In-Depth Study of the Microcrystalline Cellulose Amino-Functionalization Efficiency

Roberta Motta Neves (✉ robertamneves@gmail.com)

UFRGS: Universidade Federal do Rio Grande do Sul <https://orcid.org/0000-0002-7017-0852>

Heitor Luiz Omaghi Jr.

Universidade Federal da Integracao Latino-Americana

Benoit Duchemin

Normandie Université: Normandie Université

Ademir José Zattera

UCS: Universidade de Caxias do Sul

Sandro Campos Amico

UFRGS: Universidade Federal do Rio Grande do Sul

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Abstract

Microcrystalline cellulose (MCC) has unique properties and its use as reinforcement for polymer composites has been increasing. However, the intrinsic incompatibility with most polymers requires surface modification to improve chemical compatibility prior to its incorporation into a polymer. In this paper, an in-depth study of silanization of MCC using 3-aminopropyltriethoxysilane (APTES), at different concentration, was done. The grafting amount of APTES onto MCC was determined by different methods: from residual mass and from nitrogen content. Solid-state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR), field emission scanning electron microscopy with energy dispersive X-ray (SEM-EDX), spectroscopy plasma optical emission spectrometry (ICP), and a deep study of structural properties by X-ray diffraction were carried out. A better correlation for grafting amount of APTES onto MCC was observed for nitrogen content method than residual mass according the Pearson's correlation. ^{13}C NMR revealed all the carbon structures from cellulose and from APTES molecules and ^{29}Si NMR revealed D, T and Q Si structures. The silane treatment did not alter the shape of MCC and all treated samples showed Si characteristic peak at ~ 1.75 keV. From ICP was observed higher Si content before MCC addition than after, evidencing, once again, APTES grafting. The exposure to APTES in acidic medium caused several effects on the MCC, splitting larger I_β crystallites in half and along the more reactive hydrophilic sides. The diameter of the smaller IV_1 crystallites was largely reduced by the treatment, especially when the silane concentration was 1:5 (m/v), above which the diameter increases again.

1. Introduction

Microcrystalline cellulose (MCC) is applied in several fields, including as reinforcement in composites, since it combines renewable source with good thermal and mechanical properties. However, cellulose-based fillers and polymers are not chemically compatible in general. Thus, surface modification of cellulosic reinforcements is recommended in order to produce a stronger interface between them, improving the final composite properties (Trache et al., 2016).

There are different types of silanes used for the chemical modification of cellulose. In particular, the 3-aminopropyltriethoxysilane (APTES) has the amino functional groups and is recommended for polymers such as epoxy, polyethylene, polyvinyl chloride, butyl rubber and polyacrylate (Xie et al., 2010). The chemical groups at the surface of the reinforcement can be modified to chemically interact with other materials (Xie et al., 2010; Neves et al., 2020), obtaining tailor-made materials for specific applications.

The surface groups of cellulose-based materials can be studied using different methods such as nuclear magnetic resonance, thermogravimetric analysis or elemental analysis (Abdelmouleh et al., 2004; Baer et al., 2013; Sun et al., 2019). X-ray diffraction is widely used to determine crystal type, size of crystallites and crystallinity index. The most widely known and easiest way to analyze cellulose crystallinity is to use the Segal's method (Segal, et al., 1959). This method has relatively low accuracy but it is well-accepted for comparison purposes (Segal et al., 1959; French & Santiago, 2013; French, 2014, 2020). Posteriori methods, which rely on the preliminary knowledge of lattice or other parameters, are based on curve-fitting procedures, such as the Debye or the Rietveld method (Thygesen et al., 2005; Driemeier, 2014). All the methods have

drawbacks, and most are based on the identification of prominent peaks, which are not considered to overlap in the 10° – 50° range of 2θ .

Duchemin (2017) developed a free spreadsheet program that determines the shape, orientation, and crystallinity of cellulose I β using X-ray raw data. To summarize, a semi-empirical background is set and a small number of adjustable parameters are iterative-simulated until convergence. This software was successfully applied on raw, non-treated, microcrystalline cellulose (Duchemin, 2017) and on cellulose nanocrystals (Fernandes et al., 2020), but not for silane-modified MCC.

Thus, this study focuses on the determination of the APTES grafting index on the surface of MCC using two methods, followed by an in-depth structural characterization by X-ray diffraction, along with thermogravimetric and elemental analysis. Complementary techniques to evaluate the effect of the silanization included Fourier-transform infrared spectroscopy (FTIR), plasma optical emission spectrometry, solid-state ^{13}C and ^{29}Si nuclear magnetic resonance, and field emission scanning electron microscopy with energy dispersive X-ray spectroscopy.

2. Materials And Methods

2.1 Materials

The materials employed in this paper were: microcrystalline cellulose (Sigma-Aldrich – average diameter of $20\text{ }\mu\text{m}$), 3-aminopropyltriethoxysilane (APTES) (Sigma-Aldrich, MW: 221 g/mol). For the APTES hydrolysis, ethanol 99.5% and glacial acetic acid (Química Moderna- São Paulo-Brazil) were used.

2.2 Surface modification of MCC

The modification of the MCC surface was reported in previous work (Neves et al., 2020) and is illustrated in Fig. 1 along with the characterization carried out at each step. Briefly, (i) the MCC is homogenized in an alcoholic solution (75% v/v) acidified at pH 4–5 using acetic acid and kept under stirring for 30 min at room temperature (rT); (ii) The silane undergoes hydrolysis and is also kept under stirring for 30 min at rT; (iii) APTES and MCC are stirred together for 2 h at (rT) for the condensation, followed by washing of the unreacted silane and centrifugation; (iv) the MCC is grafted at 105°C for 15 min. The samples were named: MCC (raw microcrystalline cellulose) and MCC-Si (1:X) (m/v). The APTES relation chosen was 3, 4, 5 and 10 ml.

2.3 Characterization

The amount of silane grafted onto the MCC surface was determined by thermogravimetric analysis (TG) and elemental analysis (CHN). Complementary analysis performed included: solid-state ^{13}C and ^{29}Si Nuclear Magnetic Resonance (NMR), Plasma Optical Emission Spectrometry (ICP-OES), Field Emission Scanning Electron Microscopy (FEG-SEM) coupled by Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD).

The thermogravimetric analysis (TG) was performed on all samples (modified or not) using Shimadzu TGA-50 equipment in an N_2 atmosphere with a $50\text{ mL}\cdot\text{min}^{-1}$ purge rate, using a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ from

25 to 700°C, and *ca.* 10 mg of sample mass. The amount of APTES grafted onto the MCC surface was quantitatively determined based on the TG residue (char) according to Eqs. (1)-(2):

$$\text{Silane grafted amount (mequiv/g)} = \frac{10^3 \cdot W_{150-380}}{[100 - (W_{150-380})] \cdot M} \quad (1)$$

$$\text{Silane grafted amount (\%)} = \frac{100 \cdot W_{150-380}}{100 - W_{150-380}} \quad (2)$$

where $W_{150-380}$ is the weight loss between 150 and 380°C and M ($\text{g} \cdot \text{mol}^{-1}$) is the molecular weight of the grafted silane molecules, according to (Piscitelli et al., 2010; Loof et al., 2016);).

The carbon, hydrogen and nitrogen content in the silanized samples were determined using elemental analysis (Elementar, Vario MACRO Cube equipment, Germany). The content of APTES (M_{APTES}), in mmol silane/g sample, onto the MCC surface was determined according to (Yang et al., 2012), using Eq. (3).

$$M_{\text{APTES}} = \left(\frac{W_N}{M_N} \right) \quad (3)$$

where W_N is the content (mass%) of nitrogen from the elemental analysis and M_N is the molar mass of N (14.01 g/mol).

Solid-state ^{13}C measurements were performed using resonance frequency of 125 MHz, spinning rate 10 kHz, cross-polarization (CP) contact time 7 ms, recycle delay 5 s, SPINAL-64 1H decoupling and acquisition time 43 ms. The chemical shift was referenced against hexamethylbenzene (38.3 ppm). ^{29}Si NMR measurements were performed using resonance frequency of 99.3 MHz and chemical shift was referenced against talc (-90 ppm). Samples with lower silane content (MCC-Si (1:3) and (1:4)) were analyzed for ^{29}Si at longer exposure times, once they have the lowest APTES content. Both analyzes were performed on an Agilent DD2 500 MHz spectrometer (California, US), equipped with a 4mm dual broadband CP- MAS probe. The morphology and composition of the MCC-Si samples were characterized using Tescan brand equipment – model FEG Mira 3 (Czech Republic) by SEM and EDX. All samples were previously coated with Au and the acceleration voltage used was 15 kV.

Quantification of silicon content in the aqueous solution was performed by ICP after the APTES hydrolysis (step (ii), Fig. 1) and after the condensation (step (iii), Fig. 1). The analysis was performed in a SMEWW 3120 B in ICP (ThermoScientific - ICAP 7000 SERIES) equipment. The samples were submitted to a digestion in SMEWW 3030-E. The Si analysis had the limit of quantification of 0.01 mg/L.

FTIR-ATR was performed with the help of a Nicolet device, model IS10 Thermo Scientific. Each spectrum was the accumulation of 32 scans in the $4000 - 400 \text{ cm}^{-1}$ wavenumber range. The data treatment was performed with Orange 3.27 (Demšar et al., 2013). Three regions were treated separately: the -OH region between 3600 and 3050 cm^{-1} , the -CH region between 3000 and 2700 cm^{-1} and the region between 1800 and 650 cm^{-1} . The regions were baseline subtracted (linear baseline for the two first regions and rubber band correction for the last one) before being area normalized. A second derivative transformation was performed in order to

determine peak positions with a Savitsky-Golay filter (99 points window, 2nd order polynomial approximation).

XRD measurements were performed with a Shimadzu XRD-6000 diffractometer at 40 kV and 30 mA with a CuK_α beam ($\lambda = 0.1542 \text{ nm}$). The intensities were measured in the $2^\circ < 2\theta < 30^\circ$ range ($0.05^\circ/4 \text{ s}$). The results were interpreted with the help of a routine reported in (Duchemin, 2017; Khelifi et al., 2018; Leboucher et al., 2020). Briefly, a Rietveld analysis was performed with the hypothesis that the diffraction signal was constituted of three components: cellulose I_β with large crystallites and relatively long-range order, a form of native cellulose with small crystallites (usually below 2 nm in lateral cross-section) and a background signal with a constant value over the whole angular range. This bimodal size distribution is justified by the co-existence of protofibrils aggregates, and it has been successfully used to explain anisotropic recrystallization, or decrystallization (Khelifi et al., 2018; Leboucher et al., 2020).

The concept of multimodal size distributions has recently been reported by another team using a simulation matching approach (Rosén et al., 2020). In contrast, the approach used here is based on Rietveld refinement and it enables more parameters to be fitted from the experimental data. The larger crystallites were modelled after the I_β coordinates originally published by Nishiyama et al., (2003). The fitting parameters were intensity, lattice parameters, March-Dollase (0 0 h) texture, and crystallite dimensions and shape. The line shape was described with a Pearson VII function and a shape parameter of 1.88. The geometry of these crystallites was assumed to be that of a superellipsoid, as described in (Rosén et al., 2020). The smaller crystallites were modelled using the IV_1 unit cell assuming the absence of a preferred orientation, and only two parameters were refined, crystallite diameter (the crystallites were considered spherical) and relative intensity.

3. Results And Discussion

3.1 Amount of APTES grafted onto MCC surface

According to the TG curves (Fig. 2a), the initial mass loss observed in the 30–200°C temperature range could be attributed to the evaporation of physically adsorbed water from the surface. The values found for MCC, MCC-Si (1:3) and MCC-Si (1:4) were 5.75 wt%. For higher MCC content, (1:5) and (1:10) samples, the values were 4.5 and 3.7 wt%, respectively. This is indicative of the relatively hydrophobic nature of the silanized MCC.

Usually, cellulose shows a one-step degradation from 300 to 400°C (Fig. 2b) due to the depolymerization of cellulose chains (Ornaghi et al., 2020). For MCC, a shoulder around 310°C was observed associated with the dehydration of cellulose to dehydrocellulose as reported by Das et al., 2010). Additionally, the chemical modification of MCC decreased the T_{max} of all samples. Some literature has associated this reduction in thermal stability to the reducing ends (RE) of the cellulose chain, whose C-OH bonds can form aldehyde groups that are susceptible to oxidation and reduction reactions (Puls et al., 2011; Agustin et al., 2016).

Since the silanization process occurred in an acidic medium (pH: 4–5), some breaking of the $\beta 1-4$ glycosidic bonds may happen, producing more REs. The reduced MCC chains would tend to thermally degrade more easily than the original cellulose chain. This behavior was more pronounced for MCC-Si (1:5). A similar trend was reported by (Agustin et al., 2016) who studied the thermal characteristics of nanocrystals of cellulose,

(Matsuoka et al., 2011) who studied MCC thermal glycosylation and degradation reactions, and (Leboucher et al., 2020) who studied hydrolyzation of cellulose nanocrystals. In all cases, the thermal stability was related to the chain ends rather than to crystallinity.

The results for grafted aminosilane amount onto MCC surface from TG curves are displayed in Fig. 2c. It is possible to observe that increasing the APTES content in the sample, increase the silane grafting amount. In other words, by increasing APTES in the solution, the quantity of aminosilanes able to bond with MCC slightly increases. These results corroborate with (Piscitelli et al., 2010) finds when they treated sodium montmorillonite clay with this silane.

The content of carbon (C), nitrogen (N) and hydrogen (H) elements in MCC-Si can be found in Table 1. The MCC treated with higher content of APTES showed a slightly higher nitrogen content, being the highest for MCC-Si (1:5). According to Hassanpour et al. (2017), higher N content can be related to a successful grafting of the aminosilane onto the cellulose surface. Saini, Belgacem, Salon, & Bras, (2016) also found that the initial silane concentration significantly affected the grafting efficiency. The content of APTES (M_{APTES}) in MCC calculated from the N amount, is also shown in Table 1.

Table 1
Elemental analyses and the calculated APTES content in the MCC-Si samples.

Sample	C (%)	H (%)	N (%)	M_{APTES}^a (mmol Si/g sample)
MCC-Si (1:3)	39.219	7.237	0.448	0.0320
MCC-Si (1:4)	39.565	7.266	0.441	0.0315
MCC-Si (1:5)	39.669	7.269	0.563	0.0402
MCC-Si (1:10)	39.553	7.302	0.508	0.0363

^a Determined using Eq. (3).

A Pearson correlation plot was done to identify possible correlations among the variables (Fig. 3). The red and blue ellipses refer to positive and negative correlations, respectively, and the smaller the ellipse, the stronger the correlation between the variables (also indicated by the p-value). The results indicate a better correlation between the (M_{APTES}) (Table 1) and the N content than between the silane grafted amount and the residual TG (Fig. 2c).

3.2 Solid-state ¹³C and ²⁹Si NMR results

In a previous publication (Neves et al., 2020), NMR spectra of solid-state ¹³C from 130 to 30 ppm and NMR spectra of solid-state ²⁹Si from – 20 to -100 ppm were reported, from which cellulose carbons C1 to C6, characteristic of cellulose samples, and three Si structures of: T¹ (dimer), T² (linear) T³ (three-dimensional

structures), of the siloxane structure were reported. In the current paper, NMR measurements we performed at higher exposure times (total time of the analysis: 60h), extending the ppm axis.

Figure 4 shows the ^{13}C NMR spectra of MCC and MCC-Si samples, and the chemical shift assignments of the ^{13}C are summarized in Table 2. It was possible to observe all the chemical shifts characteristics of cellulose: C1, C2, C3, C4, C5 and C6 (Maunu et al., Sundquist, 2000) and the location at the anhydroglucose unit (AGU) (Haslinger, Hietala, Hummel, Maunu, & Sixta, 2019; Idström et al., 2016). In addition, three peaks from 45 to 5 ppm were obtained for MCC-Si samples, assigned as $\gamma\text{-C}$ ($-\text{CH}_2\text{-NH}_2$), $\beta\text{-C}$ ($-\text{CH}_2-$) and $\alpha\text{-C}$ ($-\text{Si-CH}_2-$). According to Brochier et al. (2005) and Fernandes et al. (2013), these peaks are resonances from the aminopropyl groups of the APTES, which are grafted onto the MCC, confirming the silane coupling onto the MCC surface.

Table 2
Isotropic ^{13}C chemical shift assignments (in ppm) for MCC and MCC-Si and its representations.

	MCC	MCC-Si (1:3)	MCC-Si (1:4)	MCC-Si (1:5)	MCC-Si (1:10)
C1	104	104	104	104	104
C2	73	72	72	72	72
C3	73	72	72	72	72
C5	73	72	72	72	72
C4	84	85	85	84	84
C6	63	62	63	62	62
$\gamma\text{-C}$	-	42	42	43	41
$\beta\text{-C}$	-	22	22	24	23
$\alpha\text{-C}$	-	10	10	10	11

Figure 5 shows the ^{29}Si NMR spectra of MCC and MCC-Si samples, from - 5 to -35 ppm and the chemical shift assignments of the ^{29}Si are summarized in Table 3. All the presented chemical shifts are corroborated with the literature (Cabrera, Berlioz, Fahs, Louarn, & Carriere, 2020; Rachini, Troedec, Peyratout, & Smith, 2011; Robles, Csóka, & Labidi, 2018).

Table 3

Isotropic ^{29}Si chemical shift assignments (in ppm) for MCC-Si samples.

	MCC-Si (1:3)	MCC-Si (1:4)	MCC-Si (1:5)	MCC-Si (1:10)
D ¹	-11	-9 to -13	-10 to -13	-11
D ²	-19	-17 to -20	-18 to -23	-18 to -24
T ¹	-45 to -50	-46 to -50	-46 to -50	-46 to -51
T ²	-57 to -62	-56 to -63	-52 to -62	-53 to -61
T ³	-63 to -68	-64 to -68	-64 to -76	-63 to -73
Q ²	-85 to -90	-82 to -89	-85 to -90	-84 to -89
Q ³	-91 to -97	-90 to -94	-90 to -97	-90 to -94
Q ⁴	-105 to -108	-105 to -109	-104 to -110	-104 to -114

The type of structure formed is given by the self-condensation of the silanol groups, i.e. “T” structures. However, in the current study, two other structures appeared, “D” and “Q”, due to the longer exposure times in the ^{29}Si NMR analysis. The notations “D”, “T”, and “Q” represent the different types of silicate structures commonly encountered in ^{29}Si NMR studies, with two, three and four Si–O– bonds, respectively (see Fig. 5b). More information can be found in (Glaser & Wilkes, 1989, Brochier et al., 2005). Based on Fig. 5, “T” structures were found to be dominant, and more pronounced for higher contents of APTES (MCC-Si (1:5) and (1:10)). In all samples, “D” and “Q” structures also appeared. The chemical modification of cellulose is applied, in general, to add functional groups that will interact with some polymers, producing a stronger cellulose/polymer interface in a composite. Since the chemical condensation and grafting of APTES onto cellulose happens through Si-O-C bonds (Abdelmouleh et al., 2004), “T” and “Q” structures are interesting for having more oxygen to bond with cellulose.

3.3. Chemical and Morphological Characterizations

Figure 6 shows SEM micrographs and EDX spectra of MCC-Si samples. All samples presented the same pattern, already discussed in (Samat et al., 2013; Neves et al., 2020). All modified samples with APTES presented the Si characteristic peak at ~ 1.75 keV, confirming the silanization process.

Plasma Optical Emission spectrometry (ICP-OES) has been used to identify silicon (Si) (Grümping et al., 1998; Yang et al., 2018). In this paper, the ICP-OES was used as an indirect measurement of grafted Si and the results are reported in Fig. 7. The difference in Si amount before and after APTES condensation onto MCC surface was 230, 685, 814 and 515 mg/L for MCC-Si (1:3), (1:4), (1:5) and (1:10), respectively. These results evidence that APTES has been grafted onto the MCC surface, and the higher difference in Si amount before and after APTES condensation was found for MCC-Si (1:5) sample. These results corroborate the previous TG, EA, and ^{29}Si NMR findings.

The FTIR study showed marked differences between the different samples (Fig. 8 and Table 4). In general, in the –OH region, the bands assigned to the weak intramolecular O(2)H···O(6), to the intermolecular O(6)H···O'(3) and to the intramolecular O(3)H···O(5) showed a displacement towards higher wavenumber values (Table 4) which is assigned to a constrained mobility of these –OH groups. The “weak” band is often assigned to the most accessible cellulose portions and it is strongly shifted after APTES treatment, which supports a grafting at the periphery of the crystalline portions. The main –CH band near 2900 cm⁻¹ is also affected by the treatment and it shows a slight wavenumber increase of 4 cm⁻¹ at the lowest relative concentration (MCC-Si 1:3), which progressively disappears as the concentration is increased. It is often thought that this band has little sensitivity to treatments, but this is in fact not true and it can be affected both by chemical and thermal treatments (Leboucher et al., 2020). The MCC-Si 1:10 treatment condition stands apart with respect to the intermolecular O(6)H···O'(3), to the intramolecular O(3)H···O(5) and to the –CH band (Table 4 and Fig. 8), and this supports the assumption of a different grafting architecture. The relative amount of free water in the 1800 – 650 cm⁻¹ region was also evaluated by measuring the relative area of the band near 1650 cm⁻¹. Unsurprisingly, the amount of free water is lower after silanization, which is consistent with the higher hydrophobicity provided by the treatment. Eventually, there are several distinct Si-O peaks at 1456, 1464 and 1473 cm⁻¹ (as seen in PCA, not reported here) that indicate successful silane grafting. The relative prominence of the 1456 cm⁻¹ band for 1:10 sample confirms a different grafting architecture also.

Table 4

– Band positions as a function of the band assignment, method of determination and treatment parameters.
 (*): as described by (Watanabe et al., 2006)

Band assignment	Intramolecular O(2)H···O(6) “weak type” (*)	Intermolecular O(6)H···O'(3)	Intramolecular O(3)H···O(5)	Intramolecular O(2)H···O(6)	Max –CH	Free - OH water
Method	From 2nd derivative		From max intensity	From 2nd derivative	From max intensity	Integral from 1800 to 1550 cm ⁻¹
MCC	3480	3415	3340	3271	2899	8.7%
MCC-Si 1:3	3446	3409	3334	3276	2895	1.8%
MCC-Si 1:4	3445	3409	3333	3274	2896	3.5%
MCC-Si 1:5	3446	3410	3334	3275	2897	2.4%
MCC-Si 1:10	3446	3407	3332	3276	2899	2.5%
APTES	/	/	/	/	2973	/

3.4 Structural study

The X-ray diffraction spectra were analyzed using a bimodal size distribution model, shown. The results are shown Fig. 8 and Table 4. The crystallite thickness in the direction orthogonal to the (200) plane is $\sim 2.R_x \pm 7\%$ and an increase of this value can be understood as a co-crystallization occurring on the more hydrophobic planes, as detailed in previous works (Duchemin, 2017; Leboucher et al., 2020). In contrast, the crystallite thickness in the direction orthogonal to the (010) plane is equal to $2.R_y$ and an increase of this value can be understood as a co-crystallization occurring on the more hydrophilic $\{110\}$, $\{1\bar{1}0\}$ and $\{010\}$ planes. Several things can therefore be assessed from the X-ray fitting work. Regarding the MCC sample, the relative allomorphic content, the crystallite shape and the dimensions of the two allomorphs are very much in line with our previous work, despite differences in the MCC origin and measurement setup (Duchemin, 2017). The exposure to the APTES in the acidic medium had several effects on the initial MCC. Regarding the dimensions of the larger cellulose I_β crystallites, their diameter $2.R_x$ is decreased by $\sim 25\%$ along the hydrophobic sides for all the treatment conditions except for the treatment with the highest APTES concentration (MCC-Si 1:10) for which $2.R_x$ remains the same (Table 4). More strikingly, the diameter $2.R_y$ is roughly halved by all of the treatment conditions, but this is also slightly less marked for the MCC-Si 1:10 sample. This means that, statistically, the silanization splits the larger I_β crystallites in half and along the more reactive hydrophilic sides. The diameter of the smaller IV_1 crystallites is also largely reduced by the action of the treatment and this action is more pronounced as the silane concentration increases up to the 1:5 ratio, after which point this diameter is large again. The 8–10 Å size observed for the 1:4 and 1:5 treatment conditions is actually in line with the hypothesis of protofibrils ~ 2 –3 chains in width. Interestingly, the allomorphic content is also showing two distinct groups: one in which small IV_1 crystallites are rather dominant (54% for MCC and 61% for MCC-Si 1:10), and one in which larger I_β crystallites are prevalent (between 74 and 81% for MCC-Si 1:3 to 1:5) (Fig. 9).

Table 5
Fitting parameters of the model

		MCC	MCC-Si (1:3)	MCC-Si (1:4)	MCC-Si (1:5)	MCC-Si (1:10)
I_β	Lattice parameter a (Å)	7.95	7.94	7.95	7.93	7.97
	Lattice parameter b (Å)	8.29	8.00	7.93	7.96	8.15
	Lattice parameter c (Å)	10.59	10.30	10.30	10.30	10.50
	γ (°)	95.66	95.24	95.17	95.11	96.82
	March-Dollase strength	1.51	0.80	0.73	0.77	0.94
	Ellipsoid diameter $2.R_x$ along the b x c axis (Å)	62	48	46	46	60
	Ellipsoid diameter $2.R_y$ along the b axis (Å)	56	26	24	24	30
	Ellipsoid radial squareness n	1.85	0.10	0.10	0.10	0.10
IV_1	Diameter (Å)	22	16	10	8	26
Relative area	Background	28%	22%	18%	18%	32%
	% I_β	33%	57%	65%	66%	26%
	% IV_1	39%	20%	17%	16%	42%
Fitting	Correlation coefficient	0.999	0.998	0.998	0.998	0.998
	R-pattern	0.027	0.043	0.043	0.042	0.036

These measurements can be interpreted in the light of the previous ^{29}Si NMR and ATR-FTIR results. During the APTES treatment, reactive silanols are created and they condense with the hydroxyl groups of cellulose. Since these hydroxyl groups are found in priority along the hydrophilic surfaces, the condensation reaction should occur on these sites first. This is what is observed here since the $2.R_y$ values are halved after the APTES treatment, meaning that the crystallites were split apart along the $\{110\}$ $\{1\bar{1}0\}$ and $\{010\}$ planes. Interestingly, the silane treatment is therefore able to act as a spacer between the hydrophilic sides of the cellulose crystallites. This transformation is correlated with the cross-sectional shape of the I_β phase: a swap from a lateral diamond shape (MCC) to a square shape occurs at all treatment conditions (Fig. 9 and Table 5). It is also correlated with the content reduction of slender IV_1 crystallites with respect to larger cellulose I_β , possibly due to dynamic reorganizations and perhaps recrystallization of the former phase.

When the highly reactive silanol structures are formed, they can also react to some extent with the less reactive “hydrophobic” cellulose sides, which explains the crystallite size change along a (R_x values). However, when the APTES concentration is increased in the acidic solution, the acidic hydrolysis of the APTES moieties evolves and certain forms become more frequent. For instance, the prevalence of the more reactive T^3

structure seems to be at an optimum for the 1:5 concentration (Fig. 6a), resulting in the lowest R_x values observed (Table 5). However, when the APTES concentration is too high, self-condensation might occur and bulkier, less reactive silanols are created that are unable to react along with the accessible “hydrophobic” groups. This explains the similarities between the initial and 1:10 condition in terms of crystallite size (R_x remains the same), lattice parameters (less lattice distortions due to lower reactivity), and allomorphic content (the unchanged prevalence of the IV_I form).

4 Conclusions

An in-depth study regarding MCC surface-functionalized using different ratios of APTES was performed. In all samples, APTES was grafted onto the MCC surface as proved by two different methods, CHN and TG residual mass. For the latter, higher APTES content yielded higher grafting amount, whereas for the former, the highest grafting amount was found for the MCC-Si (1:5) sample. A higher Pearson correlation was found for the grafting amounts calculated from the %N content.

Moreover, the solid-state ^{29}Si NMR of the MCC-Si samples presented dominant “T” structures (three Si–O– bridges) compared to “D” and “Q” structures (two and four Si–O– bridges, respectively). The allomorphic content obtained by XRD analysis presented dominance of IV_I crystallites for MCC and MCC-Si (1:10), and prevalence of I_β crystallites for MCC-Si (1:3) to (1:5)). During the APTES treatment, the condensation reaction occurred mostly along the hydrophilic surfaces, acting as a spacer between the hydrophilic sides of the cellulose crystallites. For the MCC-Si (1:10), due to the high concentration, the greater similarity with the initial MCC is justified in terms of self-condensation and due to the less reactive silanols which could not react any further with the accessible hydrophobic groups.

Declarations

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Ethical standard: This research did not involve the participation of humans or animals

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Figures

Figure 1

Illustration of the whole silanization process and the characterization carried out.

Figure 2

(a) TG curves, (b) DTG curves of all samples, (c) silane grafted amount of the MCC-Si.

Figure 3

Pearson correlation plot of the silanized samples and the variables of this study. C, N, H and MAPTES data from Table 1 and silane grafting amount and residue TG from Fig. 2c.

Figure 4

Solid-state ^{13}C for MCC and MCC-Si samples.

Figure 5

a) Solid-state ^{29}Si for MCC-Si samples, b) Possible silicate structures formed in the silanization process, where R is the silane functional group and X is the chain where the silane is grafted (adapted from Glaser & Wilkes, 1989).

Figure 6

SEM images and EDS spectra for: a) MCC-Si (1:3), b) MCC-Si (1:4), c) MCC-Si (1:5), d) MCC-Si (1:10).

Figure 7

Si amount (mg/L) before and after APTES condensation onto MCC for the MCC-Si samples.

Figure 8

Absorbance FTIR spectra of the samples before and after APTES condensation on MCC. The spectra were area normalized for each region of interest in order to improve readability.

Figure 9

X-ray diffractograms of all samples (black line) and simulated components: background (yellow), small cellulose IV₁ crystallites (green) and large cellulose I_β crystallites (blue). The relative IV₁ (or I_β) contents are indicated as percentages in the legend, along with a schematic of the estimated I_β cross-section (size and shape).