



**HAL**  
open science

# Chemical functionalization of nano fibrillated cellulose by glycidyl silane coupling agents: A grafted silane network characterization study

Isis Castro Cabrera, Sophie Berlioz, Armand Fahs, Guy Louarn, Pascal Carriere

## ► To cite this version:

Isis Castro Cabrera, Sophie Berlioz, Armand Fahs, Guy Louarn, Pascal Carriere. Chemical functionalization of nano fibrillated cellulose by glycidyl silane coupling agents: A grafted silane network characterization study. *International Journal of Biological Macromolecules*, 2020, 165, pp.1773-1782. 10.1016/j.ijbiomac.2020.10.045 . hal-03011559

**HAL Id: hal-03011559**

**<https://hal.science/hal-03011559v1>**

Submitted on 25 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

## Chemical functionalization of nano fibrillated cellulose by glycidyl silane coupling agents: A grafted silane network characterization study

Isis Castro Cabrera<sup>a</sup>, Sophie Berlioz<sup>a</sup>, Armand Fahs<sup>a</sup>, Guy Louarn<sup>b</sup>, Pascal Carriere<sup>a\*</sup>

<sup>a</sup> Université de Toulon, Laboratoire MATériaux, Polymères, Interfaces et Environnement Marin (MAPIEM), CS 60584, 83 041 Toulon Cedex 9, France

<sup>b</sup> Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, IMN, 2 Rue de la Houssinière, 44 000 Nantes, France

### Abstract

Nano fibrillated cellulose (NFC) has turned into a material widely studied due to its desirable performance for numerous organic systems. Nevertheless, its surface is not very compatible with most organic systems; hence, chemical functionalization methods offer a path to solve this problem. In this study, NFC is successfully functionalized with two silane coupling agents: 3-glycidyloxypropyl trimethoxysilane (GPS) and 3-glycidyloxypropyl dimethylethoxysilane (GPMES) by a simple, direct, and environmentally friendly method. Different analyses have been carried out in order to confirm the chemical modification of NFC. ATR-IR, XPS, and <sup>29</sup>Si NMR spectroscopies confirmed the chemical modification that allowed the understanding of the structure and the conformation onto the modified NFC surface. SEM and AFM microscopies were performed to study possible alterations in morphology; a slight change was observed. Thermal properties were also analyzed by TGA analysis. It remains stable after chemical functionalization. Grafted NFC showed good performance compared to the pristine one. It allows a better dispersion into organic systems improving their properties.

Keywords: surface chemical modification, nano fibrillated cellulose, silylation, GPS, GPMES

### 1. Introduction

Nano fibrillated cellulose (NFC) has drawn the attention of several researchers because of its excellent mechanical properties and the rising demand for environmentally friendly materials. NFC offers many advantages like abundance, low cost, low density, biodegradability, relatively high tensile, and flexural modulus, and it can be obtained from several sources<sup>1, 2</sup>. NFC has been used in different fields such as reinforcement filler for polymers, electronic devices, coating systems, drug delivery systems, tissue engineering materials, enzymatic immobilization, among others.<sup>3, 4, 5, 6, 7</sup>

However, the use of pristine NFC is limited due to its hydrophilicity character. Besides, NFC presents a poor dispersibility into a non-polar organic matrix<sup>8, 9</sup>, so a strong tendency for self-

agglomeration<sup>2</sup> due to the presence of several hydroxyl groups which form hydrogen bonds. Surface chemical modification is an excellent pathway to overcome these difficulties. The reaction between the hydroxyl groups and an organic agent may improve its hydrophobicity, and consequently promotes a better dispersion, which is the first parameter to increase composites mechanical properties. Some reactions have been explored in the literature, such as nucleophilic substitution<sup>7</sup>, oxidation<sup>6, 7</sup>, amidation<sup>7</sup>, silylation<sup>10</sup>, polymer grafting<sup>6</sup>, resulting in a modified NFC. These modifications have been employed in different matrices<sup>11, 12, 13, 14</sup>.

Inasmuch NFC is an eco-friendly material; the surface modification should be as much as possible a sustainable and scalable method, including low energy cost, benign solvent conditions, not expensive, and finally does not alter the good mechanical properties of the pristine NFC. Silylation achieves these requirements and has proved to be an efficient method to modify the NFC surface<sup>5, 15</sup>. Chemical interactions between cellulose and silane agents have been widely studied<sup>15, 16, 17, 18</sup>. Researches show that several mechanisms are involved between NFC and silane coupling agents: a) hydrolysis, the alkoxy groups of the silane are catalyzed in acid conditions forming silanol. b) physisorption, the adsorption of silanol groups onto the hydroxyl groups of cellulose surfaces. c) condensation, giving rise to the chemical sorption/grafting, i.e., the bond Si-O-Cellulose<sup>4, 19</sup>, nonetheless, self-condensation Si-O-Si cannot be dismissed<sup>20</sup>. Figure 1 illustrates the different steps of chemical functionalization.

Systems like  $\gamma$ -aminopropyl triethoxy silane (APS)<sup>18</sup>,  $\gamma$ -methacryloxypropyl trimethoxy (MPS)<sup>21</sup>,  $\gamma$ -mercaptopropyl trimethoxysilane (MPRS)<sup>22</sup>, hexadecyl trimethoxysilane (HDS)<sup>18</sup>, methyltrimethoxysilane (MS)<sup>23</sup>, N-2-aminoethyl-3-aminopropyl trimethoxysilane (AAPS)<sup>16</sup>, among others have been used to modify nano fibrillated cellulose surface for its use as a reinforcing agent as an alternative to traditional glass fibers<sup>24</sup>. Even though many questions remain in a large number of siloxane conformation studies onto the NFC surface, the results are promising<sup>25</sup>. Indeed, the silane self-condensation induces a more or less dense siloxane networks surrounding NFC within incomplete condensation far away from cellulose<sup>26</sup>. Therefore, the fiber/matrix adhesion is not optimal because of their poor ability in loads transfer. Indeed, the better fiber/matrix adhesion is promoted by the capacity of the matrix to restrict the deformation in the elastic zone of the NFC/matrix interphase. Soxhlet extraction, which is traditionally used in composite fiber development, is assumed to overcome this drawback by releasing weak linked or adsorbed silanes. Despite the importance of soxhlet extraction on the interphase properties and the ultimate performance of composite materials, most of the studies, related to silane grafted NFC as reinforcement into a matrix, have not given particular attention on the condensation state of silanes after

soxhlet extraction. Inasmuch, the siloxane network is not finely described even though. Spectroscopies and microscopies have proven to be suitable tools to describe siloxane network, according to grafting methods and to coupling agent performed in different studies<sup>27, 28</sup>. Nevertheless, as far as we know, none of them deal with their characterizations after soxhlet extraction. Therefore many questions still subsist about siloxane network in the interface fibril-matrix<sup>5,15</sup>.

It is interesting to fill this gap by undergoing a detailed investigation of functionalized NFC. This may pave the way for choosing the better functionalization protocol and for understanding clearly the interface properties when using the modified NFC as filler in a non-polar polymer matrix.

This study aims to present a detailed surface characterization of functionalized NFC with epoxy silanes by using a simple grafted method. 3-glycidyloxypropyl trimethoxysilane (GPS) and 3-glycidyloxypropyl dimethylethoxysilane (GPMES) were chosen because of their reactivity, the presence of oxirane groups which could be used to promote a post-reaction for future applications, their low cost, and no need for hazardous solvents to dissolve them. In addition, the GPMES can only generate a chemistry grafted monolayer onto the surface. In contrast, the GPS allows the development of a monolayer or a tridimensional covalent network onto the NFC chains. The monofunctional silane agent is used as a reference to provide pieces of information about different condensation states which might be observed with GPS onto NFC surface.

The NFC functionalized with the GPS and GPMES were chemically characterized by Attenuated Total Reflection Infrared Spectroscopy (ATR-IR), solid-state <sup>13</sup>C and <sup>29</sup>Si Nuclear Magnetic Resonance (NMR), X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive X-ray Analysis (EDX). In order to observe any change in NFC morphology, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were performed. The thermal stability was studied by Thermogravimetric Analysis (TGA).

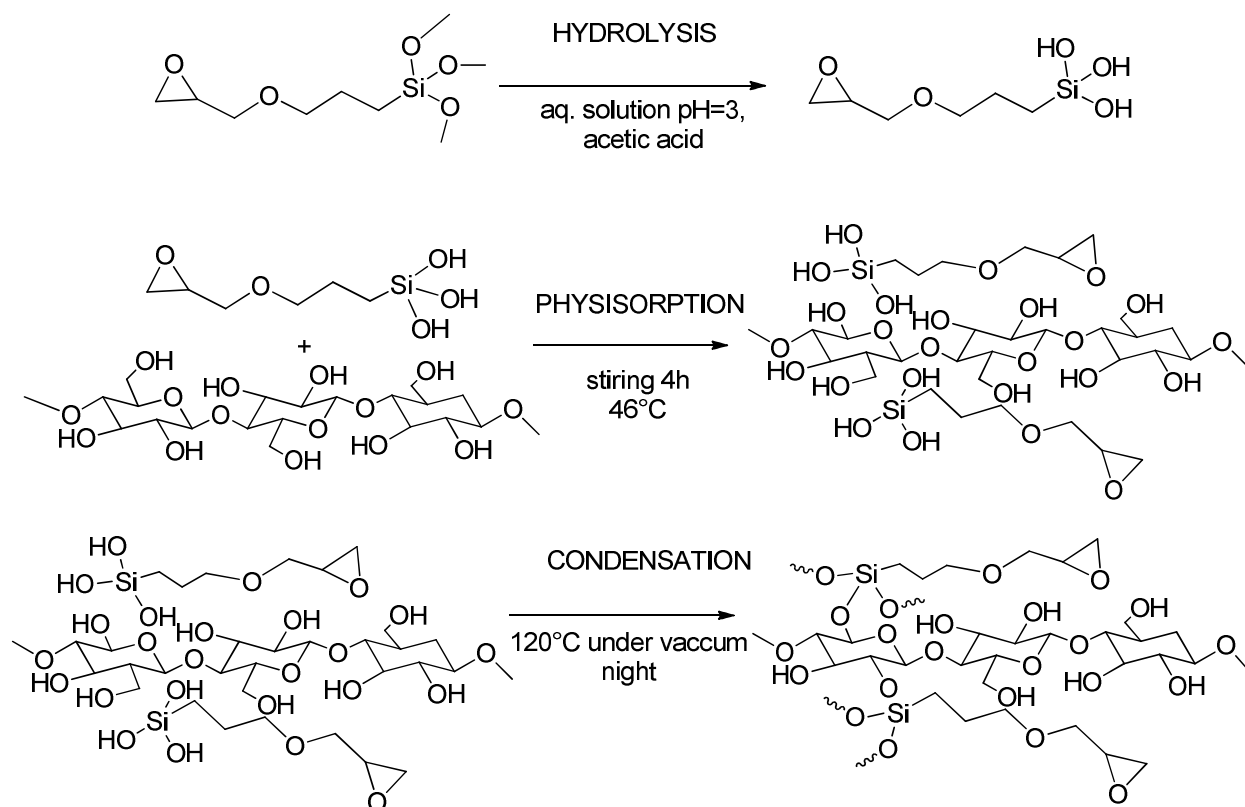


Figure 1. Functionalization steps of NFC surface by a silane coupling agent

## 2. Materials and methods

### 2.1 Materials

Nano fibrillated cellulose 1 % wt in aqueous, and ethanol suspension were supplied from INOFIB (Grenoble, France), 3-(glycidyloxypropyl) trimethoxysilane (GPS;  $C_9H_{20}O_5Si$ ; purity  $\geq 98\%$ ) and 3-(glycidyloxypropyl) dimethylethoxysilane (GPMES;  $C_{10}H_{22}O_3Si$ ; purity  $\geq 97\%$ ), were supplied by ABCR (Karlsruhe, Germany), glacial acetic acid and absolute ethanol provided by Aldrich.

### 2.2 Surface modification of NFC

Two different protocols of NFC functionalization with trifunctional GPS were performed:

For the first one, 3% wt. GPS was directly added to the NFC aqueous suspension, then the pH was adjusted to 3 by adding glacial acetic acid, and the suspension was magnetically stirred during 4h at 46°C. In order to thoroughly study the GPS grafting onto the NFC surface and better understand its network structure, the GPMES, a monofunctional silane, is used because of its analogous chemical structure compared to GPS. This allows to complete the understanding of the degree of substitution on the NFC chain and the effect of silane reactivity. The same protocol followed to graft the GPS has been used to graft the GPMES (3% wt). The NFC samples functionalized with this protocol were respectively named NFC-GPS acid and NFC-GPMES acid.

For the second one, 3% wt. GPS was directly added to the NFC suspension in ethanol (1% wt in EtOH) and magnetically stirred during 4h under reflux. The functionalized NFC, according to this protocol, is named NFC-GPS EtOH.

After this first step, the mixtures were filtered and washed with EtOH/H<sub>2</sub>O mixture (8:2; v/v) and then with acetone to remove acetic acid and weakly adsorbed silane molecules. Lastly, they were dried in a vacuum oven at 120°C for 12 hours to allow hydroxyl cellulose-silanol condensation. The obtained compounds are a white powder.

The last step consists in a soxhlet extraction during 48h in acetone to eliminate any residue of physisorbed silane onto the modified NFC samples.

### 2.3 Characterization of modified NFC

#### *Attenuated total reflection infrared spectroscopy (ATR-IR)*

Untreated and treated nano fibrillated cellulose samples were characterized by Fourier transform infrared (FT-IR). A spectrometer Nicolet IS50 FT-IR (Thermo Nicolet) with an attenuated total reflection universal accessory was used. Samples were analyzed in absorbance mode in the range of 700 to 4000 cm<sup>-1</sup>, a scanning resolution of 1 cm<sup>-1</sup>, and 32 scans for each sample. All samples were dried at 100°C during 1h before the analysis to discard the presence of water.

#### *X-ray photoelectron spectroscopy (XPS)*

XPS experiments were done on an Axis Nova spectrometer (Kratos Analytical) using the Al K(alpha) line (1486.6 eV) as the excitation source. The analysis chamber was maintained below  $2 \times 10^{-7}$  Pa, and the analysis area was  $700 \times 300 \mu\text{m}^2$ . For survey spectra, the analyzer was operated in constant pass energy of 80 eV. The core-level spectra (C (1s), O (1s)) were acquired with an energy step of 0.1 eV and using a constant pass energy mode of 20 eV (energy resolution of 0.48 eV). Binding energies of the spectra were calibrated by setting the C1s peak at 284.8eV. The chemical composition (expressed in atom percentage) was determined using integrated peak areas of each component, and peak fitting was made with mixed Gaussian–Lorentzian (70-30%) components.

#### *Nuclear Magnetic resonance spectroscopy (NMR)*

Solid-state <sup>29</sup>Si NMR was carried out at a resonance frequency of 79.49 MHz on a Bruker Avance IV HD 400 spectrometer (Rheinstetten, Germany), furnished with a 7 mm dual broadband CP-MAS probe (around 250 mg), a spinning rate 5kHz, a cross-polarization (CP) with a contact time of 5 ms, a recycle delay of 2 s, SPINAL64 1H decoupling at 64 kHz and an acquisition time of 43 ms.

Solid-state  $^{13}\text{C}$  NMR was carried out at a resonance frequency of 100.61 MHz on a Bruker Avance III 400 Ultrashield spectrometer, furnished with a 4 mm dual broadband CP-MAS probe (around 100 mg). The spinning speed was set at 12 kHz.

*Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray analysis (EDX)*  
SEM microscope (Zeiss Supra 40VP Field Emission) was used in secondary electron mode to observe the morphology of different nano fibrillated cellulose. Aqueous suspension of modified and unmodified NFC (0.01 %wt) were prepared and deposited onto silicon wafers. The water was then evaporated at room temperature, and the samples were covered by a carbon conductive layer. Experiments were carried out with a field emission gun of 3 kV in a vacuum of  $10^{-6}$  mbar.

EDX was carried out in order to confirm the presence of Si onto nano fibrillated cellulose modified with silanes. NFC powders were fixed on carbon conductive support, and the analysis was handled under a field emission gun of 20 kV.

#### *Atomic force microscopy (AFM)*

AFM experiments were operated on a Multimode 8 microscope (Bruker) by using Peak Force mode. Samples were prepared by placing a drop of 0.001 wt. % of an aqueous suspension of pristine NFC or modified NFC onto mica surfaces, the water was then evaporated at room temperature. The scans were performed on an area of  $1\ \mu\text{m} \times 1\ \mu\text{m}$ , collecting images with 512 pixels at a scan rate of 0.8 Hz. The nominal spring constant of the cantilever was 0.4 N/m. All measurements were carried out under ambient conditions.

#### *Thermogravimetric analysis (TGA)*

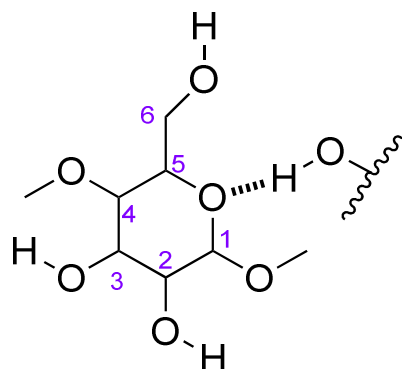
TGA analysis was run using a TA instruments (Q600) in a range of  $25^\circ\text{C}$  to  $800^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen flow of  $100\ \text{mL min}^{-1}$ .

### 3. Results and discussion

#### 3.1 Chemical characterization of functionalized NFC

As the first investigation, ATR-IR was employed to ascertain NFC modification by following the singular absorbing peaks of pristine NFC<sup>28, 29</sup>. A detailed description of the region  $1450\text{-}1315\ \text{cm}^{-1}$  and  $1200\text{-}800\ \text{cm}^{-1}$  of NFC was given by Maréchal et al<sup>30</sup>. The band at  $1160\ \text{cm}^{-1}$ , due to antisymmetric glycoside vibration, was taken as a reference. All spectra were normalized as a function of this band to compare the intensity of the different FT-IR spectra after both silane modification and soxhlet extraction. Figure 2 shows infrared spectra in the range  $1250\text{-}750\ \text{cm}^{-1}$ , the full spectra are given in Figure S1. The band at  $1200\ \text{cm}^{-1}$  related to symmetric glycoside vibration is constant for all different NFC samples. This fact indicates that the glycoside units were maintained after surface treatment. Besides, the  $\beta$ -glucoside linkage at  $895\ \text{cm}^{-1}$  and the C-O vibration of the carbohydrate ring of cellulose at  $1071\ \text{cm}^{-1}$

were maintained. Therefore, we can assume the integrity preservation of the NFC structure after acidic or ethanol treatment and soxhlet extraction.



Scheme 1. Cellulose ring

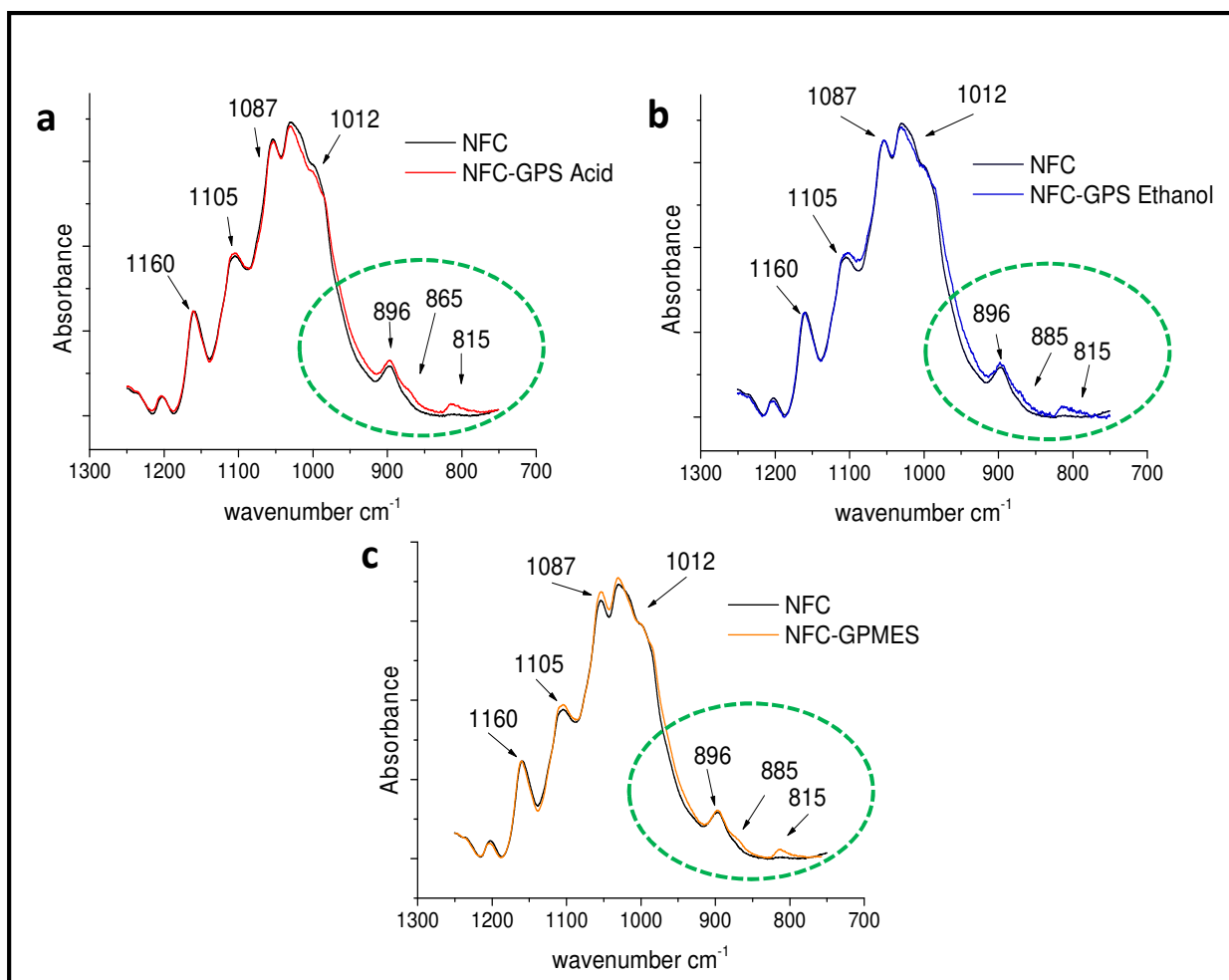


Figure 2. Infrared spectra of a) NFC-GPS acid, b) NFC GPS-EtOH and c) NFC GPMES-acid

Once nano fibrillated cellulose was modified, some changes are undeniable for each NFC modification protocol by silane (Figure 2). The most notable are at 1109-1090, 865, and 815  $\text{cm}^{-1}$ , corresponding to GPS glycidoxy group, the propyl chain, the  $-\text{Si}-\text{O}-\text{C}$  bond, and  $-\text{Si}-\text{O}-\text{Si}$  bond respectively <sup>31</sup>.



Figure 3 brings together the experimental spectra of NFC pristine and modified and their respective deconvolution attributed to the different functional groups in the region comprised between 1200 to 800  $\text{cm}^{-1}$ . The black line corresponds to the experimental data and the red line to the summation of all deconvoluted signals.

Figure 3a displays the deconvolution of all vibration bands of the NFC *pristine*: the peaks at 1034, 1018, 994, and 986  $\text{cm}^{-1}$  correspond to the primary alcohols, and 1105 and 1054  $\text{cm}^{-1}$  to the secondary alcohol. No difference in infrared spectra can be observed before and after the soxhlet extraction of the NFC confirming the preservation of the carbohydrate rings.

Figure 3b shows the normalized spectrum of NFC pristine convoluted (the red line) overlapped on the NFC-GPS acid spectrum (the black line). Two regions show significant differences: 940-1054  $\text{cm}^{-1}$  and 800-930  $\text{cm}^{-1}$ . To explain these differences, the vibration bands of the GPS<sup>29, 30</sup> were added to the normalized spectrum of the NFC pristine. The intensity of GPS vibrations were adjusted until equaled the NFC-GPS experimental spectrum. Figure 3c summarizes this analysis.

The GPS bands at 805 and 815  $\text{cm}^{-1}$  are the primary references for NFC-GPS grafting because of the non-overlapping of NFC and GPS bonds vibrations in this region. The GPS band added at 805  $\text{cm}^{-1}$  is linked to Si-C and Si-O stretch; the vibrations at 813, 965, 1096  $\text{cm}^{-1}$  correspond to propyl chain; 867 and 926  $\text{cm}^{-1}$  vibrations are related to epoxy, and finally, 951, 1109 and 1143  $\text{cm}^{-1}$  bands are associated to glycidoxy<sup>31</sup>. The results in the range 800-930  $\text{cm}^{-1}$  allow to conclude that silane is both adsorbed and covalently grafted to NFC by acidic treatment.

Besides, at the range of 940-1054  $\text{cm}^{-1}$  multiple GPS vibrations are present, linked mainly to glycidoxy. Moreover, the vibration bands at 1035 and 986  $\text{cm}^{-1}$  of the NFC-GPS acid spectrum slightly decrease. It is related to a diminishing of alcohol vibration from NFC.

All these considerations allow to assume a chemical grafting of epoxy silane onto the NFC surface. It is important to remark that the Si-O stretch at 813  $\text{cm}^{-1}$ <sup>31, 32</sup> can be linked to the presence of a silicon network that cannot be discarded in the analysis.

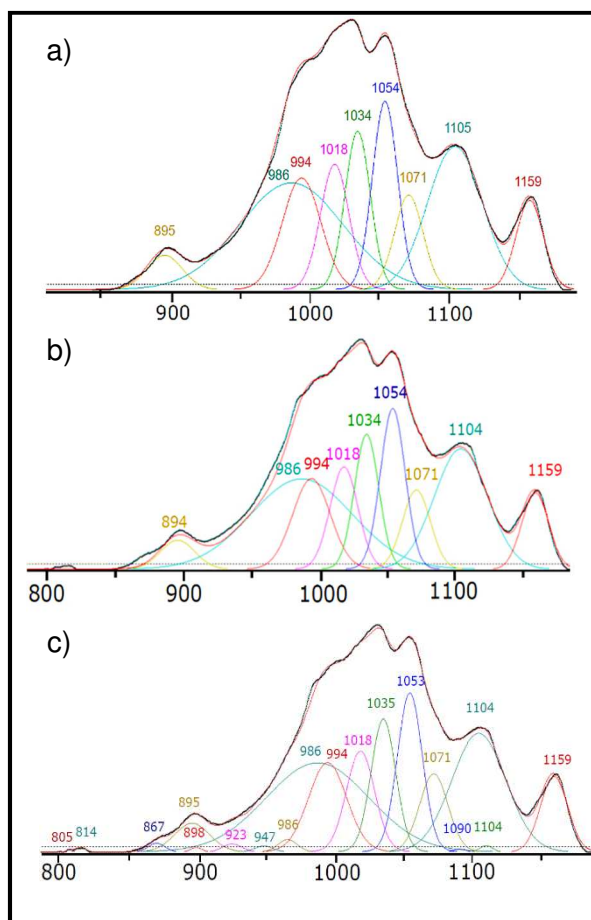


Figure 3. Deconvolution of a) NFC after soxhlet extraction and its deconvoluted bands, b) NFC-GPS acid overlapped by NFC pristine deconvoluted bands, c) NFC-GPS acid overlapped by NFC and GPS deconvoluted bands

EDX experiments were carried out before and after soxhlet extraction to confirm the chemical silane grafting. Three different signals at 0.277, 0.252, and 1.75 keV associated with C, O, and Si K $\alpha$ , respectively, were observed. This result confirms the presence of silicon, even after soxhlet extraction (Figure S2).

In order to quantify and analyze the chemical composition of functionalized NFC, X-ray photoelectron spectroscopy was performed on the different samples. Figure 4 and Table 1 present the XPS spectra obtained after soxhlet extraction and the relative atomic concentration as well as the oxygen to carbon ratios. The survey spectrum of pristine NFC has two peaks at 532 and 286 eV corresponding respectively to oxygen (O 1s) and carbon (C 1s)<sup>33, 34, 35</sup>. Moreover, all grafted NFC present a third peak at 102 eV confirming once again the presence of Si element for the modified NFC. The O/C atomic ratio for pristine NFC found by XPS is 0.75. The theoretical one is 0.83, considering the chemical formula of the cellulose<sup>5</sup>.

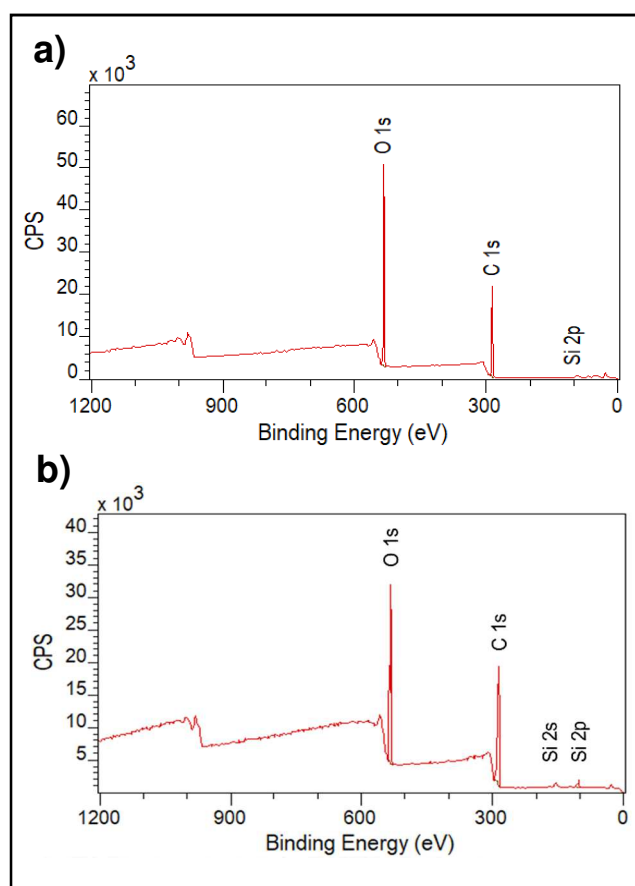


Figure 4. XPS survey spectra of a) pristine NFC and b) NFC-GPS Acid.

Sample	C 1s	O 1s	Si 2p	O/C
Pristine NFC	57.3	42.7	-	0.75
NFC-GPS EtOH	58.4	40.3	1.3	0.69
NFC-GPS Acid	65.6	32.3	2.1	0.49

Table 1. Relative atomic concentration (%) obtained by XPS analysis of pristine and modified NFC.

Once the NFC were modified with GPS silane under acid or ethanol conditions, the O/C ratios were decreased to 0.69 (for NFC-GPS in EtOH) and 0.49 (for NFC-GPS at pH acid). This result is due to the bonding of GPS on the NFC surface and/or to the presence of self-condensed silanes, as demonstrated later in the NMR analysis. XPS analysis reveals an atomic concentration Si of 2.1% when grafting GPS in an acid condition. However, this value is 1.3% in the case of ethanol (Table 1). Thus, the affinity of GPS toward the NFC surface is more important in aqueous acidic conditions than in ethanol.

To go further in the investigation of the more reactive silane (trifunctional GPS) with NFC, the peaks corresponding to C1s in the XPS spectra have been deconvoluted, and the results are presented in Figure 5 and Table 2.

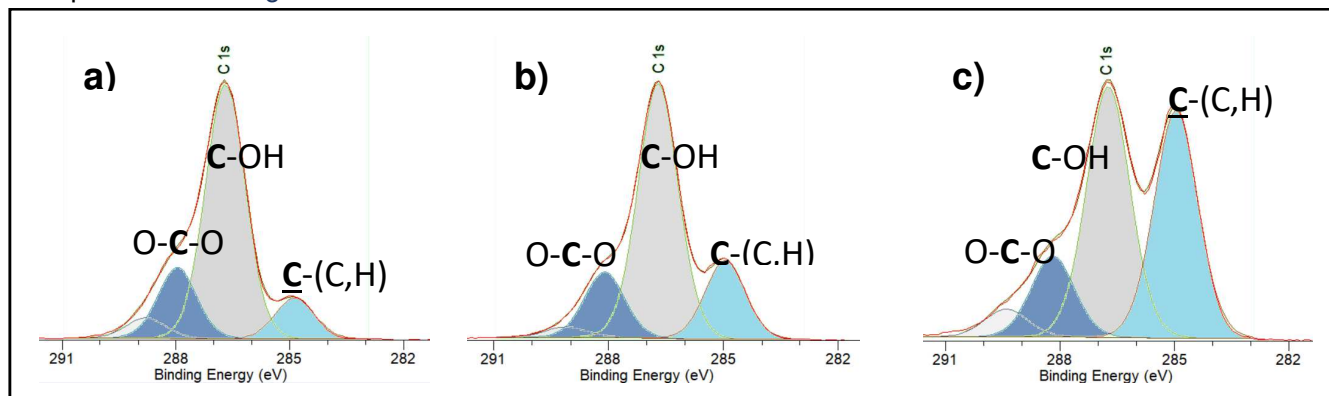


Figure 5. Deconvolution of C1s XPS spectra a) pristine NFC, b) NFC-GPS EtOH and c) NFC-GPS Acid

Sample	Sub-peak 1 at 284.8 eV	Sub-peak 2 at 286.7 eV	Sub-peak 3 at 288.0 eV
Pristine NFC	11.2	69.4	19.4
NFC-GPS EtOH	19.7	63.9	16.4
NFC-GPS Acid	40.7	44.8	14.5

Table 2. Positions and intensities (%) of the C1s sub-peaks of pristine NFC and GPS-modified NFC

The deconvolution shows three main sub-peaks (at 284.8 eV, 286.7 eV, and 288.0 eV), which can be attributed to three types of carbon bonds and a weak sub-peak at 289 eV (see Figure 5). This peak, corresponding to carbonyl group, is usually observed in pristine NFC according to the preparation process. There is some sample variability of the amount of the carbonyl groups. Likewise, the sub-peak at 284.8 eV corresponding to aliphatic carbon in pristine NFC is attributed to chemical defects inherent to NFC. The positions and the intensities of the C1s sub-peaks found for pristine and GPS-modified NFC are summarized in Table 2. The intensity of the sub-peak at 284.8 eV significantly increases from 11.2% for pristine to 19.7% for NFC-GPS EtOH, and up to 40.7% for NFC-GPS Acid. This increase is mainly due to the presence of the propyl groups of GPS. In fact, variability of the aliphatic and carbonyl groups in the pristine NFC has a slight impact on the deconvolution peaks of C1s. Therefore, one can assume silane grafting onto NFC.

Like in infrared analyses, this result shows that the grafting of silane in ethanol is less efficient than in acid condition. This result suggests that the average silane substitution in ethanol may be divided by two comparing to the acid method. A quick calculation shows that 2.1 % of NFC-GPS acid equals to an average of one silane per two glucosidic units;

meanwhile, 1.3% of Si from NFC-GPS EtOH, gives an average of only one silane per four glucosidic units.

However, the GPS can form a covalent network more or less grafted on NFC. Indeed, a previous study has shown how different silane network morphologies can be formed from a functional covalent group<sup>36</sup>. Therefore, to elucidate the structure of a siloxane or siloxane network grafted onto the NFC surface, Solid-state NMR <sup>29</sup>Si was used to provide more information on the NFC-GPS acid. The chemical shift of silicon is determined by the chemical nature of its neighbors, namely, the number of siloxane bridges attached to a silicon atom<sup>20</sup>. In the literature, it was described how the condensation takes place onto the NFC surface, the self-condensation and both effects simultaneously cannot be rejected<sup>15, 26, 37</sup>.

Figure 6a illustrates the self-condensation evolution, from a dimer to a network denominated T0, T1, T2, and T3. This evolution was studied by Salon et al.<sup>20</sup> using different silane systems, as well as the homopolycondensation process and the different signals derived from each one. Figure 6b displays different silanes configurations related to the self-condensation onto the cellulose surface before and after soxhlet extraction. Before and after extraction, the average chemical shifts are almost the same,  $\delta = -39, -48, -58$  and  $-66$  ppm, corresponding to T0, T1, T2 and T3 respectively. Because of the multiplicity of reactive sites on cellulose (C2, C3; C4 and C6), the peaks are broad and second signals surround the common area of T1, T2, and T3 as already described by Salon et al.<sup>20</sup>. The hypothesis of side reactions between alcohol or silanols and epoxy have been tested and can be discarded. Indeed, a <sup>13</sup>C NMR analysis of GPS and GPMES under acid conditions at 46°C shows only few oxirane ring opening. Neither reactions between these residual alcohols with silanols nor reactions between epoxy with silanols can be highlighted at this temperature (see supplementary informations 4).

T0 corresponds to the grafting of GPS directly onto the NFC surface without any connection with another silane, meanwhile T1, T2 and T3 correspond to different degrees of self-condensation. The silicon atom fraction directly grafted to cellulose T0 is limited to 20% inducing free silanols. More than 70% of silanes are chain-ends and linear grafting whereas only 10% are involved in a three dimensional siloxanes networks.

The presence of self-condensation structures grafted onto NFC has been reported in the literature<sup>15, 26</sup>. Signal T3 has been shown as the most abundant conformation, followed by T2 and T1. For instance, Robles et al.<sup>28</sup> explored APS grafting by using different methods, T3 conformation was always the most abundant structure. Belgacem et al.<sup>15</sup> have reported the different steps and kinetics of silanes grafting process since silane hydrolysis to self-condensation T3. In our study of GPS grafting under acid condition, T3 is not the most

abundant structure (Table 3) neither before nor after soxhlet extraction. This result corresponds to optimized silane grafting conditions<sup>20</sup> to avoid a condensed network surrounded the NFC.

After Soxhlet treatment, these peaks are narrower and their intensity are reduced (figure 6b). The eliminated relaxation peaks are attributed to GPS self-condensed physisorbed on the cellulose surface. However, soxhlet extraction eliminates preferentially T3 structures from the siloxane networks because they are weakly grafted onto NFC. Silanes grafted networks closer to cellulose, T0, and T1 show an apparent increase after soxhlet extraction. This remark lets to think that, before soxhlet extraction of the functionalized NFC, a significant amount of the siloxane network surrounds NFC without necessarily direct Si covalent bond to the cellulose. Therefore, the soxhlet treatment allows to eliminate the physisorbed polycondensated GPS, and makes chain-ends and flexible linear silanes available for further reactions involving epoxy groups.

Signal	Before soxhlet extraction (%)	After soxhlet extraction (%)
T0	15	19
T1	40	45
T2	35	32
T3	10	4

Table 3. Values of relative concentration of GPS networks before and after soxhlet extraction.

At our knowledge, no report exists about a single silane unity grafting onto NFC. It could be expected that using GPMS to functionalize NFC, a monolayer grafting might be performed.

Figure 6c shows the chemical shifts of GPMS carried out under acid conditions after soxhlet extraction. There are only two signals,  $\delta = 18$  and 8 ppm, attributed to a linkage between GPMS-NFC and the self-condensation as dimers, respectively. Indeed, after soxhlet extraction, only T1, coming from dimers is shown. This GPMS dimers amount near NFC isn't meaningless. Contrary to GPS for which complete three dimensional self-condensation was not favorable in an acid environment, self-condensation for GPMS is more important. The GPMS grafted monolayer doesn't allow to screen out hydrogen bonds or Van der Waals interactions between NFC and the dimers. The limited oxirane rings opened during hydrolysis promote the dimers physisorption onto NFC. As already discussed for GPS, the hypothesis of secondary reactions between silanes and cellulose could not be established. The physisorption of GPMS dimers is strong and it isn't discarded after soxhlet extraction.

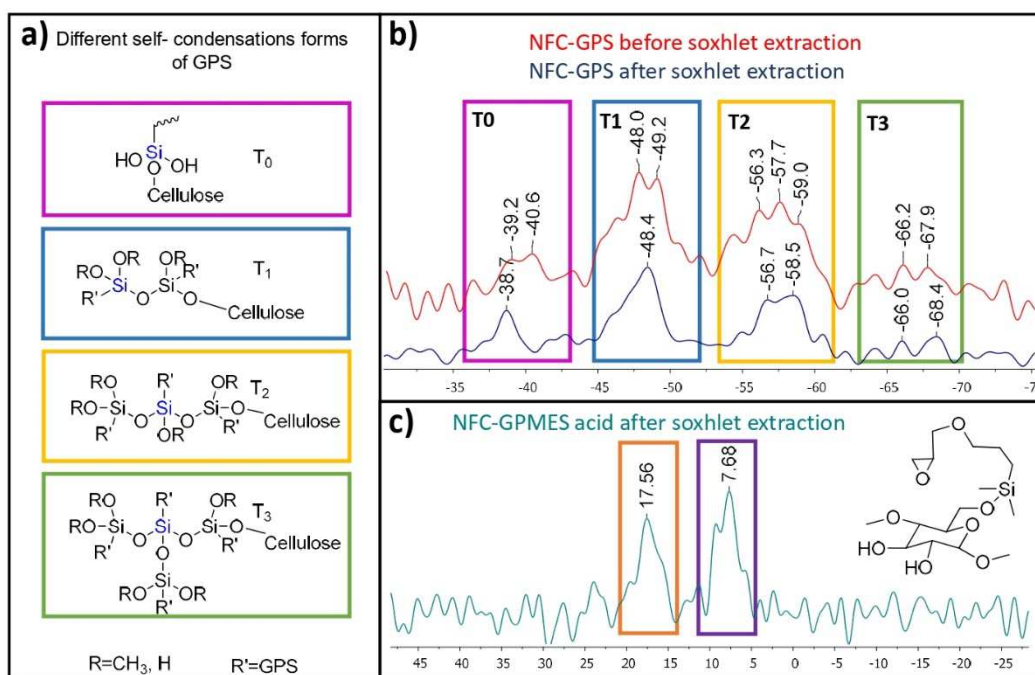


Figure 6. Solid-state  $^{29}\text{Si}$  NMR spectra of NFC functionalized with GPS under acid condition. a) Different condensation forms of GPS silane, b) NFC-GPS before and after soxhlet extraction under acid conditions, and c) NFC-GPMES – acid after soxhlet extraction.

To go further in the understanding of the siloxane network structure, solid-state  $^{13}\text{C}$  NMR has been carried out. In Figure 7, the spectra show different signals attributed to cellulose carbon and GPS silane. Cellulose chemical shifts have been widely studied and identified. The regions from 62 to 66 ppm correspond to C6; from 71 to 77 ppm, the peaks are attributed to C2, C3, and C5; from 85 to 90 ppm, the peak is assigned to C4; finally, from 104 to 108, peak corresponds to C1<sup>38, 39</sup>. For GPS case, it is possible to identify some chemical shifts at 8.2, linked to  $\text{CH}_2\text{-O-Si}$ , and at 22.4 ppm associated with  $\text{CH}_2\text{-CH}_2\text{-O-Si}$ . These two chemical shifts were corroborated in Figure. S4, which shows the spectrum of GPS before hydrolysis and condensation.

In the GPMES case, the chemical shifts were similar to the GPS case excepting a chemical shift at 0.2 ppm, corresponding to methylene extra in GPMES molecule comparing to GPS.

The smallest chemical shift at 45.9 ppm is related to the oxirane which is predominantly remained after acid treatment<sup>40, 41</sup>.

Finally, the peak at 31.1 ppm corresponds to the acetone that was not possible to eliminate after drying the samples. To corroborate this affirmation, an experiment acetone-free was carried out (Figure S5).

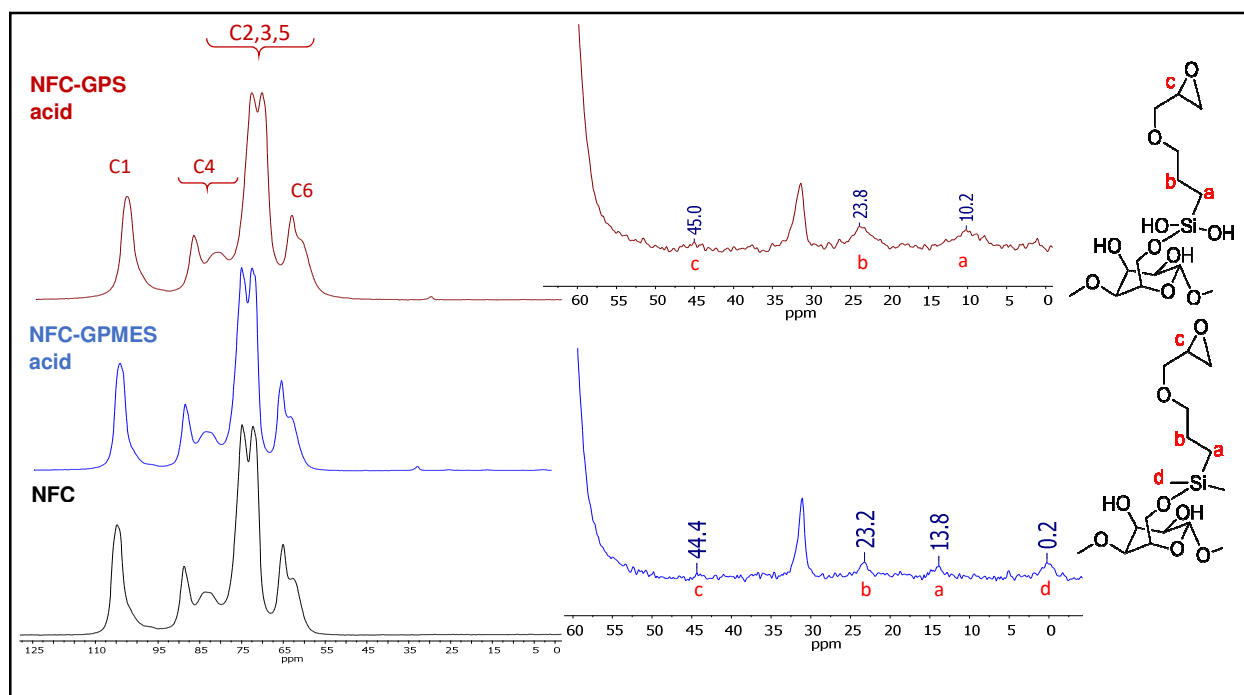


Figure 7. Solid-state  $^{13}\text{C}$  NMR spectra of pristine NFC, NFC-GPS acid and NFC-GPMES acid after Soxhlet.

### 3.2 Structural characterization of functionalized NFC

To determine the effect of the silane grafting on the morphology of NFC, SEM images of nano fibrillated cellulose were recorded before (Figure 8a) and after chemical functionalization (Figure 8b,c, and d). Table 3 summarizes the diameters measured from the obtained images. (See also Figure S6). The diameter of pristine NFC increases once it is modified. After soxhlet extraction, the diameter decreases but still being higher than NFC pristine. It is important to remark that before the soxhlet extraction, the standard deviation is higher than after extraction. These results suggest the presence of a siloxane network physisorbed onto the modified NFC, which is partially removed after the soxhlet extraction, inducing an NFC surface covered by a heterogeneous siloxane network.

	Pristine NFC	NFC-GPS EtOH before Soxhlet	NFC-GPS EtOH after Soxhlet	NFC-GPS acid before Soxhlet	NFC-GPS acid after Soxhlet
<b>Diameter (nm)</b>	38	58	52	63	54
<b><math>\Sigma</math></b>	9	27	15	25	16

Table 4. Measured diameter of pristine NFC and modified NFC.

The chemical functionalization does not seem to sharply alter the width dimension or the morphological aspect of the NFC at the microscale. Similar results have been obtained by Herrera-Franco et al.<sup>17</sup>



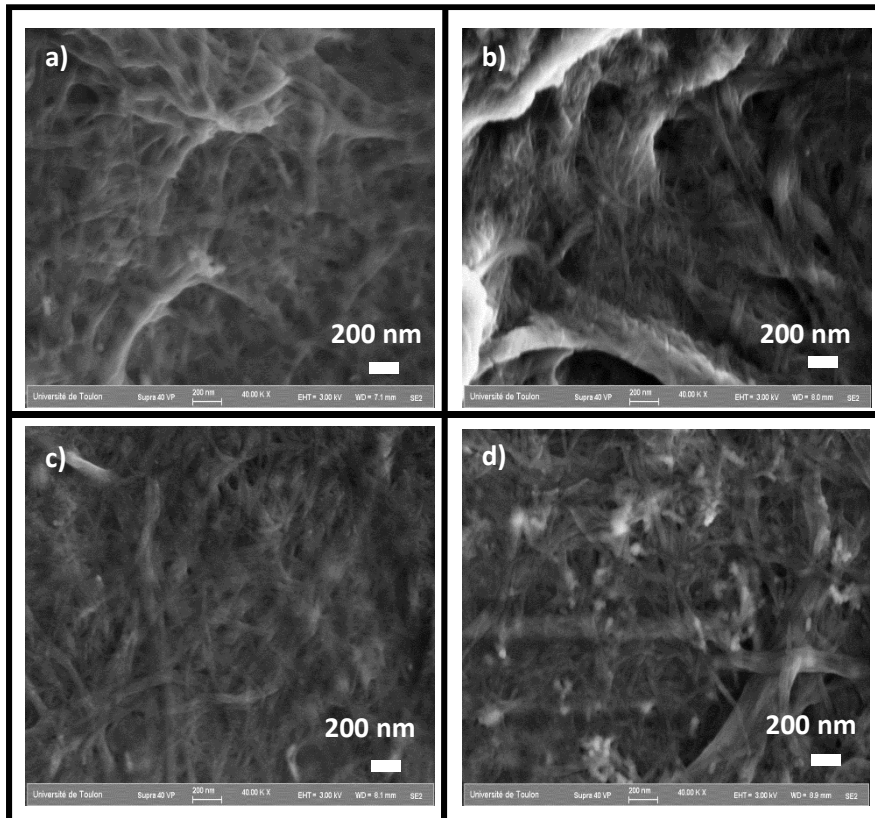


Figure 8. Surface morphology recorded by SEM microscopy of a) pristine NFC, b) NFC-GPS EtOH, c) NFC-GPS acid, and d) NFC-GPMES acid.

To get more insight into the morphology of NFC, AFM analysis was executed on the unmodified and modified NFC samples. As shown in Figure 9, AFM topographical images show no change in NFC organization after being modified, which is consistent with SEM observations.

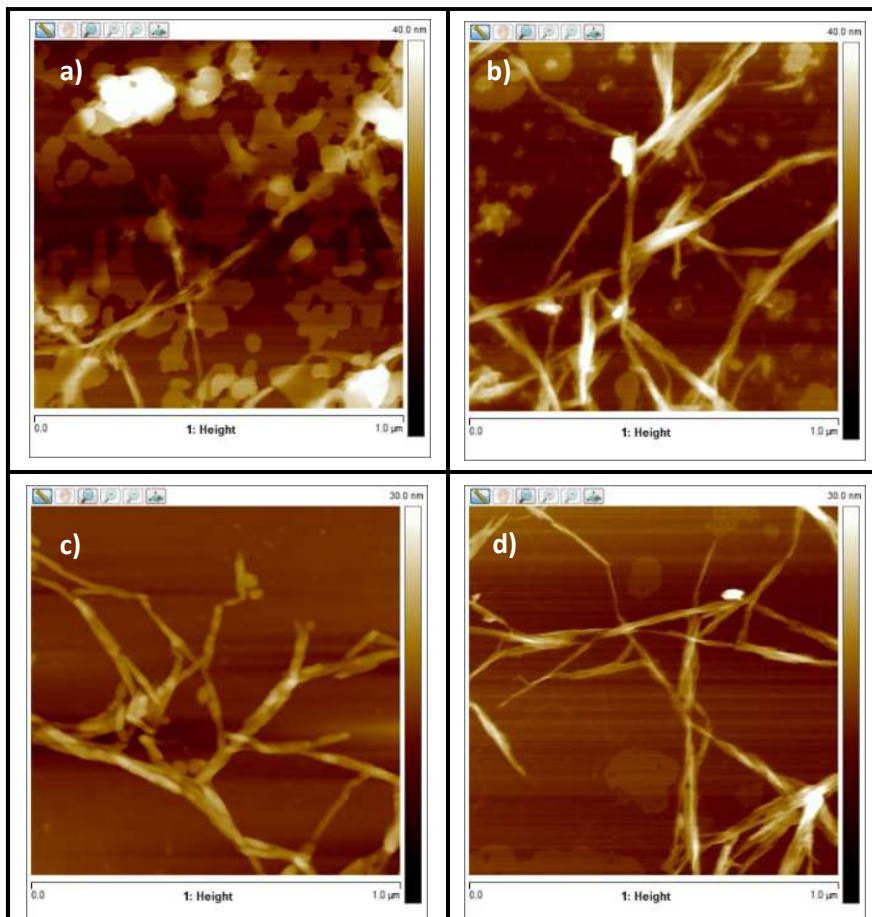


Figure 9. AFM topographical images (1  $\mu\text{m} \times 1 \mu\text{m}$ ) of a) pristine NFC, b) NFC-GPS EtOH, c) NFC-GPS acid, d) NFC GPMS acid.

### 3.3 Thermal properties of functionalized NFC

At the final stage of this study, the thermal stability of the modified NFC was evaluated by TGA analysis. Figure 10 shows the differences and similarities of pristine and modified NFC. Before 380°C, the weight loss is similar but, at superior temperatures, the thermal stability of modified NFC is higher than pristine NFC. This behavior could be associated with a polysiloxane layer formed onto NFC surfaces, which delays the thermal decomposition<sup>42</sup>. This result strengthens the assumption of NFC-GPS grafting.

Moreover, a difference between the two grafting methods is observed: samples fabricated under acid condition present a higher performance than those fabricated with ethanol reflux. This performance is related to the polysiloxane layer formed onto the surface. This behavior is due to the higher quantity of siloxane grafted and physisorbed onto the NFC surface under the acid condition, as previously demonstrated by the XPS study. TGA study supports that statement. The rise of thermal stability is mainly due to the layer formed onto the surface to protect NFC. This phenomenon has been observed in several silane coupling agent systems, as with APS<sup>42</sup>, CPTES<sup>43</sup>, MPS<sup>44</sup>.

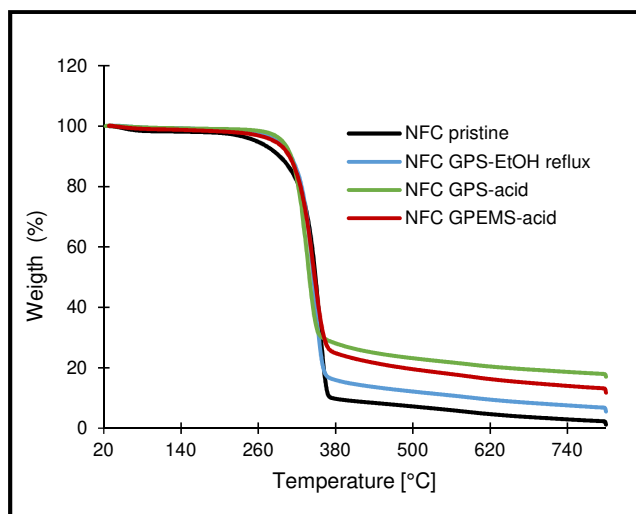


Figure 10. Thermogravimetric analysis of pristine and modified NFC.

### 3. Conclusions

The chemical functionalization of nano fibrillated cellulose (NFC) with 3-(glycidyoxypropyl) trimethoxysilane (GPS) and 3-(glycidyoxypropyl) dimethylethoxysilane (GPMS), was successfully realized by simple protocols. Besides, the characterization was achieved by employing different methods. Functionalization under acid conditions is more efficient than

ethanol reflux; besides that, it allows to keep the desired amount of epoxy groups available for further applications. The network morphology is studied in detail by various techniques.  $^{29}\text{Si}$  and  $^{13}\text{C}$  solid-state NMR allows establishing the existence of four different silicon configurations of the siloxane network. These configurations remained after soxhlet extraction even if the elimination of weakly grafted network is performed. Silanes self-condensation process under acid conditions is not the dominant reaction. These results indicate that grafted silanes are probably not fully self-condensed, and mainly consisting of linear dangling silane chains with heterogeneous NFC substitution.

Furthermore, the NFC functionalization with GPS or GPMES improved thermal stability. This behavior is associated with the presence of silanes, the slightly microscopical modification of NFC morphology, and the apparent persistence of the glucosidic units.

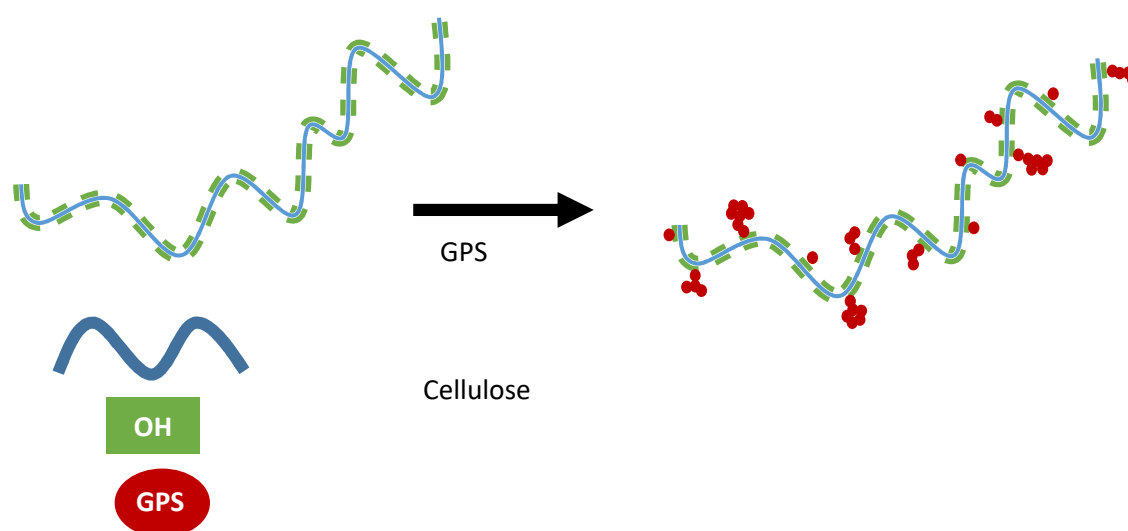
The results of this study allow to elaborate NFC functionalized with epoxy groups still chemistry reactive; for instance, they can be used as reactive bio-fillers for epoxy-amine systems. The results also cleared up the condensation state of the grafted silanes network and let us elucidating the surrounding network to the cellulose surfaces. It is essential to provide and adjust the final properties and dimensions of the functionalized NFC-polymer matrix interface in the next study.

## 5. Acknowledgments

The authors would like to acknowledge :

The Mexican Council of Science and Technology (CONACyT), through scholarship No. 471702, for financially supporting this work.

The Bruker BioSpin company, Silberstreifen 4, 76287 Rheinstetten, Germany (Dr Gerhard Althoff-Ospelt)



## References

---

- <sup>1</sup> M. Jawaid, H.P.S. Abdul Khalil, Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review, *Carbohydr. Polym.* 86 (2011) 1–18.
- <sup>2</sup> A. Dufresne, Nanocellulose: A new ageless bionanomaterial, *Mater. Today*. 16 (2013) 220–227.
- <sup>3</sup> S. Kalia, A. Dufresne, B.M. Cherian, B.S. Kaith, L. Avérus, J. Njuguna, E. Nassiopoulos, Cellulose-based bio- and nanocomposites: A review, *Int. J. Polym. Sci.* 2011 (2011) ID837875.
- <sup>4</sup> A.S. Singha, A.K. Rana, Effect of Aminopropyltriethoxysilane (APS) Treatment on Properties of Mercerized Lignocellulosic *Grewia optiva* Fiber, *J. Polym. Environ.* 21 (2013) 141–150.
- <sup>5</sup> J. Lu, P. Askeland, L.T. Drzal, Surface modification of microfibrillated cellulose for epoxy composite applications, *Polymer (Guildf)*. 49 (2008) 1285–1296.
- <sup>6</sup> M. Gericke, J. Trygg, P. Fardim, Functional cellulose beads: Preparation, characterization, and applications, *Chem. Rev.* 113 (2013) 4812–4836.
- <sup>7</sup> D. Li, Y. Wang, F. Long, L. Gan, J. Huang, Solvation-Controlled Elastification and Shape-Recovery of Cellulose Nanocrystal-Based Aerogels, *ACS Appl. Mater. Interfaces*. 12 (2020) 1549-1557.
- <sup>8</sup> S. Eyley, W. Thielemans, Surface modification of cellulose nanocrystals, *Nanoscale*. 6 (2014) 7764–7779.
- <sup>9</sup> Y. Habibi, Key advances in the chemical modification of nanocelluloses, *Chem. Soc. Rev.* 43 (2014) 1519–1542.
- <sup>10</sup> T. Heinze, T. Liebert, Unconventional methods in cellulose functionalization, *Progress in polymer science*. 26 (9) (2001) 1689-1762.
- <sup>11</sup> A.L. Goffin, J.M. Raquez, E. Duquesne, G. Siqueira, Y. Habibi, A. Dufresne, P. Dubois, From interfacial ring-opening polymerization to melt processing of cellulose nanowhiskered poly(lactide)-based nanocomposites, *Biomacromolecules*. 12 (2011) 2456–2465.
- <sup>12</sup> E. Ten, J. Turtle, D. Bahr, L. Jiang, M. Wolcott, Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers composites, *Polymer (Guildf)*. 51 (2010) 2652–2660.
- <sup>13</sup> I. Navarro-Baena, V. Sessini, F. Dominici, L. Torre, J.M. Kenny, L. Peponi, Design of biodegradable blends based on PLA and PCL: From morphological, thermal and mechanical studies to shape memory behavior, *Polym. Degrad. Stab.* 132 (2016) 97–108.
- <sup>14</sup> D.N. Sahed, J.P. Jog, Natural fiber polymer composites: a review, *Advances in Polymer Technology: Journal of the Polymer Processing Institute*. 18 (1999) 351-363.

- 
- <sup>15</sup> M. Abdelmouleh, S. Boufi, A. Ben Salah, M.N. Belgacem, A. Gandini, Interaction of silane coupling agents with cellulose, *Langmuir*. 18 (2002) 3203–3208.
- <sup>16</sup> M.C. Matías, M.U. De La Orden, C.G. Sánchez, J.M. Urreaga, Comparative spectroscopic study of the modification of cellulosic materials with different coupling agents, *J. Appl. Polym. Sci.* 75 (2000) 256-266
- <sup>17</sup> P.J. Herrera-Franco, A. Valadez-González, A study of the mechanical properties of short natural-fiber reinforced composites, *Compos. Part B Eng.* 36 (2005) 597–608.
- <sup>18</sup> M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne, A. Gandini, Modification of cellulose fibers with functionalized silanes: Effect of the fiber treatment on the mechanical performances of cellulose-thermoset composites, *J. Appl. Polym. Sci.* 98 (2005) 974–984.
- <sup>19</sup> M. Castellano, A. Gandini, P. Fabbri, M.N. Belgacem, Modification of cellulose fibres with organosilanes: Under what conditions does coupling occur?, *J. Colloid Interface Sci.* 273 (2004) 505–511.
- <sup>20</sup> M.C.B. Salon, G. Gerbaud, M. Abdelmouleh, C. Bruzzese, S. Boufi, M.N. Belgacem, Studies of interactions between silane coupling agents and cellulose fibers with liquid and solid-state NMR, *Magn. Reson. Chem.* 45 (2007) 473–483.
- <sup>21</sup> P. Threepopnatkul, N. Kaerkittha, N. Athipongarporn, Effect of surface treatment on performance of pineapple leaf fiber-polycarbonate composites, *Compos. Part B Eng.* 40 (2009) 628–632.
- <sup>22</sup> J. Girones, J.A. Méndez, S. Boufi, F. Vilaseca, P. Mutjé, Effect of silane coupling agents on the properties of pine fiber/polypropylene composites, *J. Appl. Polym. Sci.* 103 (2007) 3706-3717.
- <sup>23</sup> J.M. Urreaga, M.C. Matías, M.U. De la Orden, M.L: Munguía, C.G Sánchez, Effects of coupling agents on the oxidation and darkening of cellulose materials used as reinforcements for thermoplastic matrices in composites, *Polym. Eng. Sci.* 40 (2000) 407-417.
- <sup>24</sup> A.K. Mohanty, M. Misra, L.T. Lawrence T. Drzal, *Natural fibers, biopolymers, and biocomposites*, Taylor & Francis, 2005.
- <sup>25</sup> Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: A review, *Compos. Part A Appl. Sci. Manuf.* 41 (2010) 806–819.
- <sup>26</sup> M.C. Brochier Salon, M. Abdelmouleh, S. Boufi, M. N. Belgacem, A. Gandini, Silane adsorption onto cellulose fibers: Hydrolysis and condensation reactions, *J. Colloid Interface Sci.* 289 (2005) 249–261
- <sup>27</sup> H. Khanjanzadeh, R. Behrooz, N. Bahramifar, W. Gindl-Altmatter, M. Bacher, M. Edler, T. Griesser, Surface chemical functionalization of cellulose nanocrystals by 3-aminopropyltriethoxysilane, *Int. J. Biol. Macromol.* 106 (2018) 1288–1296.

- 
- <sup>28</sup> E. Robles, L. Csóka, J. Labidi, Effect of reaction conditions on the surface modification of cellulose nanofibrils with aminopropyl triethoxysilane, *Coatings*. 8 (2018).
- <sup>29</sup> W. Qing, Y. Wang, Y. Wang, D. Zhao, X. Liu, J. Zhu, The modified nanocrystalline cellulose for hydrophobic drug delivery, *Appl. Surf. Sci.* 366 (2016) 404–409.
- <sup>30</sup> Y. Maréchal, H. Chanzy, The hydrogen bond network in I $\beta$  cellulose as observed by infrared spectrometry, *Journal of molecular structure*. 523 (2000) 183-196.
- <sup>31</sup> I.M. Šapić, L. Bistričić, V. Volovšek, V. Dananić, K. Furić, DFT study of molecular structure and vibrations of 3-glycidoxypropyltrimethoxysilane, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 72 (2009) 833–840.
- <sup>32</sup> J.S. Yeo, O.Y. Kim, S.H. Hwang, The effect of chemical surface treatment on the fracture toughness of microfibrillated cellulose reinforced epoxy composites, *J. Ind. Eng. Chem.* 45 (2017) 301–306
- <sup>33</sup> K. Missoum, J. Bras, M.N. Belgacem, Organization of aliphatic chains grafted on nanofibrillated cellulose and influence on final properties, *Cellulose*. 19 (2012) 1957–1973.
- <sup>34</sup> L.S. Johansson, J.M. Campbell, K. Koljonen, P. Stenius, Evaluation of surface lignin on cellulose fibers with XPS, *Appl. Surf. Sci.* 144 (1999) 92-95.
- <sup>35</sup> D. Briggs, G. Beamson, High resolution XPS of organic polymers: The Scienta ESCA 300 database, John Wiley & Sons (1992).
- <sup>36</sup> Y. Dufil, V. Gadenne, P. Carrière, J.M. Nunzi, L. Patrone, Growth and organization of (3-Trimethoxysilylpropyl) diethylenetriamine within reactive amino-terminated self-assembled monolayer on silica, *Appl. Surf. Sci.* 508 (2020)145210
- <sup>37</sup> K.C. Vrancken, L. De Coster, P. Van Der Voort, P.J. Grobet, E.F. Vansant, The role of silanols in the modification of silica gel with aminosilanes, *J. Colloid Interface Sci.* 170 (1995) 71-77.
- <sup>38</sup> E. Alonso, L.A. Pothan, A. Ferreira, N. Cordeiro, Surface modification of banana fibers using organosilanes: an IGC insight, *Cellulose*. 26 (2019) 3643–3654.
- <sup>39</sup> K. Wickholm, P.T. Larsson, T. Iversen, Assignment of non-crystalline forms in cellulose I by CP/MAS <sup>13</sup>C NMR spectroscopy, *Carbohydrate Research* 312 (1998) 123-129.
- <sup>40</sup> A. M. Zaper, A. Cholli, J. L. Koenig, Applications of Solid-State Magic Angle NMR Spectroscopy to Fiber Reinforced Composites, *Molecular Characterization of Composite Interfaces* (1985) 299-312 Springer, Boston, MA.
- <sup>41</sup> E. Bayer, K. Albert, J. Reiners, M. Nieder, D. Müller, Characterization of chemically modified silica gels by <sup>29</sup>Si and <sup>13</sup>C cross-polarization and magic angle spinning nuclear magnetic resonance *Journal of Chromatography A*. 264 (1983) 197-213.

---

<sup>42</sup> L. Yue, A. Maiorana, F. Khelifa, A. Patel, J.M. Raquez, L. Bonnaud, R. Gross, P. Dubois, I. Manas-Zloczower, Surface-modified cellulose nanocrystals for biobased epoxy nanocomposites, *Polymer (Guildf)*. 134 (2018) 155–162.

<sup>43</sup> F. Rafieian, M. Mousavi, Q. Yu, M. Jonoobi, Amine functionalization of microcrystalline cellulose assisted by (3-chloropropyl)triethoxysilane, *Int. J. Biol. Macromol.* 130 (2019) 280–287.

<sup>44</sup> A. Rachini, M. Le Troedec, C. Peyratout, A. Smith, Chemical modification of hemp fiber by silane coupling agents, *J. Appl. Polym. Sci.* 123 (2012) 601-610.