Available online at www.sciencedirect.com

SCIENCE DIRECT®

Bioresource Technology 97 (2006) 1696–1702

BIORESOURCE TECHNOLOGY

Cellulose acetates from linters and sisal: Correlation between synthesis conditions in DMAc/LiCl and product properties

Beatriz A.P. Ass, Gabriela T. Ciacco, Elisabete Frollini *

Instituto de Química de São Carlos, Universidade de São Paulo, C.P. 780, CEP 13560-970, São Carlos, SP, Brazil

Received 26 April 2004; received in revised form 6 September 2005; accepted 1 October 2005
Available online 28 November 2005

Abstract

We report the acetylation of celluloses from sisal (untreated and alkali treated) and cotton linters (alkali treated), under homogeneous solution conditions, using DMAc/LiCl as solvent system. Our target was to evaluate the effects of cellulose dissolution and reactions conditions on the product properties. The products were characterized in terms of degree of substitution (DS) by ^{1}H NMR, and molar weight distribution (MWD) by size exclusion chromatography. Changes in the DS of the products were correlated with reaction conditions and solution properties. It was found that the dissolution of celluloses and degree of substitution of cellulose derivatives depends on a fine adjustment of the dissolution/derivatization conditions, as well as on the origin (sisal or linters) of celluloses.

Keywords: Linters; Sisal; Cellulose; Cellulose acetate; DMAc/LiCl; Size exclusion chromatography (SEC)

1. Introduction

Cellulose derivatives, as esters, are produced industrially in a heterogeneous medium. In this two-phase medium, in which the macromolecule is suspended in a reagent solution, the amorphous part of the cellulose reacts first, and next the crystallites. Hence, at intermediate steps of the reaction, the cellulose exhibits block substitution, that is, highly-substituted regions alongside non-substituted regions. A consequence of this is that it is difficult to control the process. The use of homogeneous processes for industrial-scale derivatization of cellulose is one of the possible solutions to this problem (Nelson and Oliver, 1971; Nevell and Zeronian, 1985; Toyoshima, 1993).

Due to the complex morphology of the crystalline and amorphous regions and to the inter- and intramolecular hydrogen bonds, cellulose is not soluble in conventional solvents. Therefore, special solvents are required to process fibers or films, as well as in the controlled synthesis of cellulose derivatives under homogeneous conditions (Morgenstern and Kammer, 1996). The dissolution of cellulose and its derivatives rarely leads to complete dispersion of the polymer chains, owing to the strong tendency of cellulose to form hydrogen bonds (Morgenstern and Kammer, 1999; El Seoud et al., 2000; Schulz et al., 2000). These interactions between chains are conducive to aggregation (irreversible process) or association (reversible).

A great advance in cellulose chemistry occurred when non-aqueous solvent systems were proposed as a reaction medium for the derivatization of cellulose, allowing products to be made with a more homogeneous distribution of functional groups (Dawsey and McCormick, 1990). Prominent among these systems are solutions made of *N*,*N*-disubstituted amides, such as *N*,*N*-dimethylacetamide (DMAc) and a lithium halide, preferably LiCl (Morgenstern and Kammer, 1996).

A polymeric material is generally considered to be dissolved when a clear solution is obtained. In reality, it seems that only solutions of weakly polar polymers are almost fully-dispersed down to the molecular level. This has led to the view that a polymer is either dissolved or not. However, this generally accepted rule does not always

---

[*] Corresponding author. Tel.: +55 16 3373 9951; fax: +55 16 3373 9952.
E-mail address: elisabete@iqsc.usp.br (E. Frollini).

0960-8524/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2005.10.009

hold, because intermediate stages between swelling and complete solution seem to exist (Schulz et al., 2000).

In the case of celluloses, the introduction of groups such as acetates breaks hydrogen bonds and introduces new interactions between the substituents, which depend on the degree of substitution (DS) and the nature of the substituents. As a result, cellulose derivatives are generally soluble in a wide range of solvents (El Seoud et al., 2000).

However, in a previous study it was found that the solubility properties of acetates, after they were isolated from DMAc/LiCl (in which they were synthesized), can also depend on the previous reaction conditions, such as the LiCl concentration (Ass and Frollini, 2001). The results discussed in the present work confirm this dependence. This is an important finding, for it indicates that in many cases it is not possible to compare data on a cellulose ester by correlating only the DS and solubility in a given solvent, as is usually done, even when the molar mass and crystallinity index are similar for the samples considered.

Celluloses from differing sources (e.g. linters, sisal, sugarcane bagasse, wood) vary significantly in terms of their degree of polymerization, α-cellulose (pure cellulose) content and crystallinity index. Hence, they also exhibit varying properties with regard to solubilization and the aggregation/association of chains, which in turn influence the degree of substitution of the cellulose acetate. Thus, to discover the best conditions for dissolution of cellulose and synthesis of the acetate, each variety needs a separate, detailed study.

The choice of raw materials (linters and sisal) derived from the fact that the present work is part of a larger project aiming at the study of cellulose reactions in homogeneous medium, using celluloses obtained from several plant sources, such as linters, cotton, sisal and sugarcane bagasse, which grow much more rapidly than trees, from which wood, the main current source of cellulose, is obtained (Ciacco et al., 2000; Marson et al., 2000; Ass and Frollini, 2001).

The present study concerns the preparation of cellulose acetates in homogeneous medium, starting with celluloses obtained from sisal and cotton linters. The influence of cellulose properties, such as molar mass and crystallinity index, on the process of dissolution in DMAc/LiCl was investigated, along with the influence of this dissolution step on the properties of the derivatives obtained. The properties examined were the degree of substitution and molecular weight distribution of the acetates formed, the aim being able to obtain information about the influence of aggregation or association among the chains during the dissolution and/or derivatization of the cellulose on the DS of the obtained acetates.

2. Experimental

2.1. Materials

The celluloses used as raw material here were (a) untreated sisal, kindly provided by Lwarcel (Lençóis Paulista, SP, Brazil) and treated sisal (mercerized) and (b) mercerized cotton linters, kindly provided by Indústria Fibra S/A, Americana, SP, Brazil. *N*,*N*-dimethylacetamide (DMAc, VETEC) and acetic anhydride (Mallinckrodt) were dried over 4 Å molecular sieves. Lithium chloride (Mallinckrodt) was dried at 90 °C under vacuum and afterwards stored in a desiccator. Methanol (Synth) and sodium hydroxide (Synth) were used as received.

2.2. Cellulose characterization

(a) *Degree of polymerization* (*DP*): this was determined by viscometry, using an Ostwald viscometer to measure the characteristic viscosity of cellulose dissolved in Cuen (copper ethylene diamine) solution (1:1). The average molar mass is given by $\overline{\mathrm{Mv}} = \overline{\mathrm{DP}} \times 162$ (TAPPI, 1990).

(b) *Crystallinity index* (*CI*): this was determined by X-ray diffraction, using a VEB CARL ZEISS-JENA URD-6 Universal Diffractometer operating at 40 kV/20 mA and λ (Cu Kα) = 1.5406 Å (Buschle-Diller and Zeronian, 1992).

(c) *Alpha-cellulose content*: this is given by the loss of mass after treatment of cellulose with 17.5% NaOH solution. It is defined as: %α-cell = (mass of dry α-cell/mass of dry cell) × 100 (Browning, 1967).

2.3. Cellulose mercerization

Sisal and linters celluloses were mercerized in 20% NaOH solution (material:licor ratio 1:50) at 0 °C for 1 h. The alkali-swollen material was washed with distilled water until the pH of the distilled water was unchanged. The mercerized product was dried in air and afterwards at 60 °C under vacuum (Buschle-Diller and Zeronian, 1992).

2.4. Cellulose dissolution and acetylation

The dissolution and acetylation steps were based on those of Edgar et al. (1995) with some modifications. A mixture of cellulose (2.00 g) and 100 ml of DMAc (see Table 2) was heated to 150 °C and stirred for 1 h, in a glass reactor equipped with a mechanical stirrer and reflux condenser, under N_2 flow. After that, lithium chloride (see Table 2) was added and the reflux condenser was substituted by a short-path distillation apparatus. The mixture was heated to 170 °C and 10% of the solvent volume was distilled off with the aim of eliminating most of the residual water present in both solvent and cellulose. After that, the reaction mixture was cooled to room temperature and allowed to stir overnight. A clear cellulose solution was obtained and the temperature was raised to 110 °C, under the reflux and N_2 flow. Acetic anhydride was added dropwise, in appropriate molar ratios to the anhydroglucose units (AGU) (see Table 2). The system was kept at 110 °C for 1 or 4 h, according to the source of the cellulose (see Table 2), and then cooled to