

# Comparison of the Thermal Degradation of Natural, Alkali-Treated and Silane-Treated Hemp Fibers Under Air and an Inert Atmosphere

Ali Rachini, Marianne Le Troedec, Claire Peyratout, Agnès Smith

Haute-Vienne, GEMH-ENSCI, Groupe d'Etude des Matériaux Hétérogène (EA 3178), Ecole Nationale Supérieure de Céramique Industrielle, 47 à 73 Avenue Albert Thomas, 87065, Limoges Cedex, France

Received 26 May 2008; accepted 24 September 2008

DOI 10.1002/app.29412

Published online 22 December 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** To estimate the contribution of all major components to the thermal properties of natural hemp fiber bundles, the thermal decomposition of hemp fibers following several chemical treatments was studied by the differential thermogravimetric analysis (DTA/TGA). Contrary to what was observed with measurements conducted under air, the thermal degradation of all major hemp fiber components (pectins, hemicellulose, cellulose, and lignin principally) could be easily detected and deconvoluted under inert atmosphere. The intensity of the TGA peaks observed at 235°C (characteristics of pectin) and at 265°C (characteristics of hemicellulose) decreased after all fiber chemical treatments. This resulted in an overall increase of the cellulose percent-

age. Based on the onset temperature of DTA, it was found that the thermal stability decreased in the following order: NaOH-treated fibers, silane-treated fibers, solvent extracted fibers (water/ethanol mixture, 20/80 v/v), and untreated hemp fibers. Moreover, the difference of the mass loss (%) between TGA under argon of silane-treated fibers and untreated fibers showed that some silane molecules were chemically attached to hemp fiber bundles. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 226–234, 2009

**Key words:** hemp fibers; alkali treatment; solvents extraction; silane grafting; differential thermal analysis; thermogravimetric analysis

## INTRODUCTION

In the recent years, natural fibers, especially bast fibers, such as flax, hemp, jute, and henequen, have been successfully used as fiber reinforcement for composite materials. Natural fibers have a low density and a low cost. Moreover, they are renewable and biodegradable materials. Thus, they are interesting for various applications, in particular for the building industry.<sup>1–9</sup>

Natural fibers including cellulose, hemicellulose, lignin, pectins, waxes, and water-soluble substances are complex assemblies.<sup>10</sup> Cellulose is a semicrystalline polysaccharide which consists of D-glucopyranose units, linked together by  $\beta$ -(1-4)-glucosidic bonds. Hemicellulosic polymers are branched, fully amorphous and have a significantly lower molecular weight than cellulose. Hemicellulose is strongly tied to cellulose fibrils, presumably by hydrogen bonds. Lignins are amorphous and mostly aromatic phenylpropane polymers. Pectins are polysaccharide acids polymers. These chemicals (hemicellulose, pectins, lignin) are not thermally stable and tend to degrade at relatively low temperature (below 500°C).<sup>11,12</sup> Fur-

ther processing of a composite requires thermal stability information for materials selection and process operation. Removal of noncellulosic materials from fiber surface was suggested to achieve this purpose. Therefore, several methods have been applied to hemp fiber.<sup>10</sup>

Alkalization is widely used chemical process which removes noncellulosic components and part of the amorphous cellulose.<sup>13,14</sup>

The alkaline treatment has also a lasting effect on the mechanical behavior of fibers, especially on fiber strength and stiffness.<sup>15</sup> The mechanical properties of treated fibers/polymer matrix composites were also modified following chemical treatment of the cellulosic fibers.<sup>16–18</sup>

Silane coupling agents were already used to let glass fibers adhere to a polymer matrix and to stabilize the composite material: Following a prehydration from alkoxy-silanes to silanols, these functions react with the hydroxyl groups of the fiber, forming stable covalent bonds on the fiber surface and thus reduce the number of cellulose hydroxyl groups at the fiber-matrix interface.<sup>13</sup>

Silane coupling agents were also used to modify natural fiber-polymer matrix interface and to increase the interfacial strength. Bast fibers such as flax,<sup>16</sup> sisal,<sup>19</sup> henequen, and oil palm fibers<sup>4,13</sup> were already modified with functionalized silane molecules.

Correspondence to: A. Rachini (alirachini26@hotmail.fr).  
Contract grant sponsor: Région Limousin (France).

All these examples show that chemical treatment of natural fibers lead to a modification of the mechanical properties of the resulting composite material. For example, interaction between silane modified fibers and the organic matrix leads to composites exhibiting higher tensile strength than composites fabricated with alkaline-treated fiber.<sup>10,13</sup>

However, little information was obtained on the structure and on the configuration of the coupling agent grafted at the fiber surface. The complexity of the silane chemistry and the coexistence of self-condensation reactions made it difficult to obtain such evidence. Thus, several mechanisms, such as grafting and/or self-condensation of grafted silane at the hemp fiber surface were proposed.<sup>17</sup>

Additionally, few researches have been developed to evaluate the treatment impact (alkali, solvents, silanes, ...) on the thermal decomposition of natural fibers.<sup>20,21</sup>

In this context, we are presenting a detailed study of the thermal degradation of hemp fibers before and after chemical treatments (alkali, ethanol/water extraction, silane), under air and under inert atmosphere (argon). The thermal decomposition of natural hemp fibers will be discussed and compared with signals of the individual extracted components, namely, hemicellulose, pectins, and cellulose.

## EXPERIMENTAL

### Materials

Cortical hemp fibers (*Cannabis sativa*) were supplied by Agrofibra (Barcelona, Spain). Their density, measured with a pycnometer (Accupic helium pycnometer, Creil, France) was equal to  $1.58 \text{ g cm}^{-3}$ . The basic unit consists of cellulose polymeric chains, aligned and gathered in microfibrils. They are linked to each other by lignin, pectin, and hemicellulose.<sup>22</sup>

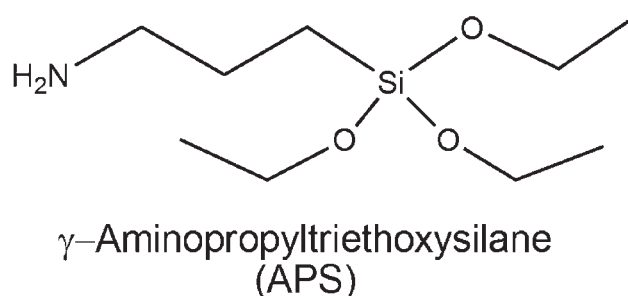
The organofunctional trialkoxysilane,  $\gamma$ -aminopropyltriethoxysilane (APS) (Scheme 1, molecular mass is  $221.37 \text{ g mol}^{-1}$ ) was a high purity product (Aldrich, Saint Quentin Fallavier, France).

All other reagents and solvents were commercial products of high purity.

## METHODS

### Fiber Cut

Before any treatment, hemp fibers were cut to approximately 5 cm long pieces, after which they were ground in a blade mixer (Waring Laboratory) for 1 min. The final length of the fiber was about 2 cm.



**Scheme 1** The chemical structure of the silane coupling agent (APS).

### Separation of components in hemp fibers

The quantity of cellulose, hemicellulose, lignin, pectins, and fat or waxes contained in the hemp was determined after successive extractions. The procedure was the following<sup>22</sup>: hemp fibers were crushed, sifted at  $500 \mu\text{m}$ , and stored for 24 h at room temperature in a dessicator to remove adsorbed water molecules. The dry fibers were first treated with ethanol (80 wt %) for 20 min in reflux, which led to the removal of fats and waxes. The residual material was boiled twice in water for 20 min. Thus the materials were soaked in a 1 wt % ammonium oxalate solution at  $85^\circ\text{C}$  for 2 h to extract the pectins. The lignins were removed by treating the residue with  $\text{NaClO}_2$  and  $\text{CH}_3\text{COOH}$  ( $80^\circ\text{C}$  for 1 h). The remaining hemicelluloses were solubilized first with a 24 wt % KOH aqueous solution ( $25^\circ\text{C}$  for 24 h) and then with a 4.3 wt % NaOH aqueous solution ( $25^\circ\text{C}$  for 24 h). After these extractions, the remaining insoluble material was considered to be the cellulosic residue. The mass percentage of each fraction was then calculated.

### Fiber alkali treatment

Fiber bundles were soaked in  $0.06 \text{ mol L}^{-1}$  NaOH ( $\text{pH} = 12.8$ ) solution during 48 h and then neutralized with 1 vol % of acetic acid. Fibers were then washed with deionized water until the pH value was 7. Subsequently, the fibers were dried at  $40^\circ\text{C}$  for 24 h. The alkalization conditions are relatively mild to leave the cellulosic part of the fiber bundles unscathed.<sup>23</sup>

### Fiber silane treatment

The isothermal adsorption of silane was obtained by adding APS ( $0.2 \text{ mol L}^{-1}$ ) to a 5 w/w % fiber suspension, in a 80/20 v/v ethanol/water mixture and by stirring at  $120^\circ\text{C}$  under a nitrogen atmosphere for 2 h. APS was previously prehydrolyzed at room temperature for 2 h in the same medium that was used for isothermal adsorption. The hemp fibers

**TABLE I**  
**Chemical Components of Hemp Fibers and Their Mass Percentage (wt %)**

Fiber	Component and wt %				
	Pectins	Lignins	Hemicellulose	Cellulosic residue	Waxes, fats
Hemp from Agrofiba (Barcelone, Spain)	16.8	6	14.2	58.7	4.3
Hemp from la Chanvrière de l'Aube (Bar-sur-Aube, France) <sup>22</sup>	20.1	6	10.9	56.1	7.9

were then centrifuged at 2500 rpm for 20 min and washed three times in an 80/20 v/v ethanol/water mixture. This treatment probably removed fat and waxes from the fibers. Subsequently, the fibers were dried at room temperature for 2 days. Finally the fibers were submitted to a 24 h Soxhlet extraction in ethanol and dried.

### Thermogravimetric analysis and differential thermal analysis

Dynamic experiments were performed using a Linseis instrument (L81 for TGA and L62 for DTA). Tests were conducted between 25 and 800°C under air and inert atmosphere (argon), at a heating rate of 10°C/min. The sample mass was 100 ± 4 mg and 30 ± 2 mg for thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurements, respectively.

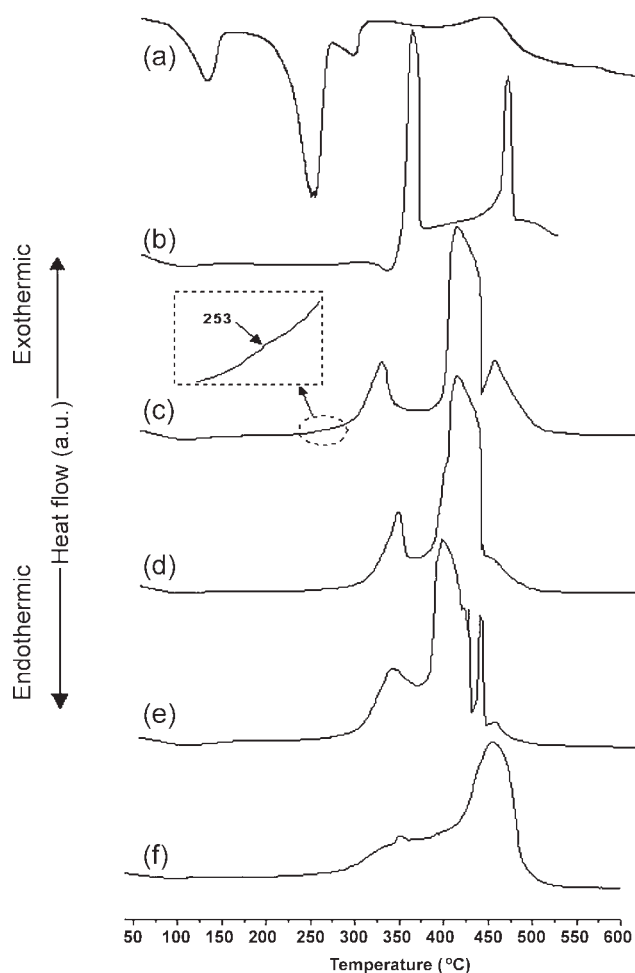
### Attenuated total reflectance infrared spectroscopy

The FTIR analysis was performed using a Perkin-Elmer instrument (spectrum one, Boston, USA), which allows measurements between 500 and 5000 cm<sup>-1</sup>. Attenuated total reflectance infrared spectroscopy (ATR FTIR) spectra (50 scans, 4 cm<sup>-1</sup> resolution) were collected with a multireflection horizontal ATR accessory, having a Germanium crystal fixed at an incident angle of 45°. The fibers were mounted on top of the ATR crystal and pressed gently by a premounted sample clamp. All spectra were corrected and normalized using the "spectrum one" software.

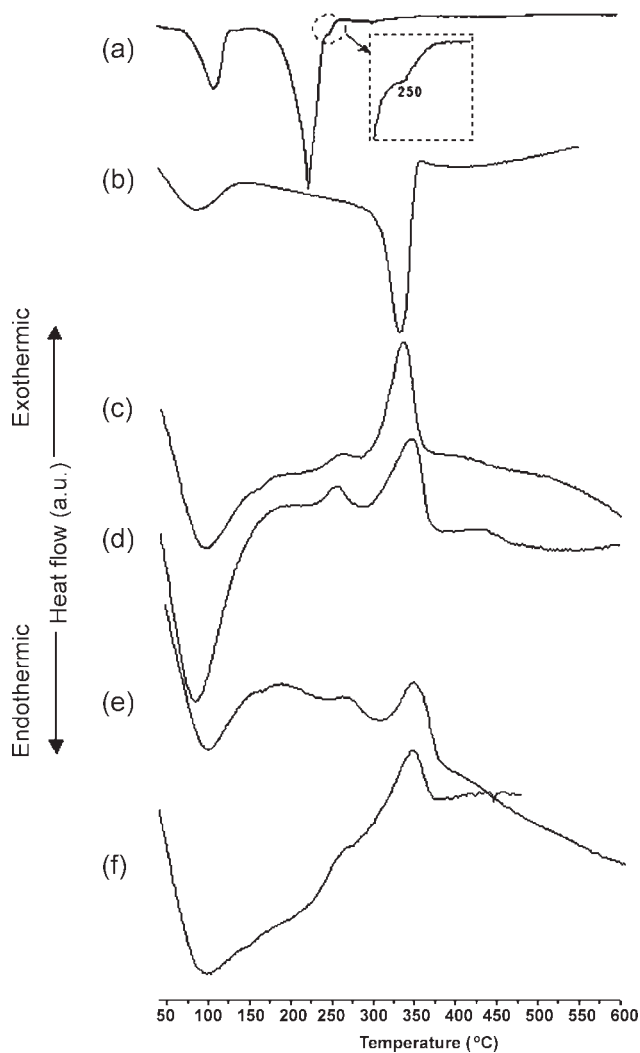
## RESULTS AND DISCUSSION

After separation of the components, hemp fibers used in this study contain 58.7 wt % of cellulose, 16.8 wt % of pectins, 14.2 wt % of hemicellulose, and 6 wt % of lignin (Table I). The component percentages were slightly different compared with those obtained from other hemp sources (la Chanvrière de l'Aube, Bar-sur-Aube, France).<sup>22</sup> These discrepancies can be attributed to climatic conditions, age, and digestion process, which influence the chemical composition of the fibers and their chemical characteristics.

The differential thermal analysis (DTA) under air and argon of extracted pectins, extracted cellulose, natural hemp fiber, NaOH treated hemp fiber, ethanol/water extracted hemp fiber, and APS treated hemp fiber are presented in Figures 1 and 2. The corresponding weight loss (%) and its derivative DTG (wt %/°C) are shown in Figures 3 and 4. Tables II and III present the maximum temperatures of decomposition and the corresponding weight loss (%), under air and argon, respectively.



**Figure 1** DTA under air of (a) extracted pectins, (b) extracted cellulose, (c) hemp fiber bundles, (d) NaOH treated hemp fibers, (e) ethanol/water extracted hemp fibers, and (f) APS treated hemp fibers.



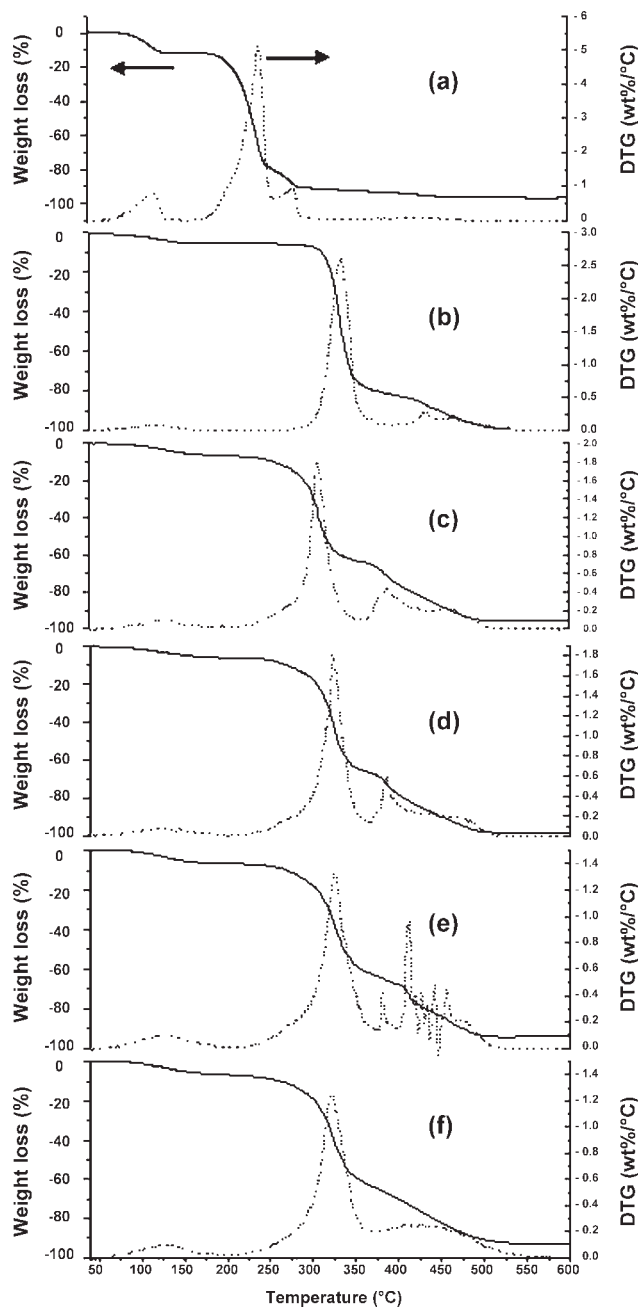
**Figure 2** DTA under argon of (a) extracted pectins, (b) extracted cellulose, (c) hemp fiber bundles, (d) NaOH treated hemp fibers, (e) ethanol/water extracted hemp fibers, and (f) APS treated hemp fibers.

### Natural hemp fibers

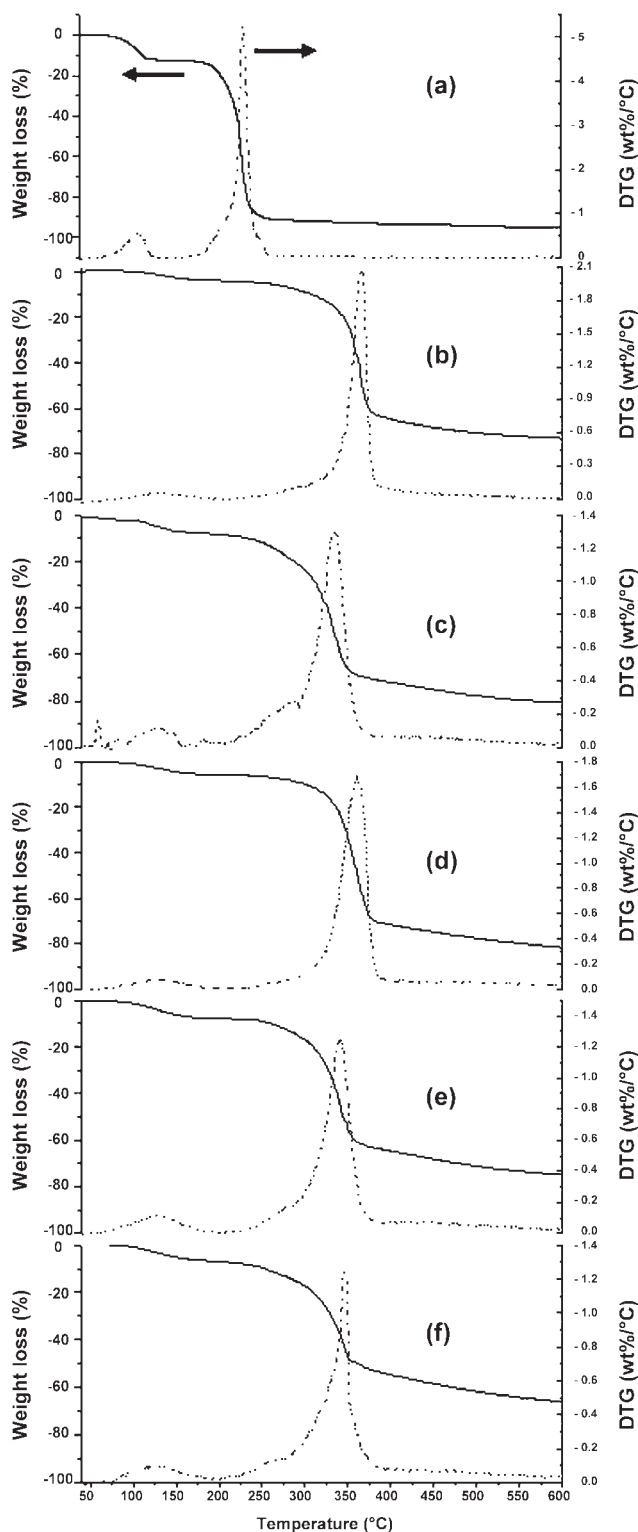
DTA curves under air and argon of natural hemp fibers [Figs. 1(c) and 2(c)] show an initial endothermic peak between 50 and 150°C, which corresponds to a mass loss of the adsorbed moisture and physisorbed water<sup>20</sup> of approximately 7% (Tables II and III). After this peak, the DTA under air showed a peak of low intensity between 220 and 280°C, and other three exothermic peaks centered around 312, 395, and 437°C.

DTA of extracted pectins [Figs. 1(a) and 2(a)] presents different endothermic peaks at 235 and 277°C under air, and at 224 and 250°C under argon. These results are in agreement with the literature, which stated that pectins are degraded at low temperature. The maximum decomposition is observed between 200 and 280°C, which the position of the

peak depending on the heating rate.<sup>24</sup> Under identical experimental conditions, the difference in the maximum temperature of pectins decomposition depends on the mass loss rate under air and argon. The first derivative of the TGA, presented in Figures 3(a) and 4(a), is representative of the mass loss rate (DTG). As the DTG of decomposition of pectins is slightly higher in argon than under air, it can be concluded that the pectin decomposition is faster



**Figure 3** Weight loss (%) and DTG (wt %/°C) under air of (a) extracted pectins, (b) extracted cellulose, (c) hemp fiber bundles, (d) NaOH treated hemp fibers, (e) ethanol/water extracted hemp fibers, and (f) APS treated hemp fibers.



**Figure 4** Weight loss (%) and DTG (wt %/°C) under argon of (a) extracted pectins, (b) extracted cellulose, (c) hemp fiber bundles, (d) NaOH treated hemp fibers, (e) ethanol/water extracted hemp fibers, and (f) APS treated hemp fibers.

under argon. Other studies state that hemicellulose starts its exothermal decomposition<sup>25</sup> at 220–315°C. Therefore, the exothermal peak at 260°C obtained

from the DTA under argon of natural hemp fibers corresponds to the simultaneous thermal depolymerization of hemicellulose and pectins (Tables II and III). The corresponding weight loss was about 10%. The endothermal decomposition of pectins is largely counter balanced by the exothermal depolymerization of hemicellulose.

The exothermic peak at 312°C from DTA under air of natural hemp fiber contains a contribution due to the cellulose decomposition [Fig. 1(c)]. Its weight loss (%) was of about 50% [Fig. 3(c) and Table II], corresponding to almost all the cellulosic residue measured in the sample (58.7 wt %). Under argon, this peak is shifted to 333°C. In fact, at this temperature, the decomposition rate (DTG) under air is higher than that obtained under argon [Figs. 3(c) and 4(c)].

The DTA and TGA under argon of the extracted cellulose [Figs. 2(b) and 4(b)] confirm the decomposition of cellulose at 333°C. However, the cellulose decomposition is generally endothermic under inert atmosphere. This is not the case with the DTA of natural hemp fiber under argon atmosphere, where the peak attributed to the cellulose decomposition is exothermic at about 333°C. This result may be explained by the contribution of lignin to the exothermic thermal decomposition. For lignin, the decomposition range is between<sup>25</sup> 280 and 500°C. Another study<sup>26</sup> reveals that the pyrolysis of cellulose mostly takes place at 315–400°C, whereas that of lignin covers a broader temperature range at 150–900°C. At low temperatures (< 500°C), the pyrolysis of hemicellulose and lignin in nitrogen involves exothermic reactions, whereas those of cellulose are endothermic (Table II and III).

Moreover, Kifani-Sahban et al. suggested that the coal yield from lignin is clearly higher than those obtained from hemicellulose and cellulose after the pyrolysis of eucalyptus.<sup>25</sup> In fact, the weight loss (%) of hemicellulose, cellulose, and lignin are 28, 37, and 11%, respectively. The coal yield of eucalyptus is 24%, which decomposes as follows: 7% from hemicellulose, 6% from cellulose, and 11% from lignin. Also, Tang noted that, for a wood containing 24% of lignin, the coal yield is 22% and the volatile compounds yield<sup>27</sup> is about 78%. In fact, the lignin contributes with 11% of the coal production and the 11% remaining is obtained from hemicellulose and cellulose pyrolysis. Moreover, the volatile materials obtained from lignin are of 13% compared with those of hemicellulose and cellulose that are of 65%. Generally, the contribution of hemicellulose and cellulose on the thermal degradation is of much higher importance than that of lignin. On the contrary, the situation is reversed when the case is that of the coal production. In conclusion, we observe that, under argon, the endothermal peak corresponding to the

**TABLE II**  
**Maximum Temperatures of Decomposition and the Corresponding Weight Loss (%) Under Air**

Material	Temperature range (°C)					
	40–150		150–380		380–600	
	Peaks	Weight loss (%)	Peaks	Weight loss (%)	Peaks	Weight loss (%)
Pectins extracted from hemp fiber	113 (endo)	11.8	235 (endo) 277 (endo)	66.0 15.5	437 (exo)	03.4
Cellulose extracted from hemp fiber	88 (endo)	05.0	344 (exo)	75.0	452 (exo)	20.0
Hemicellulose	–	–	265 (exo) <sup>a</sup>	–	–	–
Lignins	–	–	225 (exo) <sup>a</sup>	–	370 (exo) <sup>b</sup>	–
Hemp fiber bundles	87 (endo)	07.2	253 (exo)	10	395 (exo)	27.3
NaOH treated hemp fiber	87 (endo)	05.2	312 (exo)	51.0	427 (exo)	28.8
Ethanol/water extracted hemp fiber	98 (endo)	05.0	330 (exo)	64.8	397 (exo) 440 (exo)	27.9
APS treated hemp fiber	90 (endo)	05.3	324 (exo)	62.1	383 (exo) 424 (exo)	27.5
			327 (exo)	61.8	455 (exo)	

Exo, exothermic; Endo, endothermic.

<sup>a</sup> Ref. 25.

<sup>b</sup> Ref. 26.

cellulose decomposition at 333°C is hidden by the exothermic reaction of lignin.

Above 380°C, the DTA under air of natural hemp fibers presents two exothermic peaks [Fig. 1(c) and Table II] at 395 and 427°C and the weight loss (%) is about 27%. These peaks are attributed to the oxidative decomposition of the charred residue. Under argon, these peaks do not exist [Fig. 2(c) and Table III]. This result confirms that under air, these two peaks are produced by the residue loss. Decomposition of natural hemp fiber under air was complete and proceeded at a lower temperature than under argon. The decomposition under argon is due to the presence of free radicals.<sup>20,28</sup>

#### NaOH treated hemp fibers

The DTA and TGA under air and argon of NaOH treated hemp fibers are shown in Figures 1(d), 2(d), 3(d), and 4(d). The maximum temperatures of decomposition and their corresponding weight loss (%) are presented in the Tables II and III. We noticed the presence of an endothermic peak in the 40–150°C temperature range, which corresponds to a mass loss of the adsorbed moisture and physisorbed water of about 5% compared with 7% obtained for natural hemp fiber. This indicates that the alkali treatment removes a part of the adsorbed molecules like fats, waxes, and others.

**TABLE III**  
**Maximum Temperatures of Decomposition and the Corresponding Weight Loss (%) Under Argon**

Material	Temperature range (°C)					
	40–150		150–380		380–600	
	Peaks	Weight loss (%)	Peaks	Weight loss (%)	Peaks	Weight loss (%)
Pectins extracted from hemp fiber	107 (endo)	12.3	224 (endo) 250 (endo)	71.0 08.5	–	01.5
Cellulose extracted from hemp fiber	87 (endo)	03.2	333 (endo)	61.3	–	08.0
Hemicellulose	–	–	268 (exo) <sup>a</sup>	–	–	–
Lignins	–	–	365 (exo) <sup>a</sup>	–	–	–
Hemp fibers bundle	92 (endo)	07.4	260 (exo)	11.0	–	09.0
NaOH treated hemp fiber	84 (endo)	04.4	333 (exo)	52.0	–	10.0
Ethanol/water extracted hemp fiber	91 (endo)	06.4	254 (exo)	03.0	–	11.4
APS treated hemp fiber	97 (endo)	05.4	346 (exo)	65.0	–	12.0
			262 (exo)	06.0		
			340 (exo)	56.0		
			260 (exo)	06.0		
			345 (exo)	47.3		

Exo, exothermic; Endo, endothermic.

<sup>a</sup> Ref. 26.

Under air, in a 280–350°C temperature range, an exothermic peak is observed at 330°C, which corresponds to the cellulose decomposition with a weight loss of 65% [Fig. 3(d) and Table II] compared with 60%, obtained from natural hemp fiber [Fig. 3(c) and Table II]. This indicates that the cellulose percentage increased after treatment, which was also confirmed by the increase of the cellulose crystallinity index, obtained by X-ray diffraction in a previous study.<sup>29</sup> This main degradation temperature increased from 312°C (natural hemp fibers) to 330°C for the NaOH treated hemp fibers. The alkali treatment increases the thermal stability of hemp fibers. Moreover, the shoulder of the DTA peak at about 220–260°C, which was observed on Figure 1(c) and attributed to the depolymerization of hemicellulose and pectins, disappears after alkali treatment.

On the other hand, under argon, the DTA of NaOH treated hemp fibers presents two exothermic peaks [Fig. 2(d)] at 254 and 346°C. The peak at 254°C is attributed to the pectin and hemicellulose decomposition. The corresponding weight loss (%) is about 3% compared with 10% obtained from the natural hemp fiber in the same temperature range (Table III). This result confirms the removal of a large part of hemicellulose and pectins under alkali treatment. The second peak detected at 346°C represents the cellulose decomposition with a higher weight loss of 65%. This temperature is also higher than that detected for the natural hemp fiber under argon, which was 333°C. This confirms the improvement of the thermal properties of hemp fibers, due to the alkali treatment. As in the case of the natural hemp fiber, this peak is affected by the lignin decomposition within this temperature range [Fig. 2(d) and Table III].

The decrease of hemicellulose and pectin quantity was also confirmed by FTIR spectroscopy (not shown). The vibration peak at 1732 cm<sup>-1</sup> attributed to the C=O stretching of methyl ester and carboxylic acid in pectin decreases in the case of the NaOH treated fibers. This indicates a partial removal of pectin and hemicelluloses by alkalization. Pectin contains both esterified and carboxylic acid groups in its structure. Ouajai et al.<sup>20</sup> attributed the disappearance of the C=O stretching to the removal of pectin and hemicelluloses from the mercerized hemp fibers (8% NaOH). Besides, the absorption band at 1555 cm<sup>-1</sup>, characteristic of the ketone and carbonyl groups was also reduced, which confirms the partial removal of these two chemicals.

### Silane (APS) treated hemp fibers

The thermal decomposition of natural hemp fiber treated with an aminopropyltrimethoxysilane (APS) in an ethanol/water (80 : 20; v : v) mixture was eval-

uated. Before the study, it is important to characterize the effect of the mixed solution on the thermal stability of the hemp fiber under air and argon. Then, we will report the results obtained in the presence of the silane coupling agent (APS).

In comparison with the natural hemp fiber, within the 200–280°C temperature range, the ethanol/water extracted hemp fiber presents a first decomposition under air at 265°C (very low peak). On the other hand, under argon, the maximum decomposition is about 265°C compared with 260°C of the natural hemp fiber. It is interesting to notice that this first decomposition is easily detectable from the DTA under argon [Figs. 1(e) and 2(e)]. This decomposition corresponds to the thermal degradation of hemicellulose and pectins. The weight loss (%) obtained is low (6%) compared with that obtained from the natural hemp fiber (10%) within the same temperature range. Part of hemicellulose and pectins was removed due to the ethanol/water extraction.

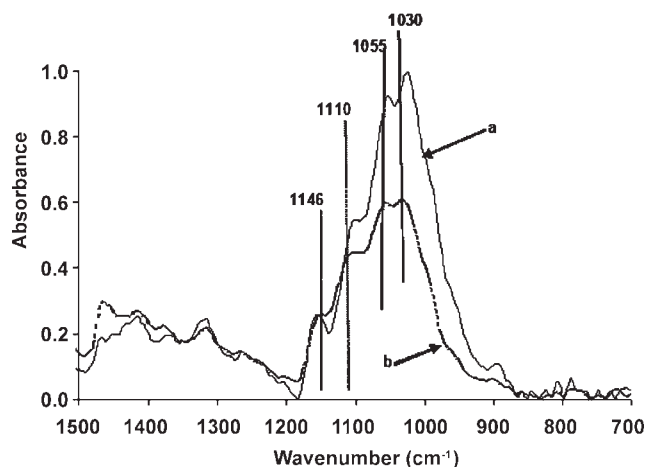
Within the 280–380°C temperature range, the ethanol/water extracted hemp fiber shows an exothermic peak at 324°C under air, and at 340°C under argon [Figs. 1(e) and 2(e)]. These temperatures of decomposition are higher than that obtained for the natural hemp fiber under air and argon [Figs. 1(c) and 2(c)]. The corresponding weight loss (%) is slightly higher than that obtained for the natural hemp fiber suggesting a low increase of the cellulose percentage (The cellulose weight loss (%) was 56% compared with 50% for natural hemp fiber). It is necessary to indicate that the thermal decomposition of cellulose is influenced by the lignin decomposition within this temperature range.

Beyond 380°C, the presence of several exothermic peaks under air is attributed to the exothermic reactions of the charred residue. These peaks are not detected under argon atmosphere.

We conclude that the ethanol/water extraction allows the removal of some hemicellulose and pectins and consequently, the increase of the cellulose percentage. The thermal decomposition of the hemp fiber is shifted toward slightly higher temperatures.

The presence of the silane coupling agent (APS, 0.2 mol L<sup>-1</sup>) in the medium does not change the temperature ranges of thermal decomposition up to 380°C, compared with those obtained for the ethanol/water extracted hemp fiber. The decomposition of hemicellulose and pectins is hardly detectable under air [Fig. 1(f)]. On the contrary, under argon, this decomposition is easily obtained at 266°C (exothermic peak) [Fig. 2(f)]. The correspondent weight loss is about 6% [Fig. 4(f) and Table III].

It is noticeable that the DTA of the APS treated hemp fiber does not present any peak corresponding to the thermal decomposition of physically adsorbed silane. It is necessary to remind that the fibers were



**Figure 5** ATR FTIR spectra (1500–700  $\text{cm}^{-1}$ ) of (a) ethanol/water extracted natural hemp fibers and (b) APS (0.2  $\text{mol L}^{-1}$ ) treated hemp fibers.

subjected to 24 h Soxhlet extraction in ethanol to remove all nonchemically grafted silanes.

In the next temperature range (above 380°C), the weight loss is attributed to the decomposition of cellulose, lignin, and grafted silane.

Generally, the thermal decomposition of the grafted aminosilane on a clay surface is detected within the 300–600°C temperature range.<sup>30</sup> In our case, the oxidative degradation (380–600°C) makes it difficult to obtain the weight loss corresponding to the degradation of grafted silane under air [Fig. 3(f)]. On the contrary, under argon, the situation is different [Fig. 4(f)]. In fact, beyond 380°C, the weight loss (%) of the APS treated hemp fiber [Fig. 4(f)] is lower compared with that of ethanol/water extracted hemp fiber [Fig. 4(e)]. This result may be attributed to the presence of grafted silanes, which do not decompose under argon environment. The grafting of the silane was also confirmed by ATR FTIR analysis (Fig. 5). Within the 1500–700  $\text{cm}^{-1}$  wavenumber range, we noticed the presence of several bands at 1030, 1055, 1110, and 1146  $\text{cm}^{-1}$ , characteristic of the Si–O–Si and Si–O–C bonds.<sup>4</sup> This seems to confirm the occurrence of a chemical reaction between the hydrolyzed silane and the natural hemp fiber and also indicates the existence of a polysiloxanes network.

Moreover, from the difference on the weight loss (%) under argon within the 150–380°C temperature range (Table III), it is possible to calculate the quantity of grafted silanes onto the surface fibers as follows:

Grafted silanes ( $\text{mg g}^{-1}$  of hemp fiber) =  $W_{150-380} \times 1000$ , where  $W_{150-380}$  is the difference (%) of the weight loss in the presence and in the absence of APS.

Then, grafted silanes ( $\text{mmol g}^{-1}$  of hemp fiber) = grafted silane ( $\text{mg/g}$  of hemp fiber) /  $M$ , where  $M$  is the molecular mass of the hydrolyzed silane.

In our case,  $M$  equals 138  $\text{g mol}^{-1}$  and  $W_{150-380}$  equals 8.7%, which gives an amount of grafted silanes of about 0.6  $\text{mmol g}^{-1}$  of hemp fiber, with an initial silane concentration of 0.2  $\text{mol L}^{-1}$ .

## CONCLUSIONS

The analysis and comparison of differential thermogravimetric data under inert atmosphere (argon) can be used to detect and identify the nature of the main components present in the hemp fiber structure. Moreover, it allows the obtention of information about the removed quantity of noncellulosic materials after alkalization, solvent extraction, and silane treatment. These treatments improve the thermal decomposition of the hemp fibers. Finally, TGA results under argon associated with FTIR ATR spectroscopy measurements suggests the possible formation of a chemical bond between the hydroxyl groups of the hemp fibers and the hydrolyzed silane molecules. The amount of the grafted silane was about 0.6  $\text{mmol g}^{-1}$  of hemp fiber for an initial silane concentration of 0.2  $\text{mol L}^{-1}$ . Mechanical characterization of the chemically treated fibers and of composites with clay and lime are currently being investigated.

## References

- Singleton, A. C. N.; Baillie, C. A.; Beaumont, P. W. R.; Peijs, T. *Compos Part B Eng* 2003, 34, 519.
- Keller, A. *Compos Sci Technol* 2003, 63, 1307.
- Rana, A. K.; Mandal, S.; Bandyopadhyay, S. *Compos Sci Technol* 2003, 63, 801.
- Valadez-Gonzalez, A.; Cervantes-Uc, J. M.; Olayo, R.; Herrera-Franco, P. J. *Compos Part B Eng* 1999, 30, 321.
- Oksman, K.; Skrifvars, M.; Selin, J. F. *Compos Sci Technol* 2003, 63, 1317.
- Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
- Paul, A.; Joseph, K.; Thomas, S. *Compos Sci Technol* 1997, 57, 67.
- Rouison, D.; Sain, M.; Couturier, M. *Compos Sci Technol* 2004, 64, 629.
- Sedan, D.; Pagnoux, C.; Smith, A.; Chotard, T. *J Eur Ceram Soc* 2008, 28, 183.
- Li, X.; Tabil, L. G.; Panigrahi, S. *J Polym Environ* 2007, 15, 25.
- Vignon, M. R.; Dupeyre, D.; Garcia-Jaldon, C. *Bioresource Technol* 1996, 58, 203.
- Garcia-Jaldon, C.; Dupeyre, D.; Vignon, M. R. *Biomass Bioenerg* 1998, 14, 251.
- Agrawal, R.; Saxena, N. S.; Sharma, K. B.; Thomas, S.; Sreekala, M. S. *Mat Sci Eng A* 2000, 277, 77.
- Fisher, T.; Hajaligol, M.; Waymack, B.; Kellogg, D. *J Anal Appl Pyrol* 2002, 62, 331.
- Jähn, A.; Schröder, M. W.; Fütting, M.; Schenzel, K.; Diepenbrock, W. *Spectrochim Acta A* 2002, 58, 2271.
- van de Weyenberg, I.; Ivens, J.; De Coster, A.; Kino, B.; Baetens, E.; Vepoes, I. *Compos Sci Technol* 2003, 63, 1241.
- Mehta, G.; Drzal, L. T.; Mohanty, A. K.; Misra, M. *J Appl Polym Sci* 2006, 99, 1055.



18. Mishra, S.; Mohanty, A. K.; Drzal, L. T.; Misra, M.; Parija, S.; Nayak, S. K.; Tipathy, S. S. *Compos Sci Technol* 2003, 63, 1377.
19. Rong, M. Z.; Zhang, M. Q.; Liu, Y.; Yang, G. C.; Zeng, H. M. *Compos Sci Technol* 2001, 61, 1437.
20. Ouajai, S.; Shanks, R. A. *Polym Degrad Stabil* 2005, 89, 327.
21. Ray, D.; Sarkar, B. K.; Basak, R. K.; Rana, A. K. *J Appl Polym Sci* 2002, 85, 2594.
22. Sedan, D.; Pagnoux, C.; Chotard, T.; Smith, A.; Lejolly, D.; Gloaguen, V.; Krausz, P. *J Mater Sci* 2007, 42, 9336.
23. Mwaikambo, L.; Ansell, M. *J Appl Polym Sci* 2002, 84, 2222.
24. Einhorn-Stoll, U.; Kunzek, K.; Dongowski, G. *Food Hydrocolloid* 2007, 21, 1101.
25. Kifani-Sahban, F.; Belkbir, L.; Zoulalian, A. *Thermochim Acta* 1996, 284, 341.
26. Yang, H.; Yan, R.; Chen, H.; Lee, D. H.; Zheng, C. *Fuel* 2007, 86, 1781.
27. Tang, W. K. Effect of Inorganic Salts on Pyrolysis of Wood  $\alpha$ -cellulose and Lignin Determined by Dynamic Thermogravimetry; USDA For Serv, F. P. L., Madison, WI, 1961; p 71.
28. Shafizadeh, F.; Bradbury, A. G. W. *J Appl Polym Sci* 1979, 23, 1431.
29. Troedec, M. L.; Sedan, D.; Peyratout, C.; Bonnet, J. P.; Smith, A.; Guinebretiere, R.; Gloaguen, V.; Krausz, P. *Compos A* 2007, 39, 514.
30. He, H.; Duchet, J.; Galy, J.; Gerard, J. F. *J Colloid Interf Sci* 2005, 288, 171.