Modification of carboxymethyl cellulose through oxidation

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ABSTRACT

The periodate oxidation reaction of carboxymethyl cellulose involve the primary and secondary hydroxyl groups of the pyranose ring. The reaction is accompanied by the opening of the pyranose ring and resulting product is dialdehyde carboxymethyl cellulose along with some hydrated forms. In this process the glucosidic bond becomes weaker; the formation of carboxyl groups induces a depolymerization, thus reducing the polymerization degree and the physical and mechanical strength of the material. The reaction has been has been carried out at pH 3.5, temperature 45 °C for 0.5–4 h.

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1. Introduction

Cellulose is the most extensively used natural polymer and represents a renewable natural source for organic materials. The main reactions acting on the structure of cellulose and causing its structure alteration are photo-degradation, acid hydrolysis, oxidation, and biodegradation. A complete analysis of them is quite complex, since these phenomena are all related to each other. In order to a better understanding of the structural changes of cellulose related to oxidation, in the present paper we will consider only the oxidation process. The oxidation reactions of cellulose involve the primary and secondary hydroxyl groups of the pyranose ring and result in carbonyl and carboxyl groups (Qingxi, Wei, Zehua, Bo, & Liangliang, 2008). This reaction can be accompanied by the opening of the pyranose ring. In this case the glucosidic bond becomes weaker; the formation of carboxyl groups induces a depolymerization, thus reducing the polymerization degree (DP) and the physical and mechanical strength of the material (Margutti, Conio, Calvini, & Pedemonte, 2001).

The conversion of dihydroxyl groups to dialdehyde by periodate oxidation is a useful method widely used in derivatization of cellulose to active the polymer at further reactions (Rahn & Heinze, 1998). Periodate oxidation is a highly specific reaction to convert 1,2-dihydroxyl (glycol) groups to paired aldehyde groups without significant side reactions and is widely used in structural analysis of carbohydrates (Bruneel & Schacht, 1993; Gal'braikh & Rogovin, 1971; Kim, Kuga, Wada, & Okano, 2000; Maekawa & Koshijima, 1984; Nevell, 1963; Schacht, Bogdanov, Bulcke, & Rooze, 1997; Uraz & Güner, 1997). When applied to glucose in the carboxymethyl cellulose chain, this reaction cleaves the C2–C3 bond, according to the mechanism of Malaprade reaction (Cremonesi, Focher, & Angiuro, 1971, 1972). The resulting compound is the dialdehyde cellulose (DAC) (Maekawa & Koshijima, 1991; Varma & Kulkarni, 2002). The application or the quantitative understanding of this reaction has been hampered by complication arising from hemiacetal formation of aldehyde and crystalline nature of cellulose (Kuniak, Alince, Masura, & Alfödi, 1969; Rowen, Forziati, & Reeves, 1951; Spedding, 1960). The structure of dialdehyde cellulose, as shown in Fig. 1, has been suggested to include the hydrated form

[–CH(OH)$_2$], the 2,3-hemialdal form [–CH(OH)–O–CH(OH)–], the 2,6- or 3,6-hemiacetal forms [–CH(OH)–O–CH$_2$–], as well as the reactive free aldehyde form. The, former three types correspond to addition of one molecule of water per each aldehyde group, addition of one molecule of water per two aldehyde groups, and rearrangement between an aldehyde group and one of the remaining alcohol groups without addition of water. All forms act as free aldehydes under appropriate conditions. According to a kinetic study, free or hydrated aldehyde groups react about 300 times faster than hemialdal groups, and hemiacetal groups come in intermediate between both forms (Maekawa & Koshijima, 1953).

2. Experimental

2.1. Materials

Carboxymethylcellulose sodium salt (low viscosity), Sigma Aldrich was used as cellulose sample. Periodic acid, sulphuric acid, sodium bicarbonate, hydrochloric acid, potassium iodide, sodium thiosulphate, starch were of reagent grade. Distilled water was used throughout the experiments.
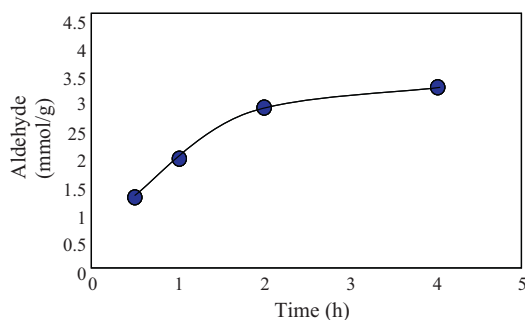
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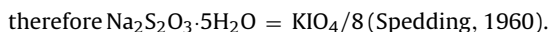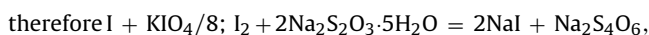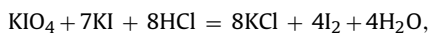
Fig. 1. Aldehyde content increasing per time.

2.2. Oxidation of carboxymethyl cellulose

Different concentrations of carboxymethyl cellulose were taken into consideration, i.e. from 0.5 wt% to 2 wt%. Finally 1 wt% was found the most suitable because of its optimum viscosity and good solubility in aqueous medium.

Added 1 g CMC in 100 ml distilled water, stirred it at room temperature for 6 h, after getting the clear solution added 3 ml of 0.45 M periodic acid. The pH of the solution was adjusted to about 3.5 using dilute sulphuric acid to decrease and sodium bicarbonate to increase the pH of the solution. The oxidation reaction conditions were carried out at temperature 45 °C (Qingxi et al., 2008). The reaction kettle was wrapped with several layers of aluminum foil to prevent exposure to light, i.e. to avoid auto oxidation. Oxidation reaction was carried out for 0.5–4 h which fulfill our requirements for detailed studies of oxidation of CMC for further experiments.

2.3. Determination of aldehyde content

The aldehyde content has been determined by iodometric titration of residual periodic acid present in the reaction mixture. Five ml of aliquot of reaction mixture was added to 10 ml 0.5 N KI and 20 ml HCl. The I_2 formed was titrated with 0.2 N sodium thiosulphate until the endpoint marked by disappearance I_2 was visualized by addition of soluble starch. The similar titration was also performed with a blank sample. All experiments were done in triplicate (Balakrishnan, Lesieur, Labarre, & Jayakrishnan, 2005; McSweeny et al., 2008). The following equations from Lange (1961) described the reactions involved in the analysis (except for the periodate cation being K):

$$KIO_4 + 7KI + 8HCl = 8KCl + 4I_2 + 4H_2O,$$

$$\text{therefore } I + KIO_4/8; \ I_2 + 2Na_2S_2O_3 \cdot 5H_2O = 2NaI + Na_2S_4O_6,$$

$$\text{therefore } Na_2S_2O_3 \cdot 5H_2O = KIO_4/8 \text{ (Spedding, 1960)}.$$

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra have been recorded for the determination of various peaks of oxidized carboxymethyl cellulose regarding aldehyde groups. Approximately 1 mg of dry sample was pressed into a pellet with 200 mg of potassium bromide and FTIR spectroscopy studies of the samples were carried out on Perkin Elmer Spectrum-BX FTIR system. FTIR of the samples were recorded in transmittance mode.

2.5. Thermogravimetric analysis (TGA)

TGA was carried out to determine the thermal stability changes occur while converting CMC to OCMC. TGA studies of the samples
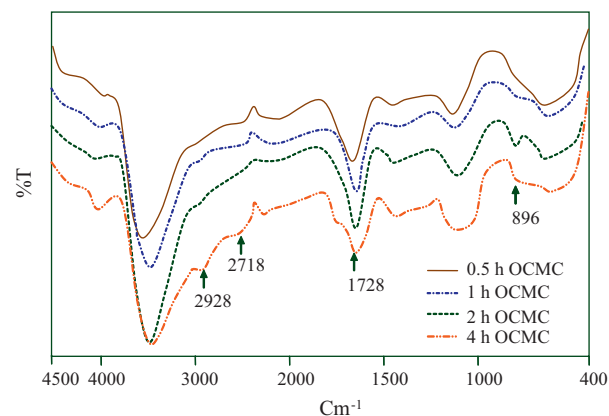

Fig. 2. FTIR spectra of 0.5 h, 1 h, 2 h and 4 h OCMC.

have been recorded with Perkin Elmer TGA-7 system. The thermograms were obtained under nitrogen atmosphere at a uniform heating rate of 20 °C/min in the temperature range of 50–600 °C.

2.6. X-ray diffraction (XRD)

X-ray diffraction has been applied to observe the crystallinity changes of CMC and OCMC. X-ray diffraction of the films was measured by the X-ray diffractometer Xpert PRO PANalytical, Holland. X-ray diffraction pattern were recorded with Cu-Kα radiation (λ = 1.54 °A). The voltage and current were recorded 40 kV and 30 mA respectively. Samples were scanned from 5° to 60° 2θ.

3. Results and discussion

3.1. Aldehyde content

Periodate oxidation of cellulose proceeds gradually from the amorphous to the crystalline phase, it cause the changes in the physical and chemical properties of carboxymethyl cellulose. In this study several oxidations with different time period were carried out. Increasing the reaction time degrades the sample more extensively. In Fig. 2 we can see the periodate oxidation of carboxymethyl cellulose forming dialdehyde cellulose.

Consumption of sodium thiosulphate by the sample is the measure of excess periodic acid. It is known that one periodic acid forms two aldehyde groups so by the amount of periodic acid we calculated the amount of aldehyde groups formed during periodate oxidation. We carried out our experiment from 0.5 h to 4 h. As the oxidation time is increased aldehyde content also get increase Table 1 and Fig. 1.

3.2. FTIR

In Figs. 2 and 3 the three bands, i.e. at 1728, 2928 and 2718 cm^{-1} confirm the oxidation. The oxidation leads to the presence of one more characteristic band of OCMC in 880 cm^{-1} regions. The broad band at 880 cm^{-1} can be assigned to the hemiacetal and hydrated form of the dialdehyde cellulose (Bruneel & Schacht,

Table 1
Aldehyde Content (mmol/g) per time (h).

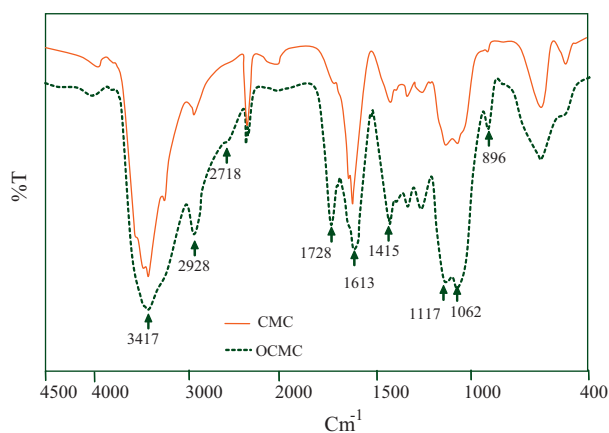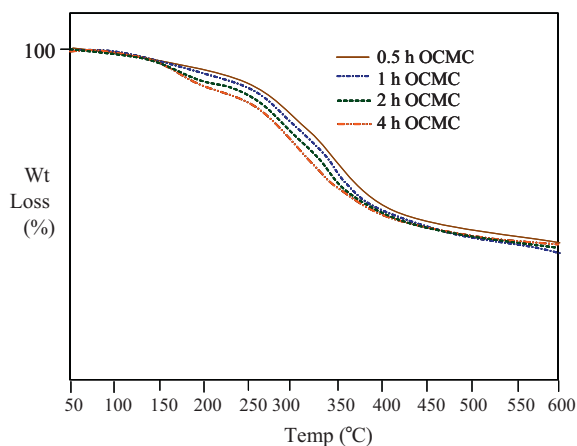| Time (h)	Aldehyde content (mmol/g)
0.5	1.2
1	1.9
2	2.8
4	3.1

Fig. 3. FTIR spectra of CMC and OCMC.

Fig. 4. TGA of 0.5 h, 1 h, 2 h and 4 h OCMC.

1993; Kuniak et al., 1969; Maekawa & Koshijima, 1984; Michell & Purves, 1942; Nevell, 1963; Rowen et al., 1951; Schacht et al., 1997; Uraz & Güner, 1997; Veelaert, Polling, & Wit, 1994), the sharp band at 1728 cm^{-1} is characteristic of carbonyl groups stretching (Gal'braikh & Rogovin, 1971; Kuniak et al., 1969; Spedding, 1960), bands at 2928 and 2718 cm^{-1} show the C–H stretching of aldehyde group. FT-IR analysis of both CMC and OCMC is complicated owing to the high affinity of the samples with water. In fact sometimes the band at 1613 cm^{-1} can be very broad and can hide the
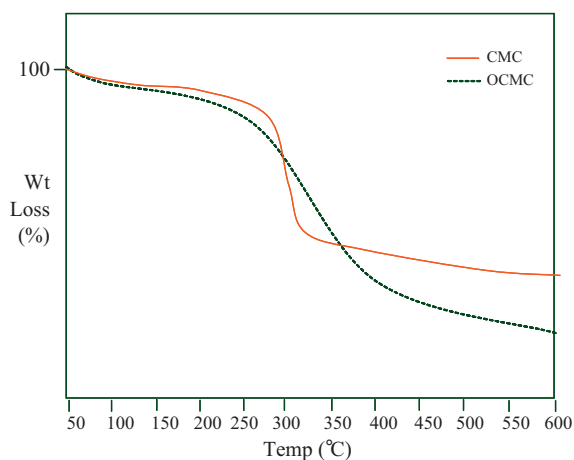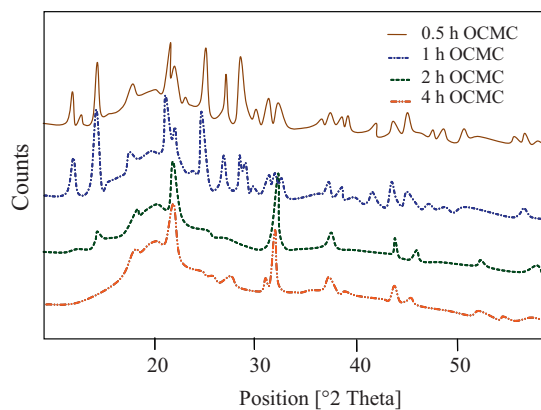

Fig. 5. TGA of CMC and OCMC.

Fig. 6. XRD of 0.5 h, 1 h, 2 h and 4 h OCMC.

bands of the carbonyl groups. Here we can observe the gradual change in the bands from 0.5 h to 4 h for oxidized CMC. Moreover, in the oxidised samples the identification of the functional groups is complicated because aldehyde, keto and carboxyl groups of oxy-cellulose absorb in a very narrow region of the spectrum, between 1720 and 1780 cm^{-1}. Bands at 1117 and 1062 cm^{-1} correspond to the C–O–C stretching vibration of pyranose ring skeleton and bands at 1117 and 1062 cm^{-1} correspond to the C–O–C stretching vibration of pyranose ring skeleton. For samples oxidised with periodate, the identification of the aldehyde group is more difficult since dialdehyde carboxymethyl cellulose can exist in partially or completely hydrated form. These hemiacetal or hemialdal forms do not show the classical bands of the aldehydic carbonyl.

3.3. TGA

Here we can see the loss of crystallinity by periodate oxidation of carboxymethyl cellulose. Thermogravimetric studies of different OCMC show similarity in the weight loss pattern from 0.5 h to 4 h is observed, weight loss started at 200 °C and it become almost stable at 600 °C (Fig. 4).

In thermal degradation studies of OCMC two distinct zones are observed where the weight is being lost Fig. 5. The initial weight loss is due to presence of small amount of moisture in the sample up to 100 °C. The second loss is due to loss of CO_2 from polysaccharide (100–200 °C) while in case of CMC the rapid weight loss occurred at 300–340 °C. It has been observed that in initial stages of weight loss (200–400 °C) oxidized samples started to decompose at lower temperatures (150 °C) than that starting carboxymethyl cellulose (300 °C), reflecting the reactive nature of OCMC which is due to the ring opening and formation of dialdehyde groups in OCMC.
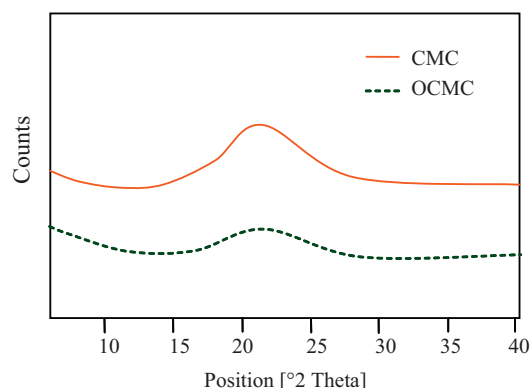

Fig. 7. XRD of CMC and OCMC.

3.4. XRD

In Fig. 6 the well-defined CMC pattern diminished with the increase of oxidation time and the product became almost amorphous after 4 h. A gradual decrease has been observed in crystalline structure from 0.5 h to 4 h OCMC. It has been observed that 0.5 h OCMC posses the most crystalline structure and the 4 h OCMC has the least crystalline structure.

In Fig. 7 in X-ray diffractogram of OCMC amorphous nature of oxidized carboxymethyl cellulose has been observed, CMC has a broad peak at 21° of 2θ showing its crystalline structure which has been almost diminished in OCMC. It is then concluded that periodate oxidation makes OCMC structure less crystalline as compared to CMC and crystallinity decreases as the oxidation time is increased. The loss of crystallinity is considered to result from opening of glucopyranose rings and destruction of their ordered packing.

4. Conclusion

The studies here reported give an insight in understanding the structural changes occurring when carboxymethyl cellulose is oxidised. The oxidation reaction has been performed by periodic acid which is a specific reaction and cleaves the C2–C3 bond only to form dialdehyde carboxymethyl cellulose. The quantitative evaluation of oxidation degree, usually underestimated due to the transformation of carboxymethyl cellulose to hydrated forms like hemiacetals. Quantification of aldehyde groups has been performed by iodometric titration method; by this chemical method the number of aldehydic groups introduced in oxidised materials is rapidly evaluated. FTIR peaks prove the oxidation of carboxymethyl cellulose to dialdehyde carboxymethyl cellulose. TGA observations reveal the reactive nature of oxidised carboxymethyl cellulose due to the presence of two reactive aldehyde groups in the compound so this compound will be used for various derivatization reactions. XRD studies show the decrease in the crystallinity of oxidized material as compared to the original sample. This makes the resulting material mechanically slightly weak. This product, i.e. dialdehyde carboxymethyl cellulose is very useful because aldehyde groups present in this new compound will be used for converting silver into nano silver which will be utilized for the preparation of cellulose based antimicrobial material.

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