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Preparation of sulfoacetate derivatives of cellulose by direct esterification☆

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Abstract

A new and efficient method for the preparation in one step of water-soluble cellulose acetate sulfate derivatives (CAS) is reported. Acetylation and sulfation were carried out simultaneously, using a mixture of acetic anhydride and sulfuric acid in glacial acetic acid. The reaction time and the amount of acetic anhydride were optimized and the method provided water-soluble esters, with a degree of acetylation in the range 1.6 and 2.4 and a degree of sulfation of 0.3. This method has been successfully applied to pure cellulose and to cellulose-enriched materials obtained from agricultural by-products. The product exhibited a high viscosity in aqueous solution suggesting interesting rheological properties. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Cellulose; Wheat bran; Maize bran; Esterification; Acetylation; Sulfation; Water-soluble ester

1. Introduction

Cellulose, a (1→4)-linked β-D-glucopyranosyl polysaccharide is the main plant cell-wall constituent and gives plants their structural support. Its annual formation rate amounts to 180×10^9 tons.[1] Cereals bran is rich in cellulose but poorly exploited except for its use for animals feeding. Cellulose, water-insoluble in its native form, is often modified to prepare new materials, e.g., paper, filtration membranes or food additives. Hydrogen atoms of the primary and secondary hydroxyl groups may be replaced by reactive groups such as methyl, ethyl, carboxymethyl, acetyl. Amongst cellulose derivatives, the production of cellulose acetate is the most important because of its broad application in plastics and fibers. Whatever the process of acetylation, the product obtained is cellulose triacetate.[1] A lower degree of substitution is obtained by partial deacetylation.

Water-soluble polymers are important commercial products and are used for a number of applications (cosmetics, paints, detergents, food products ...). Various cellulose ethers (e.g., hydroxypropylcellulose, carboxymethylcellulose, methylcellulose) and esters (e.g., cellulose sulfate) are well known for their solubility in water, and cellulose ethers are used on a commercial scale. Cellulose acetates with a degree of substitution lower than 1 are water-soluble.[1] Water-soluble cellulose monoacetates are made from cellulose triacetate by controlled deacetylation in an aqueous mineral acid solution[2,3] or by metal-catalyzed methanolysis using for example molybdenum trioxide or zinc chloride.[4,5]

We describe, in this paper, the one step preparation of a water-soluble cellulose acetate derivative from microcrystalline cellulose or cellulose-enriched materials obtained from maize bran (MB) and wheat bran (WB). Various parameters of acetylation, such as reaction time, amount of acetic anhydride and sulfuric acid catalyst were studied in order to obtain water-soluble cellulose derivatives. The chemical characterization and some physico-chemical properties of these derivatives are also presented. Their rheological behaviour has been investigated and is presented in Part II of this series of papers.

☆ Water-soluble cellulose esters, Part 1.

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Table 1
Composition (mg/g) of cellulosics residues of WB and MB and viscosity-average degree of polymerization ($\overline{\mathrm{DP}}_v$)

Treatment	Avi [a]	WB_1 [b]	WB_2 $NaClO_2$ [c]	WB_3 $NaClO_2$; KOH [d]	WB_4 $NaClO_2$; KOH+$NaBH_4$ [e]	MB_1 KOH $NaBH_4$ [f]	MB_2 KOH H_2O_2 [g]
Cellulose	974	383	581	554	587	603	729
Heteroxylans [h]	0	110	102	218	237	212	138
Lignin	0	169	132	7	6	7	8
Protein	0	101	30	2	1	2	3
Ash	0	5	1	26	25	29	17
$\overline{\mathrm{DP}}_v$	210	330	270	940	1150	1250	720

[a] Cellulose Avicel.
[b] WB industrial acid treatment.
[c] $NaClO_2$ treatment of WB_1.
[d] WB extracted with KOH 2 mol/L, liquid (mL)/solid (g) ratio (L/S) = 10/1.
[e] WB extracted with KOH 2 mol/L + 1% (w/w) $NaBH_4$, L/S = 10/1.
[f] MB extracted with KOH 1.5 mol/L + 1% (w/w) $NaBH_4$, L/S = 10/1.
[g] MB extracted with KOH 1.5 mol/L + 1% (v/w) H_2O_2, L/S = 10/1.
[h] Heteroxylan content = sum of the contents in arabinose, xylose, galactose and glucuronic acid.

2. Results

2.1. Composition of cellulose substrates

Chemical treatments used to obtained cellulose-enriched residues from MB and WB have been previously described.[6,7] The various substrates had a cellulose content varying from 380 to 730 mg/g and were contaminated by residual lignin (6–169 mg/g) and heteroxylans (102–237 mg/g). According to the extraction procedure, the viscosity-average degree of polymerization of cellulose varied from 270 to 1250 (Table 1). A very low cristallinity, probably of Type I was observed whatever the cellulose-enriched sample.[6]

2.2. Optimization of esterification conditions

The conditions for esterification were optimized on a cellulose enriched product obtained from wheat bran (WB_2) by varying the amount of acetic anhydride and the reaction time at 40 °C. Esterification experiments led to a heterogeneous mixture containing residual insoluble materials, water-insoluble esters that precipitated by addition of water and water-soluble derivatives (Fig. 1). The proportion of the various reaction products as a function of the acetic anhydride amount for a reaction time of 30 min is shown in Fig. 2. The amount of residual material was almost constant until addition of 1 molar proportion of acetic anhydride per mole of anhydroglucose (about 0.95 g of residual particles per g of starting material). This amount then decreased until addition of acetic anhydride reached 3 mol/mol of anhydroglucose and remained constant (0.3 g/g) at higher concentration. Meanwhile, the amount of water-soluble derivative increased up to 1.3 g/g but decreased when the amount of acetic anhydride exceeded 6 mol/mol of anhydroglucose. The amount of water-insoluble esters was low (< 0.1 g/g) up to 8 mol/mol of anhydroglucose but increased very rapidly for higher concentrations. A sharp range of acetic anhydride was

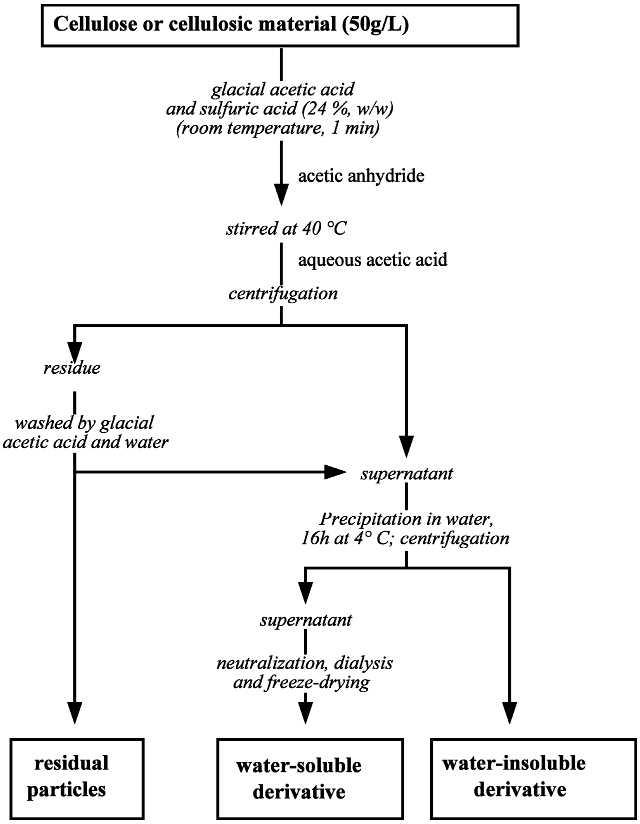

Fig. 1. Esterification of cellulosic material.

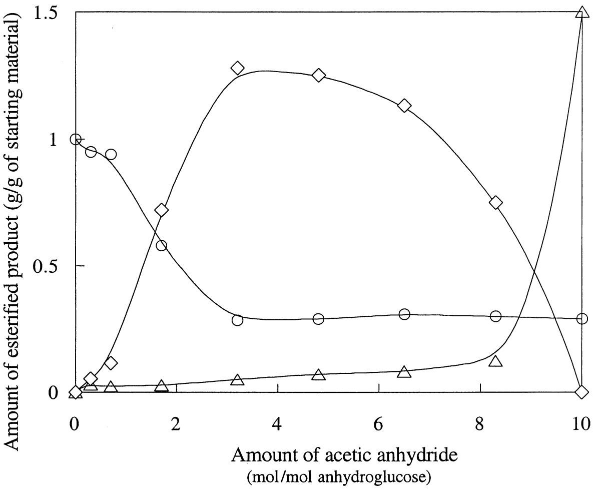

Fig. 2. Influence of the amount of acetic anhydride on the yield in water-soluble ester by esterification of Wac2 at 40 °C for 30 min. Residual particles, circle; water-insoluble ester, triangles; water-soluble ester, lozenges.

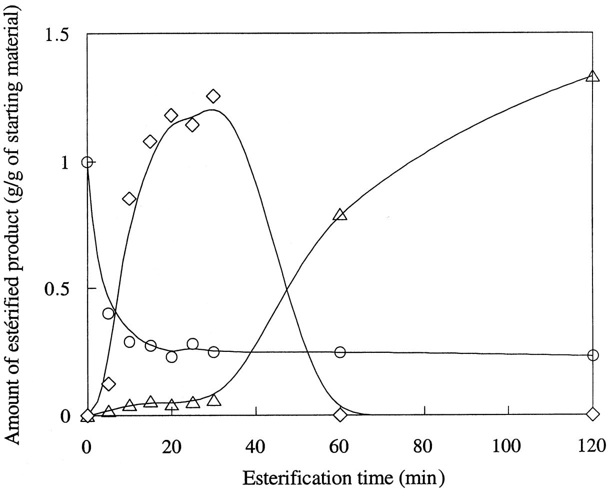

Fig. 3. Kinetics of esterification of WB_2 at 40 °C (3.2 mol/mol Ac_2O/anhydroglucose). Residual particles, circle; water-insoluble ester, triangles; water-soluble ester, lozenges.

finally found for the formation of water-soluble derivatives: below 3 mol/mol of anhydroglucose, a low yield of esterification was obtained but over 8 mol/mol, water-insoluble derivatives were obtained.

The composition of water-soluble derivatives is reported in Table 2. The cellulose content slightly increased with the amount of reagent (between 474 and 561 mg/g range) and a small amount of non-cellulosic sugars was also present (between 60 and 80 mg/g). The acetate content reached about 300 mg/g and the DS_{Ac} varied from 1.6 to 2.0. This is the first time that a direct partial acetylation (in one step) is described. The DS_{Ac} obtained was unusual for a water-soluble cellulose acetate which is generally described with DS_{Ac} between 0.5 and 1.[1–5]

The kinetic of the reaction was then studied (Fig. 3). An amount of acetic anhydride of 3.2 mol/mol of anhydroglucose was selected. The amount of residual particles decreased rapidly in the first 10 min of reaction and reached a constant value of 0.3 g/g; a sharp optimum was obtained for the formation of water-soluble derivative, between 20 and 30 min. The formation of water-insoluble esters increased significantly over this time.

The composition of unesterified material, water-soluble and water-insoluble derivative was investigated. A low amount of unesterified glucose and non-cellulosic sugars (between 30 and 70 mg/g) was present in the insoluble material, which was probably rich in lignin. The water-insoluble ester portion was rich in xylose (~ 300 mg/g) and the DS_{Ac} reached 2.8 as previously described by Tanghe and coworkers.[2] The chemical compositions of the water-soluble ester part was similar whatever the reaction time (Table 2). The esterified product was rich in glucose (~ 450 mg/g), in acetate groups (~ 300 mg/g) and poor in non-cellulosic sugar component (~ 60 mg/g). The DS_{Ac} varied from 1.9 to 2.2 as previously described.

Table 2
Influence of reaction time (min) and amount in acetic anhydride (mol/mol anhydroglucose) on composition (mg/g) and degree of acetylation (DS_{Ac}) of water-soluble cellulose esters prepared from WB_2

Composition	Acetic anhydride reaction time: 30 min				Reaction time acetic anhydride: 3.2 mol/mol		
	1.7 mol/mol anhydroglucose	3.2 min	4.8	6.5	5	10	20
Noncellulosic sugars [a]	81	62	60	68	69	56	53
Cellulose	474	493	505	561	469	458	441
DS_{Ac}	1.8	2.0	1.6	2.0	2.1	1.9	2.2

[a] Noncellulosic sugars = arabinose + xylose + mannose.

Table 3
Yield in CAS (g/g), and their chemical composition (mg/g), degrees of acetylation (DS_{Ac}) and sulfation (DS_{Sulf}) of water-soluble CAS

Yield in CAS	Avi 1.7	WB_2 1.3	WB_3 1.2	WB_4 1.2	MB_1 1.2	MB_2 1.3
Arabinose	2	3	17	15	19	14
Xylose	9	49	64	87	73	53
Mannose	0	10	8	12	8	8
Glucose	531	493	408	434	443	445
Esterified acetic acid	330	295	320	285	262	308
Free acetic acid	4	43	7	35	15	13
DS_{Ac}	**2.3**	**2.0**	**2.4**	**1.9**	**1.8**	**1.8**
Esterified sulfuric acid	83	85	100	95	70	87
Free sulfuric acid	2	0	0	0	0	0
DS_{Sulf}	**0.3**	**0.3**	**0.4**	**0.3**	**0.3**	**0.3**

2.3. Effect influence of cellulose content

The different cellulosic material were acetylated using the optimized conditions, i.e., 3.2 moles of acetic anhydride per mole of glucose and 30 min of reaction at 40 °C. Water-soluble derivatives were obtained for all the substrates and the amount of esterified product increased with the cellulose content of the starting material (Table 3). Indeed, cellulose Avicel (Avi) led to 1.7 g/g of water-soluble esters whereas esterification of cellulose-enriched residues produced both water-soluble esters (~ 1.2 g/g) and residual particles (~ 0.3 g/g). A small amount of water-insoluble esters (≤ 0.05 g/g) was also formed whatever the starting material.

The composition of water-soluble esters is reported in Table 3. They were mainly composed of glucose (between 400 and 530 mg/g) and acetate groups (between 260 and 330 mg/g). They contained a small amount of non-cellulosic sugars (between 62 and 114 mg/g) when cellulose-enriched materials were used. Free acetic acid (less than 45 mg/g) was also detected. The DS_{Ac} varied from 1.8 to 2.4, which was unusual for a water-soluble cellulose acetate as already indicated. Sulfate groups linked to sugars were detected in the water-soluble derivative (between 70 and 100 mg/g). A DS_{Sulf} of 0.3 was calculated for all of the samples except WB_3 (0.4). Therefore, 15–30% of hydroxyl groups remained free after the esterification reaction. Thus, the water-soluble derivative was a mixed acetate and sulfate ester of cellulose and is referred as a cellulose acetate sulfate (CAS) in the following part of this paper.

2.4. Kinetic of sulfation

The amount of sulfate esterified to cellulose was followed as a function of time (Fig. 4). Esterification of cellulose by sulfuric acid was very fast and about 80% of sulfuric acid present in the reaction mixture was in the form of cellulose esters in the first min of the reaction. This rate of esterification corresponded to a DS_{Sulf} of 0.6. Then, DS_{Sulf} decreased with reaction time and reached about 0.2 after 2 h of reaction, as previously described by Tanghe and coworkers.[2] An esterification time of 1 h led to a water-insoluble ester due to a high extent of acetylation ($DS_{Ac} \sim 2.8$) and a low DS_{Sulf} (~ 0.2).

So, both the presence of bound sulfate and a balance between free hydroxyl groups and hydrophobic acetate groups probably favored the solubility in water of cellulose derivatives. Sulfate conferred a polyelectrolyte character increasing the hydrophilic character and then the water solubility.

2.5. Solubility and reduced viscosity of the water-soluble ester

Solubility of CAS was determined in pure water, in ethanol–water mixtures (0, 10, 25, 50, 70, 80, 90 and

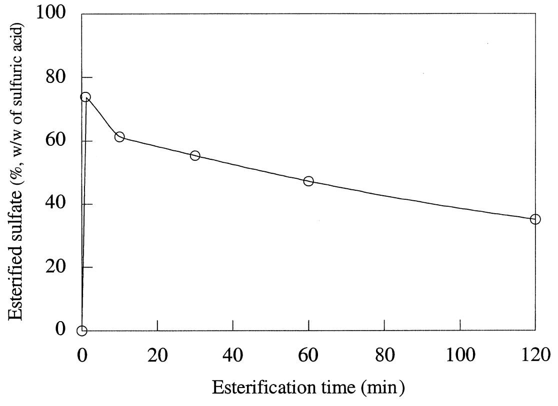

Fig. 4. Kinetics of esterification of WB_2 by sulfuric acid (sulfuric acid: 24% w/w; acetic anhydride of 3.2 mol/mol Ac_2O/anhydroglucose).

Table 4
Solubility of the CAS (10mg/mL) made from Avicel (Avi), WB_2 and MB_2 in water and in mixtures of ethanol and water (v/v)

Concentration in EtOH (%, v/v)	0	10	25	50	70	80	90	99
Avi	100	100	100	100	86	80	35	12
WB_2	100	99	99	98	97	97	11	5
MB_2	100	99	97	93	94	90	27	0

100%, v/v, Table 4) and in 5×10^{-3} mol/L NaCl aqueous solution. In our conditions, CAS was totally soluble in water (~ 100% of neutral sugar recovered in the filtrate after filtration), almost insoluble in the presence of salt and soluble in aqueous ethanol at concentration lower than 50% (between 93 and 100% of neutral sugar recovered). The solubility decreased over 4:1 ethanol–water and CAS was insoluble in pure ethanol.

A quasi-linear relation was observed between reduced viscosity and concentration above 0.6 mg/mL (Fig. 5). However, the reduced viscosity increased for the more diluted concentration (below 0.6 mg/mL) indicating a polyelectrolyte effect, which was the consequence of the presence of ionic sulfate groups. The reduced viscosity at 0.5 mg/mL was used to compare samples. A very high value of reduced viscosity (between 629 and 2.126 mL/g) was observed. These values could not be related to the degree of polymerization of the starting cellulose (Table 1), since Avicel cellulose having the shortest chain length led to CAS with the highest reduced viscosity, whereas long chain cellulose (e.g., MB_1 with $\overline{DP}_v = 1250$) led to cellulose esters with the lowest reduced viscosity. The comparison of DS_{Ac} (Table 3) and reduced viscosity (Table 5) suggested that the two parameters might be linked.

When the reduced viscosity was determined in a solvent less polar such as a mixture of ethanol and water, the reduced viscosity decreased for Avicel and remained almost constant for WB_3 (Table 5). The decrease in viscosity could be related to a decrease of the hydrodynamic volume of the polymer in the solvent since it was less polar. It also probably indicates the presence of hydrophobic interaction that led to supermolecular structures and explains the high reduced viscosity.

3. Discussion

Cellulose acetate can be prepared by various methods[2,8–12] and sulfuric acid is often used as catalyst.[2,8,9] In opposition with previously published work,[4,13–15] this study showed that it is possible to prepare water-soluble cellulose acetate derivatives directly from cellulose without involvement of the triacetate as intermediate. The amount of acetic anhydride (3.2 mol/mol of anhydroglucose) and the reaction time (30 min) at a temperature of 40 °C were optimized. The amount of sulfuric acid and acetic anhydride, and the reaction time are critical parameters in the preparation of stable CAS. In the present study, the amount of sulfuric acid was higher than that usually used (0.02–0.16 g/g;[1,2,8]). Usually, acetylation with sulfuric acid as a catalyst leads to unstable CAS as an intermediate product.[16] Remaining esterified sulfates groups are destroyed during the final step of stabilization of the ester[16] and a cellulose acetate with high DS_{Ac} (2.8) is obtained.[2,17]

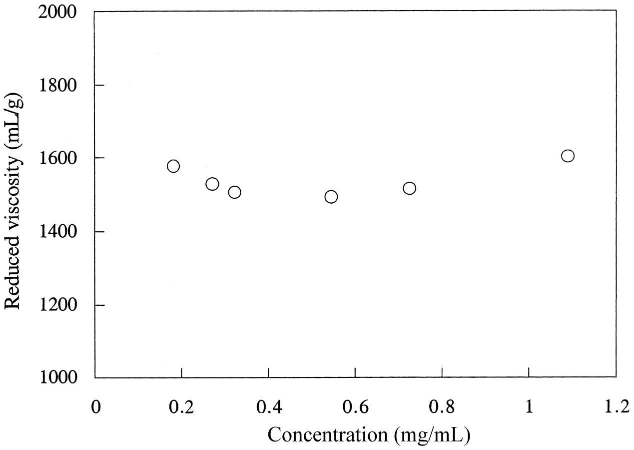

Fig. 5. Determination of the intrinsic viscosity in water at 25 °C of cellulose acetate sulfate prepared from Avi.

Table 5
Reduced viscosity (η_{red}) at 0.5 mg/mL of CAS determined in de-ionized water and in a mixture of ethanol and water (1:9, v/v)

$\eta_{red,\ 25\ °C}$	Solvent	
	Water	EtOH:water
Avi	2126	1145
WB_1	1493	1800
WB_2	882	nd
MB_1	629	nd
MB_2	745	nd

nd: not determined.

Preparation of water-soluble cellulose acetate sulfate has been previously reported in the literature. Tunc[18] prepared this derivative by acetylation of cellulose sulfate or by sulfation of cellulose acetate.[18–20] In both cases, cellulose esters have very interesting properties such as high water solubility, important water retention or good filmogenic properties. Direct acetosulfation of cellulose using a mixture of acetic anhydride and sulfur trioxide or chlorosulfonic acid in *N*,*N*-dimethylformamide was also reported.[16] The product obtained was water-insoluble but had a high water retention capacity and a DS_{Sulf} between 0.2 and 1.3. A cellulose sulfate was finally obtained by deacetylation and it was water-soluble when the DS_{Sulf} was higher than 0.3.

Generally, acetic anhydride is used in large excess, about 10 mol/mol of glucose[1,2,8,16] to allow this heterogeneous reaction. The limited amount of this reagent in our conditions probably allowed to control the reaction and to isolate water-soluble CAS before formation of cellulose triacetate.

According to the results, a mechanism of esterification may be proposed. A first step might be the esterification of cellulose by sulfuric acid; indeed, about 80% of sulfuric acid was found esterified to cellulose in the first min of the reaction. The accessibility of cellulose and therefore its reactivity are then probably improved by a swelling effect induced by the bulky sulfate groups.[6] Then, a transesterification reaction could occur,[21] sulfate being partially and slowly removed or replaced by acetate. DS_{Sulf} then decreased as the degree of acetylation increased until CAS became soluble in acetic acid. Transesterification reactions were previously evidenced for the sulfation of cellulose acetate or cellulose nitrate.[16,22]

The water solubility of CAS was surprising because of the DS_{Ac} values—1.6–2.4—largely higher than usually obtained for water-soluble cellulose acetate (0.5–1.0). The formation of CAS has been previously described by sulfation of cellulose triacetate.[20] The esterified product had interesting hydrophilic character but was not water-soluble. Aikhohodzaev and coworkers[23] already described the preparation of a water-soluble cellulose acetate (DS between 0.9 and 2.0) by direct acetylation of cellulose in the presence of a large amount of sulfuric acid (100–240 g per 100 g of cellulose). However, such amount probably induced an important decrease of the cellulose chains length and influenced the rheological properties of the cellulose ester.

The sulfation may be the cause of solubility since it confers an ionic character to the resulting polysaccharide and both sulfate and the remaining hydroxyl groups increase the hydrophilic character and then the water solubility.

The chemical compositions of water-soluble esters were similar whatever the cellulose used as starting material. However, the amount of esterified product obtained was lower when cellulose-enriched samples were used. This was mainly due to a lower cellulose content since the recovery of cellulose in cellulose esters (80 and 90%) was only slightly lower as compared to the case when pure cellulose was used as starting material. A lower accessibility of cellulose, which could be embedded in an amorphous network comprising residual heteroxylans and/or lignin, could also explain a lower reactivity of cellulose.

DS_{Ac} varied from 1.6 to 2.4, which suggested that solubilisation of cellulose acetate in acetic acid occurred when DS_{Ac} reached about 1.5. DS_{Ac} variations in the samples were probably the consequence of the nature of cellulose and particularly of the method of purification of cellulose. DS_{Sulf} was the same for all the samples and was dependent on the reaction time, and probably on the amount of sulfuric acid.

The high-reduced viscosity observed for our derivatives suggested interesting thickening properties. The rheological properties of our CAS are presented in the second part of this study.

4. Experimental

4.1. Materials

Destarched WB and cellulose-enriched samples recovered after treatment of WB with sulfuric acid (WB_1) were provided by ARD (Pomacle, France). Destarched MB was provided by Ulice (Chappes, France). Cellulose Avicel PH-101 (Avi) was purchased from Fluka.

Cellulose-enriched materials (WB_2, WB_3 and WB_4 from WB; MB_1 and MB_2 from MB; Table 1) were prepared as previously described.[6,7] Heteroxylans were extracted by alkaline treatment and removal of lignin was improved by addition of hydrogen peroxide in the alkaline medium[24,25] or by treatment of the bran with sodium chlorite.[26] In some experiments (WB_2 and MB_1), sodium borohydride was used to prevent cellulose chains from oxidative peeling.

4.2. Chemical modification (Fig. 1)[27]

Cellulosic material (1 g) was immersed at room temperature (rt) in 20 mL of glacial AcOH and stirred for 15 min. Acetic acid was removed by centrifugation (2250*g*, 10 min, 20 °C). This step was repeated two times. The residue was immersed in 20 mL of a mixture of H_2SO_4 (0.24 g/g of cellulosic material) in glacial AcOH and shaken for 1 min at rt (Fig. 1). Acetic anhydride was added (0–10 mol/mol of anhydroglucose); the mixture was shaken for 1 min at rt and finally stirred at 40 °C for 0–2 h. At the end of the reaction, a mixture of glacial AcOH in water (7/3, v/v) was added to stop the reaction and the mixture was slowly stirred at rt for 30 min. The supernatant was removed by centrifugation (2250*g*, 10 min, 35 °C), and the residue was washed with glacial AcOH (× 3, 20 mL) then with water (× 3, 20 mL). The supernatants were recovered by centrifugation (2250*g*, 10 min, 35 °C) and the residue was freeze-dried.

The supernatant was slowly added to de-ionized water and water-insoluble esters were precipitated for 16 h at 4 °C. The precipitate was removed by centrifugation (17,500*g*, 20 min, 4 °C) and the supernatant was adjusted to pH 7.5 with NaOH (4 mol/L). Temperature (~ 10 °C) was controlled during the neutralization to minimize possible saponification of the product. The precipitate formed upon neutralization disappeared after dialysis against de-ionized water (4 days). Water-soluble cellulose esters were finally freeze-dried.

4.3. General methods

All the results are expressed relative to the dry matter content determined by drying at 120 °C for 3 h.

The methods used to characterize cellulose-enriched residues (contents in ash, protein, lignin, uronic acid and neutral sugar) were previously described in details.[6,28]

Individual neutral sugars were analyzed by gas-liquid chromatography (GLC) after total hydrolysis of the polysaccharide to sugars and derivatization of the sugars into alditol acetates.[29] Conditions of hydrolysis was optimized (data not shown) and cellulose derivatives were hydrolyzed 6 h in 2 mol/L H_2SO_4 at 100 °C.

Acetic acid was analyzed by HPLC on Aminex HPX-87H (300 × 7.8 mm, Biorad) with a differential refractometer (ERMA-ERC 7510) detection.[30] Free AcOH was extracted with water for 16 h at rt and AcOH was released by saponification in 0.4 mol/L NaOH prepared in 1:1 water–EtOH, for 16 h at rt. The column was eluted at 35 °C with 5×10^{-3} mol/L H_2SO_4 at 0.6 mL/min and succinic acid was used as internal standard.

Sulfate was quantified by HPAEC on an ION PAC II column, with a conductimetric detection (AS II DIONEX, Sunnyvale, U.S.) using an external calibration.[31] The separation was carried out at 20 °C at a flow rate of 1 mL/min, with a 0.01 mol/L NaOH. Total sulfate was determined after hydrolysis with 2 mol/L TFA (2 h, 120 °C) and the free sulfate was quantified after aq extraction (2 h, 25 °C). The esterified sulfate was estimated by difference between total and free sulfate.

The degree of acetylation (DS_{Ac}) of cellulose derivatives in the text refers to the molar ratio between acetic acid and total neutral sugars, and the degree of sulfation (DS_{Sulf}) refers to the molar ratio between sulfuric acid and total neutral sugars.

The viscosity-average degree of polymerization ($\overline{DP}_v$)of water-insoluble cellulose was determined from the values of intrinsic viscosities in cupriethylenediamine determined as previously described.[6] Reduced viscosity of water-soluble cellulose derivatives was determined with an Ubbelhode viscometer (diameter 0.52 mm, Viscologic TI.1 SEMATech, Nice-France). Six determinations were carried out at 25 °C for each dilution (1.5, 1.0, 0.75, 0.5, 0.38 and 0.25 mg/mL). Solutions were prepared in water or in 9:1 water–EtOH and were filtered (pore diameter 15 μm) before measurement.

Solubility was determined after dispersion of the sample (20 mg/2 mL) in water, mixtures water–EtOH (EtOH content: 0, 10, 25, 50, 70, 80, 90 and 100%, v/v) and a 5×10^{-3} mol/L NaCl aq solution. The dispersions were stirred during 16 h at 25 °C. Then, the dispersion was filtered (pore diameter 15 μm) and total neutral sugars were determined in the filtrate by the orcinol method[32] using D-glucose as standard.

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