



Linters Cellulose: Characterization and Acetylation in N,n-dimethylacetamide/Lithium Chloride

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Abstract: Different celluloses exhibit differences with respect to dissolution and the trend towards aggregation (irreversible) and/or association (reversible) of their polymer chains in solution. Such variations may influence the degree of substitution of a derivative synthesized in homogeneous medium. Thus, each type of cellulose must be studied in detail to discover the best conditions, not only to maximize its solubility but also to optimize the synthesis of products. In the present work, before derivatization the linters cellulose was submitted to mercerization and the fibers were characterized by Scanning Electron Microscopy, X-ray diffraction, viscosimetry and α -cellulose content. It was shown that the treatments induced small changes in the cellulose. The acetylation degree of these fibres was found to follow a linear behavior with the stoichiometry between acetic anhydride and glucose unit, but this linearity obeyed high rate up to a DS of 2.0.

Keywords: linters cellulose, cellulose acetate, DMAc/LiCl, mercerization

Introduction

Generally, the solubility of cellulose depends strongly on its molecular weight and degree of crystallinity(1) and it is necessary to explore separately the conditions of solubility for cellulosic material from each source(2,3,4,5). In fact, different celluloses exhibit differences with respect to dissolution and the trend towards aggregation (irreversible) and/or association (reversible) of their polymer chains that may occur in solution. Such variations may influence the degree of substitution of a derivative whose synthesis involves making a solution of cellulose first, that is a derivative prepared in homogeneous medium. Thus, each type of cellulose must be studied in detail to discover the best conditions, not only to maximize its solubility but also to optimize the synthesis of products.

For instance, the cellulose from cotton linters used in this study is very pure, with a high degree of crystalline order, so that the polymer chains are closely packed and do not dissolve in DMAc/LiCl, unless the linters are first mercerized with alkaline solution (6), as described later.

As already mentioned, the properties of the linters cellulose have an influence on its solubility in DMAc/LiCl and hence on the properties of the derivatives made by modifying the polysaccharide in this medium. Moreover, various reaction conditions should be tested, to discover the best conditions for each cellulose-solvent-reagent combination. In the work reported here, linters cellulose mercerized was investigated in detail, and the conditions of acetylation, such as the time of reaction and molar ratio of the reagent to the anhydroglucose unit, were varied in an attempt to optimize the synthesis of linters cellulose acetate.

Experimental

The cellulose used as raw material here was cotton linters, kindly provided by Indústria Fibra S/A, Americana, SP, Brazil. Cellulose from linters was mercerized in 10, 20, 30 and 40% NaOH solution (material : liquor ratio 1:50 w/w) at 0°C for 1.0 h(7).

Cellulose characterization

The cellulose samples were characterized considering the crystallinity index, I_c , by X-ray diffraction(7), degree of polymerization, DP, by viscosimetric methods(8) and α -cellulose content(9).

Solubilization and acetylation of linters in DMAc/LiCl

The dissolution and derivatizing steps were carried out based on Edgar et al.(10) procedure, with some modifications, using 2.0 g of cellulose, 100 mL of DMAc, 6.0 g LiCl. The molar ratio of acetic anhydride to anhydrous glucose unit (AGU) of celluloses and reactional time are showed in Table 2. Degree of substitution of the acetates, DS, was determined by $^1\text{H NMR}$ (10).

Results

Characterization of cellulose

The surface of mercerized linters is smoother than that of untreated linters, which indicates that there are no fragments stuck

to the fibers, suggesting that such fragments have been eliminated during the mercerization procedure (figures not shown).

During the treatments, cellulose chains can be degraded by the hydrolysis of the glycosidic bonds, resulting in a reduced degree of polymerization. This hypothesis was not observed in our case, since even at the highest concentrations of NaOH (30 and 40%), this degradation was very mild (DP = 407 and 405, respectively), as summarized in Table 1, which presents the data obtained from the characterization of cellulose. This could be attributed to the mild conditions used in this study, namely: low temperature (0°C) and short treatment time (1.0 h) of the mercerization.

Regarding to crystallinity index, it decreased around 10% with increase of NaOH concentration and this is due to lower crystallinity of cellulose II (after mercerization) comparing with cellulose I (linters – before mercerization).

Table 1 shows small changes in the alpha-cellulose content because linters is already a pure material before its treatment with NaOH solution.

Table 1. Degree of polymerization (DP), crystallinity index (Ic) and alpha-cellulose content (α -cell) of untreated and treated linters celluloses

Cellulose	DP	Ic (%)	α -cell(%)
linters	414	79	92
10% NaOH mercerized linters	414	67	93
20% NaOH mercerized linters	408	72	94
30% NaOH mercerized linters	407	69	94
40% NaOH mercerized linters	405	69	93

Characterization of cellulose acetates

The concentration of NaOH used for mercerization was varied over the range 10%-40% (acetates 1-4, Table 2), with the aim of evaluating its effect on the separation of bundles of cellulose fibers, which in turn might influence the solubility in DMAc/LiCl and thus the amount of aggregation and the DS of the acetates synthesized. The working hypothesis before this experiment was that a higher concentration of alkali would lead to greater penetration between polysaccharide chains, increasing their separation and reducing their packing efficiency. As a consequence, this would facilitate the dissolution of the cellulose in DMAc/LiCl and promoting a lower degree of aggregation in solution, which would probably be reflected in higher DS values and more uniform acetylation, as more of the hydroxyl groups would be available for reaction.

However, the experimental results of mercerization at 0°C, presented in Table 2 (acetates 1 to 4), show that while raising the strength of the alkaline solution does lead to looser bundles, allowing fibers to move further apart, as it was showed by SEM images (figures not shown) it has no effect on cellulose solubility and, consequently, none on the acetylation step that follows; i.e., DS values of acetates derived from cellulose samples mercerized at different NaOH concentrations are near the same (Table 2). The other experiments described in Table 2 were then carried out in an attempt to find the best reaction conditions for the synthesis of cellulose acetates from linters, the target being the stoichiometric DS of 3.0 substituents per AGU. It should be stressed that many of the reactions were carried out in duplicate, to verify the reproducibility of results. The divergence was always very small (around 4%), implying low error levels in the data reported below.

The time of acetylation was increased stepwise from 1.0 to 5.5 hours. In Table 2 (acetates 2, 5, 6 and 7), it can be seen that this did not raise the DS, which remained near 1.9 for each of the 4 reaction times. Therefore, the DS attained in acetates produced from linters cannot be altered significantly either by pretreatment of the cellulose or by varying the reaction time.

In view of the importance of stoichiometric control of the reaction, it was investigated the relation between the number of moles of Ac₂O per AGU in the initial solution in DMAc/LiCl and the DS of the acetate produced (acetates 8-13). The reaction time was 1.0 h (Table 2 and Figure 1).

Table 2. Reaction conditions and degree of substitution of cellulose acetates

Acetate	Cellulose	Acetylation time (h)	Molar ratio Ac ₂ O : AGU	Degree of substitution (DS)	
1	mercerized in 10% NaOH	1.0	3.0	1.9	
2	mercerized in 20% NaOH			1.9	
3	mercerized in 30% NaOH			1.8	
4	mercerized in 40% NaOH			1.9	
5	mercerized in 20% NaOH	2.5	1.5	1.9	
6		4.0		1.9	
7		5.5		1.9	
8		1.0		2.0	0.6
9		2.5		1.1	
10		2.8		1.2	
11		4.5		1.3	
12	6.0	2.1			
13			2.2		

It can be seen in Figure 1 that for products with DS values from 0.6 to about 1.9, there is an approximately linear

relation between DS and the molar ratio of reactants Ac₂O:AGU (which ranges from 1.5 to 3.0). The significance of this relation is that it can be used to achieve a desired DS in the acetylation of linters cellulose in DMAc/LiCl. Moreover, products with any DS from 0.5 to 2.0 and the acetate groups spread uniformly along the chain can be made in this way; such control over this range would be hard to obtain in the heterogeneous reactions used on the industrial scale.

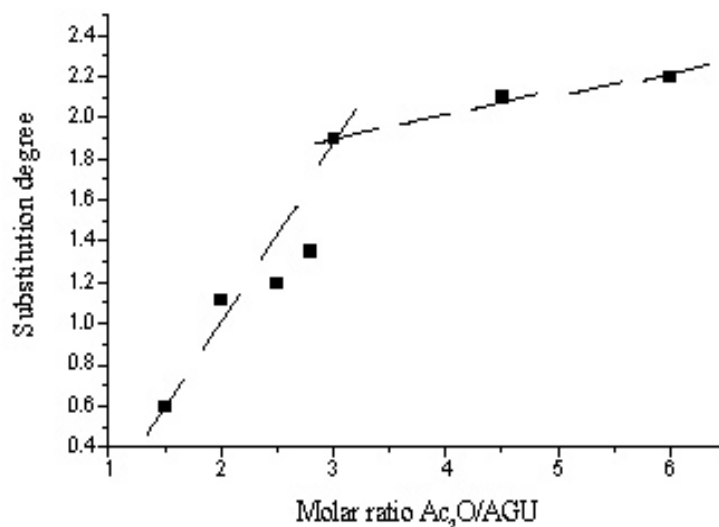


Figure 1. DS of cellulose acetate as a function of molar ratio of acetic anhydride to AGU. Linters mercerized in 20% NaOH reacted with Ac₂O in DMAc/LiCl solvent for 1.0h at 110°C

When the reactant ratio is above 3.0, yielding acetates of DS exceeding about 2, the gradient of the data line in Figure 1 falls sharply and DS rises very little with additional Ac₂O. In any event, when the desired DS is near 3, the heterogeneous reaction is normally adequate, since problems relating to the uniformity of substitution are less severe or absent when few -OH groups remain.

The fact that substitution was incomplete under the present conditions, even when a large excess of Ac₂O was used, may indicate that the accessibility of some hydroxyl groups to attack by the reagent was hindered by aggregation or association of cellulose chains. Such interactions between the dissolved chains could be intermolecular hydrogen bonds, either present in the original fibers and left intact by the solvent or formed during solubilization in DMAc/LiCl.

Another possibility is that some of the ester formed (and indeed the anhydride reagent) may be hydrolyzed, lowering the maximum DS that can be attained, since it is virtually impossible to eliminate all water from the reaction mixture, given that cellulose and the other ingredients are very hygroscopic. Evidence that water in the medium can influence the DS of cellulose acetate was obtained in parallel work (to be published soon), in which linters were acetylated in another solvent system: dimethyl sulfoxide / tetrabutylammonium fluoride trihydrate (DMSO/TBAF.3H₂O). Owing to the water of hydration in the salt, a much greater quantity of Ac₂O was needed to obtain a given DS than in the DMAc/LiCl solvent.

Conclusion

In the present work, the acetylation of a cellulose obtained from a rapidly - growing source (cotton linters), in the solvent system DMAc/LiCl, has been thoroughly investigated. It was shown that the reaction can be controlled, with excellent reproducibility, this factor being of fundamental importance for eventual large-scale application.

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