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Synthesis and characterization of methylcellulose from sugar cane bagasse cellulose

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Abstract

In the present paper, methylcellulose was produced from cellulose extracted of sugar cane bagasse, using dimethyl sulfate in heterogeneous conditions. The infrared spectra of the cellulose and of the methylcellulose present significant differences at the regions from 3600 to 2700 cm^{-1} and from 1500 to 800 cm^{-1}. The ratio between the absorption intensities of the O—H stretching band (~3400 cm^{-1}) and the C—H stretching band (~2900 cm^{-1}) in the spectra of the methylated samples is lower than that in the cellulose spectrum, evidencing the methylation of the samples. The effect of using toluene and acetone during the synthesis was studied. Without using the solvent, the degree of substitution (DS) of the methylated sample was 0.70, reaching a DS of 1.2 when using acetone. The produced methylcellulose presents chemical and physical properties that increase its range of application and aggregate value to this agro-industrial residue.

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1. Introduction

Lately, the literature has presented a series of papers about the use of residues of several agro-industrial activities (Sun, Sun, Zhao, & Sun, 2004). One of these residues is the sugar cane bagasse, which, in Brazil, comes from the production of sugar and alcohol from sugar cane. Sugar cane bagasse contains about 30–50% of cellulose and 20–24% of lignin, what makes possible to use this residue by producing cellulose derivatives and by partially substituting phenol for producing phenolic resins (Pandey, Soccol, Nigam, & Soccol, 2000; Tita, Paiva, & Frollini, 2002). Due to its high crystallinity, cellulose is insoluble in most of the traditional organic solvents, what reduces significantly its applicability at its original form. An alternative path for increasing the cellulose applicability is chemically modifying it by incorporating many kinds of chemical groups on the hydroxyl groups of the glycosidic units. According to this procedure, several cellulose derivatives may be produced, as for example, carboxymethylcellulose, cellulose acetate and methylcellulose. The cellulose derivatives have in common an increase on the solubility in the most common organic solvents. In addition, the increase on the water solubility is observed in methylated and carboximetilated cellulose derivatives (Ott, 1943).

One of the most important cellulose derivatives is the methylcellulose, which is extensively used in several activities, according to its degree of substitution. For example, it may be used as a thickener in the food industry (Reibert & Conklin, 1999), as admixture for concrete in civil construction (Fu & Chung, 1996), as an agent for modifying the water viscosity in the petrochemical industry for recovering heavy oils (Borchardt, 1991), and as a matrix for the

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controlled release of drugs in the pharmaceutical industry (Mitchel et al., 1993). This polymer is obtained by replacing the cellulose hydroxyl groups by methoxyl groups. In this process, the hydrogen bonds, which are predominant on the cellulose and responsible for the high crystallinity of this polymer, are weakened and therefore, methylcellulose containing a degree of substitution between 1.4 and 2.0 is usually water-soluble (Li et al., 2002). However, the solubility, as well as other methylcellulose properties, depends on how uniform the methoxyl groups are distributed along the polymeric chain. Cellulose is usually modified in heterogeneous conditions due to its insolubility in the most usual solvents. At those conditions, the distribution of the substituted groups is not very uniform. When methylcellulose is produced in homogenous conditions, it is water-soluble having a degree of substitution lower than those samples that were obtained in heterogeneous conditions (Mansour, Nagaty, & El-Zawawy Waleed, 1994; Desbrières, Hirrien, & Rinaudo, 1998). The difference between the properties of the methylcellulose that is produced according to each route is related to the formation of a gel fraction in aqueous medium. This gel is formed due to hydrophobic interactions between the chains having methoxyl groups, which replaced the hydroxyl groups on the glycosidic rings on the original cellulose during the synthesis. The hydrophobic blocks also get associated due to an unfavorable interaction with water, what results in a viscosity increase, conducing to the formation of a three-dimensional network (Desbrières et al., 1998).

As the chemical modification in heterogeneous conditions is made from the alkali-cellulose in aqueous medium, it is possible to form gel during the process. This gel leads not only to a little uniform distribution of the replacing groups, but also to a decrease on the degree of substitution that the samples can reach. Mansour et al. (1994) studied the conditions of the heterogeneous methylation by adding several organic solvents during the synthesis, trying to alter the pattern of the cellulosic hydrogen bonds and the hydrophobic interactions of the methylated blocks for destroying the structure of the formed gel and increase the degree of substitution of the produced samples.

Cellulose derivatives have been successfully produced from the cellulose extracted of the sugar cane bagasse. This may be observed on the production of cellulose acetate (Rodrigues Filho et al., 2000) and on the studies related to the production of methylcellulose (Viera, Meireles, Assunção, & Rodrigues Filho, 2004) and carboxymethylcellulose (Morais & Campana Filho, 1999) from sugar cane bagasse. In this paper, methylcellulose was produced from sugar cane bagasse. The cellulose was modified in heterogeneous conditions, evaluating the effect of organic solvents during the synthesis. The polymers produced were characterized through Fourier Transform Infrared spectrometry (FTIR), chemical determination of the methoxyl groups and Differential Scanning Calorimetry (DSC).

2. Experimental

2.1. Purification of sugar cane bagasse (Rodrigues Filho et al., 2000)

The 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 left in 76.0 mL of distilled water to remove the water-soluble extractives. After 24 h, it was filtered and 76.0 mL NaOH (0.25 M) was added to the bagasse. After 18 h, this mix was vacuum filtered. The bagasse was put in reflux with three successive portions of a mixture containing 20% (v/v) of nitric acid in ethanol. After each hour, the mixture was replaced. After the reflux, the mixture was filtered and washed with distilled water until the filtrate did not turn to pink when phenolphthalein and a drop of NaOH (0.5 M) were added to it. The bagasse was dried at 105 °C during 3 h, and after that, it was ground in a blender.

2.2. Characterization of the sugar cane bagasse and purified sugar cane cellulose

2.2.1. Klason lignin

A 2.000 g sample of sugar cane bagasse, without extractives, was transferred to a round bottommed flask. Fifteen milliliter of sulfuric acid (72%) was slowly added to it under stirring. The sample was kept under stirring in a bath at room temperature for 2 h. Subsequently, 560 mL of distilled water was added to the round bottommed flask, diluting the acid solution to 3%. The system was heated up, under reflux, until its boiling temperature. Then, the system was left to stand for sedimenting the insoluble residue, which was filtered in a previously weighed sintered crucible, and washed with 500 mL of distilled hot water. The residue was dried in an oven for 12 h at 105 °C and, after dry, weighed for quantifying the amount of Klason lignin.

2.2.2. Holocellulose

5.000 g of sugar cane bagasse was added to a 250 mL beaker, containing 0.7500 g of sodium chlorite, 0.5 mL of concentrated acetic acid, 100 mL of distilled water was added and the mix was stirred until the chlorite dissolved. The beaker was then covered with a watch glass and placed on a thermostat bath at 75 °C for 1 h with occasional stirring. The same amount of reagents was added to the beaker every hour for 2 more hours, totalizing a digestion period of 3 h. The system was cooled to 10 °C in ice water, and then filtered through a sintered crucible. The material was now nearly completely white. The residue was washed six times with ice water and dried in an oven at 105 °C for 6 h. After this period, the residue was weighed to quantify the holocellulose.

2.2.3. Determination of the alpha cellulose content

Three grams of holocellulose was put into a 250 mL Erlenmeyer flask and mixed with 100 mL of a 5% KOH solution in inert atmosphere, which was obtained by adding nitrogen gas to the mix during the first 10 min of extraction. The flask was put in a water bath at 25 °C for 2 h, with constant stirring. The mix was filtered in a sintered crucible, and washed with 50 mL of a 5% KOH solution, and then with 100 mL of distilled water. The filtrate was put into a 1 L Erlenmeyer flask and the precipitation was performed by adding a solution containing equal parts of acetic acid and ethanol. The precipitate was hemicellulose-A.

The fibrous residue retained on the sintered crucible was transferred to a 250 mL Erlenmeyer flask, and the same procedure that was performed to obtain hemicellulose-A was followed. However, a 24% KOH solution was used. The fibrous residue on the sintered crucible was washed with 25 mL of a 24% KOH solution, then with 25 mL of 10% acetic acid solution and finally with 100 mL of distilled water. The filtrate was recovered in a 1 L Erlenmeyer flask into which a solution containing equal amounts of acetic acid and ethanol was added. The precipitate was hemicellulose-B.

The fibrous residue at the end of the process described above was washed with distilled water until the filtrate pH was neutral. Then, it was washed with 50 mL of acetone and dried at 105 °C for 3 h. After this period the residue was weighed to quantify alpha cellulose.

2.3. Methylation of the sugar cane bagasse

The methylation of the bagasse cellulose was made according to the method described by Mansour et al. (1994). The procedure is described as follows: cellulose (1.0 g) was mercerized using a 50% NaOH solution for 1 h at room temperature. The excess of the NaOH solution was taken out, and then dimethyl sulfate (3 mL) was added to produce sample 1. For samples synthesized using solvents, after addition of DMS, 9 mL of acetone or 9 mL of toluene was added to prepare samples 2 and 3, respectively. The mix was left in a water bath at 50 °C for 3 h, being occasionally stirred. 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. The methylcellulose was dried in an oven at 50 °C for 6 h.

2.4. Characterization of the bagasse, bagasse cellulose and methylcellulose by FTIR

A Perkin-Elmer Spectrum 1000 Fourier Transform Infrared Spectrophotometer (FTIR) was used to record the IR spectra of the dried powered polymers (sugar cane bagasse, cellulose extracted of sugar cane bagasse and methylcellulose). The samples were prepared by mixing the materials and KBr in a proportion of 1:100 (w/w). For all spectra, 28 scans were accumulated with a 4 cm^{-1} resolution.

2.5. Determination of the methoxyl groups

The determination of the methoxyl group content was made through the modified procedure of Viebock and Schawappach, described by Chen et al. (Chen, 1992).

Fig. 1 shows a scheme of the system used in this determination. 0.1000 g of phenol, 1.2000 g of potassium iodide, 2.00 mL of orthophosphoric acid and 50.00 mg of methylcellulose were added to the reaction flask (Fig. 1A). The washing tube (Fig. 1B) was filled with 3.00 mL of a saturated solution of sodium bicarbonate.

1.50 mL of a solution containing 20% sodium acetate in acetic acid was added to the first absorption tube (Fig. 1C). Ten drops of bromine were added to this solution under light stirring, and then this tube was filled up with the 20% sodium acetate solution. This solution was then distributed among the three absorption tubes by inclining the system.

The reaction was maintained for 1 h at 150 °C in an inert atmosphere produced by nitrogen flow, which drags the formed methyl iodide. After this period, the content of the absorption flasks was transferred to an Erlenmeyer containing 1.500 g of sodium acetate and 60.00 mL of distilled water. In order to remove the excess of bromine of the absorption solution, five drops of formic acid were added to the solution, under agitation. Finally, the formed iodine is titrated by a standard solution of sodium thiosulphate, using a starch solution as indicator.

2.6. Characterization of the methylcellulose by DSC

The DSC analysis was carried out in Rheometric Scientific DSC-SP equipment. Two milligrams of methylcellulose in powered form were sealed in aluminum pan with lid, and purged with ultra-pure dry nitrogen at a flow rate of 20 mL/min. The temperature ramp was set at 10 °C/min and the heat flow was recorded from 25 to 300 °C. Indium was used as standard to calibrate the temperature and energy scales of the DSC instrument.

3. Results and discussion

The sugar cane bagasse, used as raw material for obtaining cellulose, was chemically characterized, and its α-cellulose and lignin content were, respectively, 44.9% and 23.8%. After the purification of sugar cane bagasse, the extracted cellulose has a lignin content of 3.84%. This value is lower than that found for unbleached Kraft pulps of soft woods (4.7%) (Isogai, Ishizu, Nakano, Eda, & Kato, 1985).

The main differences in relation to the functional groups in the sugar cane bagasse and in the cellulose that was extracted from it may be observed on the FTIR spectra presented in Fig. 2.

The main alterations are found at the region from 2000 to 700 cm^{-1}. The absorption bands at 1730, 1620, 1595 and 1512 cm^{-1} are not observed on the spectrum of the

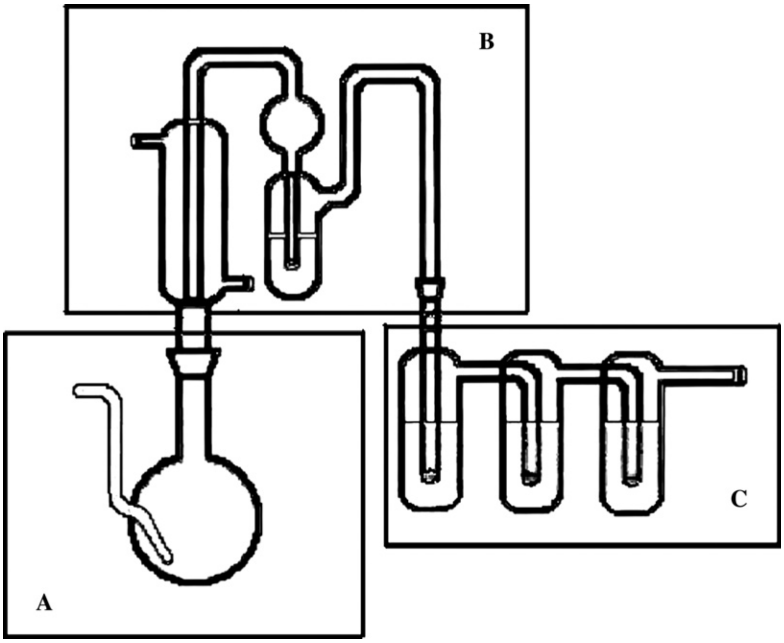

Fig. 1. Scheme of the system used in methoxyl group determination.

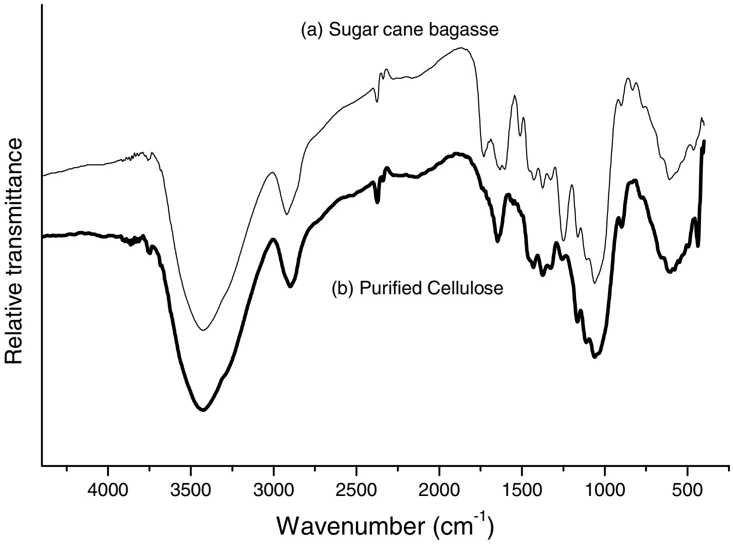

Fig. 2. FTIR spectra: (a) Sugar cane bagasse and (b) purified cellulose.

cellulose that was extracted from sugar cane bagasse, Fig. 2b. These absorptions are attributed to the functional groups that are present in the lignin that is associated to the sugar cane bagasse before the process of purification for removing the lignin. The assignment for each one of these absorption bands may be seen in detail in Table 1.

Two absorption bands must be emphasized: the bands at 1512 and 1250 cm^{-1}. The band at 1512 cm^{-1} is not present and the band at 1250 cm^{-1} is drastically reduced on the purified cellulose spectrum. These two absorption bands are important since their absence in the purified cellulose spectra indicates that most of the lignin was removed. However, the band at 1250 cm^{-1} has another function, its return to the cellulose spectrum after the chemical reaction of methylation is an evidence of the chemical substitution of the hydroxyl groups when the methylated derivative of the cellulose is formed.

The assignment of the bands was employed to evaluate the chemical modification of the cellulose during the methylation reaction. Fig. 3 presents the infrared spectra of the methylated samples. The main differences between the spectra of the methylated samples and the spectrum of the purified cellulose are seen at the region from 3600 to 2700 cm^{-1} and from 1500 to 800 cm^{-1}.

At the first region, the ratio between the intensities of the O—H stretching band (~3400 cm^{-1}) and the C—H

Table 1
Assignment of main absorption bands in cellulosic materials (Colom et al., 2003 & Adebajo & Frost, 2004)

Wave number (cm^{-1})		Assignment
Unpurified sugar cane bagasse	Purified sugar cane bagasse	
3426	3426	OH stretching
2922	2900	CH stretching of CH_2 and CH_3 groups
1730		C=O stretching of acetyl or carboxylic acid
	1648	H—O—H bending of absorbed water
1634		Carbonyl stretching with aromatic ring
1620–1595		C=C stretching of aromatic ring (lignin)
1512		C=C stretching of aromatic ring (lignin)
1429	1432	CH_2 bending
1376	1374	C—H deformation
1335	1335	OH in plane bending
1250 (medium)	1250 (weak)	C—O stretching of ether linkage
1166	1160	C—O—C antisymmetric bridge stretching
1062	1062	C—O symmetric stretching of primary alcohol
904	896	β-Glucosidic linkages between the sugar units

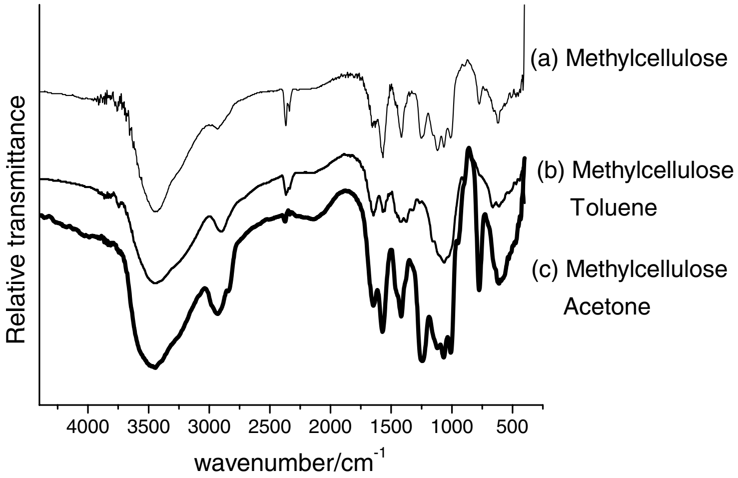

Fig. 3. FTIR spectra: (a) methylcellulose (1:3 (w/v) cellulose/DMS), (b) methylcellulose (1:3 (w/v) cellulose/DMS and 1:9 (w/v) cellulose/toluene) and (c) methylcellulose (1:3 (w/v) cellulose/DMS and 1:9 (m/v) cellulose/acetone).

stretching band (~2900 cm^{-1}) is lower in the spectrum of the methylated samples than the observed for the purified cellulose. This effect is even more evident for the sample that was synthesized using acetone as solvent. The decrease in the ratio of these two bands is an evidence of the effectiveness of the cellulose methylation, since the hydroxyl groups of glycosidic units are replaced by the methoxyl group during the methylation reaction, increasing the amount of methyl groups in relation to the amount of hydroxyl groups.

Another important aspect at this region of the infrared spectra of the methylcellulose samples is the alteration in the shape of the band in approximately 2922 cm^{-1} and the displacement of this to higher frequencies when compared to the purified cellulose. The same displacement may be observed for the O—H stretching band of the methylated samples. The substitution of the hydroxyl groups by methoxyl groups significantly changes the amount of methyl groups, and that is clearly observed in unfolding of the band, which is attributed to the C—H stretching of the CH_2 and CH_3 groups. The substitution of hydroxyl groups by methoxyl groups in cellulose changes the pattern of the hydrogen bonds on the methylated cellulose, what sensibly changes the O—H stretching region (Sekiguchi, Sawatari, & Kondo, 2003). It is important to emphasize that these changes become more evident for the samples that were produced using solvent. The added solvents change the intermolecular interactions of the cellulose during the methylation, improving the accessibility of the alkylating agent to the hydroxyl groups for the chemical modification. The acetone acts at the original structure of the cellulose by modifying the hydrogen bonds between the chains, making them more accessible. On the other hand, the toluene acts by modifying the interactions between the hydrophobic blocks that were formed from the sample that has already been methylated, avoiding the gel to be formed during the synthesis (Mansour et al., 1994).

At the region between 1500 and 800 cm^{-1}, it may be observed significant modifications at the absorption bands of the methylcellulose samples spectra, especially the appearing of a high intensity band at approximately 1250 cm^{-1}, mainly for the sample that was methylated without solvent and for the sample that was methylated with acetone. The rise of this band combined to the modifications that were observed in the whole spectrum indicates a significant evidence of the production of methylcellulose from the sugar cane bagasse cellulose. It must be noticed that the region from 1500 to 800 cm^{-1} of the sample that was methylated with toluene presents less alterations when compared with the others and with the original cellulose. This may be attributed to the unfavorable interaction of the toluene with the structure of the original cellulose. It is possible that the toluene causes so little change on the cellulose crystalline microstructure that no big alterations are observed at this region (Rodrigues Filho et al., 2000).

The analysis of the FTIR spectra allowed to qualitatively verifying the occurrence of the methylation reaction and the benefic effect of using organic solvents. In order to investigate those in a quantitative way, the degree of substitution (DS) of the samples was calculated through the chemical determination of the methoxyl groups, using the modified procedure of Viebock and Schwappach (Chen, 1992). The results are presented in Table 2.

According to the results presented in Table 2, all the cellulose samples were successfully methylated. The differences on the DS values are due to the use of solvent and are according to what was observed in the FTIR spectra. The same procedure for determining the methoxyl groups was carried out on the starting cellulose and the result shows that this sample does not present a significant amount of methoxyl groups. This result shows that the original cellulose loses part of its residual lignin during the treatment with alkali (mercerization), what was attested by the insignificant value of the methoxyl groups and by the yellowish color of the filtrate after the mercerization.

Despite of the degree of substitution, the presented difference for the samples that were methylated with solvent shows that the accessibility to the hydroxyl groups is increased during the synthesis. However, the effect is not the same for the samples that were treated with toluene and with acetone. The sample that was treated with acetone has a higher degree of substitution, what may be related to the effective way in which this solvent interacts with the hydroxyl groups, decreasing the amount of interchain hydrogen bonds. This kind of interaction is predominant on the original cellulose and on the low DS methylcellulose during the initial steps of the synthesis. Thus, the use of this solvent since the start of the synthesis is favorable for increasing the DS of methylcellulose. Concerning the use of toluene, its main function is avoiding the hydrophobic interactions between the methylated blocks. Then, it probably acts more effectively on the final steps of the synthesis. The use of this solvent since the beginning of the reaction is unfavorable due to its little interaction with the hydroxyl groups, what makes the accessibility of the cellulose hydroxyl groups similar to that found for the material without solvent. Therefore, the obtained DS is lower than that found for the samples that were produced using acetone, but higher than the value that was observed for the sample, that was methylated without solvent. That was due to the favorable interaction of the toluene with the hydrophobic groups at the final steps of the synthesis.

Table 2
Determination of the degree of substitution of the methylcellulose samples produced from sugar cane bagasse cellulose

Samples	DS
Purified cellulose without methylation	0.010
Methylcellulose – without solvent	0.70
Methylcellulose – toluene	0.95
Methylcellulose – acetone	1.2

Due to the chemical modifications, the cellulose derivatives present very different properties when compared to the original cellulose. That may be attested by evaluating a differential scanning calorimetry thermogram of the methylcellulose containing a DS of 1.2 as presented in Fig. 4.

In most of the papers in the literature, the DSC thermograms of methylcellulose are about the study of the sol-gel reversible transition in aqueous solution (Li et al., 2002; Sekiguchi et al., 2003). The analysis of this phenomenon is made at the temperature range between 0 and 100 °C. The evaluation made in this paper intended to characterize the prepared cellulose derivative in comparison to the original cellulose, and for that reason, the DSC thermograms were analyzed in a range temperature from 25 to 300 °C.

The thermogram that is presented in Fig. 4 shows an endotherm of dehydration, in which the peak is centered at 115.68 °C. This endotherm is present on the thermograms of cellulosic materials due to the interaction of the water and the non-substituted hydroxyl groups of the cellulose derivatives. This effect may be particularly observed for the cellulose acetate (Puleo & Paul, 1989; Rodrigues Filho et al., 2000). Cellulose presents the same endotherm of physical desorption of water, with most of the water physically bonded to the polymer being eliminated before 100 °C. Even though cellulose is a crystalline polymer, its DSC thermogram does not present an endotherm of fusion, since during the DSC scanning the cellulose is degraded. For cellulose derivatives as methylcellulose, the total or partial substitution of the hydroxyl groups during the chemical modification of the cellulose significantly alters the chemical and physical properties of the produced derivative. These changes are present on the DSC thermogram that is shown in Fig. 3. On this thermogram, the Tg is observed around 184 °C and two endotherms are seen in approximately 211 and 219 °C. In the literature, methylcellulose having a DS from 1.6 to 1.9 present its glass transition at 199.5 °C, detected by dynamic mechanical analysis (DMA) (Park & Buckenstein, 2001). The difference between the value in the literature and in this paper may

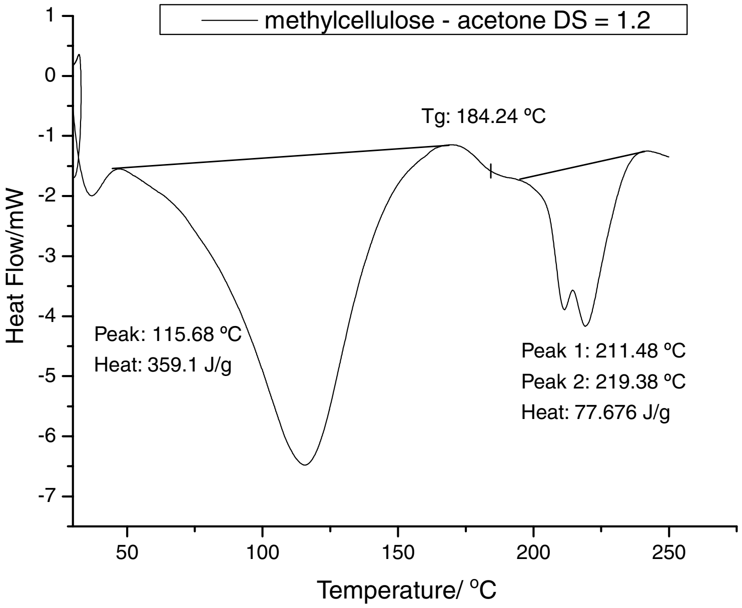

Fig. 4. DSC thermogram of methylcellulose (DS = 1.2).

be attributed to three factors: the difference on the degree of substitution of the samples, the high water content that may act as a plasticizer and reduce the Tg, and the differences regarding the sources of the cellulosic material. Obviously, there is also a difference on the Tg values due to differences in the technique used for Tg determination.

The two endotherms in approximately 211 and 219 °C are possibly due to two competitive phenomena of fusion of the crystalline regions and to the degradation of the methylcellulose. These two phenomena are possible since the methylcellulose that was produced in this paper is a material that presents low water solubility, which keeps part of the crystalline structure of the original cellulose. However, with a degree of substitution of 1.2, this material presents a higher thermal stability than cellulose, what allows it to present the two phenomena on the DSC thermogram.

4. Conclusion

It was possible to produce methylcellulose from sugar cane bagasse cellulose using DMS as an alkylating agent in heterogeneous conditions. The degree of substitution of the methylated sample without using solvent was 0.70. The use of solvent during the synthesis meant to alter the pattern of the cellulosic hydrogen bonds and the hydrophobic interactions of the methylated blocks for destroying the gel structure that may be formed during the synthesis in heterogeneous conditions in aqueous medium. When using toluene or acetone during the synthesis, it was possible to rise the degree of substitution of the samples, reaching a DS of 1.2 when using acetone. The methylated cellulose presents chemical and thermal differences from what is known for the original cellulose, what increases its applicability in relation to the cellulose, and aggregates value to this agro-industrial residue.

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