

Characterization of methylcellulose produced from sugar cane bagasse cellulose: Crystallinity and thermal properties

Guimes Rodrigues Filho^a, Rosana M.N. de Assunção^{a,*}, Júlia G. Vieira^a,
Carla da S. Meireles^a, Daniel A. Cerqueira^a, Hernane da Silva Barud^b,
Sidney J.L. Ribeiro^b, Younes Messaddeq^b

^a *Institute of chemistry, Federal University of Uberlândia, Av. João Naves de Avila 2121, P.O. Box 593, 38400-902 Uberlândia, Minas Gerais, Brazil*

^b *Institute of chemistry, UNESP, P.O. Box 355, 14801-970 Araraquara, SP, Brazil*

Received 7 September 2006; received in revised form 27 October 2006; accepted 20 November 2006

Available online 29 December 2006

Abstract

In the present work, methylcellulose produced from sugar cane bagasse was characterized by FTIR, WAXD, DTA and TGA techniques. Two samples were synthesized: methylcellulose A and methylcellulose B. The only difference in the process was the addition of fresh reactants during the preparation of methylcellulose B. The ratio between the absorption intensities of the C–H stretching band at around 2900 cm^{-1} and O–H stretching at around 3400 cm^{-1} for methylcellulose B is higher than for methylcellulose A, indicating that methylcellulose B showed an increase in the degree of substitution (DS). Methylcellulose A presents a more heterogeneous structure, which is similar to the original cellulose as seen through FTIR and DTA. Methylcellulose B showed thermal properties similar to commercial methylcellulose. The modification of methylcellulose preparation method allows the production of a material with higher DS, crystallinity and thermal stability in relation to the original cellulose and to methylcellulose A.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Sugar cane bagasse; Methylcellulose; FTIR; WAXD; DTA/TG

1. Introduction

Methylcellulose is a cellulose derivative that can be prepared from the reaction of alkali-cellulose with dimethyl sulfate (DMS) or methyl chloride [1,2]. Several products of considerable commercial importance can be developed from methylcellulose. For example, it may be used as thickener in the food industry [3], as matrix for controlled release of drugs in pharmaceutical industry [4], as admixture for concrete in civil construction [5], and as an agent for modifying water viscosity in the petrochemical industry for heavy oil recovery [6]. The use of methylcellulose in these activities depends on its

solubility in water and, consequently, on the degree of substitution (DS) of the polymer. When this polymer is prepared with a DS between 1.4 and 2.0, hot or cold water may be used to produce solutions or dispersions in low concentration [7]. For DS higher than 2.0 the polymer shows solubility in organic solvents.

Considering the great applicability of this polymer, the characterization of its physico-chemical properties is extremely important, mainly due to the fact that the methylcellulose evaluated in this work was produced from an alternative source of cellulose, sugar cane bagasse. In previous work [8], methylcellulose was produced from cellulose extracted from sugar cane bagasse. This material was produced with different DS depending on which solvent was used during the methylation reaction. Methylcellulose prepared with acetone as solvent presented a DS of 1.2, the highest value obtained.

* Corresponding author. Tel.: +55 34 3239 4174; fax: +55 34 3239 4208.

E-mail address: rosanassuncao@gmail.com (R.M.N. de Assunção).

As DS increases, large modifications on the physico-chemical properties are observed for methylcellulose in relation to original cellulose, as for example, the changes in thermal properties that were observed by DSC and TGA [7,8].

Sugar cane bagasse cellulose, shows semicrystalline pattern, is insoluble in common organic solvents and in water. In spite of its high crystallinity, cellulose decomposes before it undergoes melt flow. Therefore cellulose is normally converted into derivatives such as esters and ethers because these derivatives normally show major thermal stability compared to cellulose and can be processed through thermal treatments or solvent-casting techniques. Methylcellulose shows changes mainly in an increase of thermal stability and water solubility associated with the increase of the DS, which improve the commercial applicability of the polymer. Considering these aspects, in this work methylcellulose produced from sugar cane bagasse cellulose was characterized in relation to DS, crystallinity and thermal properties. To this end, the synthesis was modified and the produced material was compared to that obtained in previous work, in the sense of enlarging the possibility of the use of agro-industrial residues in the production of cellulose derivatives.

2. Experimental

2.1. Purification of sugar cane bagasse

Sugar cane bagasse was provided by Usina Alvorada de Açúcar e Álcool, from the 1999 harvest in Araporã-MG. For the purification, 4.0 g of ground dry bagasse was immersed in 76.0 mL of distilled water to remove the water-soluble extractives. After 24 h, it was filtered and 76.0 mL of NaOH (0.25 M) was added to the bagasse. After 18 h this mixture was vacuum filtered. The bagasse was left in a reflux with three successive portions of a mixture containing 20% (v/v) of nitric acid and ethanol, which was replaced after each hour. After the reflux, the mixture was filtered and washed with distilled water until it did not turn pink when phenolphthalein and a drop of NaOH (0.05 M) were added to it. The bagasse was dried at 105 °C for 3 h and then ground in a blender [9].

2.2. Methylation of the sugar cane bagasse

2.2.1. Methylcellulose A (3 h reaction without changing the reactants)

The methylation of the bagasse cellulose was made according to the method described by Mansour et al. [2]. The procedure is as follows: sugar cane cellulose (1.0 g) was mercerized using a 50% NaOH solution for 1 h at room temperature. The excess of the NaOH solution was removed, and acetone (9 mL) was added as a solvent. Three milliliters of DMS were added dropwise and the reaction was allowed to proceed at 50 °C for 3 h, being stirred occasionally. At the end of the reaction, the material was neutralized by a 10% acetic acid solution, filtered on a sintered crucible, and then washed

with acetone. Methylcellulose was put into an oven at 50 °C for 6 h.

2.2.2. Methylcellulose B (3 h reaction with successive change of reactants)

The same procedure in relation to mercerization and amounts of reactants, as described in Section 2.2.1, was repeated for methylcellulose B. The modification made in the process was the addition of fresh reactant for every 1 h of the reaction after filtering the system, maintaining the same previous proportions. After the end of 3 h the samples were treated as described previously.

2.3. FTIR characterization of bagasse, cellulose bagasse and methylcellulose

The powdered samples were mixed with KBr to produce tablets. Infrared spectra were obtained in an FTIR Perkin Elmer Spectrum 1000. Twenty-eight scans were collected for each spectrum with a step size of 4 cm⁻¹.

2.4. WAXD characterization of methylcellulose

X-rays diffraction patterns were obtained with a Kristalloflex Simens Diffractometer with Ni filtered Cu K α radiation from 4 to 70°.

The diffractograms were deconvoluted into peaks and halos referring to the crystalline and amorphous regions, respectively. These deconvolutions were obtained using the Pseudo-Voigt 2 peak function from Origin[®] 7.0, which is shown below:

$$y = y_0 + A \left[m_u \frac{2}{\pi} \frac{w_L}{4(x - x_c)^2 + w_L^2} + (1 - m_u) \frac{\sqrt{4 \ln 2}}{\sqrt{\pi} w_G} e^{(-4 \ln 2 / w_G^2)(x - x_c)^2} \right] \quad (1)$$

where w_L and w_G are the width at half maximum for Lorentz and Gauss components of the above equation, respectively, A is the area and m_u is the profile shape factor.

2.5. TGA/DTA characterization of methylcellulose

TGA curves were obtained in a TA Instrument thermobalance, with an SDT cell, using aluminum pans. The experiments were carried out under continuous nitrogen flow of 70 mL/min, and the temperature ramp was set at 10 °C/min. The weight loss was recorded from 10 to 900 °C. DTA measurements were performed under the same conditions.

2.6. DSC characterization of methylcellulose

DSC analyses were carried out in a Rheometric Scientific DSC-SP equipment. Six milligrams of methylcellulose in powdered form were sealed in an aluminum pan with lid, and purged with ultra-pure dry nitrogen at a flow rate of

Download English Version:

<https://daneshyari.com/en/article/5205144>

Download Persian Version:

<https://daneshyari.com/article/5205144>

[Daneshyari.com](https://daneshyari.com)