Solvent-free acetylation of lignocellulosic fibers at room temperature: Effect on fiber structure and surface properties

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ABSTRACT: Acetylation is one of the most interesting chemical treatments to improve the affinity of lignocellulosic fibers with polymeric matrices for the elaboration of several types of composites. In this paper, the acetylation of flax and wood pulp (bleached softwood Kraft pulp and thermomechanical pulp) fibers was carried out at room temperature in a solvent-free system with acetic anhydride in the presence of sulfuric acid as catalyst. The effect of acetylation on the fine structure of fibers was investigated by spectroscopic methods, while the extent of acetylation was quantified by weight percent gain. The effect of reaction time on fiber morphology was studied at macro- and microscale using scanning electron microscopy, optical microscopy, and fiber quality analysis. The evolution of the hydrophobic/hydrophilic character of fibers was determined by contact angle measurements. The wettability of fibers by liquid epoxy resin was also evaluated to confirm the improvement of the affinity of acetylated fibers with the epoxy matrix. It was found that the hydrophilic character of fibers decrease with increasing reaction time, whereas the trend was less pronounced beyond specific reaction times. Acetylated fibers can therefore be potential candidates for replacing nonbiodegradable reinforcing materials in composite applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42247.

INTRODUCTION

For more than a decade, numerous laboratories and technical centers around the world are conducting research in order to incorporate natural materials to plastics obtained from fossil fuels.[1] Cellulose is the main representative of this class of material. This biopolymer, derived from renewable resources, is more than ever the subject of numerous scientific studies. Cellulosic fibers are receiving attention for applications in reinforcing composite materials,[2] because of their low cost, low density, high mechanical properties, and biodegradability. Thus, many modern technologies have used composite materials reinforced by natural fibers with properties that cannot offer traditional materials like metals, ceramics, and polymers.[3]

Different natural fibers such as flax, jute, hemp, sisal, palm, bamboo, and wood fibers have been used as reinforcement in composite materials. However, a surface treatment is generally required to improve the fiber/matrix interfacial bonding.[4–6] The reagents used to modify the fiber surface are numerous, ranging from small molecules to macromolecules. These treatments are carried out to establish an effective interface between the different composite constituents. An even better strategy consists in creating covalent bonds between fibers and the matrix. This provides an effective stress transfer and consequently develops high-performance composites.[7]

The esterification of natural fibers reduces their hydrophilic character by substituting hydroxyl groups with less polar entities. The acetylation of fibers is among the simplest esterification reaction to modify or enhance natural fibers properties.[8] Therefore, the study of the effect of acetylation on the properties of cellulosic fibers is of increasing interest. The reaction may be carried out either in heterogeneous or homogeneous phase, with or without solvent. However, the solvent-free chemical modification is preferred since the solvent dilutes reagents and subsequently decreases the reaction rate. Moreover, the use of a solvent requires complicated separation procedures to

recover the final product after the reaction. This makes the process undesirable and increases the production cost. In addition, organic solvents are often harmful to the environment and operators.

The solvent-free acetylation reaction using acetic anhydride as the reagent can be carried out, in some instances, with a catalyst to improve the reactivity of acetic anhydride. Several catalysis systems have been evaluated such as iodine,[9,10] sulfuric acid,[9,10] and pyridine and its derivatives.[9,10] Depending on experimental conditions, a high yield of acetylated fibers can be obtained. Other researchers have opted for acetylation without catalysis. However, the reaction is carried out at high temperature.[11] The acetylation of cellulosic fibers with acetic anhydride in a homogeneous medium in presence of nonderivatizing solvents is also the subject of a detailed study, particularly in ionic liquids[12,13] and in nonaqueous saline solutions.[12,13]

The interest for the acetylation of lignocellulosic fibers in an environmentally safe way is steadily increasing.[14,15] However, the cost-effectiveness of the process and the possibility of a scale-up to industrial conditions have not been sufficiently studied. This work presents a process that increases the hydrophobicity of the fibers while respecting the environment (no solvent used) and is economically viable in terms of energy and equipment (no heating required). The main objectives of this study are (1) to evaluate the effect of acetylation time on the cellulosic fibers structure and (2) to study the influence of this chemical treatment on the wettability of fibers in order to evaluate their affinity with epoxy resins frequently used in composite materials. For this purpose, flax, Kraft, and thermomechanical pulp fibers were acetylated in a heterogeneous reaction environment, for different reaction times at room temperature and the structural modification of lignocellulosic fibers have been examined. In addition to being solvent free, the main advantage of the reaction process used in this work is that it does not require any heating. Therefore, it is very low cost and easy to implement in an industrial environment. To evaluate the effect of the acetylation treatment on fiber affinity with polymeric matrices, wettability tests have been performed using the drop shape method. Two liquids were tested: water and liquid epoxy resin to demonstrate that the modified fibers can advantageously be used as reinforcement in composite materials.

EXPERIMENTAL

Materials
Lignocellulosic fibers used in this study were obtained from different suppliers: bleached softwood Kraft pulp (Kruger Wayagamack, Trois-Rivières, Canada) thermomechanical pulp (TMP) (Kruger Trois-Rivières, Canada) and flax fibers (Safilin, Sczytno, Poland). Before treatment, the flax fibers were cut in 5 mm length from a yarn spool. Acetic anhydride (ACS reagent grade, ≥98% purity) and sulfuric acid were used as received and were supplied by Sigma Aldrich and Fisher Chemical, respectively.

Solvent-Free Acetylation of Kraft, TMP, and Flax Fibers
The acetylation of flax, Kraft, and TMP fibers with acetic anhydride was carried out in heterogeneous conditions, without solvent and using sulfuric acid as catalyst. The reagent/catalyst

ratio used in this study was determined by Olaru et al.[15] Acetic anhydride (5 mL) was manually mixed with sulfuric acid (10 μL)) in a shallow large-diameter beaker for a few seconds. Then 1 g of fibers was added and the beaker was sealed with an aluminum foil to minimize anhydride hydrolysis under the effect of humidity. The volume of added liquid (anhydride and sulfuric acid) was not sufficient to obtain a paste. The fibers were only impregnated by the liquid phase. Acetylation was performed at room temperature (22°C), without stirring, for different reaction times: 30 min and 1, 2, 3, 4, 11, and 24 h. The samples were filtered and washed with an acetone/ethanol mixture, filtered, and washed several times with deionized water until the pH of the filtrate was neutral. Next, the modified fibers were dried under vacuum at room temperature before characterization.

Infrared Spectroscopy
Fourier transform infrared (FTIR) spectroscopy was used to evaluate the effect of the reaction time on the chemical structure of fibers. Spectra were recorded with a Thermo Scientific Smart iTR spectrophotometer and the samples were scanned using diffuse reflectance mode from 4000 to 500 cm^{-1}. A total of 16 scans were taken for each sample with a resolution of 1 cm^{-1}.

Weight Percent Gain
The acetylation yield was reflected by the weight percent gain (WPG). The substitution of a hydroxyl group by an acetyl group will increase the weight of the material by 52 g mol^{-1} of anhydroglucose unit.

Nuclear Magnetic Resonance
Solid-state ^{13}C-NMR was carried out on Varian 300 INOVA spectrometer using cross-polarized magic angle spinning (CPMAS) techniques. The spectrometer was operated at 100 MHz.

Scanning Electron Microscopy
Scanning electron microscopic (SEM) has been used to examine the surface morphology of fibers before and after acetylation. Micrographs were obtained with a JEOL JSM T300 microscope operated in secondary electron mode at a beam current of 100 μA with an accelerating voltage of 15 kV.

Fiber Morphology
The chemical treatment affects fiber's morphology. For this reason, a fiber length and rectitude analysis was performed. The fiber length, curl, and kink indices were determined using an electronic sequential fiber analyzer (FQA, Optest Equipment) and the mean arithmetic values were reported. Because of technical limitations, flax fibers morphology could not be evaluated with the FQA. However, it was investigated using a Zeiss optical microscope. Each flax fiber length value is the average of 60 measurements.

Wettability
Contact angle measurements are a simple method to evaluate the affinity of fibers for liquids having different polarities. Higher affinity (better wettability) between the liquid and the surface is obtained for low contact angles between the droplet and the surface. Contact angles value at equilibrium between
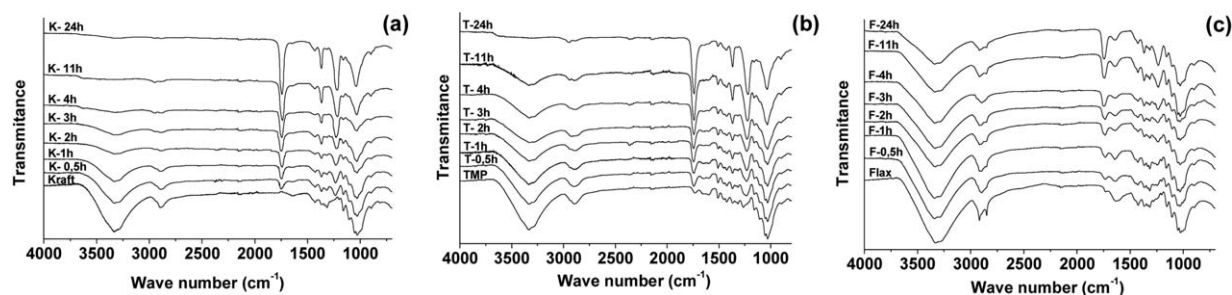
Figure 1. Evolution of the acetylation reaction by FTIR spectroscopy for: (a) Kraft; (b) TMP and (c) flax fibers.

the surface and the tangent to the water drop were obtained using FTA4000 Microdrop device (First Ten Angstroms). The instrument is equipped with a camera that monitors the contact angle with time. Measurements were carried out using water to evaluate the hydrophilic character of fibers after acetylation, and epoxy resin to evaluate the hydrophobic character and determine the efficiency of the chemical treatment for composite materials. Each reported value is the average of three measurements. To obtain a flat and smooth surface, fibers were pelletized using a hydraulic press at a pressure of 15 MPa.[16] The pellet shape diameter is about 13 mm.

RESULTS AND DISCUSSION

The FTIR spectra of untreated and acetylated flax, Kraft and TMP fibers are shown in Figure 1. All spectra show absorption bands at 1033 cm^{-1}, due to C—O stretching in holocellulose and lignin,[17] 2890 and 3474 cm^{-1}, assigned to the C—H stretching vibration of aliphatic methylene groups and the cellulose O—H vibration, respectively.[17] The structural change of treated fiber is confirmed by the appearance of three new peaks characteristic of the acetyl group. Indeed, the spectra show an intense absorption around 1740 cm^{-1} representative of the C=O bond and two other bands located at 1366 and 1215–1230 cm^{-1} arising from the C—H bond bending in —O(C=O)—CH_3 and the C—O stretching of acetyl.[15,18] As expected, for untreated fibers, these peaks are absent. We also observed that the intensity of the three peaks increase with
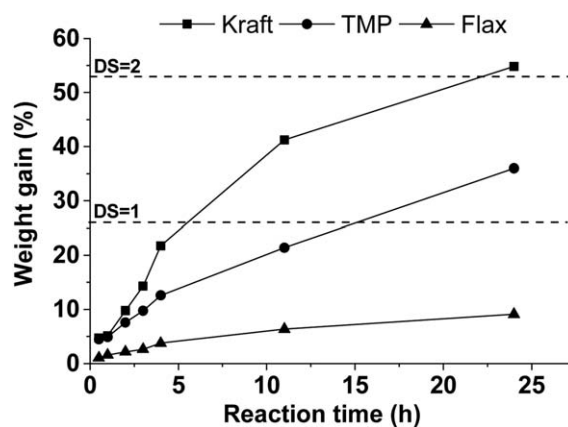
increasing reaction time for Kraft, TMP, and flax fibers, in particular the carbonyl peak, as illustrated in Figure 2. The substitution of cellulose hydroxyl groups with acetyl is also confirmed by the decreasing intensity of the O—H band at 3474 cm^{-1}. The comparison between the three fiber spectra shows that Kraft pulp fibers are more acetylated than TMP and flax. This is probably due to the presence of residual hemicelluloses and lignin in TMP and flax fibers which impedes the access of anhydride acetic molecules to hydroxyl groups. This result is confirmed by the mass yield of the acetylation reaction.

On the other hand, the absence of peaks in the 1818–1751 cm^{-1} region (due to the coupled symmetric and asymmetric stretching of the acetic anhydride carbonyl function) indicates that there is no residual unreacted acetic anhydride trapped between acetylated fibers. The spectra also prove that the samples are free of acetic acid by-product. Indeed, the modified fibers spectra do not show any absorption at 1711 cm^{-1} (C=O normal stretching of carboxylic acid dimers).[19,20]

Figure 3 shows an increase in weight gain with increasing acetylation time for the three fibers. The reaction yield is strongly influenced by the fiber type, implicitly by cellulose, hemicellulose, and lignin contents.[11] As expected, Kraft pulp fibers were more successfully acetylated than TMP and flax since the extent of acetylation is much higher and the kinetic is very fast. This is probably due to the fact that the hydroxyl groups of Kraft fibers are more accessible to acetic anhydride compared to TMP and flax for which the reactive surface is partly covered by
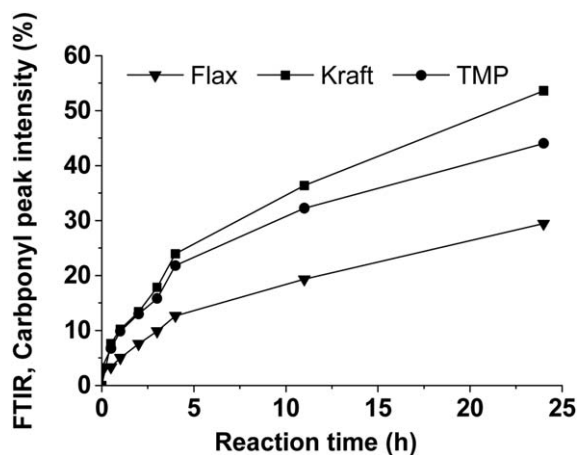
Figure 2. Carbonyl peak intensity at 1736 cm^{-1} as a function of the reaction time.

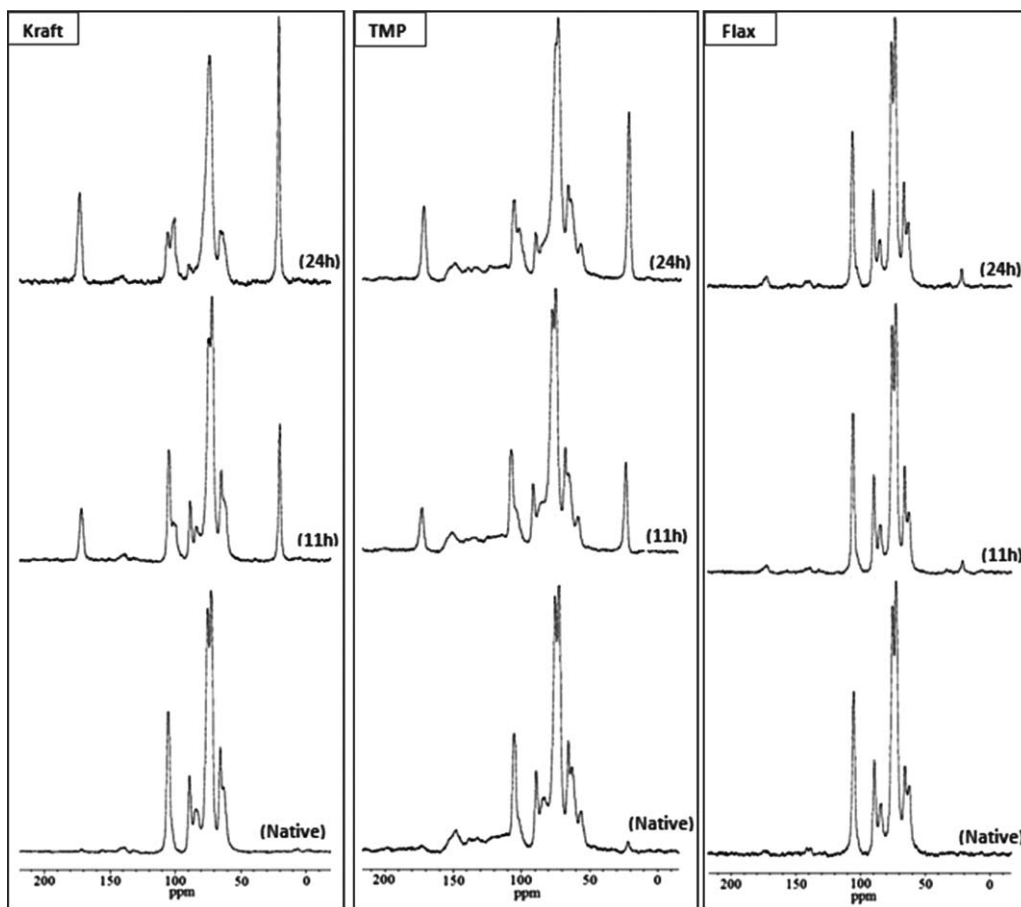**Figure 3.** Weight gain as a function of the reaction time for Kraft, TMP, and flax fibers.

Figure 4. Solid-state ^{13}C-NMR spectra of native and acetylated Kraft, TMP, and flax fibers for 11 and 24 h.

hemicelluloses and lignin. The large difference in reaction rate between the three fibers can be also related to the type of hydroxyl groups present in the structure of each fiber. Indeed, these groups can be phenolic, benzylic, or alcoholic in lignin domains, and alcoholic in carbohydrate domains. Accordingly, each of these groups will present a different reactivity towards acetic anhydride.[9] In addition, the acetic acid released during the acetylation reaction increases the reaction rate which explains the significant weight gain obtained in the case of the Kraft pulp.[21]

The theoretical degree of substitution (DS) corresponding to a specific weight gain can be calculated. The DS values of esterified Kraft pulp fibers can reach a value of two under the experimental conditions described in this work (Figure 3). However, even for long reaction times, the weights gain of flax fibers is still low, which means that the acetylation was limited to the surface or to the outer layers of the fiber cell wall. In addition, the loss of extractable material during the chemical reaction can explain the moderate weight gain of flax fibers.[22]

In order to obtain additional evidence of the occurrence of the acetylation reaction, the modified fiber samples were characterized by ^{13}C-NMR spectroscopy (Figure 4). All spectra show the typical signals of the different carbons of cellulose in the region between 60 and 110 ppm: ∼105 ppm (C-1), ∼89 and ∼84 ppm (assigned to C-4 of crystalline and amorphous cellulose, respec-

tively), ∼72 ppm (C-2, C-3), ∼75 ppm (C-5), ∼65 ppm (C-6).[18,23] We also noted that TMP spectra show the two major signals of the lignin structure with free phenolic groups: methoxy carbon (OCH$_3$) of guaiacyl and syringyl at ∼56 and ∼148 ppm (C-3 and C-4 of guaiacyl and C-3 and C-5 of syringyl units).[24–26] The spectra of acetylated fibers show new peaks at ∼21 and 171 ppm. They are assigned to the aliphatic and carboxylic carbons of the acetyl group.[18] As expected, the intensity of these peaks increases gradually with increasing reaction time for Kraft, TMP, and flax fibers. The spectra show that the extent of acetylation of flax fibers was relatively low. This result can be related to the surface of commercial flax fiber which might have been chemically treated with silicon oil which impedes the acetylation reaction.

On the other hand, the NMR signal revealed that the acetylation has taken place mainly on the hydroxyl groups at the 6 and 2 positions, since the intensity of C-6 and C-2 peaks decreases with increasing reaction time. We also noted that the hydroxyl group at position 3 of Kraft fiber cellulose was attacked at high reaction time. However, long reaction times promoted the degradation of cellulose as shown by the decrease of the C-1 peak intensity.[9,27]

The ^{13}C-NMR signals at 89 and 65 ppm, assigned to C-4 and C-6 of ordered cellulose, allow us to evaluate the crystallinity of cellulosic fibers before and after acetylation.[28,29] The decrease of
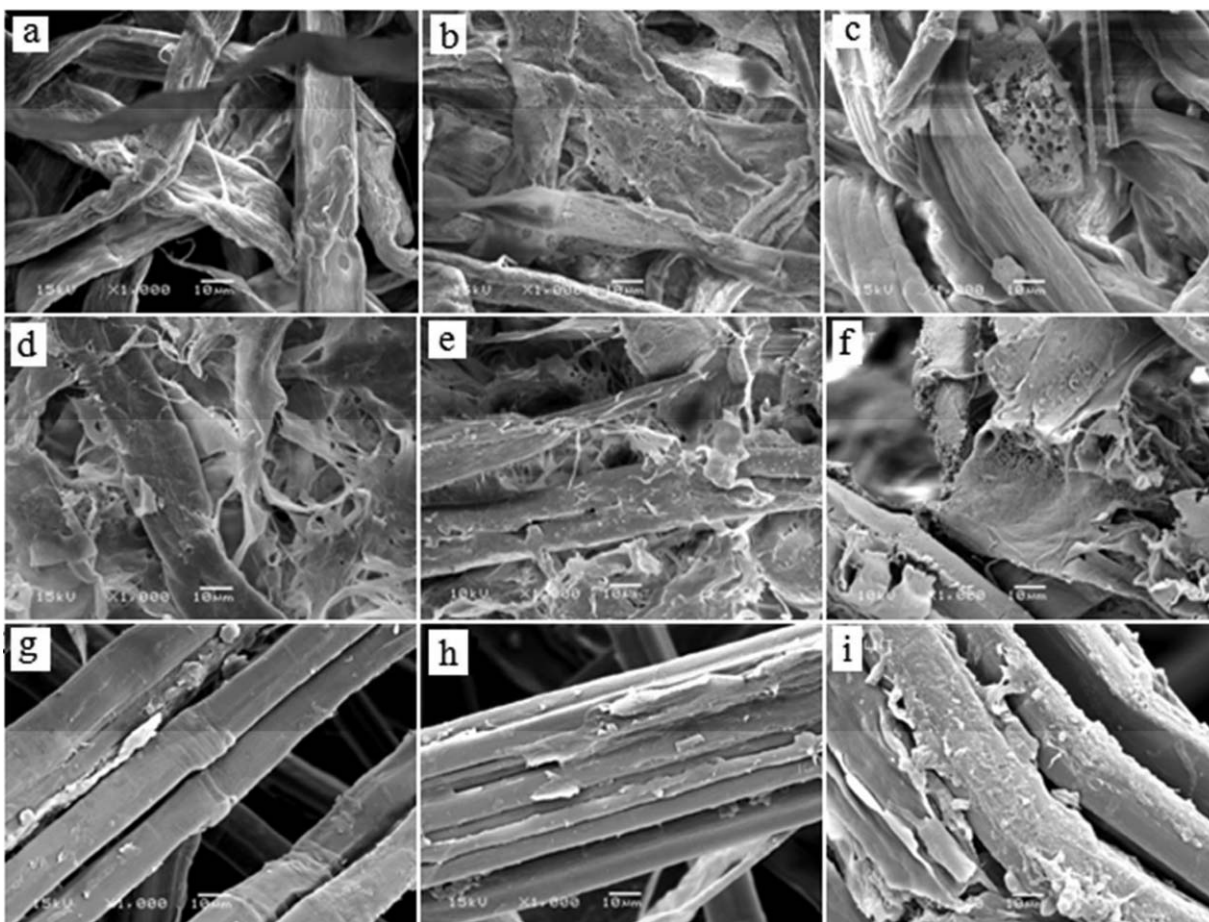
Figure 5. SEM images of fibers at 1000× magnification: kraft fibers (a) unmodified (b) acetylated 2 h (c) acetylated 24 h; TMP fibers (d) unmodified (e) acetylated 2 h (f) acetylated 24 h; flax fibers (g) unmodified (h) acetylated 2 h (i) acetylated 24 h.

the intensity of these two peaks shows that acetylation reduces the supramolecular order of Kraft and TMP fibers.[27] Indeed, the substitution of hydroxyl with acetyl groups reduces the hydrogen bonding, which is responsible for fiber crystallinity. This leads to more amorphous zones. Contrary to wood fibers, flax fibers are more ordered after the chemical treatment. This phenomenon can be related to the removal a part of amorphous components, such as natural or synthetic extractible substances, by the reaction medium.

Chemical treatments can lead to a significant change in the surface topography of fibers depending on reaction environment and reaction time.[15,30] The change in the surface morphology of the acetylated fiber was evaluated by scanning electron microscopy (SEM), optical microscopy, and fiber quality analysis (FQA). From SEM images, it is observed that the surface of flax, Kraft, and TMP fibers has changed after acetylation, as depicted in Figure 5. Indeed, the surface of esterified fibers is slightly degraded compared to untreated fibers.[3] It can also be noted that the chemical treatment causes fiber fibrillation which enhances the effective surface area of fibers leading to better fiber-matrix interfacial adhesion.[30,31] This is particularly evident in Figure 5 by comparing the unmodified (image g) and modified flax fibers (images h and i). In addition, the micrographs show degradation at fiber surface after acetylation. This effect

becomes increasingly pronounced with reaction time.[32] For composite materials applications, this suggests that the treatment duration needs to be adjusted to maximize their overall mechanical properties. The duration should be such as to maximize the fiber–matrix adhesion while minimizing the degradation of fibers.

Fiber quality analysis results for Kraft and TMP fibers are in agreement with previous observations. As shown in Figure 6,
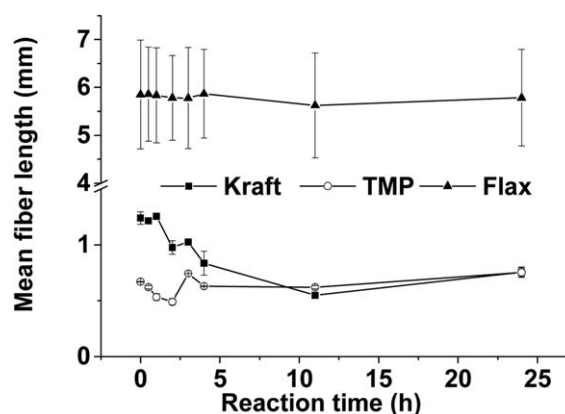
**Figure 6.** Mean fiber length as a function of reaction time.
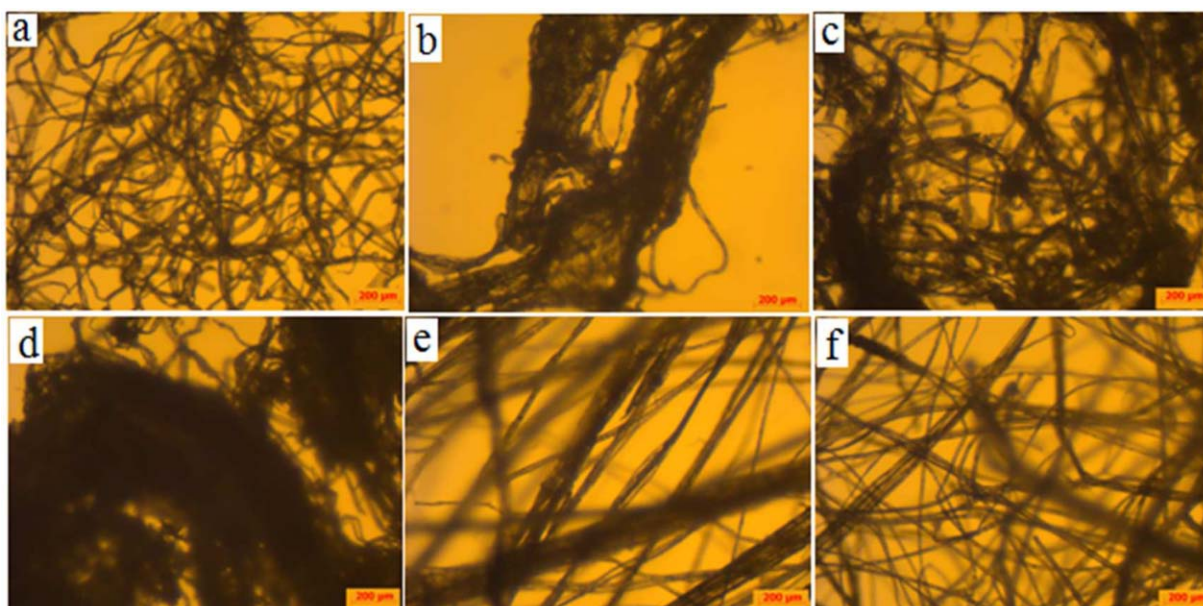
Figure 7. Optical microscopy images of Kraft fibers (a) unmodified and (b) acetylated 24 h; TMP (c) unmodified and (d) acetylated 24 h; flax fibers (e) unmodified and (f) acetylated for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the fiber length decreases with increasing acetylation time, indicating fiber degradation. However, after a determined reaction time, the value of the mean length increases. This behavior can be related to the cellular structure of the fiber in which some hydroxyl groups are substituted with acetyl groups leading to a decrease in surface polarity. In consequence, the water affinity of fibers is reduced leading to the agglomeration of acetylated fibers. The fiber length measured by the FQA device for long reaction times is then representative of the length of fiber bundles and not that of individual fibers. Usually, extremely diluted fiber dispersions are used for FQA measurements to avoid fiber agglomeration. Even after drying, acetylated Kraft and TMP fibers form agglomerates; this is not the case of untreated fibers, as shown by optical microscopy (Figure 7). The chemical treatment also affects fiber straightness [Figure 8(a,b)]. Indeed, it was observed that kink and curl indices increase with increasing acetylation time. This behavior can be related to the partial substitution of hydroxyl with acetyl groups which creates a tension

between acetylated and nonacetylated areas at fiber surface. So the fibers become more curved. However, at moderate acetylation levels, fibers become very short and cannot exhibit curvature and kink. As a result, the values of curl and kink indices decrease. However, for long reaction times, the presence of fiber agglomerates increases fiber straightness. Certainly, the FQA method is not appropriate to evaluate the real effect of acetylation beyond a specific acetylation level. However, it is observed that over two hours of acetylation, the fibers demonstrate a particular behavior in water. These results are of great importance, since they raise the possibility of using acetylated fibers in papermaking processes to produce paper layers that can be used as a binder and support of unidirectional (UD) flax fiber reinforcements.[33]

The optical micrographs of flax fibers show that the chemical treatment increases significantly the fibrillation of flax fibers and also affects the flax fiber straightness. Fibers become less
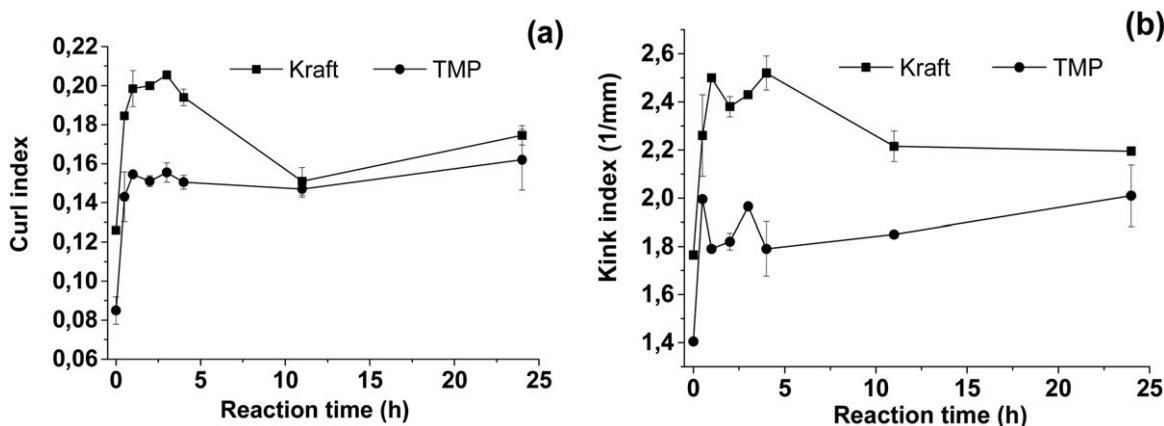
Figure 8. Morphological characteristics of acetylated and unmodified Kraft and TMP fibers: (a) curl and (b) kink indices.
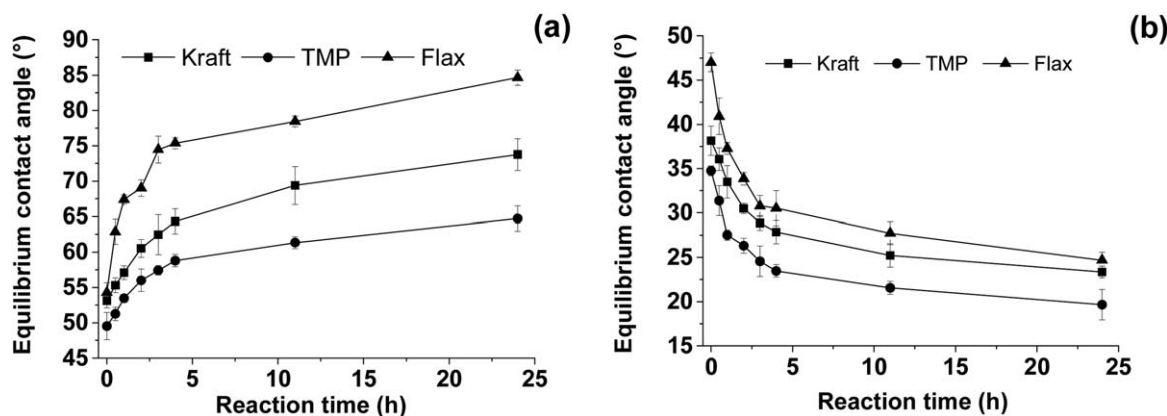
Figure 9. Equilibrium contact angle of water (a) and epoxy resin (b) as a function of the reaction time.

straight as illustrated in Figure 7(f). However, it is observed that the length distribution of flax fibers is very large which subsequently masked the effect of acetylation on fibers length, as illustrated in Figure 6.

Contact angle measurements of water and liquid epoxy resin droplets on fibers surfaces are used to evaluate the effect of acetylation on fibers hydrophilic character. Figure 9(a) gives the contact angle at equilibrium formed by a drop of water on cellulose substrates. The untreated fibers show a high affinity for water, reflected by the low values of contact angle (less than 57°, 54°, 48° for flax, Kraft and TMP, respectively). As expected, acetylation reduces the hydrophilic character of fibers and the contact angle increases with increasing reaction time due to the substitution of hydroxyl groups with less polar acetyl groups. The contact angle increased up to 84°, 73°, and 64°, for acetylated flax, Kraft, and TMP fibers, respectively. These results are in good agreement with previously reported ones.[16] The evolution of the hydrophilic character of Kraft fibers is more pronounced than TMP because of the higher accessibility of acetic anhydride to hydroxyl groups leading to a higher surface density of acetyl groups. However, the hydrophilic character of both Kraft and TMP fibers becomes weaker after 11 h of reaction. This can be explained by the fact that the surface of fibers has reached a high level of coverage with acetyl groups. The low affinity of acetylated fibers for water would reduce significantly

their humidity uptake leading to an improved durability of the material when it is used as reinforcement.

These results also suggest that the modified fibers will be more compatible with nonpolar polymers used as matrices in composite materials. Indeed, the substitution of hydroxyl groups with acetyl groups, which will more readily interact with nonpolar liquids, improves their affinity with epoxy resin. The contact angle of a drop of epoxy resin deposited on the surface of a treated fiber decreased with increasing reaction time. After 24 h of reaction, the epoxy-fiber contact angle values decreased by 15° for Kraft and TMP and by 23° for flax [Figure 9(b)].

Flax fiber exhibited a particular behavior. Their hydrophobicity increased rapidly with increasing the treatment time. In addition, it was noted that they had a low affinity for both wetting liquids of opposite characters (water and epoxy). This behavior could be related to the contamination of the surface by spinning oil, generally used to facilitate winding of flax fibers. To verify this hypothesis, the fibers were subjected to a soxhlet extraction with methylene chloride. The extract was evaporated to dryness and weighed. The recovered solids presented an oily appearance at room temperature and it accounted for $\sim$ 9% of the total fiber weight. The FTIR spectra of the flax fiber extract showed the characteristic peaks of silicon oil at $\sim$ 1250 cm^{-1} (CH$_3$ symmetric deformation of Si—CH$_3$), 1010 cm^{-1} (Si—O stretching), 790 cm^{-1} (Si—C stretching)[34,35] as illustrated in Figure 10. Gradual extraction of this oil by the reaction medium led to the direct contact of acetic anhydride with the nonpolar groups (alkyl chain and aromatic) of natural extractives of flax fibers which has further increased their hydrophobic character.[36,37]
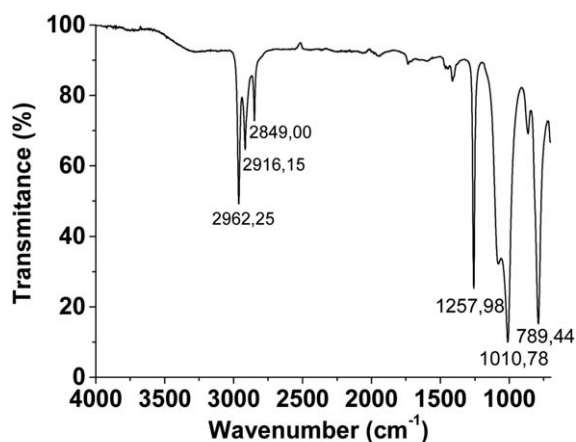
CONCLUSIONS

The results of this work show clearly that it is possible to enhance the hydrophobic character of cellulosic fibers using an environmentally friendly and economical process. Moreover, this study underlines the effectiveness of acetylation for potential composite applications. Detailed investigation into the effect of solvent-free acetylation with acetic anhydride on fibers structure is presented. We have shown that the extent of fiber acetylation increases with increasing reaction time. However, it is noted that weight gain values for TMP and flax are lower than those for Kraft pulp because of the presence of lignin and

Figure 10. FTIR spectrum of the waxy material extracted from flax fibers.

extractives which reduce the accessibility of the reagent to fiber hydroxyl groups. The extent of acetylation of flax fibers may be improved with a pretreatment to remove the silicone oil covering fiber surfaces. This oil coating can significantly reduce inter-fiber bonding and the exposure of the surface hydroxyl groups to acetic anhydride. IR and RMN analyses were used to confirm trends leading to a better study of the fine structure of acetylated fibers. The morphological studies revealed that at micro-scale, the chemical treatment makes the surface of fiber rougher and, for longer reaction times, fiber degradation has been noted. At macro-scale, it was found that the length of the fibers decreased with increasing reaction time which could be due to the degradation caused by the reaction medium. Finally, it was concluded from fiber wettability measurements that acetylation increases significantly the contact angle of water on fiber surface indicating a less hydrophilic character. Moreover, the hydrophobicity increased with increasing reaction time, the most significant changes occurring in the first five hours of treatment. It was also found that the presence of acetyl groups linked to cellulosic fibers improves their interaction with the nonpolar epoxy resin. It can be concluded that the chemical treatment of flax, Kraft, and TMP fibers with acetic anhydride can improve the adhesion between fiber and polymer matrices when they are used as reinforcement in composite materials.

ACKNOWLEDGMENTS

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