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Jérôme Peydecastaing, Samuel Girardeau, Carlos Vaca-Garcia,
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Jérôme Peydecastaing, Samuel Girardeau, Carlos Vaca-Garcia, Marie-Elisabeth Borredon. Long chain cellulose esters with very low DS obtained with non-acidic catalysts. *Cellulose*, 2006, 13 (1), pp.95-103. 10.1007/s10570-005-9012-5 . hal-02051301

HAL Id: hal-02051301

<https://hal.science/hal-02051301v1>

Submitted on 27 Feb 2019

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Peydecastaing, Jérôme  and Girardeau, Samuel  and Vaca-Garcia, Carlos  and Borredon, Marie-Elisabeth  *Long chain cellulose esters with very low DS obtained with non-acidic catalysts.* (2006) Cellulose, 13 (1). 95-103. ISSN 0969-0239

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Long chain cellulose esters with very low DS obtained with non-acidic catalysts

J. Peydecastaing*, S. Girardeau, C. Vaca-Garcia and M. E. Borredon

*Laboratoire de Chimie Agro-Industrielle, UMR 1010 INRA/INP-ENSIACET, Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, 118, route de Narbonne, Toulouse, 31077 Cedex 4, France; *Author for correspondence (e-mail: Jerome.Peydecastaing@ensiacet.fr; phone: +33-5-62885724; fax: +33-5-62885730)*

Key words: Cellulose esters, Emulsion, Fatty acids, Hydrophobicity, Solvent-free acylation

Abstract

Long-chain cellulose esters with very low degree of substitution ($DS < 0.3$), useful for specialty applications, were obtained by reaction with fatty acids (FAs) without solvent for cellulose. Non-acidic catalysts such as FA salts were used to limit the cellulose degradation when subjected to reaction at high temperatures. The surfactant character of this type of molecules was employed to create an emulsion with FA and water to favor the contact of hydrophobic FA and hydrophilic cellulose. Response surface methodology was used as a statistical optimization method to find the best proportions of octanoic acid, potassium laurate and water. A highly hydrophobic product with retention of fibrous structure was thus obtained. The reactions with higher saturated FAs (C_{10} – C_{18}) yielded lower DS values but still comparable hydrophobicity.

Introduction

Long-chain cellulose esters (LCCE) having a high degree of substitution (DS) have been widely studied, mainly due to their thermoplastic properties (Sealey et al. 1996; Jandura et al. 2000; Vaca-Garcia et al. 2003). Their preparation requires very reactive compounds to obtain high yields, by employing difficult synthesis procedures or a solvent for cellulose. All of them have been reviewed recently (Heinze and Liebert 2001). In contrast, LCCE with very low DS (< 0.3) synthesized without a cellulose solvent retain the fibrous structure of cellulose and permit them to acquire interesting properties such as water repellency (Vaca-Garcia and Borredon 1999), selective adsorption ability (Deschamps et al. 2003) or even modified gas permeability (Bras et al., personal communication).

The industrial utilization of LCCE with very low DS is still limited. Their development requires on the one hand, the understanding and the exploitation of these properties and, on the other hand, the setting up of synthesis techniques with low environmental impact.

Fatty acids (FA) are acylating agents that do not produce inconvenient by-products. However, under non-catalyzed conditions, their reactivity is extremely low towards cellulosic hydroxyl groups. The reported reactions of cellulose with FA make use of co-reagents to transform the carboxylic acids into more reactive entities: trifluoroacetic anhydride (TFAA; Arni et al. 1961), tosyl chloride (Shimizu and Hayashi 1989), mesyl chloride (Talaba et al. 1996) or dicyclohexylcarbodiimide and pyrrolidinopyridine (Samaranayake and Glasser 1993).

It was the purpose of the present research to propose a simple technique to obtain LCCE with very low DS by using FA without the use of toxic or expensive chemicals. We intended to obtain a fibrous product with low surface energy useful for specialty applications.

We propose the use of non-acidic catalysts, hydroxides and FA salts, to limit the degradation (depolymerization) of cellulose, to preserve as much as possible the fibrous structure of cellulose. Such catalysts have not been reported in the literature for LCCE synthesis.

Materials and methods

Materials

Reagent grade chemicals were purchased from Aldrich France and were used without further purification. Sigma France provided alpha-cellulose powder (4% pentosans, 7% water content, degree of polymerization 980).

Cellulose esters were prepared by two different techniques: the solvent exchange method and the emulsion method.

Solvent exchange method

Two grams (dry basis) of undried cellulose powder was stirred into 200 ml of deionized water for 15 min, then filtered over fritted glass. The swollen substrate was rinsed with ethanol then stirred twice in 100 ml of ethanol for 15 min and filtered each time. Then, the solid was rinsed with FA (the same FA used in the acylation reaction) at about 20 °C above the melting point of the FA, then stirred twice in 100 ml of FA for 15 min at the same temperature and filtered each time. The solvent-exchanged cellulose was mixed with 6.85 eq of FA/OH (36.5 g in the case of octanoic acid; OA) and 0.1 eq of catalyst/OH (quantities varied from 0.15 g to 1.18 g, according to catalyst). Water was distilled off at 130 °C for 30 min in a glass reactor equipped with mechanical stirring and a Dean–Stark distilling device. The water content of the reaction medium after this operation was verified to be lower than 0.1% (measured by Karl–Fisher titration). Acylation reaction was carried out at 195 °C for a certain time, up to 6 h in the same reactor after replacement of the distilling device by a reflux condenser.

At the end of the reaction and after cooling to about 80 °C, 150 ml of ethanol was added to recover the precipitable solubilized fraction. The solid was separated by filtration over fritted glass and purified by Soxhlet extraction with ethanol for 8 h. The purified product was then oven-dried at 105 °C for at least 24 h and to constant weight.

Emulsion method

A homogeneous mixture of OA (36.5 g, 6.85 eq/OH), FA salt (0.1 eq/OH, quantities varied from 0.15 g to 1.18 g according to catalyst), and 6 g of deionized water (9 eq/OH) was obtained by stirring in a homogenizer at 2000 rpm for 15 min at about 20 °C above the melting point of the FA. The emulsion was immediately poured over 2.0 g of undried cellulose powder for acylation reaction. Water was distilled off at 130 °C for 30 min in a glass reactor equipped with mechanical stirring and a Dean–Stark distilling device, to a content of 0.1%. The acylation reaction was carried out at 195 °C for a certain time, up to 6 h in the same reactor after replacement of the distilling device by a reflux condenser. At the end of the reaction, the cellulose ester was recovered as described in the solvent exchange method.

Degree of substitution

DS was determined by the traditional saponification method. A purified sample (0.5 g) was stirred for 30 min in 40 ml of aqueous ethanol (70%). After the addition of 20 ml of a 0.5 N NaOH aqueous solution, the stirring was continued for 48 h at 50 °C. The unreacted NaOH was back-titrated with 0.5 N aqueous HCl. The solid was recovered by filtration and thoroughly washed with deionized water and ethanol, then oven-dried at 50 °C for 48 h. The absence of ester functions in the saponified solid was confirmed by FT-IR spectroscopy. Ester content was calculated as:

$$EC(\%) = \frac{[(A - B) \times N_B - (D - C) \times N_A] \times M}{10 \times w}$$

where A and B represent the volumes (ml) of NaOH solution added to sample and blank, respectively, N_B and N_A are the respective normalities of NaOH and HCl solutions, D and C are

the respective volumes (ml) of HCl added to sample and blank, respectively, M is the molecular weight of the grafted acyl residue (127 for octanoyl) and w is the weight of the sample (dry basis, in g).

The degree of substitution was then calculated as:

$$DS = \frac{162 \times EC}{M \times 100 - EC \times (M - 1)}$$

where 162 is the molecular weight of anhydroglucose monomer.

Degree of polymerization

The cellulose esters were saponified in a mild condition (as in DS determination, above) to regenerate cellulose. The intrinsic viscosity (η) of diluted solutions of cellulose in cupriethylenediamine was measured at 25 °C with a capillary viscometer, according to the French AFNOR standard NF T 12-005. The degree of polymerization (DP) was calculated using the Mark–Houwink–Sakurada equation (Brandrup and Immergut 1975) which correlates η and the viscosimetric molecular weight (M_v) of cellulose:

$$DP = \frac{M_v}{162} = \frac{\left(\frac{\eta}{0.0133}\right)^{\frac{1}{0.905}}}{162}$$

where 0.0133 and 0.905 are the coefficients corresponding to the cupriethylenediamine system and η is expressed in ml/g. Blanks were also carried out to evaluate the reduction in DP due to the saponification. A decrease of 30% was detected and the measured values were thus corrected. Original α -cellulose showed a DP of 980.

Recovery yield

The recovery yield (RY) is defined as the ratio of the solid fraction to the theoretical total cellulose ester calculated from its DS. It is assumed that the DS of the non-precipitated part is the same as that of the precipitated fraction. The RY is calculated as:

$$RY(\%) = 100 \times \frac{W_p}{W_0 \times \frac{(162 + DS \times (M - 1))}{162}}$$

where W_0 is the weight of initial cellulose and W_p is the weight of purified product.

Optimization

The influence of the reaction parameters on the yield of the reaction were studied using response surface methodology (RSM) as a statistical optimization method, described elsewhere. A central composite design was used and both canonical analysis and discussion of the isoresponse curves were used for interpreting the results.

Contact angle

Disks (10 mm diam.) of the esterified products were obtained using a laboratory press (10 t) and a conventional pellet mold. Metal surfaces in contact with the sample were carefully cleaned to avoid contamination. A HPLC-quality water drop (2 μ l) was placed on the surface of the disk and the static contact angle was measured with a Digidrop apparatus (GBX Instruments, France), using the triple point calculation method. Three specimens were used for each sample.

Results and discussion

The natural incompatibility of FA and cellulose obliged us to use a compatibilization method to favor the reactivity between them. An adapted version of the well known solvent exchange technique was first used.

The first experiment, carried out without catalyst, resulted in no reaction. This confirmed that it is absolutely necessary to use a catalyst to achieve the acylation of cellulose by FA, even at very high temperatures (195 °C is the highest limit before important thermal degradation). We tested NaOH as a first non-acidic catalyst. It was added in ethanolic solution to ensure a better dispersion in the FA medium. Ethanol was rapidly eliminated from the reaction medium as the temperature inside the reactor increased. Partially esterified cellulose octanoates could thus be obtained (Table 1), demonstrating that an alkaline catalyst can be used for the esterification of cellulose by FA. A relatively low catalyst concentration (0.02 eq/OH) was sufficient to attain a plateau in DS. Higher concentrations of catalyst increased to some extent the biopolymer degradation, determined by diminution of the recovery yield. Indeed, the oligomers with low DP cannot be precipitated at the end of reaction and remain in the liquid phase (Vacagarcia and Borredon 1999).

Table 1. Influence of the amount of NaOH catalyst on the DS and the RY of acylated cellulose with OA (2 g solvent-exchanged cellulose, 36.5 g OA (6.85 eq/OH), 3 h, 195 °C). Experimental uncertainty: DS = ± 0.02 ; RY = $\pm 2\%$.

NaOH (eq/OH)	DS	RY (%)	θ (°)
0	0	97	0
10^{-4}	0.06	97	72
10^{-3}	0.08	97	83
2×10^{-2}	0.12	93	71
4×10^{-2}	0.10	93	68
10^{-1}	0.10	91	87

Under the high temperatures of this reaction, NaOH easily reacts with OA to yield sodium salt octanoate and water molecules, rapidly evacuated from the system due to the high temperature. We can presume that using NaOH in the presence of a FA may be equivalent to using the sodium salt of the FA. Based on this assumption, we tested the sodium and potassium salts of lauric acid as catalysts to evaluate their performance. Results presented in Table 2 demonstrate that the selected FA salts are even more efficient for this esterification reaction than NaOH. NaOH and sodium laurate gave nearly the same results. These results are consistent with the hypothesis of equivalence between the hydroxide and the corresponding fatty salt, as far as DS is concerned. Moreover, potassium laurate (KL) yielded higher DS and RY values than sodium laurate, indicating that the contra-ion may play an important role. Indeed, the O–K bond formed with the acyl group has a weaker ionic character than the O–Na bond and

therefore the acyl carbon of the salt becomes more positively charged. This situation favors the nucleophilic attack of the cellulosic hydroxyl group over the C=O carbon. The esterification reaction is thus more efficient with a potassium salt than with a sodium salt. In this work, we limited our studies to Na and K in order to avoid heavier ions that are not interesting for an environmentally friendly method.

As an alternative to the solvent-exchange method, we used emulsions to improve the compatibility between the hydrophobic fatty reagent and the hydrophilic cellulose fibers. An advantage of this approach is that the FA salt plays both roles: surfactant and catalyst of the reaction. The results presented in Table 3 show that the replacement of solvent exchange with the emulsion pretreatment led to similar DS and RY values. The experiment carried out without any pretreatment confirmed that the fatty esterification reaction cannot take place significantly if cellulose fibers are not previously swollen.

The optimum composition of the emulsion was determined by using response surface methodology. The effects of the concentration of OA, KL and water (W) on the efficiency of the esterification reaction were studied. A central composite experimental design was used to evaluate their influence on the DS and on the degradation of the polymer (evaluated through RY). Preliminary experiments suggested confining the experimental domain to the following range: OA = 5–15 eq/OH, KL = 0.01–1 eq/OH and W = 4–20 eq/OH. The

Table 2. Comparison of the effect of three catalysts on the DS and RY of cellulose octanoate (2 g solvent-exchanged cellulose, 36.5 g OA (6.85 eq/OH), 6 h, 195 °C).

Catalyst (eq/OH)	DS			RY (%)		
	NaOH	Na laurate	KL	NaOH	Na laurate	KL
10^{-4}	0.15	0.16	0.17	90	88	92
4×10^{-2}	0.18	0.18	0.28	86	86	92
10^{-1}	0.23	0.22	0.25	86	85	92

Table 3. Effect of cellulose pretreatment on the esterification efficiency of cellulose (2 g cellulose, 36.5 g OA (6.85 eq/OH), 3.5 g KL (10^{-1} eq/OH), 6 h, 195 °C).

Pre-treatment	DS	RY (%)	θ (°)
None	0.02	94	65
Solvent-exchanged	0.25	92	71
Emulsion ^a	0.22	92	91

^a[water] = 9 eq/OH.

matrix of experiments and results is presented in Table 4. The test at the center of the experimental domain (OA = 10 eq/OH, KL = 0.5 eq/OH, W = 12 eq/OH) was replicated three times to estimate the experimental uncertainty σ_e^2 . The average value of these experiences was used to extend the model matrix (X) up to nine experiments at the center of the experimental domain. Thanks to this mathematical method, the dispersion matrix $({}^tX \cdot X)^{-1}$ can better approach orthogonality and therefore minimize covariance in the multilinear regression as described elsewhere. The coefficients of the second-order equation obtained for each response are presented in Table 5.

Comparison of the coefficients against uncertainty allows the following remarks. OA and KL concentrations are the main influent factors that determine DS. However, the cellulose degradation, indirectly represented by the RY parameter, also depends on the W concentration, which seems reasonable.

The canonical analysis of the second-order equations showed that the optimum conditions regarding to DS were: (OA = 10 eq/OH,

KL = 0.01 eq/OH, W = 3.6 eq/OH). Figure 1 was plotted for a concentration of OA = 10 eq. It can be seen that by choosing the concentration of KL and water to their minimum values, a DS of 0.2 can be obtained.

The isoresponse curves of RY were plotted with the optimum acid concentration, i.e., 10 eq/OH (Figure 2). The highest values of RY are obtained for various combinations of water and catalyst concentration values. Even though the best RY (92%) is obtained at 20 eq/OH and 1 eq/OH, it would be preferable to work with the one that leads to the highest DS-value, i.e., 3.6 eq/OH and 0.01 eq/OH respectively, since the RY is not significantly different (90%).

After determining the best conditions of the reaction permitting the acquisition of optimal DS with a minimum degradation ([OA] = 10 eq/OH, [catalyst] = 0.01 eq/OH, [water] = 3.6 eq/OH). We studied the grafting of fatty chains onto cellulose and the degradation of this polymer along with the reaction time. The results are presented in Figure 3. The biggest DS value was obtained after 6 h of reaction; and a plateau is reached after this

Table 4. Experimental design for the esterification of cellulose with OA using the emulsion method as pretreatment. Values are given for degree of substitution and recovery yield obtained.

OA (X_1 ; eq/OH)	KL (X_2 ; eq/OH)	Water (X_3 ; eq/OH)	DS	RY (%)	θ (°)
7 (-1) ^a	0.2 (-1) ^a	7 (-1) ^a	0.21	86	83
13 (+1)	0.2 (-1)	7 (-1)	0.16	97	82
7 (-1)	0.8 (+1)	7 (-1)	0.14	81	71
13 (+1)	0.8 (+1)	7 (-1)	0.07	96	70
7 (-1)	0.2 (-1)	17 (+1)	0.11	92	93
13 (+1)	0.2 (-1)	17 (+1)	0.13	89	67
7 (-1)	0.8 (+1)	17 (+1)	0.09	90	70
13 (+1)	0.8 (+1)	17 (+1)	0.07	98	71
5 (-1.682)	0.5 (0)	12 (0)	0.11	95	69
15 (+1.682)	0.5 (0)	12 (0)	0.09	96	60
10 (0)	0.01 (-1.682)	12 (0)	0.18	93	73
10 (0)	1 (+1.682)	12 (0)	0.17	90	75
10 (0)	0.5 (0)	3.6 (-1.682)	0.15	89	80
10 (0)	0.5 (0)	20.4 (+1.682)	0.20	92	83
10 (0)	0.5 (0)	12 (0)	0.15	93	87
10 (0)	0.5 (0)	12 (0)	0.19	92	75
10 (0)	0.5 (0)	12 (0)	0.13	92	73
10 (0)	0.5 (0)	12 (0)	0.16	92	78
10 (0)	0.5 (0)	12 (0)	0.16	92	78
10 (0)	0.5 (0)	12 (0)	0.16	92	78
10 (0)	0.5 (0)	12 (0)	0.16	92	78
10 (0)	0.5 (0)	12 (0)	0.16	92	78
10 (0)	0.5 (0)	12 (0)	0.16	92	78

^aThe figures in brackets correspond to the normalized variables X_i .

Table 5. Coefficients of the second order polynomial model $Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j$ for DS and RY.

	Coefficient $\pm \sigma_\beta$	
	DS	RY
β_0	0.159 ± 0.010	92.14 ± 0.71
β_1	-0.011 ± 0.008	2.39 ± 0.58
β_2	-0.019 ± 0.008	-0.30 ± 0.58
β_3	-0.007 ± 0.008	1.03 ± 0.58
β_{12}	-0.008 ± 0.011	1.88 ± 0.76
β_{13}	0.015 ± 0.011	-2.63 ± 0.76
β_{23}	0.010 ± 0.011	1.63 ± 0.76
β_{11}	-0.026 ± 0.007	0.91 ± 0.54
β_{22}	0.000 ± 0.007	-0.51 ± 0.54
β_{33}	0.000 ± 0.007	-0.86 ± 0.54
F test	90%	80%

Model confidence level: $F_{6,2}$. The variance of the coefficients estimation σ_β^2 was evaluated with: $\sigma_\beta^2 = \sigma_c^2 ({}^t X \cdot X)^{-1}$.

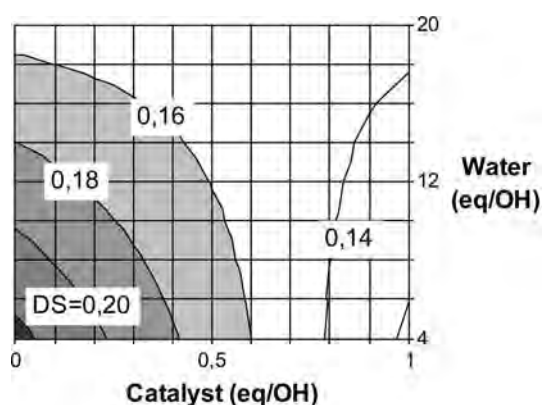


Figure 1. Isoresponse curves for the degree of substitution (DS) of the cellulose ester after acylation (6 h, 195 °C) with OA (emulsion method) as a function of the amount of catalyst and water (OA = 10 eq/OH).

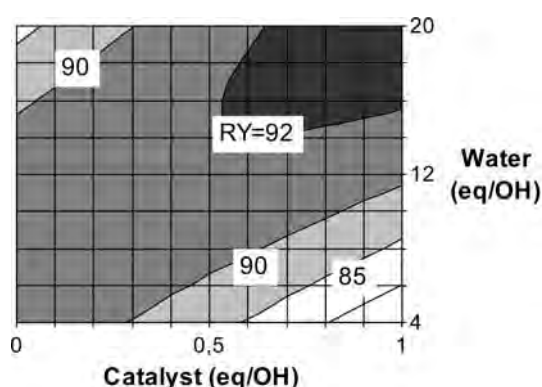


Figure 2. Isoresponse curves for the recovery yield (RY%) of the cellulose ester after acylation (6 h, 195 °C) with OA (emulsion method) as a function of the amount of catalyst and water (OA = 10 eq/OH).

time. As occurs in most esterification reactions of cellulose, a relatively important depolymerization (low RY and DP values) was observed. After the first hour of reaction, the average DP of the precipitated polymer decreased markedly, reaching a third of its initial value after 3 h of reaction, as occurs in classic esterification reactions of cellulose, such as acetylation.

We studied the performance of other basic catalysts using the optimized conditions above. Results are presented in Table 6. As observed before, all the potassium salts were more efficient than the sodium salts. Again, the hydroxide was equivalent to the corresponding fatty salt. Moreover, the length of the aliphatic chain of the catalyst had no significant influence on the efficiency of the acylation reaction. These surprising facts may be explained through the mechanism scheme shown in Figure 4. The aliphatic chain of the catalyst is first grafted to the cellulosic polymer. A hydroxide is then liberated and reacts immediately with a FA from the reaction medium and forms the corresponding FA salt. After this initial step, the new salt formed provides the way to graft the FA from the reaction medium and to regenerate a salt molecule at each step. If this hypothesis is true, the initial aliphatic chain belonging to the catalyst (laurate in this case) must also be grafted onto cellulose. This could be verified by hydrolysis of the purified cellulose ester product and consequent chromatographic analysis of the hydrolysate after conversion of the free FA salts into methyl esters. The peak of methyl laurate was observed when analyzing a sample of cellulose octanoate obtained using KL as catalyst.

As a conclusion, what we called a catalyst (KL) seems to act in reality as an initiator of the esterification reaction. Properly speaking, the actual catalyst should be the salt formed after the initial step (potassium octanoate), which was formed from the reaction medium.

Reactions with other FAs

Some linear saturated and unsaturated FAs usually derived from vegetable oil and fats (Table 7) were tested as reagents. As expected, the DS decreased when the number of carbon atoms (n) of the FA increased. Steric hindrance is more significant with long FAs.

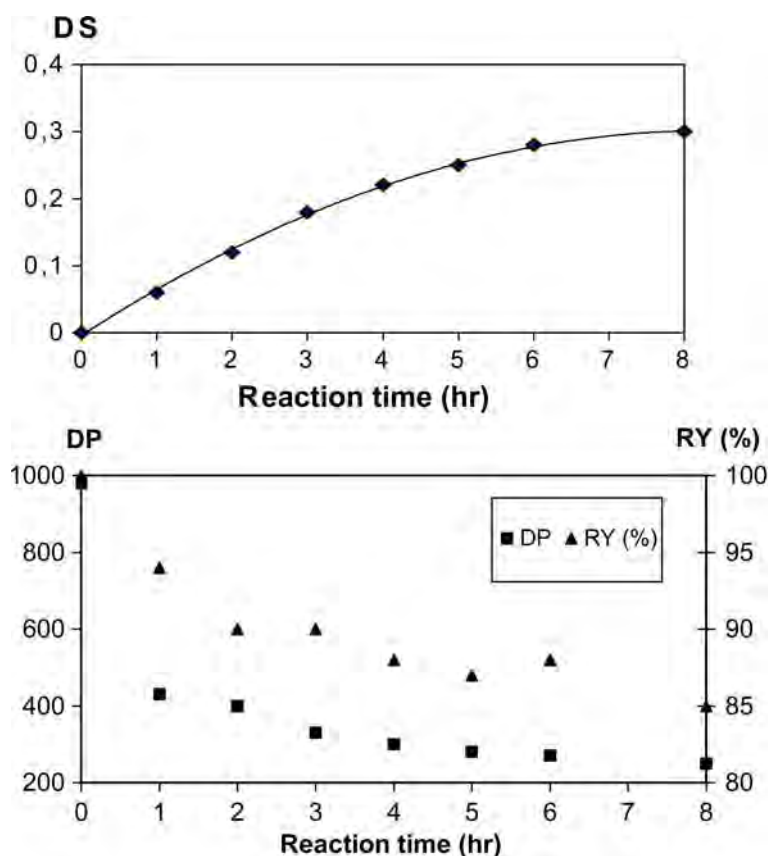


Figure 3. Evolution of the DS, the DP and the recovery yield with time for the cellulose esterification with OA ([OA]=10 eq/OH, [KL]= 10^{-2} eq/OH, [water]=3.6 eq/OH).

Table 6. Influence of the nature of the catalyst on the esterification of cellulose with OA, using the emulsion method (OA = 53.4 g; 10 eq/OH), catalyst = 3.5 g (10^{-2} eq/OH) in the case of KL and W = 2.4 g (3.6 eq/OH).

Catalyst	DS	RY (%)	θ (°)
KL	0.28	88	79
Na laurate	0.23	85	90
K stearate	0.26	85	91
Na stearate	0.20	92	73
Na acetate	0.22	88	77
NaOH	0.24	85	90
KOH	0.27	87	89
K ₂ CO ₃	0.19	86	74

Hydrophobicity

Finally, we observed the change in the surface energy of all the esterified products by measuring their static contact angle with water. Unmodified cellulose absorbed water immediately, whereas all

the esterified samples presented water repellence. Contact angles were observed to be higher at initial time, i.e., when the drop of water was put on the surface of the disk. The value of the angle decreased rapidly and reached a constant value. We considered the angle values at equilibrium after 5 min. Samples with DS superior to 0.05 presented contact angle values ranging from 60° to 90°. Results are presented in Tables 1, 3, 4, 6 and 7. From the comparison in each table and for the samples altogether, it was clear that there was no correlation between the contact angle and the DS or between contact angle and the fatty chain length grafted. This may be due to the low variation in DS values and to the heterogeneity of grafting. The latter is known to occur when solid cellulose is made to react with liquid reagents in the absence of a cellulose solvent. Esterification yield is normally higher on the surface of cellulose fibers than in their core (which accounts for the high hydrophobicity),

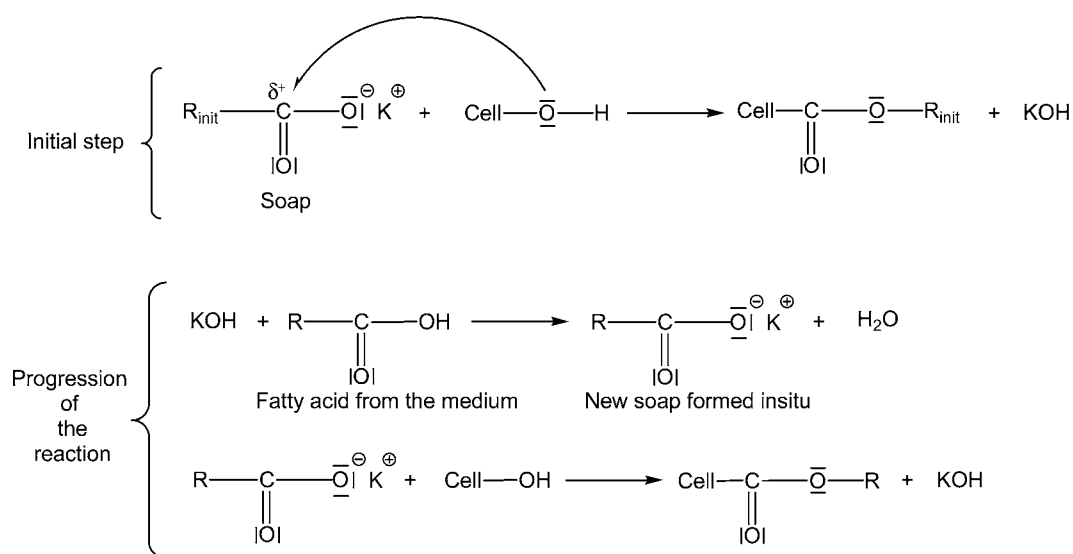


Figure 4. Proposed mechanism for the cellulose acylation by a FA in the presence of a FA salt.

Table 7. Effect of the nature of the FA on the acylation of cellulose (emulsion method). FA = 53.4 g in the case of OA (10 eq/OH), KL = 3.5 g (10⁻² eq/OH) and water = 2.4 g (3.6 eq/OH).

FA	<i>n</i> ^a	DS	RY (%)	<i>θ</i> (°)
Octanoic/Caprylic	8	0.28	88	79
Decanoic/Capric	10	0.24	85	87
Dodecanoic/Lauric	12	0.20	85	89
Tetradecanoic/Myristic	14	0.14	80	65
Hexadecanoic/Palmitic	16	0.12	78	70
Octadecanoic/Stearic	18	0.10	77	78
Oleic	18:1 ^b	0.10	80	62

^aNumber of carbons in the aliphatic chain.

^bUnsaturated FA.

but it is impossible to control the DS distribution when applying the acylation conditions in heterogeneous reaction medium as we did in our case.

Conclusions

The esterification of cellulose with a FA was possible with a FA salt yielding very low DS (< 0.30) with high recovery yield in a 6 h reaction at 195 °C. Potassium salts were more efficient than sodium salts. Carboxylic salts play the role of initiators of the reaction and rapidly generate another FA salt out of the reaction medium, which acts as the real catalyst. This reveals a new mechanism for cellulose esterification with FAs. The results obtained with a FA salt are equivalent

to those obtained with the corresponding hydroxide, as far as degree of substitution and depolymerization are concerned. The advantage of using the salt is that it allows the preparation of an emulsion before the reaction, which may favor impregnation of the cellulose fibers and avoid the solvent exchange pretreatment.

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