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Acetylation of bleached Kraft pulp: Effect of xylan content on properties of acetylated compounds

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ABSTRACT

Bleached Kraft pulp (BKP) from *Eucalyptus globulus* and cotton xylan blends (CXB) was acetylated. The effects of xylan content on cellulose acetylation and the properties of the acetylated material were studied. An increase in xylan content caused a slight decrease in the degree of substitution (2.98 to 2.68 for CXB; 2.93 to 2.84 for BKP). Thermal analysis showed that the melting temperature also decreases from 268.0 to 188.8 °C for CXB and from 221.4 to 212.8 °C for BKP. Moreover, the solubility decreased due to the partial dissolution of acetylated xylans.

The presence of xylans during Kraft pulp acetylation does not have a significant negative effect on the physical properties of the acetylated material, but the decrease in melting temperature was beneficial for the application of acetylated polymer as a natural internal plasticizer. This is considered to be an important argument for BKP utilization in the cellulose acetate manufacturing process.

1. Introduction

The growing value of lignocellulosic feedstocks, as renewable raw materials in both energy production and development of bio-based materials, has redirected the interest of researchers toward new applications and products derived from cellulose. In this context, cellulose esters are particularly attractive due to their applications in the field of bioplastics.

Much recent activity has focused on cellulose acetate (CA), which is used for manufacturing a wide variety of fibers or films (e.g., cigarette filters). Cellulose by itself is not suitable for processing, being largely insoluble in common solvents and, especially so, because its decomposition temperature (T_d) is lower than its glass transition (or fusion) temperature (T_g). To overcome its resistance to thermo-forming processes, one can replace hydroxyl with acetyl groups and thus reduce the cross-linking driving force, which in turn can reduce T_g to a level below that of T_d (Kamide & Saito, 1985).

Commercial CA is produced from ultra-pure dissolving pulp or cotton, and this is the main reason for its high production cost; therefore, its current use is restricted to expensive products (Cao et al., 2007). More abundant and economic alternative sources are lignocellulosic biomass and lower-purity cellulose pulp; thus, for example, the agriculture and forestry sector generates large amounts, which allows their potential use in manufacturing of acetylated materials and facilitates the development of sustainable processes with low production costs.

There is an abundant literature on the acetylation of different types of biomass: wheat straw (Biswas, Saha, Lawton, Shogren, & Willett, 2006; Ren, Sun, Liu, Cao, & Lou, 2007; Sun, Fang, Tomkinson, & Jones, 1999), sugarcane bagasse (Cerqueira, Filho, & Meireles, 2007; Shaikh, Pandare, Nair, & Varma, 2009), maize and rice husk (Biswas et al., 2006; Fan et al., 2013; Zhang, Huang, Jiang, Huang, & Yang, 2013), paper fibers such as recycled paper (Loo, Hashim, & Leh, 2012; Rodrigues Filho et al., 2008) and Kraft pulp (Popescu, Larsson, Olaru, & Vasile, 2012). These studies have helped to evaluate the characteristics of cellulose acetates from natural sources, but do not delve into the effect of the presence of other polysaccharides, especially hemicelluloses, in the acetylation process or into the key properties of the material (e.g., solubility, degree of substitution and thermal behavior). Hemicelluloses consist of

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heterogeneous chains of pentoses and hexoses with short branches of glucoronic acids, and they surround the wood pulp fibrils (Fengel & Wegener, 1984, chapter 5). Depending on wood type, hemicelluloses differ in their chemical composition: in softwoods, there is greater abundance of glucomannans, while xylans predominate in hardwoods (Sixta, 2006, chapter 2). As in cellulose, hydroxyl groups may be substituted by esterification to form acetates.

Previous studies have investigated the acetylation of isolated hemicelluloses, by analyzing different degrees of substitution and their effects on thermal and plastic properties (Ayoub, Venditi, Pawlak, Sadeghifar, & Salam, 2013; Egüés et al., 2014; Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012; Gröndahl, Teleman, & Gatenholm, 2003; Stepan, Höije, Schols, De Waard, & Gatenholm, 2012). In general, it has been shown that hemicelluloses can be acetylated with high efficiency and that this reaction facilitates the production of a thermoplastic feedstock with T_g close to 200 °C. However, the use of hemicelluloses in these studies was considered in isolation, without considering the interactions of these polysaccharides with the other polymeric constituents of biomass. Since naturally occurring cellulose and hemicelluloses are present in a complex matrix, it is reasonable to assume that the hemicellulose content affects acetylation efficiency and the properties of the acetylated material. It is therefore essential to develop a better understanding of acetylation of a heterogeneous material such as wood pulp or low-purity soluble pulp, as well as of interactions between different acetylated polysaccharides.

Here we report our progress in achieving these objectives by first evaluating the influence of xylan content on the acetylation of bleached Kraft pulp (BKP) and then comparing the properties of thus obtained products with model compounds containing pure cellulose and hemicelluloses. We prepared samples of acetylated BKP of *Eucalyptus globulus* (ABKP) with different initial xylan contents and acetylated cotton xylan blends (ACXB). Both Kraft pulp and cotton xylan blends are high-purity materials considering their low content of lignin, which has been thoroughly removed for the purposes of this study.

2. Materials and methods

2.1. Materials

The BKP from *Eucalyptus globulus* (~70%) and *Eucalyptus nitens* (~30%) was donated by a local industry. Commercial high-purity cotton (98% α-cellulose) was used. Xylans were obtained from *E. globulus* holocellulose. The holocellulose was prepared by the Wise method (Wise & Ratliff, 1947) which consists of two steps that delignify the extract-free (90% acetone) sawdust (45–60 mesh) with a sodium chlorite solution in acetic acid/water (1:2.5 v/v) at 90 °C. The xylans were obtained by holocellulose extraction at 20 °C, with 100 mL of 5% KOH for 110 min; they were separated from the extraction liquor by precipitation with methanol (4:1 v/v), followed by filtering and drying. High-purity reagents were used: 98% sulfuric acid, 99% methanol, 99.9% glacial acetic acid and 99.9% acetic anhydride (Merck).

2.2. Sample preparation

To study the effect of xylan on the acetylation of cellulose, two types of samples with different initial xylan contents were prepared: a model compound composed of CXB and BKP (Table 1). For CXB, aqueous solutions of isolated xylans were mixed with commercial cotton to obtain samples with xylan contents between 2.2% and 31.6%. The mixture was homogenized and oven-dried for 48 h at 25 °C until the moisture content was below 8%. Cotton, without addition of xylans, was used as control sample. For BKP, cold caustic extractions were performed using different alkaline loads. The extraction liquor with initial concentration of 0.9 M NaOH was added in proportions of 10.5%, 45% and 56% (odp) with respect to the BKP used. They were mixed and held at constant temperature for 1 h; then the alkaline solution was removed by filtration and washing. Thus obtained pulp was finally drained for 10 min in a centrifuge and oven-dried to achieve moisture content below 5%. The BKP without alkaline treatment was used as a control sample.

Table 1
Chemical composition of raw materials for acetylation.

Samples	% w/w			
	Glucose	Xylose	Lignin	Other sugars
Cotton xylan blends				
CXB1	96.1	2.2	0.2	1.2
CXB2	91.3	7.1	0.2	1.1
CXB3	86.5	12.0	0.2	1.1
CXB4	81.7	16.9	0.2	1.0
CXB5	76.9	21.8	0.2	1.0
CXB6	72.1	26.7	0.1	0.9
CXB7	67.3	31.6	0.1	0.8
Bleached Kraft pulp				
BKP1	92.1	7.4	0.4	0.0
BKP2	90.8	8.6	0.5	0.0
BKP3	85.7	13.1	0.6	0.6
BKP4	80.7	16.3	0.6	2.5

2.3. Acetylation procedure

The procedure applied to the BKP and CXB samples was adapted from that described by Sato (Sato, Uraki, Kishimoto, & Sano, 2003). Ten grams of each sample (BKP1 to BKP4 and CXB1 to CXB7; see Figs. 1 and 2) were impregnated with 200 mL of 99.9% acetic acid for 18 h. Then, 120 mL of acid was removed from the mixture and 0.5 mL of H_2SO_4 in 20 mL of glacial acetic acid was added to the sample before adding 25 mL of acetic anhydride, with continuous stirring, to achieve a homogeneous mixture. The mixture was reacted at 40 °C for 30 min. Then again, 25 mL of acetic anhydride was added to the mixture with continued stirring for 2 h. The reaction was stopped by adding 400 mL of water at room temperature and stirring for 1 min. The system was filtered and washed to remove the acid from the mixture. Finally, the acetylated material was oven-dried at 40 °C to achieve final moisture content below 2% before being ground and sieved.

2.4. Chemical analysis

2.4.1. HPLC

To determine the carbohydrate content in the BKP and CXB samples, they were subjected to hydrolysis with 72% sulfuric acid at 30 °C for 1 h, and subsequent hydrolysis with 3% dilute H_2SO_4 for 1 h at 121 °C (Mendonça, Guerra, & Ferraz, 2002). Monosaccharide distribution in the material was determined by HPLC analysis of the hydrolyzed liquid phase separated in a column (Aminex HPX-87H) coupled to an IR detector (9170 Young Lin YL) using deionized water as the mobile phase. The calibration was performed with standard solutions of L-arabinose, D-xylose, D-mannose, D-galactose and glucuronic acid (Sigma Aldrich). The same liquid phase was used for the detection of uronic acids, by analyzing it in an HPAE-PAD-ICS 5000 apparatus (Dionex) equipped with a CarboPAC PA20 column. Elution was performed using a multigradient method with 2–500 mM NaOH for 50 min. All analyses were carried out at 30 °C and 0.4 mL/min. The soluble lignin content was determined by UV spectroscopy, and the insoluble fraction by Tappi method T222 om.98. The total lignin content was calculated as the sum of the insoluble fraction after hydrolysis and the soluble fraction.

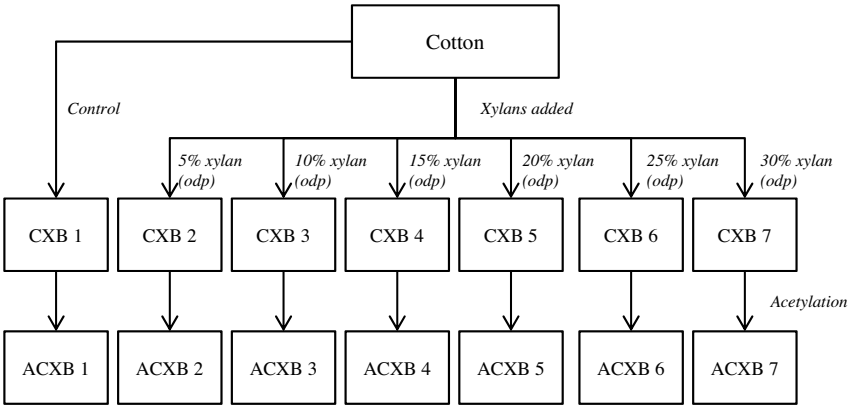

Fig. 1. Schematic representation of the treatments carried out on cotton xylan blend (CXB).

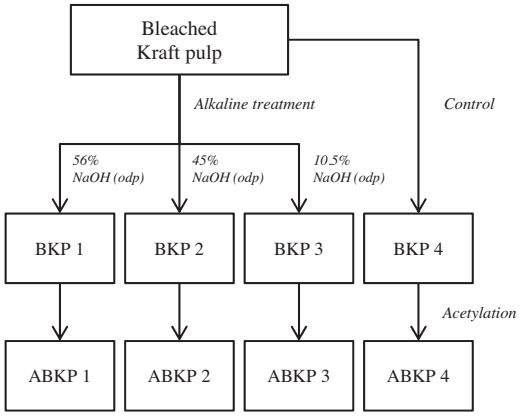

Fig. 2. Schematic representation of the treatments carried out on bleached Kraft pulp (BKP).

2.4.2. GPC-SEC

The molecular mass distribution of the xylans was determined by size exclusion chromatography (SEC) on a Young Lin YL 9170 coupled to an IR detector. Ultrahydrogel columns 120, 250 and 500 kDa of $300 \times 7.8\,mm^2$ were used, and a flow of 1 mL/min of alkaline solution of sodium acetate and sodium hydroxide 0.15 M (each) at pH 13 was applied as the mobile phase. The equipment was calibrated with pullulan standards. Injections of 20 μL were prepared by dissolving 1 mg of sample in 1 mL of the mobile phase.

2.4.3. Solubility

The solubility of the acetates was determined using the ASTM D871-96 (2004) standard. Dry-sample aliquots of 0.26 g were dissolved in 100 mL of chloroform at 25 °C. The dry weight of insoluble solid fraction was determined.

2.4.4. TGA and DSC

The thermogravimetric analysis was performed on a Netzsch TG 209 F3 Tarsus at 10 °C/min until 600 °C under pure N_2 atmosphere. The differential scanning calorimetry analysis was performed on a NETZSCH DSC 204F1 within the temperature range of 25–300 °C at a constant heating rate of 10 °C/min under inert pure N_2 atmosphere.

2.4.5. FT-IR

The FTIR spectra were recorded on a Bruker Alpha T FTIR spectrophotometer equipped with a diamond attenuated total reflectance (ATR). As many as 48 scans were collected over the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. All the FTIR spectra were recorded and processed with OPUS 7.0 software.

2.4.6. Degree of substitution (DS)

The degree of substitution was determined by adapting the ASTM D 871-96 method B, in which the acetyl groups were hydrolyzed using NaOH, and the percentage of acetyl ions (%w/w) was determined by titration with 0.5 N HCl using phenolphthalein as indicator. Having determined the percentage of acetylation in the sample, DS of cellulose in the material is calculated by the following relation (Samios, Dart, & Dawkins, 1997):

$$DS_C = (\%AC_C \times 3.86)/(102.4 - \%AC) \quad (1)$$

In materials such as xylans, in which pentoses are predominant, DS based on the percentage of acetylation is calculated by the following relation:

$$DS_X = (\%AC_X \times 3.143)/(102.4 - \%AC) \quad (2)$$

In Eqs. (1) and (2) % AC_C and $\%AC_X$ correspond to the percentage of acetylation of cellulose and xylans, respectively.

The DS_{theo} and maximum acetylation percentage ($\%Ac_{theo}$) correspond to complete acetylation of cellulose and xylans present in the material, so it is defined as the weighted sum in the content of these polysaccharides:(3)$DS_{theo} = 3X\,\%\,C/100 + 2X\,\%\,X/100$where %C and %X are percentage content of cellulose and xylans in the material.

3. Results and discussion

3.1. Acetylation

3.1.1. Raw materials

The analysis of xylans extracted from holocellulose showed that xylose is the dominant sugar in the sample and that the content of other sugars (e.g., glucose, arabinose, galactose, mannose) does not exceed 5%. The content of glucouronic acid was 2.97%, slightly lower that that reported in other studies (Gröndahl et al., 2003; Ren, Peng, & Sun, 2008). Table 1 shows the contents of carbohydrates and lignin in cotton xylan blends (CXB) and bleached Kraft pulp (BKP) used for this study. The amount of lignin does not exceed 1% for all samples, confirming the purity of the compounds obtained. The xylan content in BKP decreases when the alkali treatment is more severe, ranging from 16.3% to 7.4%. The low content of other sugars (e.g., mannose and arabinose), which does not exceed 2.5%, confirms the dominant presence of xylan-type hemicellulose in the pulp, in agreement with reports for *Eucalyptus* pulp (Sixta, 2006; Sjöstrom, 1993, chapter 3). After acetylation, in both CXB and BKP samples, the presence of glucouronic acids was detected in only a few cases, and at levels below 1%. The addition of xylans in cotton resulted in a cellulosic material with hemicellulose content between 2.2% and 31.6%.

3.1.2. Degree of substitution (DS)

The DS and acetylation percentage is the straightforward parameter that predicts the progress of the reaction between acetic anhydride and the OH groups available in cellulose (three) and hemicellulose (two). Under the conditions of our experiments, complete acetylation of pure cellulose (ACXB1 samples) was achieved; any deviation from this value can thus be attributed to the variability provided by the raw material used.

Based on the maximum acetylation potential of cellulose (44.78%) and xylans (39.82%), the maximum theoretical percentage of acetylation ($\%Ac_{theo}$) was calculated, weighted by the contents of these polysaccharides in the material (see Table 2); its comparison with the actual acetylation percentage leads to values ($\%Ac_{real/theo}$) that exceed 95% in all cases. Despite such high values, it should be noted that the degree of acetylation decreases with increasing initial xylan content in the ACXB and ABKP samples. The maximum theoretical amount was never reached in the former; it was achieved in the latter with a xylan content below 8.6%. These differences are attributed to the spatial arrangement of the hemicellulose: xylans in ABKP samples are in their natural form, around the cellulose microfibrils (Fengel & Wegener, 1984) and are distributed in the interior of the cell walls, whereas in ACXB samples they are additives in cotton fibers and presumably fail to penetrate the cell walls and thus remain only on their surface. Hemicellulose extraction in BKP leaves gaps within the fibers allowing better access of acetyl groups to the reactive cellulose moieties, with the consequent increase in the DS observed; this effect is not seen in ACXB samples, where the cotton fibers could be more compact and hardly accessible to the reactants. Popescu et al. (2012) reported that the DS of cellulose decreases toward the interior of the fiber, which indicates that the diffusion and other steric effects play an important role in cellulose acetylation. The glucouronic acid units (4-O-methyl derivatives) in the xylans 'occupy' one OH group and thus reduce the acetylation potential; nevertheless, the concentration of these units is small (<1%), so their impact on DS did not exceed 0.5%. Therefore, in a manner similar to a previous report (Jain, Sjöstedt, & Glasser, 2000), we discarded this effect as an explanation for the significant differences among samples with different xylan contents.

There is abundant evidence in the literature for a higher reactivity in the acetylation of hemicelluloses compared to cellulose, both in softwoods (Ramsden & Blake, 1997; Rowell et al., 1994) and hardwoods (Efanov, 2001). Considering the high degree of acetylation of our samples, it is reasonable to assume that the xylans of different compounds were completely acetylated ($DS_x = 2$). The DS achieved by cellulose (DS_C) was thus estimated (see Table 2): in the worst acetylation case, cellulose would have a DS_C in excess of 2.72 and, considering that the DS of commercial cellulose acetate is 2.54, this would be sufficient to maintain thermoplastic properties.

We thus conclude that the presence of xylans directly influences the DS_C, mainly due to their relative content in the material and their spatial disposition, inhibiting its complete substitution in most cases. It is evident that the DS_C tends to decrease with increasing xylan content in both types of samples; however, the different types of compounds maintain their thermoplastic properties.

3.2. Solubility

The acetyl groups are more hydrophobic than the hydroxyl groups present in cellulose. Consequently, the substitution of hydroxyl groups by acetyl groups, which occurs during cellulose and hemicelluloses acetylation, increases its solubility in apolar organic solvents. The results obtained for both samples confirm the high esterification of the polysaccharide mixtures used, since the solubility of all the samples in chloroform is higher than 80% (Samios et al., 1997).

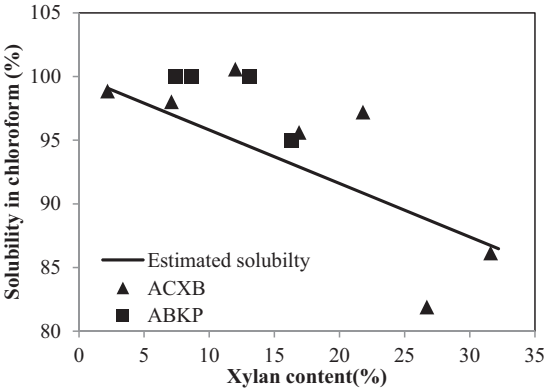

Fig. 3. Partial solubility of xylans in chloroform for different ABKP and ACXB samples.

Fig. 3 shows the solubilities of ACXB and ABKP. For ACXB samples in particular, the solubility decreases as the hemicellulose content increases; however, this effect is not so clear in the case of ABKP samples. The former decrease is thus attributed to the insolubility of xylan acetates in chloroform, in agreement with the findings of Saka and Takanashi (1998); the fact that ABKP samples did not show a clear solubility trend may be a consequence of the presence of low-molecular-weight hemicellulose, which is more soluble than the acetylated hemicellulose in ACXB samples.

The low solubility of xylan acetates can be verified by estimating the solubility parameters of the cellulose and the acetylated xylans. This was carried out using the group contribution method presented by van Krevelen and Hoftyzer (Hansen, 2007; Van Krevelen & Nijenhuis, 2009, chapter 7). For this calculation, it is considered that the polysaccharides are completely acetylated. Analyzing the parameters of cellulose triacetate and xylan diacetate, it can be concluded that the former is found at a distance of 5.54 $MPa^{0.5}$ with respect to chloroform and the latter is at 7.60 $MPa^{0.5}$. The greater the distance for a specific solvent, the lower is the affinity between these two molecules, and thus the lower their mutual solubility (Hansen, 2007). This confirms that the acetylated xylans should be less soluble in chloroform. Fundador et al. (2012) reported that the xylan acetate present in a given material has up to 58% solubility in chloroform; if this value is adopted for the xylans present in the samples, theoretical solubility can be calculated based on xylan contents that approximate the values calculated from the experimental data (see Fig. 3).

3.3. Thermal analysis

The influence of xylan content on the thermal decomposition of the acetylated mixture was analyzed by TGA. It is observed in the ABKP and ACXB samples that the degradation temperature for the 10% (Td_{10}) and 50% (Td_{50}) of the total weight tends to decrease as xylan content increases (see Table 2). Hemicellulose influence on thermal decomposition is evidenced by observing the DTG curves for both samples (see Figs. 4 and 5). Two stages are distinguished, the first attributed to degradation of xylan acetate and the second to cellulose acetate degradation (Rodrigues Filho et al., 2008; Shaikh et al., 2009). The increase in xylan content produces a clear increase in the first-stage degradation rate. However, in the second stage the degradation rate decreases as xylan acetate content increases. Therefore, the value of Td_{10} correlates with xylan degradation and that of Td_{50} correlates with cellulose degradation. This process occurs in the presence of H_2SO_4, and thus it is conceivable that sulfate formation accompanies acetylation, which in turn may affect thermal properties. Elemental analysis showed that the samples contained less than 1% sulfur which, even at this level, may

Table 2
Characterization of the acetylated samples.

Muestra	% Xylan	% Ac_{real}	%$Ac_{real/theo}$	DS_{theo}	DS_C	DS_X	Td_{10} (°C)	Td_{50} (°C)	T_m (°C)
Acetylated cotton xylan blends									
ACXB1	2.2	44.62	99.88	2.98	2.99	2.00	334.6	360.8	268.0
ACXB2	7.1	43.99	98.96	2.93	2.94	2.00	–	–	219.8
ACXB3	12.0	43.64	98.72	2.88	2.92	2.00	271.0	345.9	225.1
ACXB4	16.9	43.37	98.66	2.83	2.92	2.00	–	–	199.7
ACXB5	21.8	43.32	99.11	2.78	2.94	2.00	264.4	355.0	166.9
ACXB6	26.7	42.51	97.81	2.73	2.85	2.00	–	–	198.7
ACXB7	31.6	42.42	98.16	2.68	2.86	2.00	251.5	350.3	188.8
Acetylated bleached Kraft pulp									
ABKP1	7.4	44.52	100.23	2.93	3.01	2.00	229.8	348.0	221.4
ABKP2	8.6	44.51	100.35	2.91	3.02	2.00	227.9	347.1	222.2
ABKP3	13.1	42.02	95.21	2.87	2.72	2.00	201.0	332.0	226.3
ABKP4	16.3	42.69	97.08	2.84	2.82	2.00	214.9	332.7	212.8

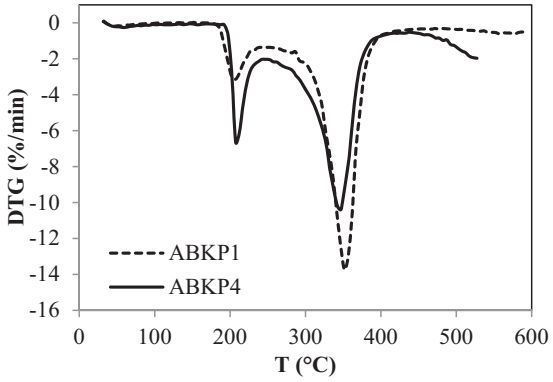

Fig. 4. DTG curves for ABKP samples.

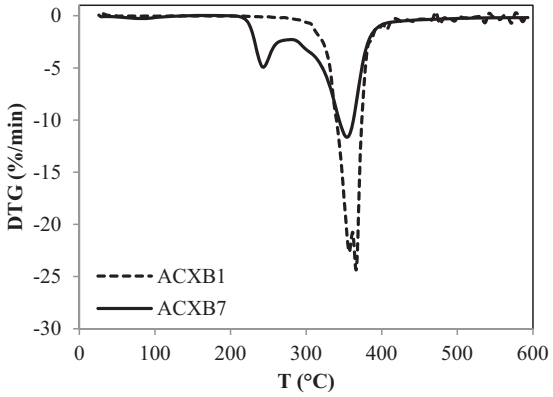

Fig. 5. DTG curves for ACXB samples.

reduce T_d; indeed, Roman and Winter (2004) reported a decrease in the maximum decomposition temperature and a broadening of the degradation profile. Our samples did not show such trends (see Figs. 4 and 5). We therefore discarded a significant sulfate effect at the expense of the widely varying acetyl group effect; we cannot rule it out, but its extent should be similar for each one of our samples. In agreement with this argument, Rodrigues Filho et al. (2008) acetylated recycled paper in the presence of H_2SO_4 catalyst, at concentration levels similar to ours, and found no evidence of a sulfate effect on the thermal properties.

In the ACXB samples, the Td_{10} values oscillate between 251.5 and 271.0 °C. These are in close agreement with results available in the literature for pure hemicellulose acetates, which are in the range of 260–290 °C (Fundador et al., 2012; Ren et al., 2007, 2008). The decrease in the degradation temperature is due to the small degree of hemicellulose polymerization in BKP. The molecular size of isolated hemicelluloses in BKP was found by size exclusion chromatography (data not shown) to vary between 0.5 and 5 kDa, while the isolated xylans from holocellulose have sizes between 3 and 32 kDa. Shaikh et al. (2009) reported that the degradation temperature Td_{10} for a sample of cellulose in sugarcane bagasse, with natural hemicellulose content of 5%, is between 210 and 220 °C, in agreement with the results obtained in our study.

The Td_{50} values did not show any major differences between ABKP and ACXB samples with similar quantities of xylans, which confirms that the differences in thermal properties are due to the presence of hemicelluloses. For ACXB the Td_{50} varies between 345.9 and 360.8 °C; for ABKP it varies between 332.0 and 348.0 °C. In both cases, these values are slightly lower than those reported in the literature for the maximum degradation temperature of cellulose acetates with a low hemicellulose content, which vary between 360 and 376 °C (Loo et al., 2012; Rodrigues Filho et al., 2008).

In all cases, endotherms associated with the melting point (T_m) of the materials were obtained by DSC analysis. The temperature at which this process occurs varies between 188.8 and 268.0 °C for ACXB, showing a decreasing tendency with the increase in xylan content (see Table 2); this is in accordance with the proposal regarding the applicability of this polymer as an internal plasticizer (Shaikh et al., 2009; Vieira, da Silva, dos Santos, & Beppu, 2011).

In ABKP, T_m increases from 212.8 °C, for the sample with 16.3% xylan, to 226.3 °C for the sample with 13.1% xylan, showing a more notable variation with respect to the xylan content than ACXB. It is also observed that the T_m of ABKP samples is close to Td_{10}, demonstrating the existence of degradation and fusion phenomena in the material, as observed in the literature for acetates of recycled paper (Rodrigues Filho et al., 2008).

3.4. FT-IR analysis

It was possible to detect the presence of functional groups and, by observation of characteristic bands, to evaluate the level of esterification in the samples. In the case of acetylation, a decrease in the band of hydroxyl groups (~3300 cm^{-1}) and an increase in the band associated with carboxyl groups (1748 cm^{-1}) is observed (see Fig. 6). A reduction in intensity of the band at 2900–2860 cm^{-1} (>CH_2 symmetric stretching) is also observed. The band at 1640 cm^{-1}, corresponding to —OH, along with the band at 1461 cm^{-1}, associated with the deformation of O—H in the cellulose plane, is seen to disappear. At 1237 cm^{-1} appears a characteristic band of C—O bond stretching in the acetyl group and the same occurs at 1375 cm^{-1}, corresponding to C—H at the acetyl group. All these changes are indicators of substitution of hydroxyl groups by the acetyl groups which takes place in each acetylation process and coincide with those reported in the literature (Adebajo & Frost, 2004; Popescu et al., 2012; Shaikh et al., 2009).

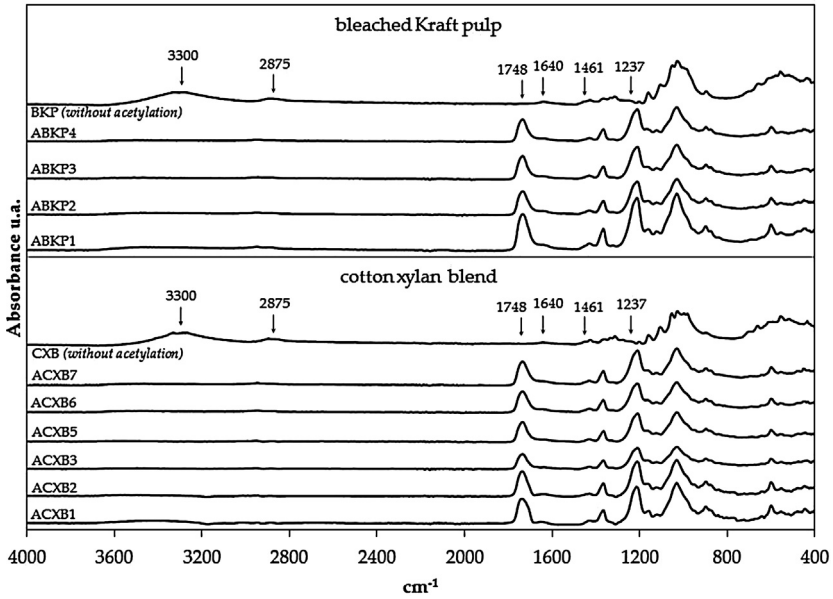

Fig. 6. FT-IR spectra of various samples with different acetylated hemicellulose contents: ABKP (top) and ACXB (bottom).

Due to the high degree of esterification achieved in all the samples, the hydroxyl group band (3200–3800 cm^{-1}) does not provide additional information regarding the hydrogen bonding interactions. The small quantity of free OH groups, as well as the presence of even minimun amounts of H_2O, interferes with the interpretation of the spectra in this region.

Similar spectra were observed for the acetylated samples (see Fig. 6): a high acetylation percent was achieved for all the samples, with very small differences in bands associated with modifications of functional groups. Nevertheless, by analyzing the deformation of carbonyl bands (1748 cm^{-1}), as well as C—H in —O—CO—CH_3 (1375 cm^{-1}), some differences in the ACXB samples can be noted: higher absorbance is obtained for sample ACXB1 and it decreases for sample ACXB6, which is in accordance with a lower esterification degree of the latter. In the ABKP sample series, the trend is even more evident: the absorbance difference is significant between simple ABKP1 (more Acetylated) and samples ABKP2, ABKP3 and ABKP4 (see Fig. 7) which have a lower DS. Despite the slight variations in acetylation degree, it was possible to establish differences in the degree of esterification by a detailed analysis of the corresponding FTIR bands.

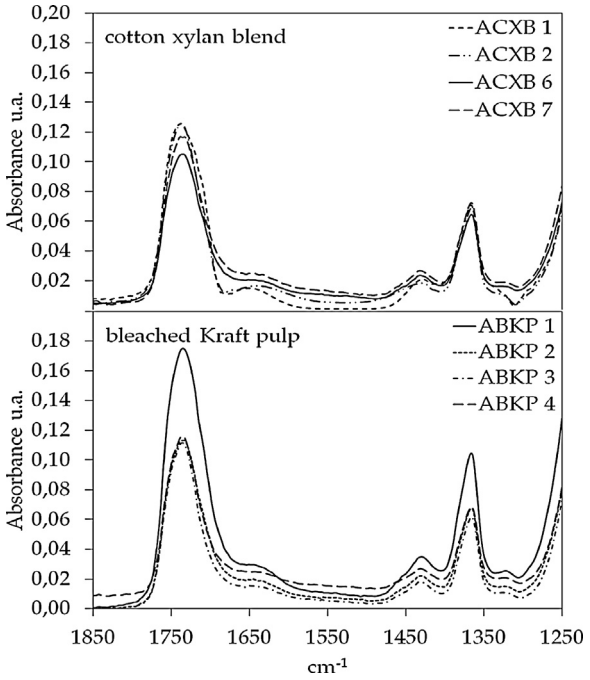

Fig. 7. FT-IR spectra in the region near 1375 cm^{-1} for ACXB (top) and ABKP (bottom) samples.

4. Conclusions

The presence of xylans in Kraft pulp acetylation does not have a significant negative effect on the physical properties of the acetylated material: minor decreases in the degree of substitution, temperature of cellulose degradation and chloroform solubility were observed. In contrast, there was a pronounced decrease in the melting temperature with increasing xylan content, which was beneficial for the application of the acetylated polymer as a natural internal plasticizer.

Both the bleached Kraft pulp (BKP) and the model samples of cotton xylan blend (CXB) exhibited a high degree of acetylation, in excess of 95%. The lower degree of acetylation in ABKP samples was attributed to differences in the distribution of xylans, bulk in the pulp *vs* superficial in the cotton. The lower thermal stability of the ABKP samples is attributed to the lower molecular weight of the xylans in them. On balance, therefore, the melting temperature decrease is the most outstanding effect, which adds value to BKP with high xylan content and makes it an improved raw material for the production of cellulose acetate.

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