Acidic Activation of Cellulose and Its Esterification by Long-Chain Fatty Acid

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ABSTRACT: Cellulose-enriched residues from wheat bran can be transformed in bioplastics after esterification of the cellulose by lauroyl chloride. Before the esterification reaction, an activation step with a swelling of the sample in dilute acid and subsequent drying was required. This activation had a marked influence on the amount of esterified product and its degree of substitution. Using pure cellulose as well as cellulose-enriched agricultural residues, we have shown that the cellulose was totally recovered after this pretreatment and that partial hydrolysis of cellulose chains occurred during the drying step, which probably improved the accessibility to chemical reagents. The possible role of sulfuric acid as catalyst for the esterification reaction of the cellulose by lauroyl chloride was discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1933–1940, 1999

Key words: wheat bran; cellulose; activation; degree of polymerization; esterification; lauroyl chloride; films

INTRODUCTION

Although plastics are vital to the economy and quality of life, their limited waste disposal issue has created the need for biodegradable plastics. To be used for this purpose, biopolymers must offer the same quality as synthetic plastics (barriers and mechanical properties, low cost, etc.).[1] Cellulose, which is the most abundant natural polymer, can form plastic after derivation. Long-chain fatty-acid esters of cellulose have been studied for their interesting filmogenic properties[2–5] and their biodegradability.[5]

Our preliminary studies have shown that it was possible to obtain cellulosic films from agricultural by-products, such as wheat bran, after extraction of heteroxylans. The cellulose-enriched residue can be esterified by lauroyl chloride and the esterified products have filmogenic properties.[6,7] We have used an acidic activation[6,7] prior to the esterification reaction to increase cellulose reactivity. In fact, alkaline activation[4,5] can be applied as well as acidic[2] pretreatment. Both have degradative effects on the cellulose chains. It is known that the alkaline activation, the so-called mercerization, increases the reactivity by a swelling effect and also decreases the crystallinity and the degree of polymerization of the cellulose.[8,9] Acidic activation has not been studied in detail; however, such treatment has been reported to facilitate enzymatic degradation, suggesting that the accessibility to cellulose is improved.[10]

We now report on the role of the acidic pretreatment, particularly its effect on the degree of polymerization, the nature of cellulose, and the

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yield of cellulose after esterification with lauroyl chloride. The results were compared to those obtained with the same samples (purified cellulose and cellulose-enriched wheat bran) activated by alkaline treatment.

EXPERIMENTAL

Materials

Destarched wheat bran and enriched-cellulose residue recovered after treatment of the bran with sulfuric acid (*R*ind) were provided by ARD (Pomacle, France). Cellulosic fiber plates (CF; Hexabio, Talence, France) were ground (Analysenmülhe A. 10, Ika Labortechnik, Staufen, Germany) before use. Cellulose Avicel PH-101 (CA) was purchased from Fluka (Saint Quentin, France) and lauroyl chloride was purchased from Aldrich Chemical Company (Saint Quentin, France) and used without further purification.

Preparation of the Cellulose-Enriched Residue

Delignification of Destarched Wheat Bran[11,12]

Destarched wheat bran (100 g) was stirred and heated in deionized water (1.5 L) until the temperature reached 70°C, then glacial acetic acid (18 mL) and sodium chlorite monohydrate (25 g) were added. After 1 h, the same amounts of acetic acid and sodium chloride were added and the mixture was stirred for 1 h. The residue was recovered by filtration (pore diameter, < 15 μm) and washed with water until washing water reached pH 5. The delignified residue was finally washed with 95% ethanol (3 times, 500 mL), then acetone (3 times, 500 mL), and dried in an oven at 40°C overnight. A dried residue of 79 g was recovered and ground (particle diameter, < 0.5 mm).

Alkaline Extraction of Heteroxylan[13]

Delignified residue (60 g) was stirred with 2 mol/L potassium hydroxide (600 mL) and sodium borohydride (0.02 mol/L) at 100°C for 2 h. The residue was recovered after centrifugation (15,000 g, 30 min) and washed with deionized water (3 times, 600 mL). The medium was adjusted to pH 6 with glacial acetic acid. The residue (*R*alk) was washed with 95% ethanol (3 times, 500 mL), then acetone (3 times, 500 mL), and dried in an oven at 40°C overnight. A dried residue of 13 g was recovered and ground (particle diameter, < 0.5 mm).

Determination of the pH of the Sample

The sample (100 mg) was stirred in deionized water (5 mL) for 16 h at room temperature; then the pH of the suspension was determined. The experiment was repeated two times for each sample.

Activation of Cellulose

Acidic Activation[2]

The sample (3 g) was immersed in 50 mL of a dilute solution of sulfuric acid of different concentrations (0.5, 0.75, and 1 mol/L) at room temperature for 1 min. After being drained on a filter (pore diameter, < 15 μm), the residue was dried at 40°C in an oven until the initial weight was recovered.

Alkaline Activation[5]

Fifty milliliters of 4 mol/L sodium hydroxide solution was cooled to about 10°C. Cellulose (10 g) was added slowly and the mixture was kept at about 10°C for 1 h. The suspension was poured into 2500 mL of an ice : water mixture (10 : 90) and kept at room temperature. After the ice melted, the cellulose was allowed to settle and the upper liquid was drawn off by siphoning. The cellulose solubilized in the supernatant was precipitated by the addition of 5% (v/v) acetic acid solution until the mixture reached pH 4, then cellulose was recovered by filtration and added to the rest of cellulose. Deionized water (3000 mL) was added to the cellulose, settling allowed, and upper liquid drawn off again. Then, 3000 mL of a 5% (v/v) acetic acid solution was added, allowed to settle for 15 min, and the upper liquid was drawn off. Finally, cellulose was washed with water until pH reached 4.5 and recovered by filtration (pore diameter, < 15 μm). The wet cellulose was finally washed with ethanol (3 times, 150 mL), then acetone (3 times, 150 mL), and dried in an oven at 40°C overnight, and in an oven under vacuum at 40°C for 24 h. An amount of 8.5 g of mercerized cellulose was recovered.

Chemical Modification[6,7]

The residue (3 g) was ground, then stirred with toluene (50 mL), lauroyl chloride (42 mL), and pyridine (15 mL) at 80°C for 5 h. Insoluble particles were removed by filtration and the ester was precipitated with 98% ethanol (100 mL) and recovered by filtration. The esterified material was dissolved in toluene and precipitated again with

98% ethanol (100 mL) to remove residual pyridine and lauroyl chloride. Cellulosic ester was then dissolved in chloroform or toluene and filmogenic properties were evaluated by visual inspection of the product obtained after evaporation at room temperature.

Chemical Composition of the Samples

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

Ash was measured after incinerating overnight at 500°C, then for 2 h at 900°C.

Sugar Composition

Individual neutral sugars were analyzed by gas–liquid chromatography (GLC)[14] after total hydrolysis and derivation of the monomers into alditol acetate. Cellulose-rich residues[7] were pre-hydrolyzed 2 h in 13 mol/L sulfuric acid at room temperature, then hydrolyzed 2 h in 2 mol/L sulfuric acid at 100°C. Cellulosic glucose was estimated by the difference between glucose content as measured by GLC with (total glucose) and without (noncellulosic glucose) pre-hydrolysis. Films (200 mg) were first de-esterified by stirring in 0.25 mol/L sodium hydroxide (10 mL) in 95% ethanol at 50°C during 16 h. The residue was recovered by centrifugation (2250 g, 40°C) for 30 min and washed with 98% ethanol (10 mL, 2 times) for 1 h at 60°C to remove any remaining traces of salt. The residue was then washed with deionized water (10 mL, 2 times) to remove any remaining trace of ethanol. The supernatants were recovered and ethanol was evaporated under vacuum at 40°C. Then both residue and supernatant were freeze-dried. Sugars were analyzed with (in the residue) or without pre-hydrolysis (in the supernatant) as already described.

Sulfate Content[15]

Sulfate was identified and quantified by HPAEC (High Performance Anion Exchange Chromatography) on an Ion Pac II column with a conductimetric detection (AS II Dionex, Sunnyvale, U.S.) against an external standard of sulfate. The separation was carried out at 20°C at a flow rate of 1 mL/min with a 0.01 mol/L sodium hydroxide solution. Total sulfate was determined after hydrolysis with 2 mol/L trifluoroacetic acid (2 h, 120°C), and free sulfate was quantified after aqueous extraction (2 h, 25°C). Bound sulfate was estimated by the difference between total and free sulfate.

Lauric Acid Determination

Lauric acid was released after saponification of cellulosic ester in a 0.25 mol/L sodium hydroxide, prepared in 95% ethanol for 16 h at 30°C. The excess sodium hydroxide was titrated with 0.1 mol/L hydrochloric acid and the amount of lauric acid was estimated by the difference between total and excess sodium hydroxide. A blank was prepared in the same conditions.

Degree of Substitution

The degree of substitution (DS) in the text refers to the molar ratio between lauric acid and total neutral sugar determined in the cellulosic film.

X-ray Diffraction

Samples (20 mg; water content, ~ 8%) were sealed between two kapton foils to prevent any significant change in water content during the measurement. Diffraction diagrams were recorded using a transmission technique with an XRG 3000 X-ray generator (Inel, Orléans, France) operating at 40 kV and 30 mA. CuK_α radiation (λ = 0.15405 nm) was selected using a quartz monochromator. A curved position-sensitive detector (CPS120 Inel) was used to monitor the diffracted intensities using 2 h exposure periods. All recorded diagrams were normalized at the same total scattering between 3 and 30° (2θ).

Degree of Polymerization

Viscosity-average degree of polymerization ($\overline{DPv}$) of the celluloses was determined from the values of intrinsic viscosities in an Ostwald viscosimeter (diameter: 0.46 mm; viscologic TI 1 SEMATech, Nice, France). Six determinations were realized at 25°C for each dilution (5.0, 3.3, 2.5, 1.7, 1.25, 0.8 mg/mL) of cellulosic solutions using 0.5 mol/L cupriethylenediamine, and the intrinsic viscosity was determined by extrapolation of the straight line of the reduced viscosity at zero concentration. The viscosity-average molar mass was determined by the Mark–Houwink–Sakurada relationship.[16,17]

$$[\eta] = 1.0110^{-4}\bar{M}v^{0.9}$$

RESULTS

Composition of the Initial Substrates

Two standards of cellulose were used and characterized (Table I). CA had short cellulose chains

Table I Composition (mg/g), Intrinsic Viscosity ([η], mL/g), and Degree of Polymerization ($\overline{DPv}$) of Cellulosic Substrates, Initially and After Acidic Activation

Substrate	Activation (mol/L)	Ara	Xyl	Glc	Ash	Bound Sulfate	[η][a]	$\overline{DPv}$
CA	no	0	2	974	0.0	0	119	200
	0.5 (H_2SO_4)	0	2	1021	0.7	14.5	115	200
	1.0 (H_2SO_4)	0	2	1015	1.1	61.1	113	200
CF	no	trace	200	748	0.0	0	1192	1590
	0.5 (H_2SO_4)	trace	202	770	1.3	50.9	206	270
	1.0 (H_2SO_4)	trace	197	836	1.5	87.9	166	220
*R*ind	no	15	69	372	5.0	0	328	440
	0.5 (H_2SO_4)	8	69	324	2.5	9.3	164	220
	1.0 (H_2SO_4)	7	44	315	4.1	12.6	184	240
*R*alk	no	62	149	634	25.0	0	863	1150
	0.5 (H_2SO_4)	66	120	658	1.7	38.9	841	1120
	1.0 (H_2SO_4)	61	118	633	2.3	145.7	145	190

[a] Intrinsic viscosity expressed in milliliters per gram of cellulose in the sample.

($\overline{DPv}$ = 200) as previously reported,[18] whereas CF had long cellulose chains ($\overline{DPv}$ = 1590). CA was almost pure cellulose since glucose constituted about 975 mg/g of the sample. CF was less pure, with glucose mainly from cellulose (750 mg/g), but also some xylose probably from contaminating xylan (200 mg/g).

The two cellulose-enriched residues *R*ind and *R*alk, obtained from wheat bran, were also characterized and their compositions (Table I) are similar to those previously reported.[7] Cellulose content was lower in *R*ind than in *R*alk (372 and 634 mg/g, respectively) because of the presence of a high amount of lignin in *R*ind (170 mg/g).[7] Some arabinoxylans were also present. However, the amount of cellulose in *R*ind was sufficient to obtain film after esterification.[7] The amount of ash was lower for *R*ind than for *R*alk (5 and 25 mg/g, respectively). The $\overline{DPv}$ of cellulose was much higher in *R*alk ($\overline{DPv}$ = 1150) than in *R*ind ($\overline{DPv}$ = 440); the degradation was probably lower in alkaline medium because of the addition of sodium borohydride, which prevented oxydative peeling.[13]

Four samples were therefore obtained with different cellulose chain lengths. Shorter chains (in CA and *R*ind) could be more accessible to lauroyl chloride during esterification; on the other hand, the properties of cellulosic films could be improved with higher cellulose chain length (in CF and *R*alk).

Composition of the Acid-Activated Celluloses

The neutral sugar composition of these samples have been determined after acidic activation (Table I). The composition of the samples are not markedly affected by the activation treatment. The slight increase in the glucose content (CA and CF) may be due to a more efficient determination of the cellulose content because of the acidic treatment and/or an overestimate glucose (CA). On the other hand, the low decrease (*R*ind) may be due to a loss of cellulose. In fact, glucose was not observed in the drained solution after activation, whatever sulfuric acid concentration used; however, a minute amount of arabinose and xylose (< 10 mg/g) was released from *R*ind and *R*alk. Therefore, the activated cellulose has a neutral sugar composition similar to the starting sample, and no loss of cellulose occurred during the activation step. After activation, the samples contained some ashes (between 0.7 and 1.5 for the standard cellulose and between 1.7 and 2.5 mg/g for *R*ind and *R*alk). The amount of ashes increased when the concentration of sulfuric acid increased.

The analysis showed that the activated samples contained free sulfate and also sulfate linked to the cellulose. The conditions of temperature and concentration (40°C, 0.5–1 mol/L) used for acid activation lead apparently to some esterification of cellulose by sulfuric acid; similar esterification has been reported during the acetylation of cellulose using sulfuric acid as catalyst.[19,20] The number of sulfate groups per anhydroglucose residue was more important for the cellulose with the highest DP; it also increased with the concentration of sulfuric acid used for the activation. It can be calculated that the degree of substitution of cellulose by sulfate group (without mention of

the other sugars) increased from 0.1 to 0.2 and 0.1 to 0.4 for CF and *R*alk, respectively, when sulfuric acid concentration increased from 0.5 to 1 mol/L. For CA and *R*ind, which had shorter cellulose chains in the starting sample, this amount was < 0.05 mol/L and also increased slightly with sulfuric acid concentration. However, CF and *R*alk also contained a high amount of xylose (200 and 149 mg/g, respectively) which could be esterified by sulfate group.

Physicochemical Characterization of the Activated Samples

The acidic pretreatment led to the hydrolysis of the cellulosic chains, but this hydrolysis depended on parameters like the crystallinity of cellulose. The $\overline{DPv}$ of samples activated with 1 mol/L sulfuric acid tend to reach 200 (220, 240, 190 for CF, *R*ind, and *R*alk, respectively), which is the $\overline{DPv}$ of CA. The $\overline{DPv}$ of CA did not decrease whatever the concentration of sulfuric acid used for activation. CA was highly crystalline as shown by its X-ray diffractograms. Sulfuric acid concentration and temperature were probably not high enough to hydrolyze such a crystalline cellulose. After activation with 0.5 mol/L sulfuric acid, the $\overline{DPv}$ of *R*ind was still close to 200, whereas $\overline{DPv}$ of CF was slightly > 200 (270), and highly above this value for *R*alk (1120). The pH of *R*alk in suspension in deionized water was 8.1 instead of about 6.8 for CF and 2.9 for *R*ind; therefore, sulfuric acid was probably neutralized by remaining alkali, due to insufficient washings; *R*alk was probably not activated with 0.5 mol/L sulfuric acid.

The acidic pretreatment, and more particularly the drying step, led to some hydrolysis of the cellulosic chains. It is unlikely that the immersion in sulfuric acid hydrolyzed the cellulosic chains because of the mild conditions (concentration: 0.5–1 mol/L; room temperature; time: 1 min) used for this step.[10] Degradation during the drying step is much more probable. The drying kinetics of CF after immersion in sulfuric acid is shown on Figure 1. Samples reached a constant weight after about 15 h, whereas $\overline{DPv}$ decreased to a constant value of about 270. At the very beginning of the kinetics, an increase of the $\overline{DPv}$ can be observed. Whatever the cellulose sample, analysis of the activated sample showed that $< 5\%$ (w/w) of the glucose became water soluble. All these results showed that activation of cellulose resulted in some hydrolysis of the cellulose chains without

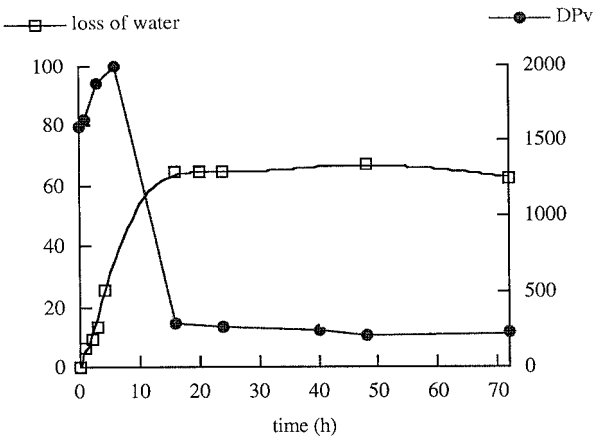

Figure 1 Kinetics of drying and $\overline{DPv}$ decrease at 40°C after immersion of CF in 0.5 mol/L sulfuric acid (25°C, 1 min).

significant production of cellodextrins. A similar decrease of $\overline{DPv}$ was observed during mercerization as previously reported[8]; $\overline{DPv}$ of 320 was determined for CF, a value only slightly above that for the acid-activated CF. So both acidic and alkaline activation led to a decrease in the cellulose chain length.

The crystallinity of native and activated samples was studied by X-ray diffraction (Fig. 2). CF was a type I cellulose with characteristic peaks at $2\theta = 14.8$, 16.6, and 22.7°; after acidic activation, a type I cellulose was still observed, whereas after mercerization, type II cellulose was observed with characteristic peaks at $2\theta = 12.2$, 20.0, and 21.8°. Both treatments led to a weak decrease in crystallinity, which is well known for mercerization.[8] For the other samples, the X-ray diffractograms did not show any change in crystallinity after activation treatment. CA was a highly crystalline type I cellulose, whereas the cellulose from wheat bran residues was highly amorphous even after acidic pretreatment. Generally, chemical treatment and high temperature increased the crystallinity of cellulose[21]; however, in our conditions, the temperature of drying was low (40°C), and only a slight decrease in crystallinity was observed.

Esterification of Activated Cellulose Samples

Amount of Esterified Product and DS

Four different samples (Table II) with different chain lengths or crystalline nature of the cellulose after activation treatment were selected. The amount of esterified product was higher in *R*ind

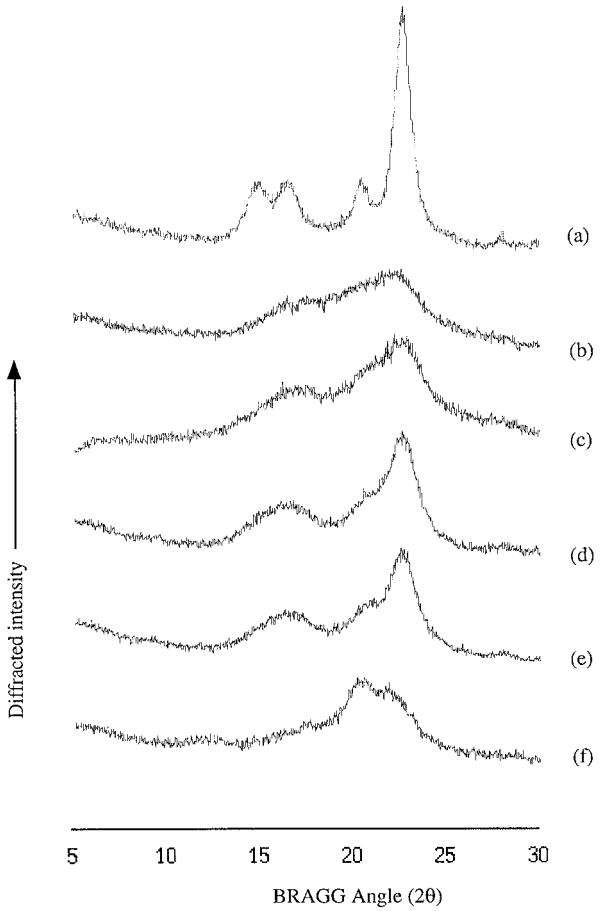

Figure 2 X-ray diffractograms of cellulosic samples. (a) Initially CA; (b) initially *R*ind; (c) initially *R*alk; (d) initially CF; (e) acid-activated CF (0.5 mol/L sulfuric acid); (f) alkaline-activated CF (4 mol/L sodium hydroxide).

than in *R*alk (0.75 and 0.66 g/g, respectively) (Table II), despite a lower cellulose content (372 and 634 mg/g, respectively) and a lower amount of sulfate linked to cellulose (9.3 and 38.9 mg/g, respectively) (Table I). It has been shown that after a pretreatment with 0.5 mol/L sulfuric acid, *R*alk had long cellulose chains. So, the hydrolysis of cellulose in chains with $\overline{DP}v \sim 200$ probably improved the accessibility of the cellulose chains to lauroyl chloride. The yield of recovered glucose was lower for CA ($\sim$ 68%) than for CF ($\sim$ 92%), but the amount of esterified products for CA was higher than for CF (2.79 and 1.93 g/g of initial sample, respectively) (Table II), which was explained by the higher DS obtained for CA (1.7) than for CF (1.2). The crystallinity of cellulose has therefore an important influence on the esterification step since the lengths of cellulose chains were similar. Furthermore, without acid activation or after mercerization, the amount of esterified product obtained for CF was < 0.3 g/g (0.28 g/g without any activation and 0.04 g/g after mercerization). Therefore, the reactivity might have been also improved by the presence of sulfate linked to cellulose chains.

The value of the DS depended on the nature of cellulose (Table II). Indeed, all the cellulose chains of CF were esterified by lauroyl chloride as shown by the yield of recovered cellulose (92%), but only the more reactive hydroxyl groups (probably the primary hydroxyl) were esterified (DS = 1.2). In contrast, crystalline cellulose (CA) exhibited lower cellulose recovery (65%) but higher DS.

Degradation of Cellulose

Three concentrations of sulfuric acid (0.5, 0.75, and 1.0 mol/L) were tested to activate CA. The amounts of ester and recovered cellulose and the degree of substitution (DS) were presented in Table II. The concentration of sulfuric acid used for the pretreatment had a great influence on the DS, which increased with acid concentration (1.7, 2.1, and 2.6 for 0.5, 0.75, and 1 mol/L, respectively). However, $\overline{DP}v$ of CA did not decrease after activation whatever the sulfuric acid concentration used. Reactivity of cellulose might have been improved by esterification of hydroxyl groups by sulfuric acid. In contrast, the optimal amount of recovered cellulose was obtained for 0.75 mol/L sulfuric acid (68%) and about 3 g of cellulosic ester were produced with 1 g of CA; how-

Table II Influence of Activation on the Yield in Esterified Product the Recovery in Cellulose and the Degree of Substitution (DS)

Substrate	H_2SO_4 (mol/L)	Yield in Ester[a] (g/g)	Recovery in Cellulose[b] (%)	DS
*R*ind	0.5	0.75	nd	nd
*R*alk	0.5	0.66	nd	nd
CF	0.5	1.93	91.8	1.2
CA	0.5	2.79	64.5	1.7
	0.75	3.12	67.9	2.1
	1.0	2.33	47.5	2.6

[a] Weight in grams of recovered esterified sample relative to 1 g of starting sample.
[b] 100 $\times$ (glucose in cellulosic film)/(glucose in initial sample).
nd, not determined.

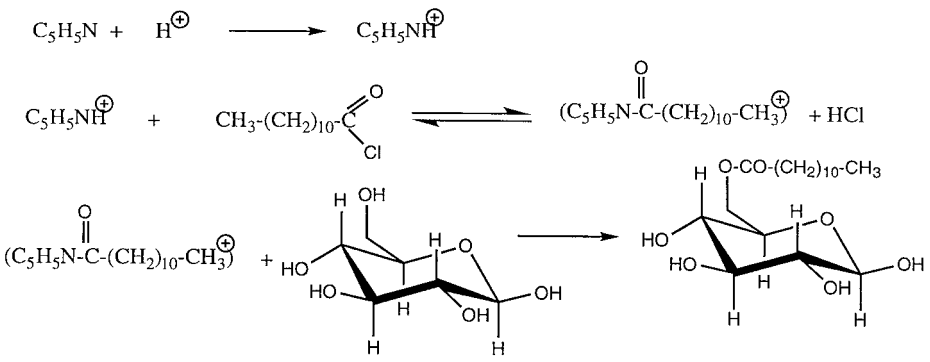

Figure 3 Proposed mechanism for esterification of activated cellulose by lauroyl chloride in the presence of sulfuric acid as catalyst.

ever, cellulose recovery decreased when sulfuric acid concentration was 1 mol/L.

Cellulose became more sensitive to degradation during the esterification when sulfuric acid concentration used for the activation increased. Both high temperature used for the esterification[22] and high sulfuric acid concentration were probably involved in the hydrolysis into small oligomers that were probably soluble in ethanol after esterification.

DISCUSSION

Four cellulosic samples were analyzed with different crystallinity, purity (37–97%), and chain length ($\overline{DPv}$ = 200–1500). The acidic activation did not significantly change the neutral sugar composition, but induced a swelling of the cellulose comparable to the effect of mercerization.[23] However, the concentration in acid and the subsequent drying at 40°C had a marked effect on the cellulose chain length. Sulfuric acid concentration increased during the drying step, leading to a partial hydrolysis of cellulose in shorten chains. Some esterification of cellulose by sulfuric acid also occurred. The reactivity of cellulose was probably improved by a swelling effect of the chains due to an ionic repulsion or by the presence of the bulky sulfate group that hampers the association between cellulose chains. It is likely that both esterification with sulfuric acid and partial hydrolysis of cellulose probably improved the accessibility to chemical reagent of cellulose, and, therefore, its reactivity.

The crystallinity of cellulose had also an important influence on the esterification by lauroyl chloride since the yield of recovered cellulose was higher for CF (92%), which is amorphous, than for CA (68%), which is highly crystalline.[24] In contrast, the DS was lower for CF than for CA. Both DS and chain length had a marked effect on the physical properties of cellulosic films[5] and biodegradability of cellulose esters.[25] Both alkaline and acidic activation led to a decrease in the crystallinity, but alkaline treatment also led to a change of crystalline type (cellulose II) that was used for cellulose ether production,[23] but seemed to be less reactive for cellulose ester production.

A degradation of cellulose occurred during esterification when sulfuric acid used for the acid activation was too concentrated; this degradation was probably due to the hydrolysis of cellulose. The optimal concentration of sulfuric acid has been shown, for crystalline cellulose, to be 0.75 mol/L.

Fritz and Shenk[26] have shown that acid catalysis occurred to a significant extent even in the presence of pyridine, which was present in a large excess over the sulfuric acid. Furthermore, pyridine was not an ideal catalyst.[27] Therefore, we suggest that sulfuric acid could catalyze the transformation of pyridine in a very reactive cation (Fig. 3), as already described for the acid-catalyzed acetylation of cellulose when sulfuric or perchloric acid was used. Pyridine might form a pyridinium salt with hydrochloric acid released by lauroyl chloride during esterification. This mechanism is further supported by the fact that alkaline activation, which also leads to a decrease in the degree of polymerization, gives a low amount of esterified product (0.04 g/g after alkaline activation, instead of 1.93 g/g after acid activation). However, Wang and Tao[4,5] have shown that it was possible to esterify cellulose with long-chain fatty acids without activation or after alka-

line activation with a large reaction time of 24 h, instead of 5 h in our procedure.

The physical properties of cellulosic films as well as their biodegradability will be investigated in further studies.

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