Chemical Modification of Hemp Fibers by Silane Coupling Agents

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

GEMH-ENSCI, Groupe d'Etude des Matériaux Hétérogènes (EA 3178), Ecole Nationale Supérieure de Céramique Industrielle, Centre Européen de la Céramique (CEC), 12, Rue Atlantis, 87068, Limoges Cedex, France

ABSTRACT: Natural hemp fibers were chemically modified using silane coupling agents to reduce their hydrophilic character. The existence of a chemical bond between coupling agents and hemp fibers was confirmed by ATR-FTIR spectroscopy, ^{29}Si Nuclear Magnetic Resonance (NMR), thermogravimetric analysis (TGA), energy dispersive spectroscopy (EDS), and BET surface area measurements. It was shown that the initial concentration and the chemical structure of the organosilane coupling agent have an effect on the grafted quantity on the hemp fiber surfaces. The grafted quantity increased proportionally to the initial concentration of silane molecules. The presence of polar amino end group (NH_2) in silane structure can cause an increase in the grafted quantity, compared with results obtained in the case of silane molecules containing methacryloxy groups. This effect is attributed to the formation of hydrogen bonds between NH_2 and unreacted hydroxyl groups of hemp fibers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 601–610, 2012

Key words: hemp fibers; silane grafting; heat treatment; surface properties; ATR-FTIR Spectroscopy; ^{29}Si CP/MAS NMR spectroscopy; differential thermogravimetric analysis (DTA/TGA)

INTRODUCTION

In the development of environment friendly composites, natural bast fibers play an important role. Indeed, this renewable and biodegradable raw material has a low density, a low cost, a high flexural strength, and thus, has been used as reinforcement in various applications, in particular for building materials applications.[1–9]
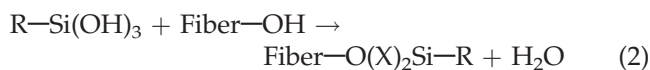
Natural fibers are complex assemblies containing cellulose, hemicellulose, lignin, pectins, waxes, and water-soluble substances.[10] The chemical composition, characteristics and component percentages can vary slightly depending on the climatic conditions, age and retting process.

The major difficulty which limits an extended use of natural fibers is their hydrophilic nature. This property affects adhesion to a hydrophobic matrix (of polymeric nature) and results in a decrease in the mechanical properties of the resulting composite material. The degree of interfacial adhesion between fibers and the matrix is one of the major contributions on the mechanical properties, affecting especially durability, and toughness. Thus, modification of the fiber surface was generally used to reduce the hydrophilic character of natural fibers for incorporation mostly in organic matrix. Therefore, many chemical treatments, such as alkaline treament, silane grafting, acetylation, benzoylation, acrylation, oxidation, and isocyanation have been applied to chemically modify natural fibers.[10]

Natural fibers were also introduced in cement matrices and are known to improve mechanical properties of mortars.[11,12] More recently, hemp fibers were treated with silane agents before mixing with clay based materials for building materials applications.[13] Grafted at the surface of natural fibers, organosilane agents decrease the number of cellulose hydroxyl groups available at the fiber/matrix interface. In the presence of moisture, hydrolysable alkoxy groups lead to the formation of silanol groups, which then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall.[14]

The reaction scheme is given as follows (1 and 2):

$$R\text{—}Si(OR_1)_3 + 3H_2O \rightarrow R\text{—}Si(OH)_3 + 3R_1OH \qquad (1)$$

$$R\text{—}Si(OH)_3 + Fiber\text{—}OH \rightarrow$$
$$Fiber\text{—}O(X)_2Si\text{—}R + H_2O \qquad (2)$$

where, R = functional carbon chain, R_1 = carbon chain and X=OH or OSi.

Silane coupling agents were already used to modify natural fiber-polymer matrix interface and to increase the interfacial cohesion strength, by

decreasing the number of hydroxyl groups at the fiber/matrix interface. Various aminopropyltrimethoxy silane molecules mixed at a 1 vol % in a solution of acetone and water (50/50 vol %) were reported to modify the surface of flax fibers.[15] Rong et al.[16] soaked sisal fibers in an alcoholic solution of aminosilane at a pH value comprised between 4.5 and 5.5, to hydrolyze the coupling agent. Silane solutions in a water and ethanol mixture were also carried out by Valadez et al. and Agrawal et al. to modify henequen and oil palm fiber surfaces.[4,14]

These studies showed that the interaction between the silane coupling agent modified fiber and the matrix is stronger than after an alkaline treatment and led to composites with higher tensile strength for silane-treated fibers than for alkaline-treated fibers.[10,14] 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 characterize the silane bonding at the fiber surface. Mehta et al. proposed a model for the grafting and the self-condensation of silane molecules on the hemp fiber surface.[17] However, the proposed reaction scheme was not clearly described.

Recently, the reinforcement capability of silane-treated jute fiber on polypropylene (PP) composites was investigated.[18] Surface of jute fibers was chemically modified using γ-glycidoxypropyltrimethoxysilane as silane-coupling agent in a methanol/water medium. Infrared spectroscopy characterization confirmed the existence of a condensation reaction between silane molecules and the cellulose polymers present in jute fibers. In addition, an intermolecular condensation occurred between adjacent silanol groups deposited on the fibers. Silane treatment increased the tensile properties of the jute-PP composites, because of an improved adhesion between the silanized jute fiber and the PP matrix.

In this study, we present the chemical modification of natural hemp fibers treated with two organosilane coupling agents. The effect of the initial concentration and the chemical structure of the organosilane on the grafting quantity will also be discussed. The untreated and treated hemp fibers were characterized using various experimental techniques, such as differential thermogravimetric analysis (TGA), [29]Si Nuclear Magnetic Resonance (NMR), infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and BET surface area measurements.

EXPERIMENTAL

Materials

Cortical hemp fibers 'Cannabis Sativa' were supplied by Agrofibra (Barcelona, Spain). The density, meas-

ured with a pycnometer (Accupic helium pycnometer, Creil, France) was 1.6 g cm^{-3}. The technical fibers used for this study consist of cellulose polymeric chains aligned and gathered in microfibrils, which are then linked to each other by lignin, pectin and hemicelluloses molecules.[19] The organofunctional trialkoxysilane (Fig. 1), γ-methacryloxypropyltrimethoxysilane (MPS) and γ-aminopropymtriethoxysilane (APS) were high purity products (Aldrich). Their molecular mass is 248.38 and 221.37 g mol^{-1}, respectively.

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

METHODS

Fiber preparation

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.

Fiber silane treatment

Different amounts of the given silane (MPS or APS) were previously prehydrolysed at room temperature for 2 h in a 80/20 vol % ethanol/water mixture. Then, 5 wt % of fibers were added. The isothermal adsorption of silane was obtained by stirring the mixture at 120°C under a nitrogen atmosphere for 2 h.

The hemp fibers were then centrifuged at 2500 rpm for 20 min and washed three times in an 80/20 vol % ethanol/water mixture. This treatment removed fat and waxes from the fibers.[13] 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.

Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

The FTIR analysis was performed using a Perkin–Elmer instrument (spectrum one, Boston), which allows measurements between 500 and 5000 cm^{-1}. ATR-FTIR spectra (50 scans, 4 cm^{-1} 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.

Solid-state [29]Si nuclear magnetic resonance spectroscopy (NMR)

[29]Si cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were
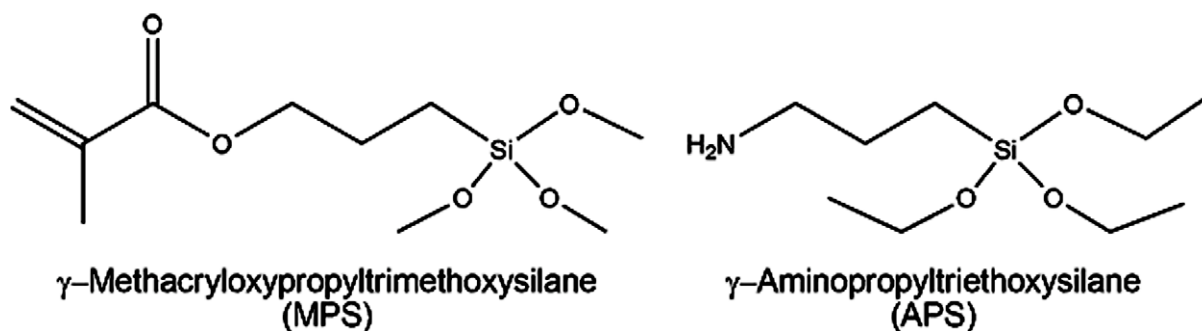
Figure 1 Chemical structures of silane coupling agents (MPS and APS).

recorded on a Bruker Avance II 400 MHz spectrometer. Samples were sealed in 7 mm zirconium rotors. The contact time was 4 and 5 ms, respectively, for APS and MPS treated hemp fibers, and the spinning rate was 5 KHz using a pulsation angle of $\pi/2$. Tetramethylsilane (TMS) was used as the external reference. To optimize the signal/noise ratio of the spectra, the acquisition time was very long (30 to 40 h/sample). This indicates a very low quantity of grafted silane molecules.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

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

Scanning electron microscopy (SEM) coupling with energy dispersive spectroscopy (EDS)

Scanning electron microscopy (SEM) was used to observe the microstructure and the surface morphology of treated as well as untreated hemp fibers. The instrument was a Cambridge Stereoscan S260 apparatus, equipped with an Energy Dispersive Spectroscopy (EDS) analysis. The fiber surfaces were coated with a thin film of carbon to render them conductive.

BET surface area measurements

Before this characterization, the fibers (2 cm) were grounded onto very small pieces ($\sim$ 500 nm) using a wood grinder. Nitrogen adsorption isotherms were measured for untreated and treated hemp fibers using a Micromeritics (Flowsorb II 2300) apparatus. The specific surface area was calculated from $\sim$ 1 g of fibers after vacuum drying for 2 h at 100°C.

RESULTS AND DISCUSSION

To investigate the effect of organosilane treatments, characterizations of all silane-treated hemp fibers were compared with results obtained with natural hemp fibers extracted in the same ethanol/water medium used for the grafting process.

Spectroscopic characterization of untreated and chemically treated hemp fibers surface by ATR-FTIR

Previous research using adsorption isotherm measurements revealed that the prehydrolyzed silane molecules used in our experiments were adsorbed onto the surface of microcrystalline cellulosic fibers.[20] This adsorption followed a mono and a multilayer deposition process depending on the ratio between the quantities of the silane molecule and the substrate. This adsorption was essentially driven by the formation of hydrogen bonds between the hydroxyl groups of silane molecules and of cellulose polymers. However, functional groups present at the end of the short aliphatic moiety of the silane structure also contributed to the adsorption process through specific interactions. The authors confirmed that the thermal treatment at 120°C induced the chemical bonding of silane grafting agents.[20]

ATR-FTIR spectra (4000–700 cm^{-1}) corresponding to ethanol/water extracted and MPS treated hemp fibers at different initial concentrations (0.05, 0.1, and 0.2 mol L^{-1}) are shown in Figure 2.

The intensity of the signals corresponding to C—H stretching at 3000–2800 cm^{-1} (s, C—H) increases compared with that of the ethanol/water extracted natural hemp fibers. This result can probably be attributed to the alkyl chain present in the silane molecule structure. Similar results (not shown) have been obtained for the APS treated hemps fibers with different initial concentrations in grafting agent.

Moreover, all MPS treated hemp fibers present two bands at $\sim$ 1720 (s, C=O) and at 1738–1734 cm^{-1} (s, C=O) (Fig. 2). These signals are attributed
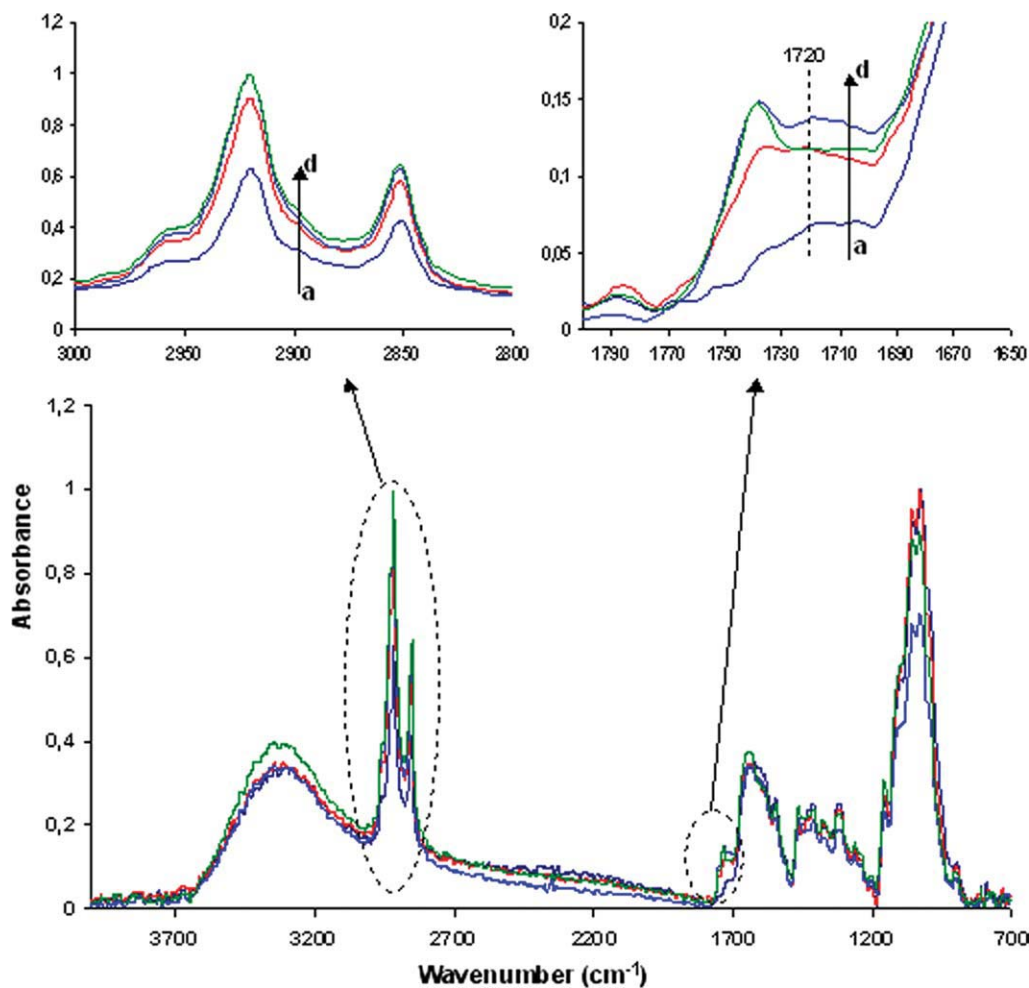
Figure 2 ATR-FTIR spectra of (a) ethanol/water extracted natural hemp fibers, (b), (c), and (d) MPS (0.05, 0.1, and 0.2 mol L^{-1}) treated hemp fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

to the stretching vibrations of the carbonyl groups. The intensity of the signal at 1720 cm^{-1} appeared clearly in the spectrum of MPS (0.2 mol L−1) treated hemp fibers, compared to that of ethanol/water extracted hemp fibers. This band was attributed to the C=O group of the acrylic moiety present in the MPS structure. From the broad shape of this peak, it was deduced that MPS had established hydrogen bonds with the hydroxyl groups on hemp fiber surface.[20] The spectrum of ethanol/water extracted hemp fibers presents a peak at 1738 cm^{-1} characteristic of hemicelluloses. The intensity of this peak increases after silane grafing agent treatment.

The detection of these different bands confirms the presence of the MPS on the surface of natural hemp fibers after Soxhlet extraction.

However, it is extremely difficult to differentiate the characteristic bands of the Si—O—Si and the Si—O—C bonds. In fact, the Si—O—Si and Si—O—C signals are generally detected at about 1030 (s, Si—O—Si), 1080 (s, Si—O), 1110 (s, S—O—Si), and

1200 cm^{-1} (s, Si—O). In addition, the hemp fibers presents several signals within the 1700–700 cm^{-1} range (Table I).[21,22] It can be observed that the components of hemp fibers are most likely alkenes, aromatic esters, ketones, and alcohol, with different oxygen-containing functional groups. Young et al. observed that the content in O—H and C—O functions is higher in cellulose polymer than in hemicelluloses polymers. However, the content in C=O is higher in hemicelluloses polymers. Lignin presents a higher methoxyl (—O—CH$_3$), C—O—C, and C=C (aromatic ring) content.[21,22]

From the spectrum of APS (0.1 mol.L^{-1}) treated hemp fibers, within the 1500–700 cm^{-1} range (Fig. 3), we can differentiate several bands at 1030, 1055, 1110, and 1146 cm^{-1}, characteristic of the Si—O—Si and Si—O—C bonds.[4,18] The presence of these bands suggests that both the grafting of silane onto hemp fiber and the intermolecular condensation between adjacent adsorbed —Si—OH groups took place. These peak assignments are in agreement with those

TABLE I
The Main Functional Groups of Hemp Fibers Within 1700–700 cm^{-1}

Wavenumber (cm^{-1})	Functional groups	Compounds
1510–1560	C=O stretching	Ketone and carbonyl
1632	C=C	Benzene stretching ring
1613 and 1450	C=C stretching	Aromatic skeletal mode
1402	C—H bending	
1232	C—O—C stretching	Aryl-alkyl ether linkage
1215	C—O stretching	Phenol
1170 and 1080	C—O—C stretching	Pyranose ring Skeletal
1108	OH association	C—OH
1060	C—O stretching and C—O deformation	C—OH
700–900	C—H	Aromatic hydrogen

reported in other studies dealing with glass surfaces treated with the same coupling agent.[23,24]

These results confirm the occurrence of a chemical reaction between the hydrolyzed silane and the natural hemp fiber and also indicates the existence of a polysiloxane network. It is interesting to note that the very low intensity of the absorption bands at 860 and 930 cm^{-1}, corresponding to Si—OH bond, reveals a low content in residual hydrolyzed silane molecules at the hemp fiber surface. This effect was also reported by other authors.[4,18] Concerning the spectra of APS (0.05 and 0.1 mol L^{-1}) treated hemp fibers, signals attributed to Si—O—Si and Si—O—C stretching bands were probably affected by those of several organic compounds present at the bast fibers surface (Table I).

Thermal decomposition of untreated and chemically treated hemp fibers

In a previous publication, we showed that organic solvent treatment increases the thermal decomposition of the hemp fiber, because of the removal by ethanol/water extraction of fats, waxes, and some of the hemicelluloses polymers.[13] The presence of the silane coupling agents MPS or APS (at different concentrations) in the medium does not influence the thermal decomposition, under air, of ethanol/water extracted hemp fibers: A first peak centered at 265°C is attributed to the decomposition of pectins and hemicellulose. The second decomposition ($\sim$ 342°C) concerns the degradation of cellulose, lignin, and grafted silane molecules. The DTA of all MPS treated hemp fibers does not present any peak corresponding to the thermal decomposition of the physically adsorbed silane molecules. This result confirms that a 24 h Soxhlet extraction in ethanol removes all nonchemically adsorbed silane molecules.[13]

Generally, the thermal decomposition of the grafted aminosilane at clay surface is detected within the 340–600°C temperature range.[25] The oxidative degradation of the charred residue (380–

600°C) makes it difficult to obtain the weight loss (%) corresponding to the grafted silane degradation under air. However, under argon and for temperatures higher than 380°C (Fig. 4), the weight loss of the MPS or APS treated hemp fibers is lower compared to that of ethanol/water extracted hemp fiber and is proportional to the initial concentration of organosilane. This result was attributed to the presence of grafted silane, which does not decompose under argon environment.

Evaluation of grafting treatment by Solid-state ^{29}Si nuclear magnetic resonance (NMR) measurements

^{29}Si CP/MAS NMR spectrum provides additional evidence for the silylation of fibers surface. ^{29}Si CP/MAS NMR spectra of APS (0.1 and 0.2 mol L^{-1}) treated hemp fibers are presented in Figure 5. Three signals are recorded at $\sim$ −67, −58, and −48 ppm and correspond, respectively, to the units of T^3 [Si(OSi)$_3$OR], T^2 [Si(OSi)$_2$(OR)R′], and T^1 [Si(O-Si)(OH)$_2$R], where R=CH$_2$—CH$_2$—CH$_2$—NH$_2$ and R′
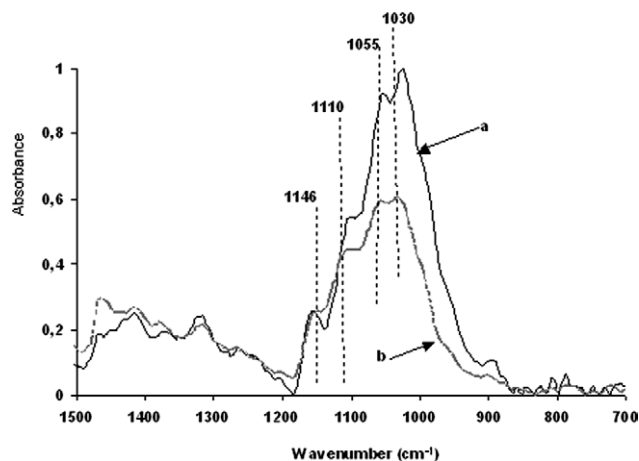

Figure 3 ATR-FTIR (1500–700 cm^{-1}) spectra of (a) ethanol/water extracted hemp fibers and (b) APS (0.2 mol L^{-1}) treated hemp fibers.
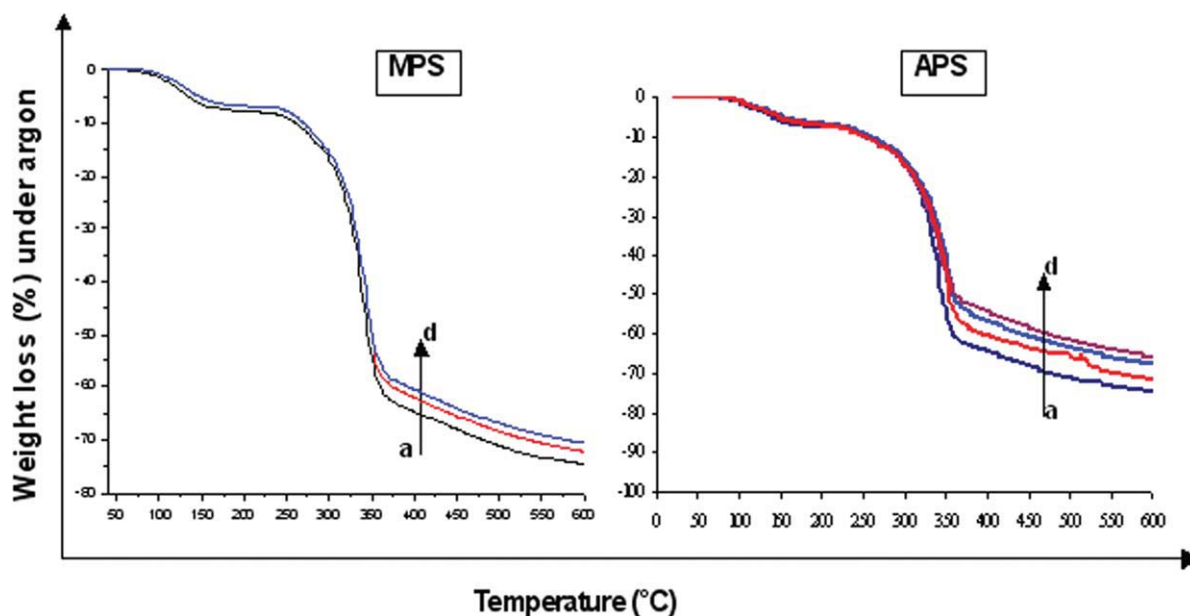
Figure 4 Weight loss (%) under argon of (a) ethanol/water extracted hemp fibers, (b), (c), and (d) silane (MPS or APS) treated hemp fibers at 0.05, 0.1, and 0.2 mol L^{-1}, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

= H or CH_2CH_3.[26–29] We can also observe that T^3 and T^2 units are present at a high percentage compared to T^1 unit. These results demonstrate grafting as well as self-condensation of APS onto the fibers surface.[27–29] The T^2 and T^3 unit signals depend on the initial concentration of APS, which is in agreement with DTA/TGA measurements under argon and ATR-FTIR spectra.

On the other hand, ^{29}Si CP/MAS NMR spectrum (not shown) of MPS (0.1 and 0.2 mol L^{-1}) treated hemp fibers do not show any signal after 48 h of acquisition for each sample. It can be explained by a very low MPS grafted quantity compared to the quantity of grafted APS in the same conditions. This result was also confirmed by the TGA measurements under argon and ATR-FTIR spectra.

Surface morphology and elementary analysis of fibers surface before and after chemical treatments

The SEM images of silane (0.2 mol L^{-1}) treated hemp fibers (Fig. 6) show a slightly smoother surface free of residues compared to that of untreated hemp fibers. This difference is due to the effect of the ethanol/water extraction, which removes part of pectin and hemicelluloses.[13]

The presence of MPS and APS does not affect the surface morphology of hemp fibers, but it changes the chemical composition of their surfaces. EDS analysis confirmed the presence of the silicium containing species on the surface of hemp fiber after the Soxhlet extraction (Fig. 7). In addition, in the case of treatment with APS, the EDS signal for the Si peak is greater than in the case of MPS treatment. It could

mean that more silane molecules are grafted after APS treatment.

Quantification of silane grafted hemp fibers

From the difference on the weight loss (%) under argon within the 150–380°C temperature range (Fig. 4), it is possible to calculate the quantity of grafted silane molecules onto the surface fibers:

Grafted silane (mg g^{-1} of hemp fiber) = $|W_{150-380}|$ × 1000, where $W_{150-380}$ is the difference (%) of the weight loss between ethanol/water extracted and silane (APS or MPS) grafted hemp fibers.
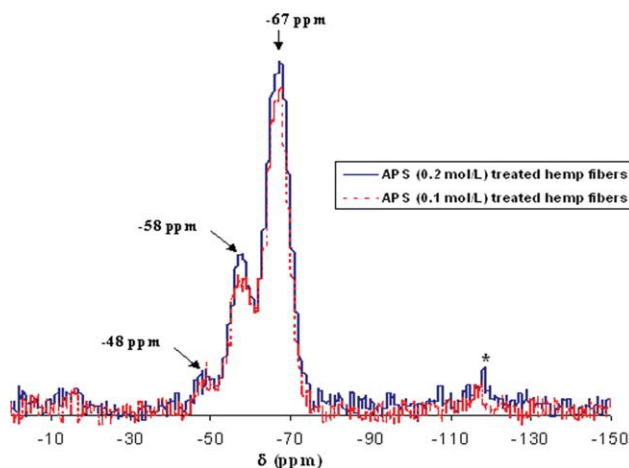

Figure 5 ^{29}Si CP/MAS NMR spectra of APS (0.1 and 0.2 mol L^{-1}) treated hemp fibers using TMS as an external reference. * rotation band. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
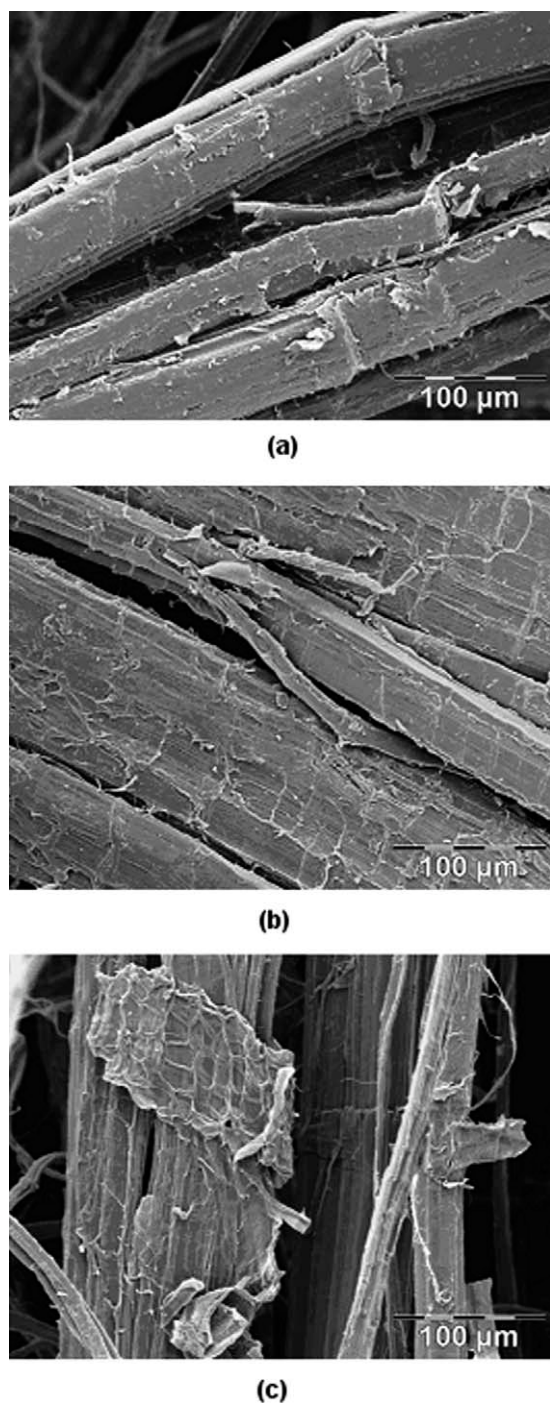
Figure 6 SEM images of (a) natural hemp fiber, (b) MPS (0.2 mol L^{-1}) treated hemp fibers, and (c) APS (0.2 mol L^{-1}) treated hemp fibers.

$$\text{Grafted silane (mmol g}^{-1}\text{ of hemp fiber)} =$$

$$\frac{\text{grafted silane (mg/g of hemp fiber)}}{M}$$

where M is the molecular mass of the hydrolyzed silane. The molecular weight of MPS is 206 g mol^{-1} and the molecular weight of APS is 138 g mol^{-1}.

The $W_{150-380}$ (%), the grafted silane quantity in mg g^{-1} and mmol g^{-1} of hemp fiber, calculated from the TGA under argon, are presented in Table II. Figure 8 represents the grafted quantity (mmol g^{-1}), according to the initial concentration of silane (MPS and APS). From these data, we can draw several conclusions:

The grafted quantity obtained in the case of APS at different initial concentrations was higher compared to that obtained in the case of MPS, in the same experimental conditions (Fig. 8). This result can be attributed to the presence of the high polar amino end group (NH_2) in APS, which favored the interaction between the coupling agent APS and the hemp fibers, driven by the formation of hydrogen bonds.[20] In addition, the presence of the bulky acryl-moeity on MPS can cause a higher steric hinderance than the amino group of APS.

On the basis of different characterizations presented above, we can propose a simplified illustration of the interaction between the silane coupling agents and the hemp surface (Fig. 9). Three main points have been taken into account:

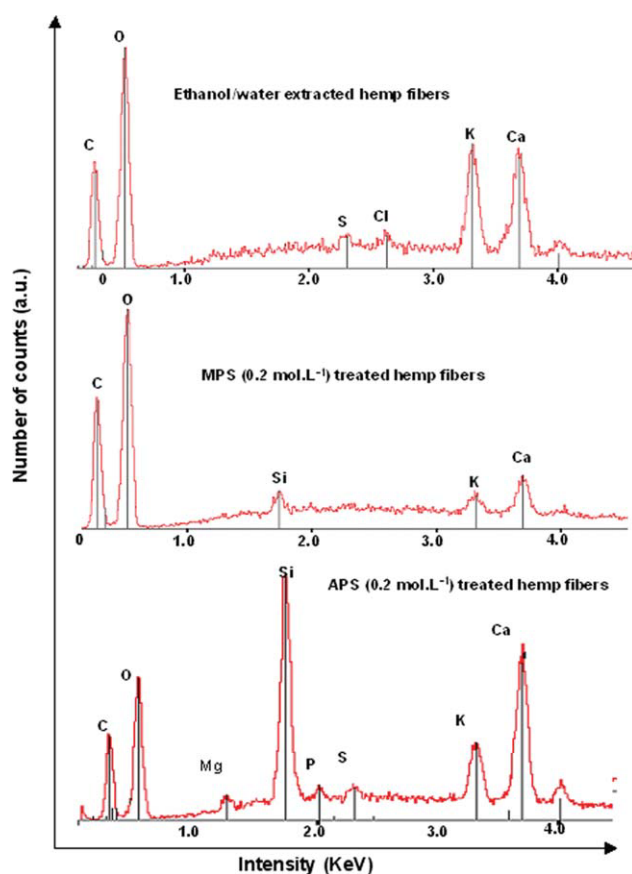• The chemical bonding between hydrolyzed silane and hydroxyl groups of hemp fibers;

Figure 7 EDS analysis of the fiber surface before and after silane grafting agent treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
The $W_{150-380}$ (%), The Grafted Silane (Mg G^{-1} and Mmo G^{-1} Of Hemp Fiber), Obtained From TGA and Argon, at Different Initial Concentration of Organosilane

Silane	[Silane]$_{initial}$ (mol L^{-1})	$W_{150-380}$ (%) (± 0.3)	Grafted silane (mg g^{-1} of hemp) (± 3)	Grafted silane (mmol g^{-1} of hemp) (± 0.02)
MPS	0	0	0	0
	0.05	−1.3	13	0.09
	0.1	−3.7	37	0.16
	0.2	−4.5	45	0.20
APS	0	0	0	0
	0.05	−3.5	35	0.24
	0.1	−7.0	70	0.49
	0.2	−8.7	87	0.61

- The self-condensation of grafted silane;
- The formation of hydrogen bonds between the end group of silane and the residual hydroxyl groups (nongrafted) of hemp fibers.

Effect of silane grafting on the specific surface area of hemp fibers

The specific surface areas of natural, ethanol/water extracted and silane treated (at different concentrations) hemp fibers are presented in Table III. The BET surface area of natural hemp fiber was about 0.7 m^2 g^{-1}. This value was also obtained for a similar length fiber ($\sim$ 500 nm) by Ouajai and al. in a previous study.[30] The surface area of the ethanol/water extracted hemp fibers was slightly higher than that of natural hemp. This variation is due to the fact that the ethanol/water extraction partly removes hemicellulose and pectins from the hemp fiber surface and renders the access of nitrogen molecules to surface pores easier.

Compared to the ethanol/water extracted hemp fibers, the specific surface area of silane treated hemp fibers was smaller. In the case of MPS, this slight decrease is proportional to the MPS grafted quantity (Table II). The lowest value (0.77 m^2 g^{-1}) was obtained for hemp fibers treated with a 0.2 mol L^{-1} MPS. The grafting of a small MPS quantity on the fiber surface decreased the accessibility toward this surface. In the case of APS, where the grafted silane quantity is more important, this decrease was significant (from 0.85 m^2 g^{-1} for ethanol/water extracted hemp to 0.44 m^2 g^{-1} for hemp fibers treated with 0.2 mol L^{-1} APS). In fact, the high decrease of the surface area correlates with the grafting yield of the silane grafting agent (Table II). The grafting and the self-condensation of APS at hemp surface (confirmed by NMR measurements) diminished the accessibility toward this surface. In consequence, the N$_2$ adsorption was lower, which led to the decrease in the specific surface area.

CONCLUSIONS

In this work we have presented the chemical modification of natural hemp fibers treated with two silane coupling agents. Silane treatment of hemp increased their hydrophobic character through a condensation reaction between hydrolyzed silane and hydroxyl groups of hemp fibers, evaluated by ATR-FTIR and ^{29}Si-NMR analysis. The grafted quantity (calculated from thermogravimetric analysis under argon) increased proportionally to the initial concentration of silane molecules. The presence of the high polar amino end group (NH$_2$) in APS can cause the high grafted quantity, compared to that obtained in the case of MPS, through the formation of hydrogen bonds due to the interaction between NH$_2$ and unreacted hydroxyl groups of hemp fibers. The presence of grafted silane molecules on fibers surface could enhance the adhesion at the interface between
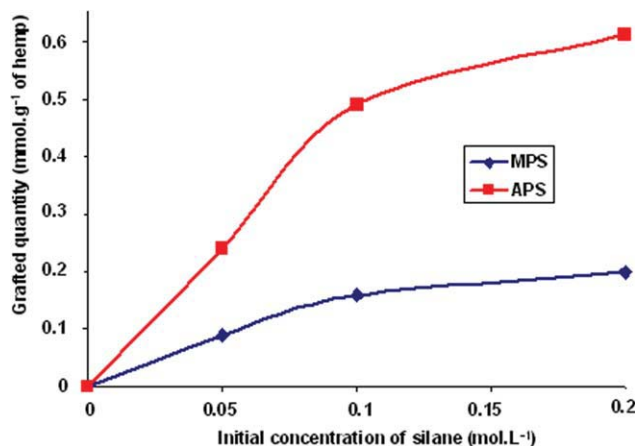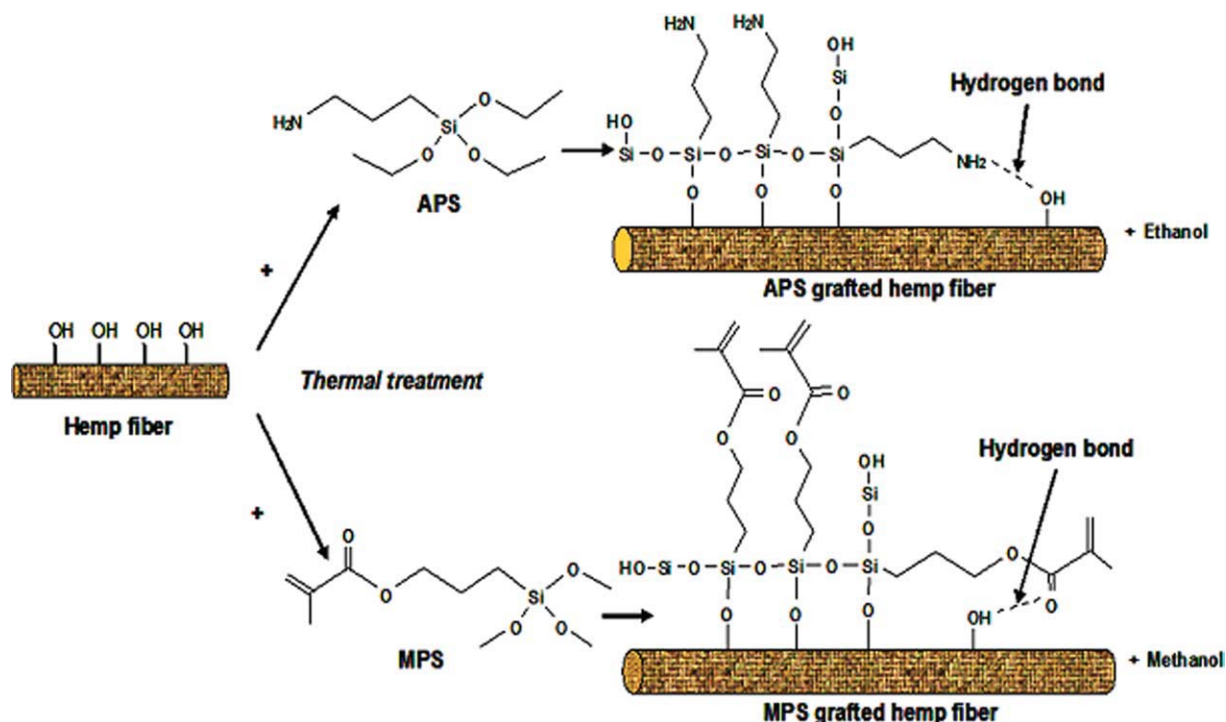

Figure 8 Grafted quantity (mmol g^{-1}) of silane molecules versus their initial concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9 Simplified illustration of silane molecules grafting (APS and MPS) on hemp fiber surfaces. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Specific Surface Area Using the BET Technique

Material	Specific surface area (m^2 g^{-1}) (± 0.2)
Natural hemp fibers	0.70
Ethanol/water extracted hemp fiber	0.85
MPS (0.1 mol L^{-1}) treated hemp fiber	0.77
MPS (0.2 mol L^{-1}) treated hemp fiber	0.73
APS (0.1 mol L^{-1}) treated hemp fiber	0.59
APS (0.2 mol L^{-1}) treated hemp fiber	0.44

grafted fibers and grafted clay particles. Actually, we try to enhance the grafting yield by testing different pretreatments (heated water, alkaline treatment) of hemp fibers before the grafting operation. These treatments could render the accessibility toward the hydroxyl functions of the cellulose polymer easier.

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