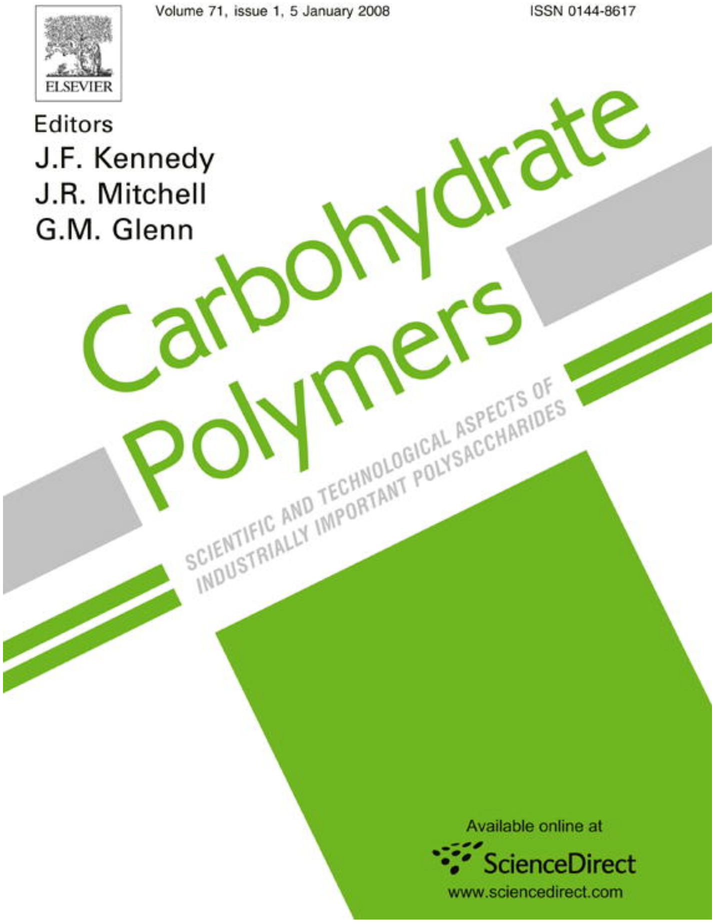

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Fast wood fiber esterification. I. Reaction with oxalic acid and cetyl alcohol

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Abstract

A method for modifying wood fiber with non-solvent media, to produce ready-to-use hydrophobic fiber suitable for use in composites, is proposed in this paper. The chemical modification was achieved by means of a consecutive reaction (cellulose/oxalic acid/cetyl alcohol) performed in a mixing chamber, at 110 °C and 30 rpm. The reaction product was washed by extraction with water and hexanes and then characterized by using spectroscopic techniques (FTIR and ^{13}C CPMAS-NMR). The results from these analyses revealed the presence of C=O groups, indicating that the esterification reaction was successful. The thermal stability of the treated samples was studied by thermogravimetric analysis (TGA); the modified fiber exhibited an increased thermal stability relative to the unmodified fiber, this increase may be related to both the formation of ester groups and the grafting of the cetyl radicals.

Keywords: Esterification; Natural fiber; Wood fiber composite; Thermoplastic composite

1. Introduction

Over the past few years, the production of fiber/thermoplastic composites with lignocelullosic fibers have found an important application for recovering, reusing and recycling a variety of by-products from industrial use of natural resources. However, the lignocellulosics and thermoplastics commonly employed in this area are not compatible enough to produce composites with the properties adequate for specific applications, especially when products with high mechanical strength are required. Incompatibility between lignocellulosics and thermoplastics is due to their differing chemical nature. Lignocellulosics (cellulose, hemicelluloses or lignin) are hydrophilic in nature because of their high content of hydroxyl groups (OH); on the contrary, many of the thermoplastics used as matrixes (polyethylene, polypropylene or polyvinyl chloride) are non-polar, hydrophobic compounds; this is why the interfacial interaction between those materials tends to be poor, in analogy with water/oil mixtures.

A number of methods exist today to improve the interfacial interaction between lignocellulosics and thermoplastics, among them: (i) the chemical modification of a lignocellulosic, either by condensation or free-radical reactions (George, Sreekala, & Thomas, 2001; Gupta & Sahoo, 2001; Huang, Zhao, Zheng, He, & Gao, 1992; Mohanty, Mubarak, & Hinrichsen, 2000; Redondo, Radovanovic, GonHalves, & Yoshida, 2002; Román-Aguirre, Márquez-Lucero, & Zaragoza–Contreras, 2004; Thiebaud, Borredon, Baziard, & Senocq, 1997), (ii) the use of a modified thermoplastic containing a compound capable of interacting or reacting with a lignocellulosic (Chauhan, Guleria, Misra, & Kaur, 1999; Fung, Li, & Tjong, 2002; Matıas,

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De la Orden, González Sánchez, & Martínez Urreaga, 2000; Navarro Cassu & Felisberti, 2001), (iii) the addition of a third component with the ability to interact simultaneously at the interface with the thermoplastic and the lignocellulosic (compatibilizer) (Feng, Caulfiel, & Sanadi, 2001; Martínez Urreaga, Matías, De la Orden, Lechuga Munguía, & González Sánchez, 2000; Matías et al., 2000; Oksman, Lindberg, & Holmgren, 1998; Rana et al., 1998). Whichever the method used (fiber modification, polymer modification or compatibilizer addition), it should not substantially increase the cost of composites.

In recent years, many research studies aimed at improving the affinity between natural fibers and thermoplastics have reported interesting fiber chemical modification procedures, as well as the effects on both the fiber surface properties and the mechanical performance of thermoplastic composites. However, a close examination of the modification techniques therein described makes clear that the reagents (cost), the modification method (several steps), and/or the time required to produce ready-to-use fiber (modification and washing processes), make of the fiber material the most expensive component of the composite formulation. All these factors must be taken into consideration when investigating methods for improving the performance of fiber/thermoplastic composites. Being by-products that can be obtained from a wide variety of industrial sources, lignocellulosics are supposed to be cheap: this is one of their most appealing features. If, to the contrary, the methods used involve expensive processes for conversion of lignocellulosics, these will become an unattractive option for manufacturing composites.

The above-mentioned considerations were taken into account in developing a method for producing chemically modified wood fiber using non-solvent media, particularly, those related to the simplicity of the method and the time required for chemical modification. By employing this method, it is possible to produce ready-to-use fiber in approximately 10 min, without the need of removing the possible reaction by-products, thus eliminating the additional washing step.

2. Experimental

2.1. Materials

The reagents and materials used in the fiber modification were oxalic acid (Aldrich Co.), cetyl alcohol (Aldrich Co.), hexanes (Aldrich Co.) and tridistilled water. A sodium oxalate solution was prepared by reacting oxalic acid with sodium hydroxide (Aldrich Co.) in a 1:2 molar ratio. All reagents were used as received. High-density polyethylene (HDPE) from Chevron (Marflex Hi-D94312; $MI = 12$; $\rho = 0.943\ \mathrm{g\ cm^{-3}}$) was chosen as the polymeric matrix. Wood fiber (ponderosa pine) was milled and then selected by sieving it through a ±60 mesh (250 μ); it was subsequently dried in an oven at 110 °C for 24 h prior to conducting the reaction.

2.2. Fiber modification

The fiber modification reaction was carried out in a Banbury mixer (60 cm^3) coupled to a Brabender plasticorder. The reaction conditions were as follows: rotor speed, 30 rpm; temperature, 110 °C; reaction time, 10 min. A typical experiment was performed using a two-step procedure. First, 54 g (1.0 eq. wt.) of wood fiber (previously milled and dried), 36 g of oxalic acid (0.8 eq. wt.) and 13.4 g of sodium oxalate (0.2 eq. wt.), were premixed in a plastic bag. Next, 50 g of the mixture were loaded into the reactor (the mixing chamber), and left to react for 5 min. It was assumed that during this first reaction, one carboxyl acid group (COOH) of the oxalic acid would react with a hydroxyl group (OH) of a glucopyranose ring, leaving the other COOH group available for the second reaction. In the second stage, 0.3 eq. wt. of cetyl alcohol was added to the mixture in the reactor and let to react for 5 min (10 min in total). In this last step, the OH group of the cetyl alcohol reacted with the COOH group available from the first reaction; hence, alkyl radicals of 16 carbons (cetyl radicals) should have grafted onto the glucopyranose rings.

2.3. Infrared spectroscopy (FTIR)

The properties of the reaction product were characterized by Fourier transform infrared spectroscopy, using a Nicolet Magna-IR 750, series II, spectrometer. Prior to recording the spectra, the modified fiber samples were washed by extraction with hexanes for 12 h, and a further 12 h with water; as for the unmodified fiber (blank), it was dried in an oven for 12 h, at 110 °C. The analyses were run using the KBr pellet technique; KBr was also employed as the reference material to acquire background.

2.4. Solids ^{13}C NMR

Nuclear magnetic resonance (NMR) spectra were collected on a Bruker 300 JCAMP-DX,V1.0, NMR spectrometer operating at 100 MHz for ^{13}C, and at 400 kHz for ^{1}H. Spectra were obtained at 6 kHz, using a 4 mm od zirconium oxide rotor. ^{13}C NMR spectra were taken in the cross-polarization mode, using magic-angle spinning (CP/MAS).

2.5. Thermal properties

The effect of esterification on the thermal properties of the fiber was studied by thermogravimetric analysis (TGA) using a TA Instruments Simultaneous TGA–DTA SDT 2960. The analyses were conducted at a heating rate of 10 °C/min under a nitrogen atmosphere. Prior to evaluation, the fiber samples were oven-dried at 110 °C for 12 h.

2.6. Scanning electron microscopy

Samples of the modified and unmodified fiber, as well as those of the fiber/HDPE composites, were examined by scanning electron microscopy (SEM), with a Jeol 5800 LV SEM. The study was performed for two purposes. First, to evaluate a possible degradation effect induced by the treatment and second, to determine the effect of the treatment on the interfacial interaction of the fiber/HDPE composites. After evaluating Young's modulus, the remaining pieces of the samples were frozen by immersing them for 10 min in a vessel filled with liquid nitrogen; immediately after freezing, the pieces were broken with an impact pendulum (Izod analyzer). Before running the SEM analyses, all the samples were coated with gold, in order to prevent static charge build-up.

3. Results and discussion

3.1. Esterification

As mentioned previously, the main objective of this study was to evaluate a fast process to produce a ready-to-use wood fiber suitable for thermoplastic composites. The most important aspects to be considered when developing methods for the chemical modification of natural fibers are the simplicity of the method and the time required for processing, since the longer and more complicated the process the higher the cost. Therefore, the technique for fiber adequacy has to be both simple and effective, to allow the production of high performing, low-cost composites. In the present work, the esterification reaction occurred in two steps, beginning with the reaction of one of the carboxyl acid groups of the oxalic acid (*HOOC*—COOH) with a hydroxyl group of the glucopyranose rings (Cell-*OH*) to produce primary ester, Cell—*OOC*—COOH. In this first step, sodium oxalate was added in order for it to reduce fiber degradation due to the acid effect, and also to act as a reactant with cellulose to produce esterification. In the second step, cetyl alcohol (Cetyl-OH) was added to the first reaction mixture to produce a second ester from the reaction between the carboxyl acid group of Cell—OOC—*COOH* and the Cetyl-*OH* hydroxyl group of Cetyl-*OH*, which yielded Cell—*OOC*—*COO*—Cetyl. It should be noted that, given the complexity of the chemical structure of lignin and the similitude between cellulose and hemicelluloses, the products of their reactions with oxalic acid and cetyl alcohol can be too complex to be identified. Therefore, to simplify the discussion, it was assumed that the reaction sites for the modification would be only the cellulose hydroxyl groups; the reaction of lignin or hemicellulose hydroxyl groups, however, cannot be ruled out at all.

The grafted alkyl radical (Cetyl = C_{16}) were expected to be long enough to induce a strong fiber/matrix interaction, since in a previous study, it has been found that the grafting of the smaller alkyl radicals (a mixture of ethyl and octyl radicals) did not improve interfacial interaction of blue agave fiber/HDPE composites, so the composites produced either with treated or untreated fiber showed very similar mechanical performance, despite the notable hydrophobicity that the fiber acquired upon the esterification reaction (Tronc et al., 2007).

The reaction by-products, e.g. Cetyl—OOC—COOH, Cetyl—OOC—COO—Cetyl, behave similarly to some additives such as estearic acid, or its calcium or zinc salts, which are commonly used as lubricants in composite formulations. It is also possible that these compounds had reacted with Cell-*OH*, during mixing with the thermoplastic, due to the heating process; this reaction may have contributed to enhance the chemical compatibility. Therefore, it is believed that for industrial applications, there will not be necessary to remove by-products, since they are not expected to have any detrimental effect on the composite performance. Of course, all the fiber samples used to characterize the modification were washed by extraction with water and hexane, in order to prevent spectral interference.

3.2. Infrared spectroscopy

FTIR spectra of both the treated and the untreated wood fiber are presented in Fig. 1. The untreated fiber (a) exhibits the characteristic signals of lignocellulosics, which include a broad peak from the cellulose hydroxyl groups (O—H) at 3429 cm^{-1}, and a small peak at 1734 cm^{-1}, corresponding to the carbonyl groups (C=O) of both the acetyl ester and the carbonyl aldehyde groups of hemicelluloses and lignin, respectively (Hassan, Rowell, Fadl, Yacoub, & Christainsen, 2000; Matuana, Balatinecz, Sodhi, & Park, 2001; Mohanty et al., 2000; Rong, Zhang, Liu, Yang, & Zeng, 2001). The peaks at 2924 and 2846 cm^{-1}, due to vibrations of the C—H (methyl groups), and those at 1070, 1040 and 900 cm^{-1}, due to the formation of C—O bonds, are both associated with the structure of the glucopyranose rings (Kontturi, Thüne, & Niemantsverdriet, 2003). The peak at 1625 cm^{-1} does not belong to the fiber; however, it is commonly observed in spectra of lignocellulosic materials, and it is associated with absorbed water (Lorıa-Bastarrachea, Carrillo-Escalante, & Aguilar-Vega, 2002; Sun, Fang, Tomkinson, Geng, & Liu, 2001).

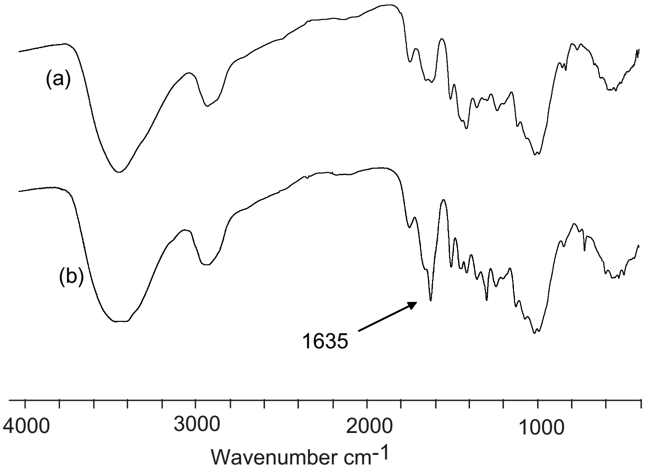

Fig. 1. Infrared spectra of (a) unmodified and (b) modified wood fiber.

On the other hand, the FTIR spectrum of the treated fiber (b) exhibits some new peaks, in particular an intense one at 1635 cm^{-1} – overlapping with the peak at 1625 cm^{-1}, seen in (a), that corresponds to C=O of ester groups. It should be noted that a similar peak of the oxalic acid is present at the same position; however, since the fiber was cleaned by extraction for 12 h with water and 12 additional hours with hexane, it was assumed that this signal did not correspond to the unreacted reagent. As for the rest of the signals, no changes were observed.

3.3. Solid-state ^{13}C NMR

Solid-state ^{13}C cross-polarization magic-angle spinning NMR spectroscopy (^{13}C CPMAS-NMR) is a useful tool to study lignocellulosics, since it allows differentiate between signals from crystalline and amorphous carbons. Fig. 2 shows the spectrum of the untreated wood fiber, it exhibits the characteristic signals of cellulose and some of lignin. Thus, the C1 (103 ppm), C4 (86.54 ppm) and C6 (63.31 ppm) peaks belong to carbons of the glucopyranose rings within crystalline cellulose packing, whereas the C4′ (82 ppm) and C6′ (60.56 ppm) peaks correspond to carbons of the glucopyranose rings within amorphous regions. In order to differentiate cellulose carbons from lignin carbons, these were named by prefixing the symbol with a letter L. So the peak at 56 ppm was assigned to methoxy carbons (–OCH_3), the signals that appeared as a wide signal between 140 and 150 ppm were assigned to L3 and L5, and a second wide signal between 125 and 135 ppm was assigned to L1 and L4. The signals from the methyl and methylene groups of lignin were barely visible in this spectrum; however, these signals should have appeared between 10 and 35 ppm, as previously reported for other lignocellulosics (Czimczik, Preston, Schmidt, Werner, & Schulze, 2002; Jandura, Kokta, & Riedl, 2000; Sun, Sun, & Sun, 2002). Similarly, the signal of the carboxyl groups (–COOH), which should have appeared between 165 and 177 ppm was not discernible; however, the FTIR spectrum (Fig. 1) exhibited a peak at 1734 cm^{-1}, indicating their presence.

^{13}C CPMAS-NMR spectrum of the treated fiber is shown in Fig. 3. The signals from cellulose were observed between 50 and 106 ppm. However, lignin signals were not clearly seen, since some of them overlapped with other more prominent ones. Before continuing the discussion, it is worth mentioning that during – cellulose/oxalic acid/cetyl alcohol – reaction the following products may be obtained: (i) cell—OOC—COOH and (ii) cell—OOC—COO—$(CH_2)_{15}$—CH_3, since a 1:1 equivalence of oxalic acid to cetyl alcohol was not used. Nevertheless, the signals from structure (i) were not easily distinguishable, since they were very similar to those of (ii). Thus, the discussion herein was based on the second structure, whose NMR spectrum gave the following signals: a peak at 15 ppm, corresponding to C24 (CH_3), and a group of signals between 20 and 33 ppm, from the methylene groups of the cetyl chain (C9–C23), which indicates that the second reaction took place (cell—OOC—COO—$(CH_2)_{15}CH_3$). The signal from the ester groups (C7 and C8) appeared as a wide peak

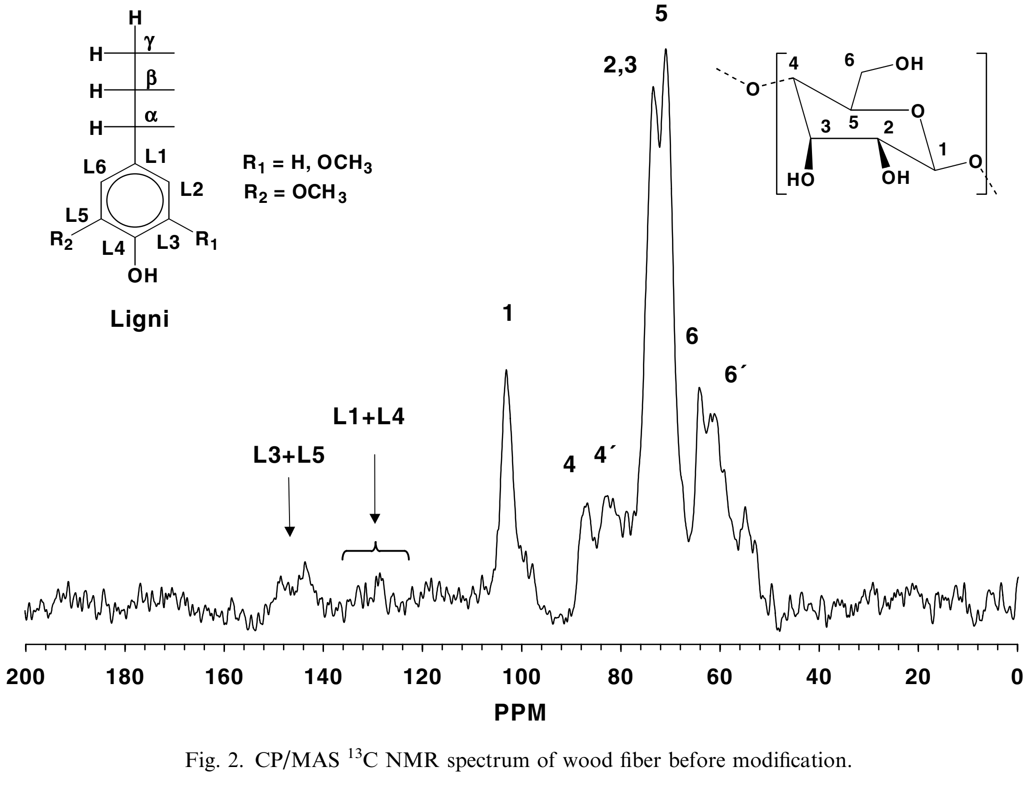

Fig. 2. CP/MAS ^{13}C NMR spectrum of wood fiber before modification.

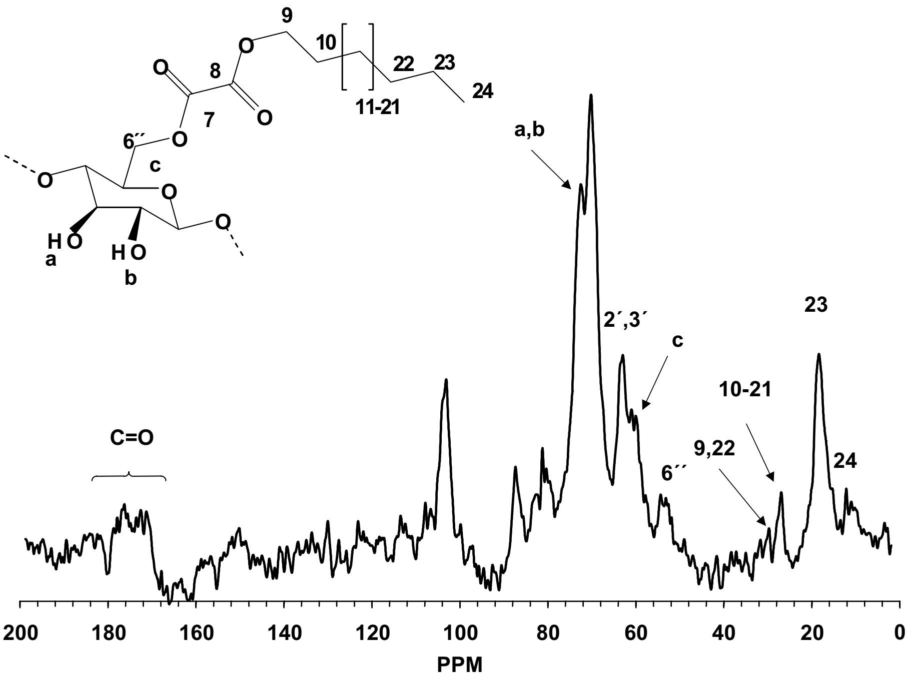

Fig. 3. CP/MAS ^{13}C NMR spectrum of wood fiber after esterification.

between 170 (–COO–) and 180 (–COOH) ppm. This signal and the one observed at 1635 cm^{-1} in the FTIR spectrum (Fig. 1) indicate that the esterification reaction actually occurred. It must be pointed out that the signal of the C=O group of the carboxylic acid appeared near 180 ppm; this is likely to be the reason for the last assigned signal to broaden; therefore, this signal indicates the presence of unesterified acid groups, as expected. It should also be noted that the glucopyranose rings have three possible points, a, b or c (Fig. 3) for the esterification reaction with oxalic acid; consequently, a change in some (or all) of C2, C3 or C6 is evidence of the reaction. As seen in Fig. 3, the C2 and C3 peaks have almost disappeared, as well as the C6′ peak. It is also worth pointing out that a new peak appeared at 55 ppm, which can be attributed to the formation of C6″ (cell—C6″—OOC—), and that the peak at 65 ppm has become wider with respect to the one in Fig. 2, corresponding to C6. These changes suggest the formation of C2′and C3′ (cell—OOC—), whose signals should appear at that position. Therefore, apparently the three points (a, b or c) reacted with the oxalic acid, in some proportion, indicating, again, that the esterification reaction took place.

3.4. Thermal analysis

Fiber thermal stability is another important aspect to be considered regarding fiber/thermoplastic composites. When the fiber of interest has a low degradation temperature, it could be unsuitable for manufacturing composites with thermoplastics, which are processed at temperatures above 200 °C. As can be seen on the TGA plots in Fig. 4, the treated fiber sample began to thermally degrade at 292 °C, a temperature higher than that at which the untreated fiber started degrading (266 °C). Similar increases in thermal stability have been reported for other treatments (Ghosh & Ganguly, 1994; Rahman et al., 2000), however, only a few researchers have reported this effect in the case of the esterification of lignocellulosics (Coutinho, Costa, Carvalho, Gorelova, & Claudio de Santa Maria, 1998; Hassan et al., 2000).

In order to determine whether or not the reaction residuals affected the fiber thermal stability, a treated, unclean fiber sample was analyzed by TGA. The thermograms of both the treated unclean fiber and the untreated one are

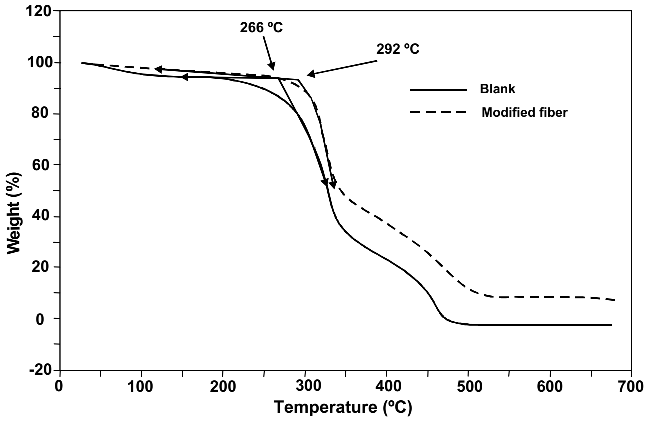

Fig. 4. TGA thermograms of modified (solid line) and blank of wood fiber (broken line).

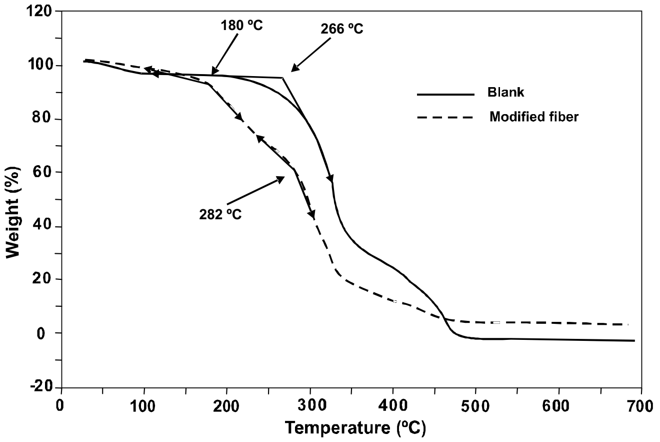

Fig. 5. TGA thermograms of modified unclean fiber (broken line) and blank of wood fiber (solid line).

shown in Fig. 5. As it can be seen, the sample of treated unclean fiber showed a first stage of degradation at 180.38 °C, which is close to the oxalic acid degradation temperature (150 °C), and a second stage at 282.18 °C, which should correspond to the modified fiber. These results suggest that the reaction residuals reduced the effect observed with esterification on the clean treated fiber (Fig. 4) at 10 °C. However, the difference with respect to the degradation temperature of the unmodified fiber is still 15 °C, which is a significant improvement. The effect observed is likely to have been promoted by the oxalic acid residuals, since it was expected that the aforementioned by-products would be unaggressive for the fiber, given their similarity with lubricant additives. Thus, washing of fiber may not be absolutely necessary in all cases.

3.5. Microscopy

After the esterification process, it was evident that the fiber had suffered some degree of degradation, since it was smaller and darker in color. Thus, some fiber samples (treated and untreated) were analyzed by SEM in order to determine the morphological changes experienced by the fiber as an effect of the treatment. Fig. 6 illustrates a couple of micrographs for both the untreated (a) and the treated fiber (b). As it can be seen, the treated fiber surface is smoother than that of the untreated one. This was attributed to the friction effect induced by the rotor and the chamber surface during the reaction. When lignocellulosics are chemically treated, some of their components can be affected, depending on the treatment. It has been reported that alkaline treatments usually affects lignin, which acts as the matrix in lignocellulosics, by causing fragility in the fiber due to lignin fragmentation (Gram, 1988). In the present study, the effect of the chemicals was evident, since the fiber was visibly darker after the treatment, as a result of the degradation of the fiber components (hemicelluloses, cellulose and lignin). Additionally, as mentioned above, fiber size was affected by the combination of fragility (chemical effect) and friction (mechanical effect) during the treatment. However, the chemical modification is considered to be more important than the chemical or mechanical degradation, since composite performance depends strongly on the fiber/matrix compatibility.

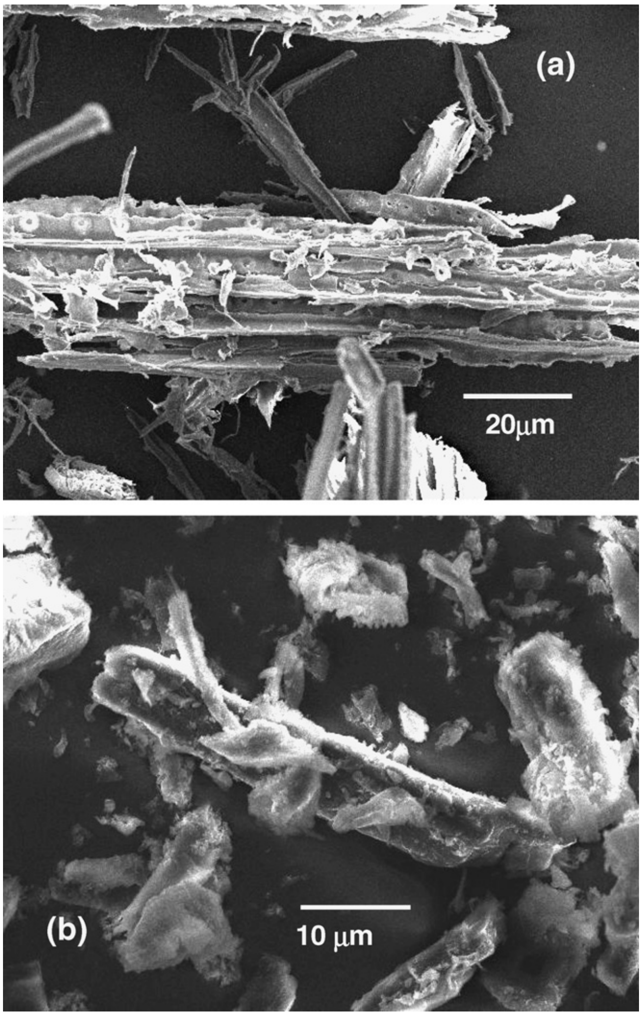

Fig. 6. SEM micrographs of wood fiber (a) before treatment and (b) after treatment.

A second part of this study will address the effect of fiber surface modification on the interfacial interaction of fiber/HDPE composites (mechanical and rehological properties). Some work has already been undertaken in this regard. A couple of composite samples have been analyzed by SEM. Fig. 7 illustrates micrographs of composites formulated with untreated (a,b) and treated fiber (c,d), at a rate of 30/70 wt% fiber to HDPE. A clear separation can be observed in micrograph (a), indicating that the fiber/matrix interface was not strong enough; moreover, (b) it shows a lot of cavities where fibers were supposed to be imbedded. It was assumed that, due to the impact during sample preparation, the fibers slipped out of the matrix because of deficient adhesion. On the other hand, micrographs (c) and (d) clearly show that the fiber is perfectly attached to the matrix, since there is no visible interfacial

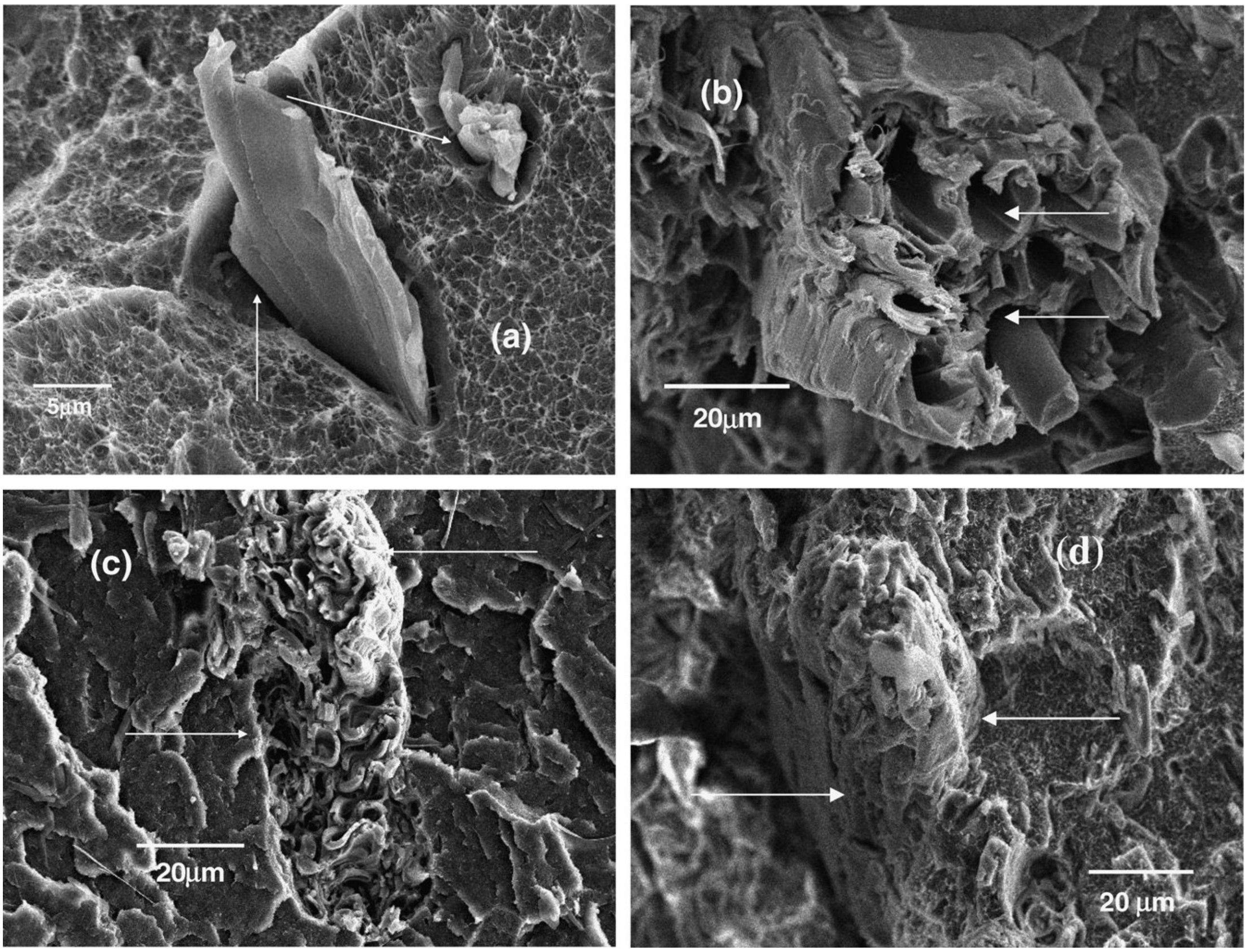

Fig. 7. SEM micrographs of fiber/HDPE composites (30 wt% of fiber) using (a,b) untreated and (c,d) treated fiber.

separation; it is also evident that the fiber is strongly imbedded in the matrix, indicating the efficiency of the treatment, which was attributed to a good interfacial interaction favored by the length of the alkyl radical entangled with the fiber.

4. Conclusion

The results of this study indicate that the esterification reaction with oxalic acid/cetyl alcohol in a non-solvent system was successfully achieved in a very short period of time. It was also found that, although fiber size was affected by the friction and the treatment, these factors did not cause any significant decrease in fiber thermal stability. Scanning electron microscopy images showed that the treatment produced a strong fiber/HDPE interfacial interaction, since both the fiber impregnation and the adherence of the fiber to the matrix were excellent. However, further evaluation of mechanical properties of this type of composites will show how efficient the treatment is. It can thus be concluded that it is possible to chemically modify lignocellulosics in the absence of solvents. The method developed in this study was found to be practical and promising; it simplifies the process, thereby shortening the time required for both the treatment and the washing steps, and reducing the cost of fiber/thermoplastic composites.

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