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Effects of acetylation in vapor phase and mercerization on the properties of sugarcane fibers

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ABSTRACT

Chemical modification of sugarcane bagasse fiber was achieved by mercerization reaction and esterification reaction with anhydride acetic vapor. This is a new acetylation procedure. The results show that the fiber length and diameter are reduced after the reactions. Fourier transform infrared spectroscopy (FT-IR) studies produced clear evidence of the partial acetylation reaction. Optical microscopy revealed fibrillation in the acetylated fiber attributed to hemicellulose dissolution. The thermal stability measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) increased after acetylation and decreased after mercerization. The higher thermal stability of the acetylated fiber as compared with modified fibers in liquid medium was attributed to the small quantity of water and acetic acid present for the reaction in vapor phase. The lesser tensile strength of the acetylated fiber was due to fibrillation. The porous structure obtained favors migration of the polymer chains into the fiber acetylated, and thus it should enhance the polymer–fiber adhesion in polymer composites.

1. Introduction

Sugarcane bagasse is an agro-industrial waste product produced on the order of millions of metric tons per year during the production of ethanol to be used as fuel. In general, the dried Brazilian sugarcane bagasse consists of approximately 51.1% fibers and 47.5% medulla. The dried fiber contains 51.1% cellulose, 26.7% hemicellulose, 20.8% lignin and 0.8% other components. The medulla is a tissue of non fibrous character that contains 47.5% cellulose, 28.5% hemicellulose, 20.2% lignin and 3% other components (Bertoti, 2004).

Cellulosic fibers, such as sugarcane, sisal, banana, coconut, wood and jute, have been incorporated in a wide variety of thermoplastics, such as polypropylene, polystyrene, polyester and polyamides, as reinforcement in polymeric composites due to their properties which can improve the material and due to the fact these materials are from renewable sources (Lee & Mariatti, 2008; Luz, Tio, Rocha, Gonçalves, & Del'Arco, 2008; Vilay, Mariatti, Taib, & Todo, 2008; Xie, King, Kilpelainen, Granstrom, & Argyropoulos, 2007). These fibers differ in biodegradability, moisture content, thermal stability, acoustic insulation, abrasion resistance, stiffness and tensile strength. Compared with other fibers, sugarcane fiber has a lower tensile strength, lower Young's' modulus, higher moisture content and better biodegradability due to its higher contents of hemicellulose (27%) and lignin (21%), compared to 13% and 13% in jute fiber and 13% and 11% in sisal fiber, respectively (Bledzki & Gassan, 1999).

Among all the natural reinforcing materials, the fiber of sugarcane bagasse appears to be a promising fiber when the aim is the biodegradation and low cost. However, to improve its properties it is necessary to improve the adhesion between the hydrophilic fiber and the hydrophobic matrix and to reduce the moisture content of the fiber. Only a few chemical modification methods of the bagasse have been described in literature, including mercerization and acrylic acid treatments (Vilay et al., 2008), mercerization and acetylation (Filho et al., 2000; Luz et al., 2008), succinylation (Liu et al., 2007), treatment with benzyl chloride (Luz, Gonçalvez, & Del'Arco, 2007) and silane (Bilba & Arsene, 2008).

The conditions of the modification reactions affect the fiber properties, including the morphology, thermal stability, tensile strength and chemical strength. Acetylation of sugarcane fiber has been performed at room temperature using a mixture of glacial acetic acid, toluene, perchloric acid and anhydride acetic, for 48 h (Filho et al., 2000) and using a mixture of acetic acid, anhydride acetic (Cerqueira, Filho, & Meireles, 2007) for 2 h up to 48 h. Higher temperatures were adopted using glacial acetic acid, sulfuric acid and anhydride acetic, at 35 °C, followed by anhydride acetic addition at 18 °C and 55 °C for 5 h (Luz et al., 2008). The conditions of the mercerization reaction reported in literature

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were aqueous NaOH solution 1% for 3 h at room temperature (Vilay et al., 2008) and aqueous NaOH solution 1.5% for 1 h at 98–100 °C (Luz et al., 2008). All these reactions were conducted in the liquid medium.

This work describes a new acetylation reaction procedure, termed acetylation in vapor phase, and its effects and the effects of the mercerization on the morphology and physical properties of sugarcane fiber, taking into consideration its possible utilization in composites materials. Acetylation in vapor phase is a new and an inexpensive methodology for modifying the surface of the sugarcane fiber, avoiding the absorption of solvents, reagents and products in the internal walls of the fibers. The reactions were confirmed by transmission Fourier transform infrared spectroscopy (FT-IR). The fibers were analyzed by density and size measurements, scanning electron microscopy (SEM), optical microscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and tensile testing.

2. Materials and experimental

2.1. Materials

Sugarcane bagasse was obtained from a local supplier, after being processed to extract liquor. Sodium hydroxide, acetic anhydride, cycle hexane and ethanol were of p.a. grade.

2.2. Fiber treatments

2.2.1. Fiber extraction

The sugarcane bagasse were cut in pieces 15 mm long and washed in water at 70 °C for complete removal of the soluble compounds. Then, they were transformed into pulp in a 1 L blender with 500 mL of water under stirring for 10 min to promote the de-aggregation of the fibers. The fibers were then washed with distilled water in a sieve with a 1.4 mm mesh, at room temperature and at 70 °C to removal small particles, medulla and soluble compounds that were adhered to the fibers. They were dried at 70 °C until they reached a constant weight. To remove the compounds soluble in organic solvents, the fibers were submitted to soxhlet extraction for 48 hr using cycle hexane and ethanol (1:1 by volume) and dried to constant weight at 60 °C. The mass percentage of fiber obtained relative to the initial mass of sugarcane bagasse was of 40%.

2.2.2. Mercerization reaction

Alkali treatment of the treated sugarcane fibers was preformed by immersing the fibers in aqueous NaOH solutions (1 fiber/5 solution, v/v) at 10% by weight for 1 h at 0 °C, under stirring at low speed. The mercerized fibers were washed with distilled water many times to achieve pH 7 and dried at 60 °C.

2.2.3. Acetylation reaction

The acetylation of the treated fibers was conducted for 1 h at 145 °C using acetic anhydride as the acetylating agent and sulfuric acid as the catalyst. Bundles of the fibers aligned vertically in the reactor were put in contact with the vapor of these substances under reflux; in this way, the reaction occurs mainly on fiber surface. The fibers were washed with distilled water up to pH 7 and dried at 60 °C.

2.3. Fibers characterization

The length of 200–250 individual fibers was determined using a paquimeter. For determination of the width, 50 individual fibers were placed on various glass plates, and the transversal section lengths were measure with a Zeiss lens and a micrometer rule. Five determinations were made for each fiber. The density was determined using a pycnometer and water.

Scanning electron microscopy (SEM) observations of the unmodified fiber were carried out using a Philips 515 SEM. The fibers were laid down on aluminum stubs using conductive tape and were sputter coated with gold prior to measurement. Optical microscopy (OM) observations of single fibers were made using an Olympus BX50 in the reflection mode.

Transmission Fourier transform infrared spectroscopy (FT-IR) was performed by means of a Spectrum BX Perkin Elmer Spectrometer, taking 32 scans with a resolution of 4 cm^{-1} using a KBr disc made from 1 mg of the powder dispersed in 150 mg of KBr. The differential scanning calorimetry (DSC) experiments and thermogravimetric analysis (TGA) were done using a Shimadsu DSC-50 and TGA-50H with the sample in powder form. Scanning speed was 10 °C min^{-1} and nitrogen flow was 50 $\text{cm}^3\,\text{min}^{-1}$. The measurements on samples weighing 8–10 mg were performed from 20 °C up to 400 °C and 20 °C up to 1000 °C for DSC and TGA experiments, respectively. Tensile testing was performed using a Contem testing machine with a load cell of 50 Kgf at room temperature, according to the standard method ASTM 12189. Bundles of 10 fibers 8 cm long were aligned and attached with adhesive tape for testing.

3. Results and discussion

3.1. Density and size

The apparent densities were 0.33 ± 0.03, 0.34 ± 0.02 and 0.44 ± 0.03 g cm^{-3}, for the unmodified, acetylated and mercerized fibers, respectively. The fiber density was not affected by the acetylation reaction, but it increased after the mercerization reaction. This means that the NaOH treatment destroyed the cellular structure of the bagasse fiber (Vilay et al., 2008), and hence reduced the void content of the fiber, as will be evidenced by the diameter measurements, while the acetylation reaction occurred mainly on the fiber surface and did not affect the structure of the internal layers of the fibers.

The fibers lengths and diameters are shown in Fig. 1. The initial length of 15 mm was reduced after the extraction procedure, giving the distribution curves in Fig. 1. The highest frequency is 8 mm long for unmodified fibers, 6 mm long for acetylated fibers and 4 mm long for mercerized fibers. The number-average length was 5.3 ± 2.7, 6.7 ± 2.9 and 7.0 ± 3.4 mm for mercerized, acetylated and unmodified fibers, respectively. There is no significant difference (at 95% level) among acetylated and unmodified results. The differences between the distribution curves of the acetylated and unmodified fibers can be attributed to shrinking of the fibers due to the hemicellulose removal. When hemicellulose is removed, the fibers became less rigid causing the rearrangements of the fibrils (Bledzki & Gassan, 1999).

The diameters with high frequency change between 0.04 and 0.06 mm for acetylated fibers, and they are 0.06 and 0.02 mm for the unmodified and mercerized fibers, respectively.

3.2. SEM and optical microscopy

The SEM photomicrograph (Fig. 2) of the unmodified fiber shows a structure with aligned fibrils and light regions that indicate the residues of materials adhered to the surface as medulla and waxy substances. These substances contribute to ineffective fiber-matrix bonding in polymeric composites (Vilay et al., 2008). The dark region indicated by the arrow represents damage on the surface caused by the stirring during the extraction process.

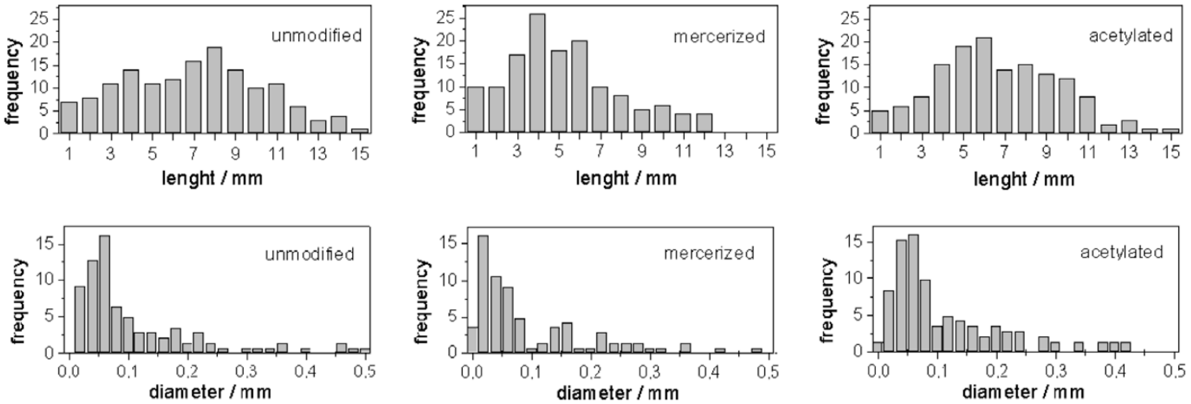

Fig. 1. Length and diameter of the: unmodified, mercerized and acetylated fibers.

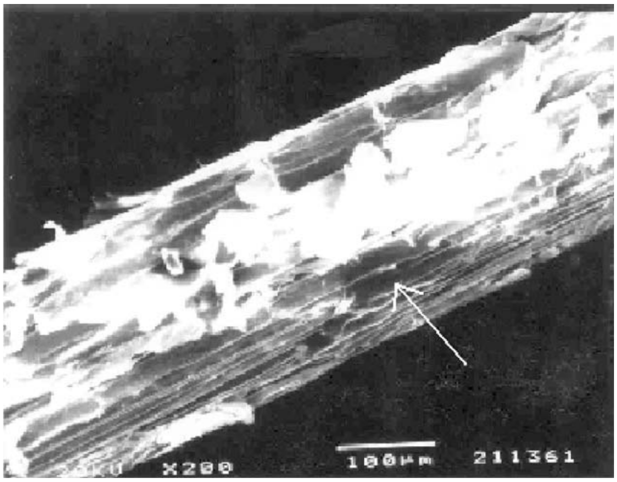

Fig. 2. SEM photomicrographs of unmodified sugarcane fiber.

Both fibrils and residues (light region) can also be observed in the optical photomicrographs (Fig. 3a).

The optical photomicrographs of the fibers reveal the changes to the fiber surface due to the chemical reactions. In the acetylated fiber there are some fibrils on the surface that are detached from the fiber, and there are void spaces between the fibrils (dark region), which are evidence of fibrillation (Fig. 3b). Because the hemicellulose is the component of the fiber that cements the fibrils, these results show that the hemicellulose was removed. The dissolution of hemicellulose during the acetylation of sisal and sugarcane fibers has been reported in the literature and is assumed to be responsible for the fibrillation (Li, Mai, & Ye, 2000; Vilay et al., 2008). The large dark region on the top left represents a region of fracture due to the extraction procedure. The residues (light region) are in lesser quantity than in the unmodified and mercerized fibers.

The fiber morphology changes drastically due to the mercerization reaction because of the aggressive action of the NaOH. The fibers become curved, their surface is rough and irregular, and the fibrils are not perceptible in Fig. 3c. It is evident that the fiber diameter decreased, as compared to the unmodified and acetylated fibers, due to the removal of some of the lignin and hemicellulose (Bledzki & Gassan, 1999). Li et al. (2000) reported the reduction in the fiber diameter and the formation of rough surface in sisal fiber after treatment with NaOH.

The surface of the acetylated fiber, due to fibrillation, has a more porous structure that the surface of the unmodified and mercerized fibers. Highly porous and uniform morphology have been obtained by homogeneous acetylation carried out in ionic liquids (Xie et al., 2007). These findings are contrary to what is reported in the literature, for fibers modified by heterogeneous acetylation reaction in liquid phase (Sreekala & Thomas, 2003). Acetylation also makes the fiber hydrophobic, and thus reduces the moisture absorption (Tita, de Paiva, & Frollini, 2002). The small quantity of residues, the hydrophobic character, and the porous structure could improve the adhesion of acetylated fibers to apolar polymers, like polypropylene and polyethylene.

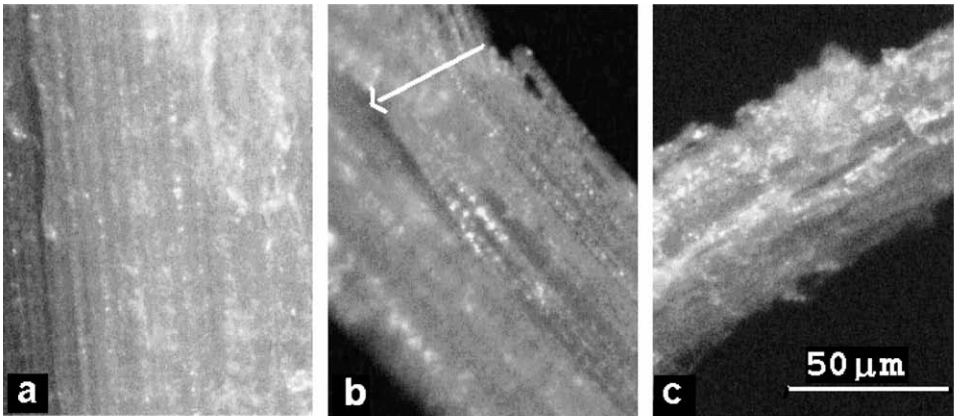

Fig. 3. Optical micrographs with reflected light (a) unmodified, (b) acetylated and (c) mercerized.

3.3. FT-IR

Fig. 4 shows the spectra of the unmodified and acetylated fibers. Observed in both spectra are the typical stretching vibrations of the $C{=}O$ group at 1740 cm^{-1} and of the $C{-}O{-}C$ group at 1257 cm^{-1} and the bending vibration of the CH_3 group at 1375 cm^{-1}, which are characteristics of the acetate group (Cerqueira et al., 2007; Filho et al., 2000; Xie et al., 2007). In the case of the unmodified fiber, the acetate groups might have originated from acetyl in hemicellulose (Zini, Scandola, & Gatenholm, 2003). The intensity of these absorption bands relative to the absorption band of the CH_2 group at 1436 cm^{-1}, is larger for the acetylated fiber than for the unmodified fiber, confirming the acetylation reaction.

In the acetylated fiber spectrum there is an absorption band of medium intensity at 1601 cm^{-1}, which is only a shoulder in the unmodified and mercerized spectra. This absorption is attributed to the $C{=}C$ stretching vibration of the aromatic ring present in the lignin structure. As compared with the CH_2 absorption, the relative intensity is higher for the acetylated fiber than for the unmodified fiber, suggesting that the lignin concentration is higher in the acetylated fiber. This result provides evidence that part of the hemicellulose was extracted during the acetylation reaction, while the lignin content was not affected. This can be explained by considering that the acetylation reaction in vapor phase occurred at 145 °C. Hence, the fiber constituents that are water soluble (such as hemicellulose) and present in the primary layer were dissolved by the water vapor, while the water insoluble constituents (such as lignin) were not affected. The large band at 3440 cm^{-1}, attributed to OH stretching (not shown), did not appreciably change upon fiber acetylation. Since only the easily accessible OH groups of the cell walls were able to react, the fibers were only partially acetylated.

3.4. Thermogravimetric analysis

The thermal stability of the fibers before and after the reactions was investigated by TGA. As shown in Fig. 5, the thermal stabilities of the modified fibers, as compared with the unmodified fiber, were altered. The acetylated fiber exhibits an initial weight loss of 5% up to 60 °C; thereafter, it remains stable up to 260 °C when the first degradation stage begins, mainly due to dehydration reactions (Scheirs, Camino, & Tumiatti, 2001). The losses for the unmodified and mercerized fibers were 10% and 12 % of weight up to 80 and 100 °C, respectively, due to the evaporation of water and solvent residues; thereafter, they remain stable up to 240 °C.

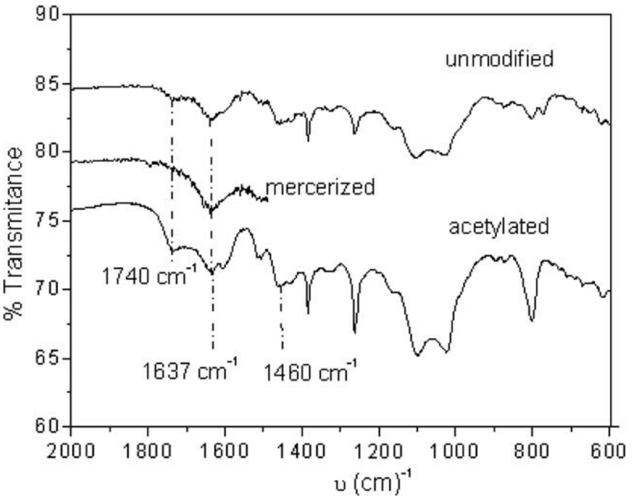

Fig. 4. FT-IR spectra of sugarcane fibers: unmodified, mercerized and acetylated.

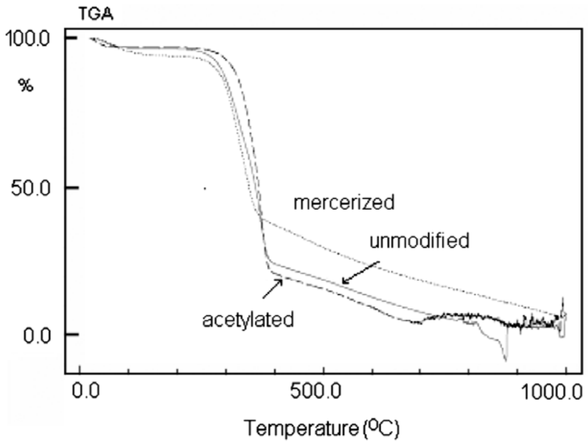

Fig. 5. Thermogravimetric analysis data for the sugarcane fibers unmodified, mercerized and acetylated.

The temperatures at the inflection points of the curves (the maximum rate of degradation) occur at 336, 368 and 378 °C for the mercerized, unmodified and acetylated fibers, respectively. In the literature, the temperature at the inflection point has been reported for unmodified flax fibers and for valerylated flax fibers as 364 °C (Zini et al., 2003); for both unmodified wood-based materials and acetylated wood (degree of substitution, DS = 92.6%), it was around 360 °C, and for benzoylated wood (DS = 94.0%), it was around 375 °C (Xie et al., 2007). Our results for the unmodified sugarcane fiber are closer to the literature results. For the acetylated sugarcane fiber, our results were 14, 18 and 3 °C higher than those of the ester modified fibers reported in the literature. Thus, the chemical treatment of the fiber via acetylation in vapor phase enhanced the thermal stability of the lignocellulosic structure of the fiber, as compared to the unmodified and mercerized fibers and ester modified fibers reported in the literature.

The higher stability of the acetylated fiber was attributed to the small quantity of water and acetic acid in contact with the fiber, since the absorbed water and the acid acetic are responsible for the acid hydrolyse of the lignin and cellulose during the heating. This can be explained by considering that: (i) at the temperature of the reaction (145 °C), the hemicellulose of the primary layer, that is, the main one responsible for the water absorption (Tita et al., 2002), was removed, as evidenced by FT-IR and optical microscopy; (ii) the quantity of acetic acid in contact with the fibers was small because acetic acid is removed in the acetylation with anhydride acetic vapor, while in the acetylation with anhydride acetic liquid it remains in solution and (iii) at 145 °C, the acetic acid and water are removed by evaporation.

The effect of the presence of acid acetic dissolved in the reaction medium on the fiber degradation have been reported by Xie et al. (2007). When acetic anhydride was used as acetylation reagent, significant degradation was observed, however, under the same reaction conditions but in the presence of pyridine, an acid acceptor, the weight percent gain increased by about 80%.

The mercerization process destabilizes the fiber due to the high content of the water retained in the fiber after the reaction. The water dissolves the hemicellulose (Tita et al., 2002) and provokes the hydrolyse of the lignin and cellulose during the heating.

3.5. Differential scanning calorimetry

DSC measurements were carried out to compare the thermal transitions of the fibers. Fig. 6 shows large endothermic curves with peak maxima at around 30, 40 and 48 °C for acetylated, mer-

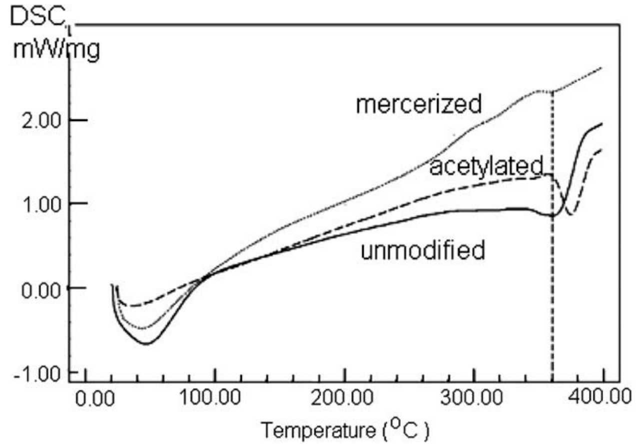

Fig. 6. DSC analysis of sugarcane fibers unmodified, mercerized and acetylated.

cerized and unmodified fibers, respectively, that are attributed to the outflow of water and solvent residues as reported by Filho et al. (2000). As evidenced by the smaller area, the acetylated fiber retained smaller quantity of these products, as also observed with TGA experiments.

The DSC endotherms, with maxima located at 350 °C (small peak), 360 °C and 375 °C for the mercerized, unmodified and acetylated fibers, respectively, were attributed to the thermal decomposition of the lignin and cellulose, also suggested by the TGA experiments (Scheirs et al., 2001). For all fibers, there are no fusion endotherms, since cellulose normally decomposes before fusing (Filho et al., 2000).

3.6. Tensile test

The tensile strength of the fibers was 0.22 ± 0.03, 0.21 ± 0.06 and 0.11 ± 0.03 MPa for unmodified, mercerized and acetylated fibers, respectively. The lesser tensile strength of the acetylated fiber was due to fibrillation provoked by the loss of hemicellulose. In the literature, a reduction of tensile strength from 445 to 320 MPa in sisal fiber was also observed, caused by the loss of the hemicellulose during acetylation (Li et al., 2000).

4. Conclusions

Acetylation in vapor phase decreases the hydrophilic properties of the fibers and enhances the thermal stability. Thus, acetylated fibers can be used as reinforcement in polymers and processed up to 370 °C without suffering thermal degradation. A surface with a more porous structure than that of the unmodified and mercerized fiber was obtained due to fibrillation. The porous structure favors migration of the polymer chains into the fiber structure, and thus it enhances polymer–fiber adhesion. These results are important if chemically modified sugarcane fibers are to be applied as reinforcement in thermoplastic polymers. The low cost and the removal of the reagents by condensation became the methodology attractive to industrial application.

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