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Synthesis of highly cationic water-soluble cellulose derivative and its potential as novel biopolymeric flocculation agent

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ABSTRACT

A water-soluble cationic cellulose derivative was synthesized by cationizing dialdehyde cellulose (DAC) produced by periodate oxidation of birch cellulose pulp by means of a reaction between aldehyde groups and cationic Girard's reagent T ((2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT) to produce cationic dialdehyde cellulose (CDAC). The effect of the aldehyde content of the DAC on its reactivity was evaluated and CDAC with a maximum of 4.27 mmol/g of cationic groups was synthesized from highly oxidized cellulose. Water-soluble CDACs were obtained from DACs having an aldehyde group content of 11.77 mmol/g or higher when the cationic group content exceeded about 3 mmol/g. Promising preliminary results were obtained regarding the use of water-soluble CDAC as a new biopolymeric flocculation agent for calcium carbonate suspension.

1. Introduction

Cellulose, the most abundant natural biopolymer, has long been investigated as a new green source to replace non-renewable materials and chemicals, but its highly ordered hydrogen bond network and high crystallinity, which both detract cellulose reactivity and solubility (Kondo, 1998), have made it difficult to exploit the full potential of cellulose materials. To overcome these problems, many new solvent systems have been studied to enable the homogeneous modification of cellulose (Ramos, Frollini, & Heinze, 2005; Wu et al., 2004). Many modifications are nevertheless still preferably conducted heterogeneously in an aqueous medium, particularly because of the advantages of this approach with regard to toxicity, volatility and price.

One potential reactive cellulose derivative that can be synthesized in a water solution is dialdehyde cellulose (DAC). The oxidation reaction introduces two reactive aldehyde groups per cellulose anhydroglucose unit (AGU) oxidized. Traditionally a high excess of oxidants and a long reaction time would be required to obtain a high aldehyde content, but as we have previously reported, the reaction efficiency can be markedly improved by using mechanical milling, high temperatures and metal salts as cellulose activators (Liimatainen, Sirviö, Haapala, Hormi, & Niinimäki, 2011; Sirviö, Hyvakkö, Liimatainen, Niinimäki, & Hormi, 2011). Ultrasound pre-treatment has also been reported to improve the reactivity of cellulose to periodate oxidation (Aimin, Hongwei, Gang, Guohui, & Wenzhi, 2004).

Due to the aldehyde functions, DAC has a high reactivity with respect to further derivatization, e.g. in Schiff base reactions to produce imines (Kobayashi, Suzawa, & Ichichima, 1990), through bisulfide addition to produce sulfonates (Hou, Liu, Liu, & Bai, 2007) and through further oxidation to produce carboxylic acid derivates (Varma, Chavan, Rajmohanan, & Ganapathy, 1997). The formation of stable imine functionalities such as hydrazones is an attractive synthesis route, as it can be conducted in an environmentally friendly manner under mild conditions and without any hazardous solvents.

A reaction between DAC and Girard's reagent T ((2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT) results in imine bond formation and introduces quaternary ammonium groups into the cellulose. GT has been used previously to obtain a cationic dialdehyde cellulose derivate with low cationicity (Van Brussel-Verraest, Besemer, Thiewes, & Verwillingen, 2003), and this insoluble product has been used as a temporary wet strength agent in papermaking. There is a scarcity of information, however, on the production of highly cationic water-soluble cellulose derivatives using the reaction between DAC and GT. We set out here to use DACs with varying aldehyde content in this reaction in order to obtain highly cationic water-soluble cellulose derivatives.

Synthetic polyelectrolytes containing high charge density are commonly used as flocculation agents in several fields such as papermaking and water purification. However, there exists growing interest to replace these oil-derived chemicals, which may

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contain toxic monomeric residues with more sustainable biopolymeric alternatives. For this purpose natural carbohydrates such as pullulan (Ghimici, Constantin, & Fundueanu, 2010), starch (Wei, Cheng, & Zheng, 2008), dextran (Ghimici & Nichifor, 2010) and cellulose (Sand, Yadav, & Behari, 2010) are considered to be the most potential ones. Consequently, we conducted a preliminary study of use of water-soluble CDAC as novel biopolymeric flocculation agent obtained from renewable source.

2. Experimental

2.1. Materials

Bleached birch (*Betula verrucosa*) commercial chemical wood pulp obtained in dry sheets was used as a source of cellulose after disintegration in deionized water. The cellulose, xylan and glucomannan contents of the pulp were 74.8%, 23.6% and 1.1%, respectively, as determined by high performance anion exchange chromatography (HPAEC-PAD) according to a similar procedure to that presented by Zuluaga et al. (2009). Lignin (TAPPI-T Method 222 om-02) and the extractive content of the pulp (SCAN-CM 49:03 standard) were 0.4% and 0.08%. The Canadian standard freeness (CSF) and Schopper-Riegler (SR) values of the pulp, which reflect its water removal efficiency, were 493 ml and 15.5, respectively, as measured according to TAPPI Method 227 om-99 and the EN ISO 5267-1:2000 standard. The average (length-weighted) length and width of the pulp fibers, as determined with a Metso FiberLab image analyzer, were 0.90 mm and 19.0 μm, respectively. The fines content, given by a L&W STFI Fibermaster analyzer, was 3.4%, and the zeta potential measured with a Mütek SZP-06 device in deionized water was −125 mV.

All the chemicals used in oxidation ($NaIO_4$ and LiCl), cationization ($[(CH_3)_3N^+CH_2CONHNH_2]Cl^-$ and 1 M HCl), precipitation ($CH_3CHOHCH_3$) and aldehyde content analysis ($NH_2OH{\cdot}HCl$, CH_3COOH and $CH_3COONa{\cdot}2H_2O$) were obtained at p.a. grade from Sigma-Aldrich and used without further purification. The acetate buffer solution used in aldehyde content analysis (an oxime reaction) was made by charging a 2.0 dm^3 volumetric flask with 27.4 g of sodium acetate trihydrate and adding 15 ml of glacial acetic acid to the flask and diluting the resulting mixture to 2.0 dm^3 with deionized water. Deionized water was used throughout the work.

The ground calcium carbonate (GCC) suspension (64 wt.%) for the flocculation tests was obtained from Omya and cationic polyacrylamide (CPAM) with a molecular weight of 1.5×10^6 g/mol and charge density of 4 meq/g, used as a reference flocculation aid, was obtained from Kemira.

2.2. Preparation of DAC by periodate oxidation

Highly oxidized cellulose was first produced by weighing 100 g of cellulose suspension with a consistency of 4% (4 g dry cellulose) into a 500 ml flask and adding 300 ml of deionized water and 10.56 g of $NaIO_4$. The reaction vessel was covered with aluminum foil to prevent the photo-induced decomposition of periodate. The reaction mixture was stirred with a magnetic stirrer in a water bath at 55 °C. After 24 h, the product was filtered and washed several times with deionized water to remove iodine containing compounds. The product was stored in a non-dried state at 4 °C.

To obtain DACs of varying aldehyde content, LiCl-assisted periodate oxidations were conducted as described previously (Sirviö et al., 2011). In brief, the cellulose was allowed to react with different amounts of periodate and LiCl (at a LiCl/cellulose weight ratio of 1.8) for 3 h at 75 °C in a vessel covered with aluminum foil.

The aldehyde content of the DACs was determined as reported previously (Sirviö et al., 2011).

2.3. Synthesis of CDAC by cationization of DAC

Non-dried DAC (0.2 g abs.) was weighed into a 100 ml flask or beaker and 20 ml of deionized water and GT with a GT/aldehyde molar ratio of 7.8, 3.9 or 1.95 were added. The pH of the reaction mixture was adjusted to 4.5 with dilute HCl and the mixture was stirred for 0.5–96 h at 20–80 °C. After cooling to room temperature, the mixture was transferred into two centrifuge tubes and 150 ml of isopropanol was added to each tube to precipitate the soluble products. The mixtures were then centrifuged for 15 min at 4500 rpm, after which the supernatants were removed. The product was washed with a water/isopropanol solution (1/9, v/v) and the centrifugation was repeated twice more. Removal of the GT was monitored by adding a small amount of $AgNO_3$ to the supernatant. When no AgCl precipitate formation was observed the washing was complete. Finally, the cationic product was oven-dried at 60 °C and the product stored in a desiccator. A schematic illustration of this cellulose oxidation and DAC cationization processes is shown in Scheme 1.

2.4. Analysis of CDAC

The cationic group content of the CDACs was calculated directly from the nitrogen content of the product as determined using a PerkinElmer CHNS/O 2400 Series II elemental analyzer.

IR spectra of the cellulose, DAC and CDAC were recorded using a Bruker FT-IR spectrometer. The samples were prepared by weighing out 2 mg of product and pressing it into a pellet with 200 mg of KBr.

The solubility of the CDACs was studied by weighing 20 mg of product into a test-tube and adding 2 ml of deionized water. The mixture was stirred for 1 h at room temperature (20 °C), after which the solubility was determined from a small sample of the mixture with an optical microscope.

2.5. Evaluation of the flocculation performance of the CDACs

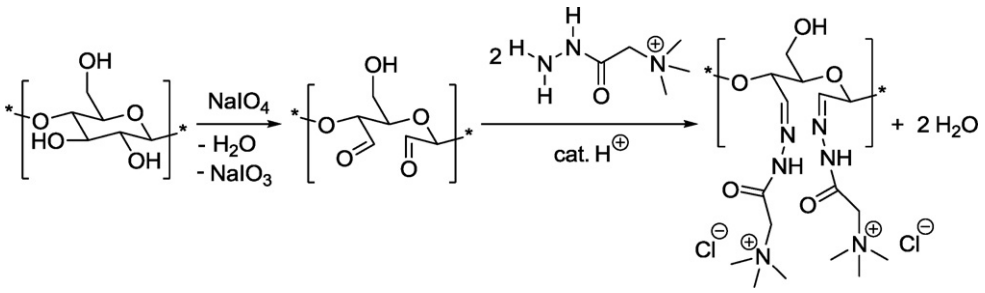
The flocculation performance of CDACs was evaluated by flocculating a GCC filler suspension (solids content of 1%) and determining its residual transmission after centrifugation at 400 rpm for 300 s at 20 °C with an analytical centrifuge (LUMiFuge, L.U.M. GmbH, Germany). The centrifuge consisted of a light source, a rotor above which the sample cuvettes containing the suspension were positioned horizontally and a CCD-line sensor below the rotor. The centrifuge measured light transmission at 800 nm over the plastic sample cuvettes simultaneously as a function of time and position. Local alterations in particle concentration and the position of the solid–liquid interface during separation were detected by changes in light transmission.

3. Results and discussion

3.1. Cationization of highly oxidized cellulose

Highly oxidized cellulose was prepared by the periodate oxidation of birch cellulose using a $NaIO_4$/cellulose AGU molar ratio of 2.0, temperature of 55 °C and a reaction time of 24 h. The aldehyde content was calculated to be 13.67 mmol/g, which corresponds 109% of oxidized cellulose AGUs. This is likely due fact that primary hydroxyl groups were also partly oxidized in addition to regioselective oxidation of hydroxyls in the carbons 2 and 3 (Ivanov, Lenshina, & Ivanova, 1957). The yield of reaction was only 30%, which indicates that these conditions highly promoted the breakdown (Vicini et al., 2004) and the dissolution of DAC (Kim, Wada, & Kuga, 2004).

The highly oxidized DAC was cationized using GT as a reagent and HCl as an acid catalyst (pH 4.5). The cationicity of the CDACs as a



Scheme 1. The synthesis of DAC and CDAC.

Table 1
Cationicity of CDAC produced from highly oxidized cellulose (13.67 mmol/g aldehyde) using different reaction times at room temperature with a 7.8-fold excess of GT.

Reaction time (h)	Cationicity (mmol/g)
1	2.85
2	2.95[a]
3	3.29[a]
12	3.70[a]
24	4.07[a]
48	4.03[a]
72	4.27[a]
96	3.89[a]

[a] Soluble at room temperature.

function of cationization time is shown in Table 1. The GT/aldehyde molar ratio used here was 7.8 and the reaction temperature 20 °C. The cationic group content increased from 2.85 mmol/g to 4.27 mmol/g as the reaction time increased from 1 h to 72 h. At a maximum, 87% of the aldehyde groups reacted with GT under these conditions. This shows the high reactivity of DAC towards the imine formation reaction.

The results of the cationization of highly oxidized cellulose using 1-h and 3-h reactions at various temperatures are shown in Table 2, in which an increase in temperature is seen to promote cationization, so that a high cationicity could be achieved with short reaction times, e.g. CDAC with a cationic group content of 4.09 mmol/g was obtained after 3 h at 60 °C.

3.2. Cationization of cellulose having a variable aldehyde content

In addition to highly oxidized DAC, we used DACs with lower aldehyde contents to study the influence of the degree of oxidation on the reaction, employing a 3-h oxidation reaction at 75 °C using LiCl as the auxiliary substance. The DACs with different aldehyde contents were obtained by using variable amounts of periodate. The results of these oxidations are presented in Table 3. Using 3.83–11.50 mmol of periodate/g of cellulose, DACs with aldehyde contents from 3.81 to 13.09 mmol/g were obtained at yields of 60–77%. Here we also observed slightly over oxidation during the DAC production.

To evaluate the time dependence of cationization in DACs with lower aldehyde contents, DAC1 was treated with GT for 15–180 min at 60 °C using a GT/aldehyde molar ratio of 3.9. The results, as presented in Table 4, showed that the maximum cationicity was achieved using a reaction time of half an hour.

Table 2
Cationic group content of CDAC produced from highly oxidized cellulose (13.67 mmol/g aldehyde) at various temperatures with a 7.8-fold excess of GT.

Reaction time (h)	Cationicity (mmol/g)			
	20 °C	60 °C	70 °C	80 °C
1	2.85	3.41[a]	3.91[a]	3.87[a]
3	3.29[a]	4.09[a]	3.83[a]	4.06[a]

[a] Soluble at room temperature.

Table 3
Aldehyde content of DAC produced using different amounts of periodate. Reaction conditions: 4 g of cellulose, 7.2 g of LiCl, reaction temperature 70 °C and reaction time 3 h.

$NaIO_4$/1 g of cellulose (mmol)	Aldehyde content (mmol/g)	Sample name
3.83	3.81	DAC1
4.79	5.70	DAC2
5.75	7.39	DAC3
7.67	9.53	DAC4
8.63	10.46	DAC5
9.58	11.77	DAC6
11.50	13.09	DAC7

The results of cationization of DACs with variable aldehyde contents for half an hour using GT/aldehyde molar ratios of 1.95, 3.9 and 7.8 at different temperatures are shown in Table 5. An increase in temperature resulted in increased cationicity with a low aldehyde content, particularly if small amounts of GT were used. The cationic group content of the CDAC from DAC2 obtained using a 1.95-fold excess of GT, for example, increased from 1.38 mmol/g to 1.92 mmol/g when the temperature was increased from 60 °C to 80 °C. The results show, however, that if the aldehyde content of the DAC is high and a large excess of GT is used the derivatization a higher cationicity is usually obtained at lower temperatures. An example of this can be seen in the DAC4 cationization experiment, where the highest conversion of aldehyde to imine was achieved at 60 °C using an 7.8-fold excess of GT.

Increasing the amount of GT had a high impact on the cationic group content of the resulting CDACs. As Table 5 shows, the cationic group content increased up to 1.8-fold at 60 °C when the excess of GT was increased from 1.95 to 7.8. In most cases, however, a fairly high cationic group content was obtained even with lower excesses of GT. In these conditions, maximum conversion of aldehyde groups on DAC to imine groups was 59–75%.

3.3. Water solubility of CDAC

The effect of cationization on water solubility was determinate by optical microscopy. Products were mixed with water at 20 °C for 1 h and solubility was confirmed by the absence of insoluble

Table 4
Cationic group content of CDACs produced from DAC1 using a 3.9-fold excess of GT at 60 °C.

Reaction time (min)	Cationicity (mmol/g)
15	1.58
30	1.92
60	1.93
120	1.79
180	1.92

Table 5
Cationization of DACs possessing different aldehyde contents in a half-hour reaction under various sets of reaction conditions.

Sample	Cationicity (mmol/g)								
	1.95 excess of GT			3.9 excess of GT			7.8 excess of GT		
	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C
DAC1	1.25	1.36	1.40	1.92	1.58	1.86	1.87	1.96	1.97
DAC2	1.38	1.77	1.92	2.04	2.05	2.18	2.55	2.60	2.61
DAC3	2.23	2.26	2.38	2.60	2.62	2.50	2.88	2.83	2.76
DAC4	2.56	2.96	2.77	2.78	2.82	2.65	3.38	3.06	3.20
DAC5	2.67	2.54	2.48	2.85	2.94	2.93	3.23	3.32	3.31
DAC6	2.55	2.75	2.65	2.91	3.13[a]	3.14[a]	3.17[a]	3.23[a]	3.41[a]
DAC7	2.69	2.81	2.92	3.13[a]	3.32[a]	3.30[a]	3.63[a]	3.65[a]	3.66[a]

[a] Soluble at room temperature.

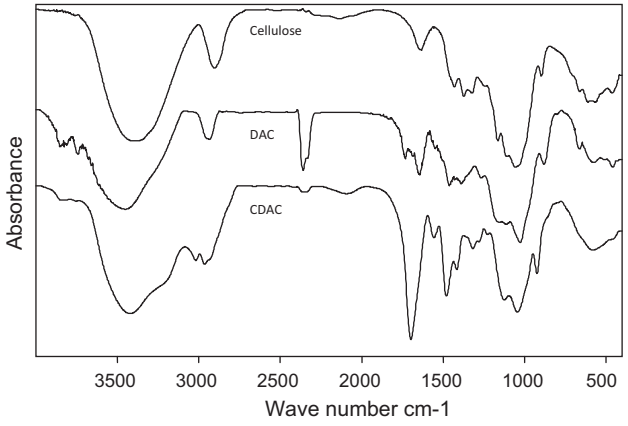


Fig. 1. FT-IR spectra of cellulose, DAC6 and CDAC.

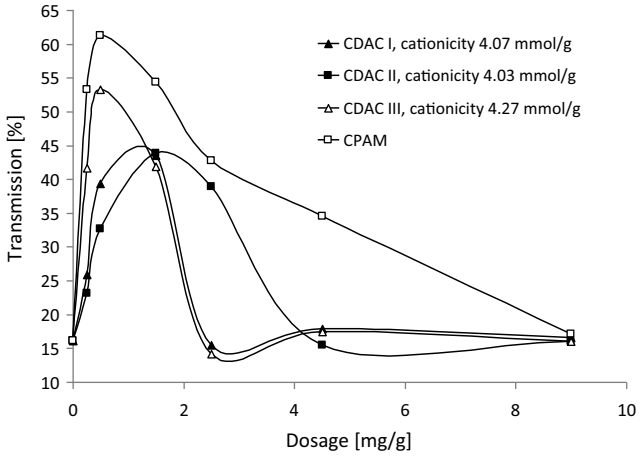


Fig. 2. Flocculation of GCC filler suspension with CDAC.

particles. CDACs prepared from DACs having an original aldehyde group content of 11.77 mmol/g or higher and a cationicity of 2.95 mmol/g or higher were soluble. The results show that the degree of oxidation has a high impact on the solubility of the resulting CDACs. CDACs with identical cationic group contents but different aldehyde group contents in their native DACs possess different solubilities. Insoluble CDAC formed a gel-like material in water.

Native cellulose is known to be insoluble to all common solvent including water. Also mildly oxidized DAC is water-insoluble while fully oxidized DAC dissolves into water at high temperatures (Kim et al., 2004). Sulphonated DAC has also reported to dissolve into water (Rajalaxmi, Jiang, Leslie, & Ragauskas, 2010). Our results show that the cationization by GT also improves solubility of DAC as our native DAC was completely water-insoluble at room temperature.

3.4. Characterization of CDAC

The synthesised DAC and CDAC were characterized by IR (Fig. 1). The spectrum of DAC shows characteristic bands at 1735 and 880 cm^{-1}, which are assigned to the aldehyde carbonyl group, hemiacetals and hydrated forms of aldehyde groups (Spedding, 1960). Formation of an imine bond in CDAC was confirmed by the band at 1569 cm^{-1}, which is characteristic of the carbon–nitrogen double bond in imines (Lin, Yao, Chen, & Wang, 2008). The sharp band at 1700 cm^{-1} is due to the carbonyl group in GT (Vojinovic et al., 2004), which overlaps with the possible remaining aldehyde carbonyl signal. The sharp band at 923 cm^{-1} is due to the nitrogen–nitrogen bond in GT (El-Ayaan, Kenawy, & Abu El-Reash, 2007), which overlaps with the hemiacetal band. The sharp bands at 1481 cm^{-1} and 1413 cm^{-1} are associated with methyl groups and the carbon–nitrogen bonds in the quaternary ammonium group, respectively (Yan, Tao, & Bangal, 2009).

3.5. Flocculation behaviour of CDAC

Since cationic water-soluble polyelectrolytes are traditionally used as flocculation agents in several fields, we conducted some preliminary tests with water-soluble CDACs to evaluate their potential as novel biopolymeric flocculants. Flocculation performance was followed by quantifying the residual transmission of flocculated ground calcium carbonate filler suspension after centrifugation. Cationic polyacrylamide with a high degree of substitution was used as a reference material. CPAM was chosen as it is one of the most common commercial flocculation agents and bears similarities to our CDAC with regarding to its high degree of substitution. As seen in Fig. 2 all water-soluble CDACs resulted in clear flocculation. The maximum flocculation efficiency was about 85% of the value obtained with the reference polymer (CPAM). Also the optimum dosage was found to be in similar range that with the reference.

The mechanism of GCC suspension flocculation is likely based on charge neutralization as the periodate oxidation remarkably reduces the molecular weight of cellulose due to which the polymeric chains are too short for efficient bridging flocculation. This was supported by the fact that the flocculation performance was promoted by increase of cationicity of CDAC, i.e. CDAC3 with the highest cationicity achieved the best flocculation performance. Thus, the high cationic charge density of CDAC3 resulted in efficient charge neutralization of anionic GCC particles.

4. Conclusions

Highly cationic water-soluble DAC derivatives were effectively produced by the formation of imine bonds between DAC and the cationic reagent GT. Maximum cationicity of 4.27 mmol/g was achieved with 72 h reaction at room temperature using highly oxidized cellulose. In all DACs, conversion of aldehyde groups to corresponding imine groups showed high reactivity.

The solubility of CDACs as determined at room temperature was shown to be highly affected by the degree of oxidation of the DAC and the cationicity of the CDAC. CDACs produced from a DAC having an aldehyde content of 11.77 mmol/g or higher were soluble when the cationicity exceeded 3 mmol/g, whereas CDACs with the same cationic group content but a lower original aldehyde content in the native DAC only formed a gel-like material in water.

Preliminary studies using water-soluble CDACs as a biopolymeric flocculation agent indicate that they have a high potential for use as new, environmentally friendly flocculation aids. Further studies on the use of CDAC as a flocculation agent are currently under way.

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