration, after correcting for the blank.

2.4. Determination of carbonyl content

The carbonyl content of the products was determined by the hydroxylamine method (Green, 1963). Briefly, an accurately weighed amount of OC (~0.5 g) and 50 ml of hydroxylamine hydrochloride (prepared by dissolving 50 g of hydroxylamine–HCl in 120 ml of 1N sodium hydroxide solution and then diluting with water to 1000 ml) were placed, separately, in 250 ml round-bottom flasks (one of the flasks had a side arm with a stopcock for evacuation), connected by a manifold. The flasks were evacuated with a water pump. The stopcock is then closed and the hydroxylamine hydrochloride solution is then transferred into the flask that contained the OC sample by tilting the assembly. The reaction mixture was then heated at 50°C for 2 h. After cooling to room temperature, a 25 ml aliquot of the reaction supernatant was removed and titrated with a 0.1N HCl solution to pH 3.2. A blank titration using a 25 ml solution of the hydroxylamine hydrochloride solution was conducted in the same manner. The carbonyl content (% w/w) in the product was calculated using the equation

$$\text{Carboxyl groups (\% w/w)} = \frac{\text{MW}_{\text{CO}}(B - S)}{10\text{Weight of sample}} \times 100$$

where B and S are milliliters of 0.1N HCl consumed in titrations of blank and sample solutions, respectively.

2.5. Determination of aldehyde content

The amount of aldehyde groups present in the products was determined according to the procedure reported by Friedlander (1996). The OC sample was reacted with a solution of 0.2 M sodium chlorite, acidified with 0.1 M acetic acid to pH 3, at a concentration of 2% (w/v) for 72 h at room temperature in the dark. The reaction mixture was filtered, and the residue obtained was washed with distilled water and then dispersed in 0.1 M HCl for 30 min in an ice bath. The latter was filtered and the solid obtained was freed from acid by washing with water. The wet material was then air dried and stored in the dark until analyzed for the carboxyl content, according to the procedure described. The aldehyde content in the product was calculated by subtracting the carboxyl content value determined in the starting OC sample from that of the chlorite-treated OC sample.

2.6. Ketone content analysis

The amount of ketone groups in the product was determined by subtracting the aldehyde content from the carbonyl content determined as described above.

2.7. Fourier-transform infrared (FT-IR) spectroscopy

The FT-IR spectra of samples were obtained as KBr pellets on a Nicolet 5DXB FT-IR spectrophotometer, equipped with the Omnic data processing software.

2.8. Degree of polymerization (DP)

The DP of OC was determined by the viscosity method using an Ostwald-Fenske capillary viscometer (size 100) and cupriethylenediamine hydroxide (Cuen, 1.0 M) solution as the solvent, according to the equation (ASTM, 1965): $\text{DP} = 190[\eta]$, where $[\eta]$ is the intrinsic viscosity. The latter was calculated from $[\eta]C$ values reported in the literature for cellulose samples exhibiting relative viscosity between 1.1 and 1.9 (ASTM, 1965) (Method A) and by plotting $\ln \eta_{\text{rel}}/C$ and η_{sp}/C versus C and extrapolating the resultant linear lines to $C = 0$ (Method B), where η_{rel} is the relative viscosity calculated by dividing the viscosity of the OC solution by the viscosity of the solvent, η_{sp} is the specific viscosity determined by subtracting 1 from η_{rel}, and C is the concentration of OC in g/100 ml. The viscosity measurements were performed as follows. An exact amount of OC sample, varying between 0.2–1 g, (on a dry weight basis), was suspended in 25 ml water in a 125 ml Erlenmeyer flask. The suspension was flushed with nitrogen to remove entrapped air from the sample. While flushing with nitrogen, 25 ml of Cuen solution was added to the suspension. The flushing with nitrogen was continued for additional 2 min. The Erlenmeyer flask was then closed with a stopper and shaken with a wrist action shaker at room temperature for 30 min. The resulting cellulose solution was equilibrated at 25 ± 0.5°C. The equilibrated solution was then filled between the marks in the viscometer. The viscometer was held vertically in the water bath, and the efflux time for the solution between the two marks was measured. The same procedure was employed to measure the efflux time for the 0.5 M cuen solution. The relative viscosity was calculated from the relationship: $\eta_{\text{solution}}/\eta_{\text{solvent}} = \text{Efflux time}_{\text{OC solution}}/\text{Efflux time}_{\text{solvent}}$.

2.9. Degree of crystallinity (DC)

This was determined by the powder X-ray diffraction method. The X-ray diffraction measurements were performed over 10–40° 2θ.range using a Phillips PW 1710 or Siemens D5000 powder X-ray diffractometer, equipped with the APD Phillips (version 2.01) or Siemens Diffrac$^{\text{PLUS}}$ (Eva, Version 2.0) data processing software, respectively, and monochromatic CuK$_\alpha$ X-rays ($\alpha_1 = 1.54060$ Å, $\alpha_2 = 1.54438$ Å). The Phillips PW 1710 diffractometer was set at a scanning rate of 3° 2θ min^{-1}, while the Siemens diffractometer used a step width of 0.02° 2θ and a time constant of 0.4 s per step. The

Table 1
Effect of different ratios of H_3PO_4 (or H_2SO_4) and HNO_3 on the carboxylic content and yields of OC

Reaction no.	HNO_3:H_3PO_4 (or H_2SO_4) v/v	COOH content % (S.D.[a])	Yield (%)
Reaction system: HNO_3/H_3PO_4–$NaNO_2$[b]			
1	11:1	18.8 (0.3)	89
2	4:1	21.4 (0.1)	92
3	2:1	23.5 (0.2)	90
4	1:1	20.5 (0.2)	88
5	1:2	21.6 (0.1)	84
6	1:4	20.8 (0.3)	86
Reaction system: HNO_3/H_2SO_4–$NaNO_2$			
7	11:1[c]	21.1 (0.2)	30

[a] Standard deviation ($n = 3$).

[b] All reactions were performed at room temperature for 48 h using a 1:14 weight-by-volume ratio of cotton linter to acid solution and about 1.4% (w/v) of $NaNO_2$.

[c] Corresponds to the same ratio used by Wanleg (1956). The ratio of cotton linter, acid mixture and $NaNO_2$ was the same as used for the HNO_3/H_3PO_4–$NaNO_2$ reaction system.

crystallinity of the samples was determined by integration of the crystalline reflections, and expressed as the percentage ratio of the integrated intensities of the sample to that of hydrocellulose, a cellulose standard that was prepared from a reaction between cotton linter and 2N HCl at boiling temperature for 30 min (Kumar & Kothari, 1999).

2.10. Scanning electron microscopy (SEM)

The samples were loaded on a stub covered with liquid graphite and then coated with gold, followed by a layer of carbon, for 4 min in an Emitech K550 coater. Photographs were then taken on a Hitachi S-4000 using Polaroid films.

2.11. Determination of volatile content

The amounts of volatile substances present in the samples were determined using a Perkin Elmer series 7 thermogravimetric analysis (TGA) system. The accurately weighted samples of OC (~4–6 mg) were heated from 21 to 260°C at a rate of 5°C min^{-1} under a constant flow of nitrogen gas. The weight loss observed between 21 and 150°C was used to calculate the volatile content.

Table 2
Effect of reaction duration on the carboxyl content and yield of OC. (The reactions were done on a 400 g. (weight of cotton linters) scale using the same conditions as used for reaction no. 2 in (Table 1))

Time (h)	COOH content % (S.D.[a])	Yield (%)
12	8.0 (0.1)	81
24	13.4 (0.3)	79
36	17.4 (0.2)	78
48	18.4 (0.1)	75

[a] Standard deviation ($n = 3$).

3. Results and discussion

3.1. Preparation of OC

In general, the oxidation of organic compounds, including cellulose, by HNO_3 alone is sluggish and frequently requires a catalyst (e.g. H_2SO_4), an initiator (e.g. HNO_2 or NO_2), and/or heating at high temperatures. This is because commercial HNO_3 contains only small amounts of NO_2 and HNO_2. Other nitrogen oxides that may be present in commercial HNO_3 include NO, N_2O_3, N_2O_5, etc. (Ogata, 1978). In this study, the use of HNO_3, in combination with H_3PO_4 and $NaNO_2$, to oxidize cellulose, was investigated. The carboxyl content and yields of OC obtained using different ratios of H_3PO_4 and HNO_3 in the reaction at room temperature for 48 h are presented in Table 1. Also included in the Table, for comparison purposes, the result of the reaction conducted using the HNO_3/H_2SO_4–$NaNO_2$ mixture reported by Wanleg (Wanleg, 1956). The ratio of cotton linter to acid solution was 1:14 and the amount of $NaNO_2$ used in the reaction corresponded to about 1.4% (w/v). The results presented in Table 1 show that irrespective of the ratio of HNO_3 and H_3PO_4 used in the reaction, the HNO_3/H_3PO_4–$NaNO_2$ reaction system produced OC in high yields (84–91%) and with a high carboxyl content (18.8–23.5%). With the HNO_3/H_2SO_4–$NaNO_2$ mixture, the carboxyl content in the OC product was about 21% while the yield decreased to about 30%. An increase in the H_2SO_4 concentration in the reaction mixture would cause further degradation of cellulose and hence a further decrease in the yield of OC. At low concentrations of H_2SO_4, this method reportedly decreases the oxidation rate (Wanleg, 1956) and hence, the oxidation levels of OC. These results clearly show that H_3PO_4, being a weak acid, slowly hydrolyzed cellulose and consequently, produced OC in high yields.

The effects of reaction duration on the carboxyl content and yields of OC are presented in Table 2. All reactions

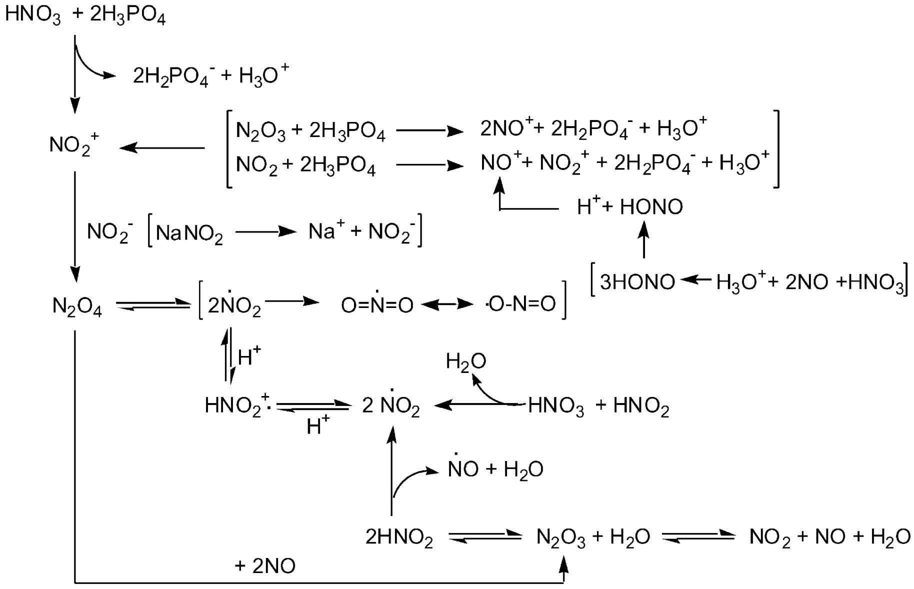


Fig. 2. Possible pathways for the generation of nitrogen oxides in situ.

were performed on a 400 g. (weight of cotton linters) scale using about 1:14 weight-by-volume ration of cotton linter and acid mixture (HNO_3/H_3PO_4 2:1) and about 1.4% (w/v) of $NaNO_2$, the same reaction conditions as was used for reaction no. 3 (Table 1). The carboxyl content in the product increased linearly when reaction time was increased from 12 to 36 h ($R^2 = 0.9927$). A further increase in the reaction time, from 36 to 48 h, caused only a small increase ($\sim$1%) in the carboxyl content only. The total carboxyl content and yield of the OC product obtained after 48 h were 18.4 and 75%, respectively. These values are lower than that obtained for the product prepared on a 5 g scale reaction (Reaction no. 2, Table 1). One possible reason for this could be that during reaction some cotton linter pieces adhered to each other and as a result the interior of these pieces was not accessible to the oxidant and hence lower oxidation level. The lower yield of OC suggests that under these conditions the end units of the cellulose chains are more susceptible to hydrolysis than the glycosidic linkages.

3.2. Oxidation mechanism

As noted above, nitrogen oxides have been widely implicated as the oxidants in the oxidation of organic compounds by HNO_3, alone or in combination with an acid and $NaNO_2$ (Ogata, 1978). Several different pathways that may lead to the generation of these species in situ are shown in Fig. 2. HNO_2, which can be formed from a reaction between: (i) a strong acid and $NaNO_2$ (Ogata, 1978), (ii) N_2O_4 and H_2O (Gert et al., 1995), or (iii) HNO_3, H_3O^+ and NO (colorless) (Ogata, 1978), is unstable. It easily and quantitatively converts to N_2O_3 and then to a mixture of NO_2 and NO. HNO_2 can also convert into NO_2 directly or through a reaction with HNO_3. The conversion of HNO_2 to NO^+ is also known. Since NO_2 and NO are odd-electron species, it is likely that the oxidation is initiated by abstracting a hydrogen atom from cellulose by such species (more likely, by NO_2 because of its high concentrations in the solution) leading to the formation of Cell–C(•)H–OH (Fig. 3), in

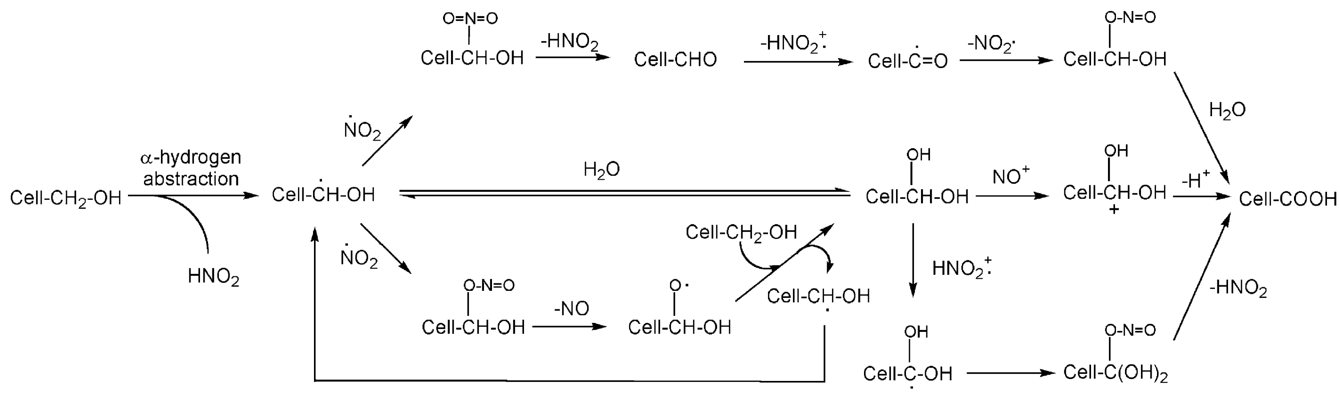
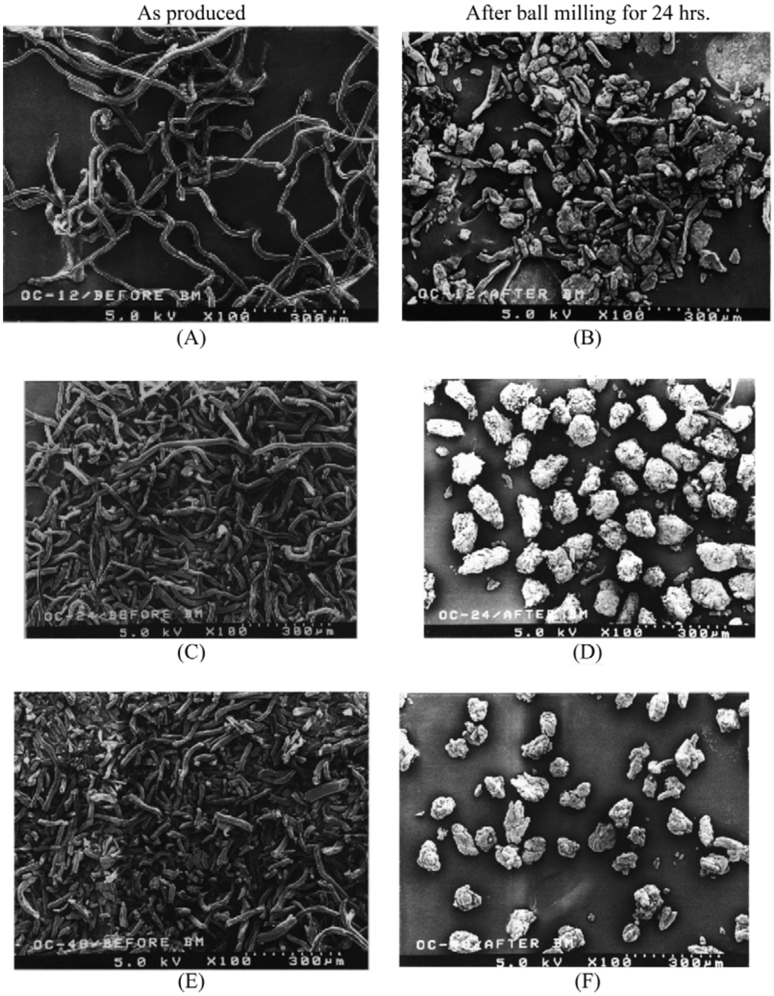


Fig. 3. Oxidation mechanism of cellulose.



(A) (B)

(C) (D)

(E) (F)

Fig. 4. SEM photographs of: (A and B) OC-12(BM), (C and D) OC-24(BM), (E and F) OC-48(BM) before and after ball milling.

accordance with the oxidation mechanism reported for alcohols by HNO_3 in the presence of nitrogen oxides and another acid (Ogata, 1978). Further attack by $NO_2\cdot$ and subsequent release of $NO\cdot$ and HNO_2 produces Cell–CH(OH)$_2$ and Cell–CHO intermediates, respectively. The formation of Cell–CH(OH)$_2$ from cellulose can also occur by abstraction of a hydride ion from the α-carbon atom by NO^+, followed by a hydrolysis reaction. The Cell–CH(OH)$_2$ may undergo a hydrogen abstraction reaction followed by an attack by $NO_2\cdot$ and subsequent elimination of HNO_2, or by a hydride abstraction mechanism involving NO^+ and then elimination of proton, to produce the Cell–COOH. In the case of Cell–CHO, an initial hydrogen abstraction reaction followed by an attack by $NO_2\cdot$ and subsequent hydrolysis of the addition product leads to the formation of Cell–COOH (Ogata, 1978).

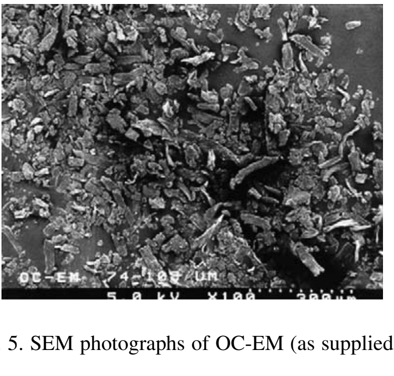


Fig. 5. SEM photographs of OC-EM (as supplied).

3.3. Characterization of oxidized cellulose

The OC products prepared after 12, 24, and 48 h, hereinafter referred to as OC-12(BM), OC-24(BM), and OC-48(BM), respectively, were characterized. They contained 8.0, 13.4, and 18.4% carboxyl content (determined by the USP method), respectively (Table 2). The amounts of carbonyl groups determined in the three products were 1.9, 3.4, and 4.5% (w/w), whereas the carboxyl content in the samples, after treatment with sodium chlorite, corresponded to 7.9, 13.3, and 18.4%, respectively. These results show that the three products contained no aldehyde groups and the carbonyl content determined in the products was solely due to ketone groups. The commercial OC-EM sample also

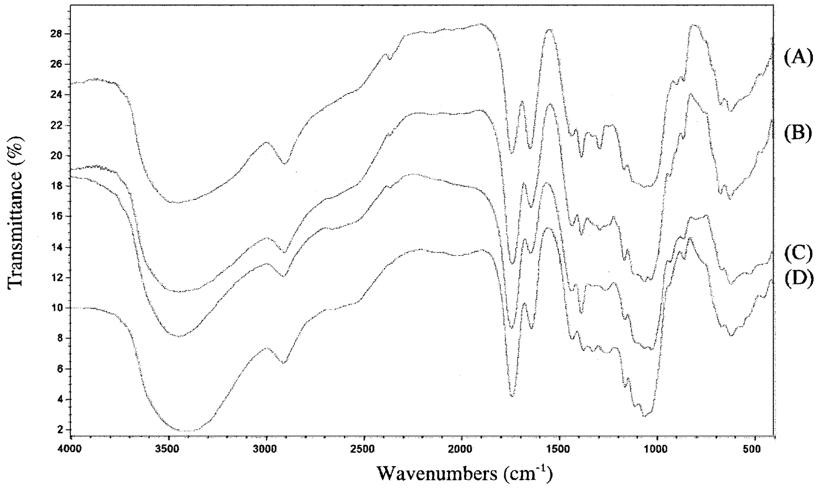


Fig. 6. FT-IR spectra of: (A) OC-12(BM), (B) OC-24(BM), (C) OC-48(BM), and (D) OC-EM.

Table 3
Degree of polymerization of oxidized celluloses

OC Sample	Degree of polymerization Method A[a]	Method B[b] average (S.D.[c])
OC-12[d]	81.1	81.1 (0.6)
OC-24[d]	63.1	60.8 (0.1)
OC-48[d]	52.8	52.6 (1.2)
OC-12(BM)	56.8	58.5 (0.5)
OC-24(BM)	51.0	51.7 (1.0)
OC-48(BM)	45.6	44.3 (1.6)
OC-EM	46.5	47.3 (0.9)

[a] Calculated using the $[\eta]$ value determined from the η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C plots.

[b] Calculated using the $[\eta]$ value obtained from the ASTM table listing $[\eta]C$ values for cellulose samples exhibiting relative viscosity of 1.1 to 1.9 (ASTM, 1965).

[c] Standard deviation ($n = 3$).

[d] As produced (i.e. before ball milling).

showed no aldehyde content. The carboxyl and ketone groups in the product were 16.1 and 5.6% (w/w), respectively.

The SEM photographs of OC-12(BM), OC-24(BM), and OC-48(BM), before and after ball milling, and that of commercial OC-EM sample are shown in Figs. 4 and 5. As is evident from the photographs, the three products, as produced, were fibrous materials. The length of fibers decreased with increasing reaction time. When ball milled for 24 h, the length of fibers decreased further and the products converted into a fine powder consisting of small fibers and aggregated particles. The commercial OC-EM sample, as supplied, had a fibrous structure (Fig. 5) similar to that of OC-12 before ball milling.

The FT-IR spectra of the three new products and that of commercial OC-EM sample are reproduced in Fig. 6. Except the characteristic carbonyl peak at 1740 cm^{-1}, whose intensity decreased in the order OC-48(BM) > OC-24(BM) > OC-12(BM), consistent with the increase in the

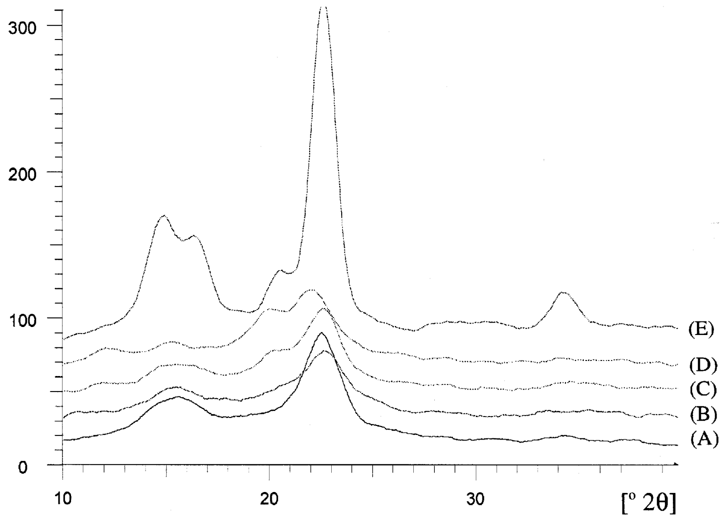


Fig. 7. Powder X-ray diffraction patterns of: (A) OC-EM, (B) OC-48(BM), (C) OC-24(BM), (D) OC-12(BM), and (E) Hydrocellulose.

Table 4
DC of cellulose and oxidized cellulose products

OC sample	Crystallinity (average), % (range)[a]
OC-12[b]	38.0 (36.8–39.2)
OC-24[b]	34.9 (33.1–36.9)
OC-48[b]	26.9 (26.6–27.2)
OC-12(BM)	33.8 (32.9–34.7)
OC-24(BM)	32.6 (31.7–33.5)
OC-48(BM)	28.7 (28.2–29.2)
OC-EM[b]	30.5 (30.0–31.0)

[a] $n = 2$.

[b] As produced (i.e. before ball milling).

carboxyl and ketone groups in the products, the IR spectra of all four materials appear similar to that of native cellulose (Klemm, Philipp, Heize, Heinze & Wagenknecht, 1998).

The DP of OC samples, before and after ball-milling, and that of commercial oxidized cellulose sample (OC-EM), calculated using the $[\eta]$ value obtained from: (i) the ASTM table listing $[\eta]C$ values for cellulose samples exhibiting relative viscosity of 1.1–1.9 (Method A) (ASTM, 1965) and (ii) the plots between η_{red} versus C and $\ln \eta_{\mathrm{rel}}/C$ versus C (Method B), are presented in Table 3. These results clearly show a good agreement between the DP values obtained by the two approaches, suggesting that either method is suitable for determining the DP of OC. The DP of the OC products decreased in the order: OC-12(BM) > OC-24(BM) > OC-48(BM), suggesting that the hydrolysis of the anhydroglucose ether linkage increased with increasing reaction time. The DP of the commercial sample (OC-EM), which was reportedly prepared by oxidation with N_2O_4 (Stillwell, Marks, Sferstein & Wiseman, 1997), was found to be about 47.

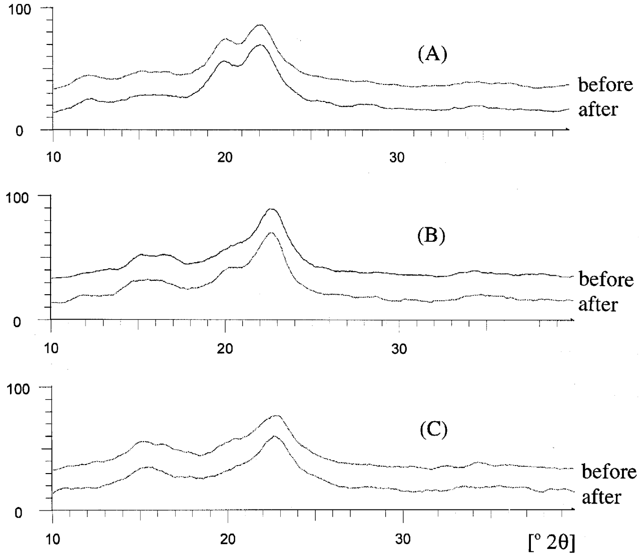


Fig. 8. Powder X-ray diffraction patterns of: (A) OC-12, (B) OC-24, and (C) OC-48 before and after ball milling.

The powder X-ray diffraction patterns of OC-12(BM), OC-24(BM), OC-48(BM), and that of the commercial OC-EM sample and hydrocellulose standards are shown in Fig. 7. OC-12(BM) showed peaks at ~12.2, 15.3, 20.1 and 22.0° 2θ. OC-24(BM) showed the same peak pattern except that the peaks at 12.2 and 20.1° 2θ showed a significantly reduced intensity. In the case of OC-48(BM), the peaks at 12 and 20° 2θ are barely visible. The degrees of crystallinity of these samples, determined using hydrocellulose as a reference standard are presented in Table 4. The results show that all OC products are low crystallinity materials compared to

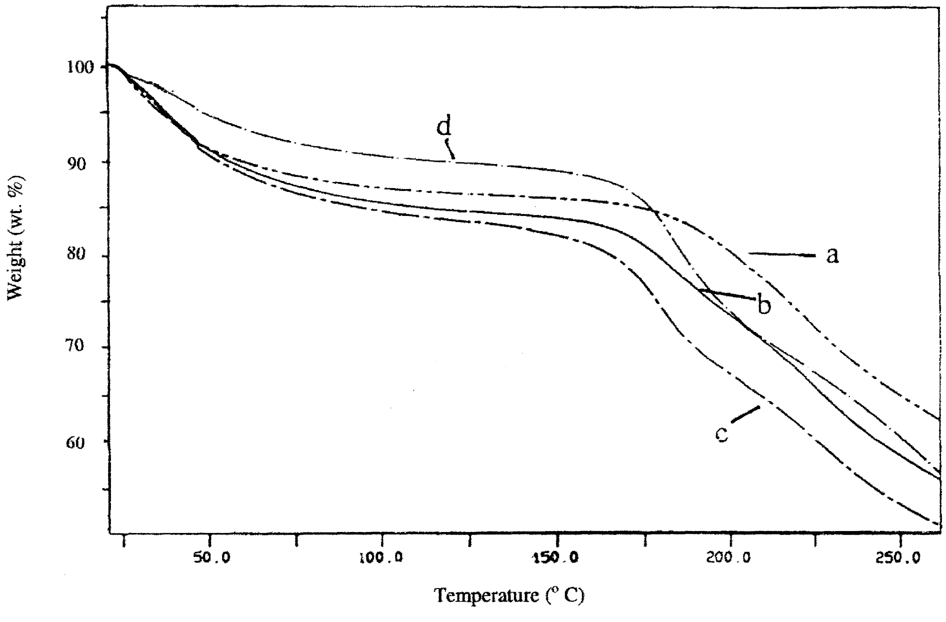


Fig. 9. TGA curves of a series of oxidized celluloses: (a) OC-12(BM), (b) OC-24(BM), (c) OC-48(BM), (d) OC-EM.

Table 5
Volatile content in oxidized celluloses as determined by TGA

OC sample	Volatile content, % (S.D.[a])
OC-12(BM)	15.1 (1.0)
OC-24(BM)	16.2 (0.6)
OC-48(BM)	17.5 (0.7)
OC-EM	10.5 (0.9)

[a] Standard deviation ($n = 3$).

Table 6
Degradation temperatures of oxidized celluloses containing different carboxyl contents

OC sample	COOH content, % (S.D.[a])	Degradation temperature °C (S.D.[a])
OC-12(BM)	8.0 (0.1)	180.9 (0.9)
OC-24(BM)	13.4 (0.3)	168.3 (0.6)
OC-48(BM)	18.4 (0.1)	164.8 (1.2)
OC-EM	16.0 (0.2)	171.9 (0.3)

[a] Standard deviation ($n = 3$).

hydrocellulose. The degree of crystallinity among the OC products decreases with increasing carboxyl content of the product. It is plausible that as the oxidation reaction progresses the disruption of hydrogen bonding between cellulose chains progressively increases, causing a linear decrease in the degree of crytstallinity of OC. Fig. 8 compares the powder X-ray diffraction patterns of the three new oxidized cellulose products before and after ball milling for 24 h. There appears to be no change in the crystallinity of any of the samples due to ball milling.

Fig. 9 shows the TGA curves for the three new OC products and for the commercial OC-EM sample. All four materials showed a weight loss due to the moisture content between 40 and 125°C. The results presented in Table 5 show that the moisture content in the product increases with increasing carboxyl content. This is because the higher the carboxyl content the greater the affinity of the material for interaction with water molecules. The decline in weights above about 150°C is attributed to the degradation of the materials. The degradation temperatures, determined from the TGA curves, are listed in Table 6. The values show that the thermal stability of OC decreases with increasing carboxyl content. Native cellulose reportedly degrades at 250°C (Klemm et al., 1998; Varma & Chavan, 1995).

4. Conclusions

The results show that OC in high yields and with different levels of carboxyl content can be prepared by reacting cellulose with a mixture of HNO_3/H_2SO_4–$NaNO_2$ at room temperature for different time intervals. In general, an increase in the reaction time increased the carboxyl content and slightly decreased the yield of the products. The different ratios of HNO_3 and H_3PO_4 used in the reaction mixture had no effect on the carboxyl content and the yields of OC. The OC products produced after 12, 24, and 48 h of the reaction period contained 8.0, 13.4, and 18.4% of carboxyl content and 1,9, 3.4, and 4.5% of ketone groups. These products showed a fibrous structure with DP values ranging between 53 and 81 and DC from 27 to 38% (with respect to a crystalline cellulose standard). The length of fibers decreased with increasing reaction time. Ball milling for 24 h decreased the length of fibers further but had no effect on the crystallinity of the products. The ball milled OC products were fine powders consisting of small fibers and aggregated particles. The TGA results revealed the OC materials to be less thermally stable than cellulose. The degradation temperature appears to decrease with increasing carboxyl content of the product.

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