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Controlled surface modification of cellulose fibers by amino derivatives using *N*,*N*′-carbonyldiimidazole as activator

Sabrine Alila [a], Ana Maria Ferraria [b], Ana Maria Botelho do Rego [b], Sami Boufi [a,*]

[a] *LMSE, Faculté des Sciences de Sfax, BP 802-3018 Sfax, Tunisia*
[b] *Centro de Química-Física Molecular (CQFM) and Institute of Nanoscience and Nanotechnology (IN), Complexo Interdisciplinar, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

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ABSTRACT

Surface grafting of different amino derivatives was carried on under mild condition using *N*,*N*′-carbonyldiimidazole (CDI) as an activator. The action of a diamine or a triamine on previously activated cellulose fibres proceeds by the reaction of one amine function giving rise to a carbamate derivative. The other terminal amino groups remained available for further reaction. In particular, their activation with CDI generates a reactive carboxamide able to condense with an aliphatic amine through a urea linkage. Evidence for the occurrence of the reaction at each modification step was confirmed by Fourier Transform Infrared Spectroscopy (FTIRS) and X-ray photoelectron spectroscopy (XPS). The contact angle measurement, using water as a probe, was used to explore the evolution of the surface wettability for the different modification sequences. It was shown that the contact angle value is determined by the ratio between polar and methylene groups and by the spatial arrangement of the molecule on the surface.

1. Introduction

Cellulose is one of the most abundant organic materials that can be easily obtained in nature with a production level approaching 10^{11} tons per year. Cellulose macromolecule has particular properties such as renewable sources, regular structure, high molecular weight, and reactive hydroxyl groups on which different reactions can be carried on. These properties have contributed to the use of cellulose as a precursor for chemical modification to prepare a broad variety of commercial polymers widely used in coating, cosmetic formulation and other industrial fields (Heinze & Lebert, 2001). Among these polymers one can find nitrocellulose, hydroxyethycellulose, carboxymethylcellulose, cellulose acetate, cellulose acetobutyrate, and so on. Although homogeneous synthesis paths are the most adopted to change the bulk properties of cellulose giving rise to new polymers easy to dissolve or to transform, the heterogeneous reaction applied to cellulose fibres is the most appropriate to change the surface properties of the material while keeping the native fibre crystalline structure and morphology responsible for the good mechanical properties. Such an approach is necessary for different applications: (i) in composite material based on natural fibres as reinforcing agents, in order to optimise the wetting of cellulose fibres surface by matrix macromolecules and to enhance the fibre-matrix adhesion in the solid composite (Abdelmouleh, Boufi, Belgacem, & Dufresne, 2007; Belgacem & Gandini, 2005) (ii) in the textile industry to develop fibres with antimicrobial effect either by grafting biocide molecule or by generating ammonium groups on the fibre surface (Navarro, Sumi, Fujii, & Matsumura, 1996), (iii) to prepare cellulose derivatives with good sorption properties towards transition metals and heavy metal ions, which could be applied as chelating sorbents in metal cation separation (O'Connell et al., 2008) (iv) to enhance the sorption properties of lignocellulosic fibres toward organic pollutants by grafting hydrocarbon structures that will act as a hydrophobic reservoir into which the organic compound could be accumulated (Aloulou, Boufi, & Labidi, 2006; Boufi & Belgacem, 2006). This latter approach was successfully adopted by our research group to greatly enhance the adsorption capacity of cellulose toward a large variety of organic compounds including herbicides (Aloulou et al., 2006; Boufi & Belgacem, 2006).

The most adopted approach for the surface modification of cellulose is a condensation reaction taking place on the hydroxyl groups available on the surface (Kadla & Gilbert, 2000; Klemm, Heublein, Fink, & Bohn, 2005; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 2001). The extent of the surface modification depends on the accessibility of these hydroxyl groups toward the reagent which is controlled by the solvent composition and the preliminary treatment of the cellulose fibres, i.e. solvent exchange, mercerisation, fibrillation, etc. It depends also on the reactivity degree of the reagent and on the activation mode used either on the surface or on the reagent. In this context, we have shown that *N*,*N*′-

* Corresponding author.
E-mail address: Sami.Boufi@fss.rnu.tn (S. Boufi).

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carbonyldiimidazole (CDI) is an efficient activator to functionalise the cellulose surface with a bulky carboxylic porphyrin acid (Boufi, Rei Vilar, Parra, Ferraria, & Botelho do Rego, 2008).

CDI was first used in 1960 by Paul and Anderson (1960) as a peptide coupling by activation of aliphatic carboxylic acids to form imidazole carboxylic ester and enabling subsequent reaction with amines. Later, CDI was used in the selective synthesis of amides (Rannard & Davis, 2000), carbamates (Rannard & Davis, 1999) and also in the synthesis of a number of pharmaceutical products, e.g. sildenafil (Dunn, Hughes, Searle, & Wood, 2003) and sampatrilat (Dale et al., 2000). In the field of carbohydrate chemistry, Heinze and collaborators have used CDI as an activator for carboxylic acid to prepare in homogeneous solutions a wide variety of cellulose ester derivatives bearing unsaturated, chiral, crownether, cyclodextrin structures and dendrons (Heinze, Pohl, Schaller, & Meister, 2007; Hussain, Liebert, & Heinze, 2004; Liebert & Heinze, 2005). The particularity of CDI is its ability to react with alcohol, carboxylic acid and amine groups giving rise to reactive carbonyl imidazole intermediates that are more easily handled and may be isolated, if necessary. The ensuing carbonyl imidazole could subsequently undergo selective reactions with primary amines or primary alcohols to form amide, carbonate or ester derivative (Rannard & Davis, 1999, 2000). The advantages of this method include the mild reaction conditions which minimize secondary reaction, the lack of formation of amine hydrochloride when using acid chlorides, and the avoiding of lengthy purification stages. Moreover, imidazole, the by-product obtained both when CDI reacts with hydroxyl and carboxylic acid and after the reaction of carbonyl imidazole with alcohol or amine, is easily removed from the reaction mixture by an acidic wash. These advantages, coupled with the relatively low cost of CDI, render this method an attractive alternative to the carbodiimide-based reagents such as *N*,*N*-dicyclohexylcarbodiimide DCC (Samaranayake & Glasser, 1993) or acid chloride.

In this work, we focus on the use of CDI in the surface activation of cellulose fibres and its subsequent reaction with different amines to graft different organic moieties on them. In particular, we will show that the modification can be carried on under heterogeneous and mild conditions. Moreover, when we use di- or trifunctional amine, it is possible to generate a reactive surface on which further reactions can be performed. Surface modification using difunctional reagents was first adopted by Gandini, Botaro, Zeno, and Bach (2001) to graft rigid aromatic diisocyanate on cellulose fibres.

2. Experimental

2.1. Materials

Bleached soda pulp from the Tunisian annual plant esparto (*alfa tenacissima*), after delignification was used as cellulose substrates to be modified by CDI. The fibres were highly porous and, in a dry state, had a specific surface area of 3 $m^2 g^{-1}$ as measured by BET. The fibre mean length and diameter, measured by optical microscopy, were 750 and 14.2 μm, respectively.

All the reagents and all the aliphatic amines used in this study were of analytical grade.

2.2. Preparation of modified cellulose fibres

After delignification treatment with NaOH solution (10%), the cellulose fibres were soaked in water to bring about expansion and then dispersed, at a concentration about 10 wt%, in a solution of toluene/DMF (60/40 vol). The mixture was introduced in a three necked flask equipped with a Dean-Stark system, and kept under reflux until all the water is removed by azeotropic distillation. The suspension (800 μmol CDI/g of cellulose fibres) was then cooled from 120 to 60 °C, CDI was added under dry nitrogen atmosphere, and the mixture was kept under magnetic stirring for 3 h. Afterwards, the reaction mixture was rapidly filtered and washed twice with dry toluene in order to eliminate all the residual CDI. The activated fibres (10 wt%) were then introduced in a three necked flask containing a 10^{-3} mol.L^{-1} aliphatic amine, melamine or diamine solution, according to the type of required modification, and kept at 60 °C under magnetic stirring and dry nitrogen atmosphere for 3 h.

In the case where further modification was carried out, the ensuing substrate was submitted to reaction with CDI followed by an aliphatic amine or acid by the procedure described above.

Finally, the recovered product was purified by Soxhlet extraction with toluene for 48 h, and dried at 40 °C for 24 h.

The various characterisation techniques used to assess the occurrence and the extents of the modifications include Fourier Transform Infrared Spectroscopy (FTIRS), Nuclear Magnetic Resonance (NMR) spectroscopy, contact angle measurements and X-ray Photoelectron Spectroscopy (XPS).

2.3. FTIRS analysis

The FTIR spectra were obtained from KBr pellets using a Perkin-Elmer BX II spectrophotometer under transmission mode with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}. The fibres were mixed with high purity KBr (weight ratio: 5/200). Each spectrum was recorded with a total of 10 scans. KBr pellet spectrum was used as background.

2.4. CP/MAS ^{13}C solid state NMR

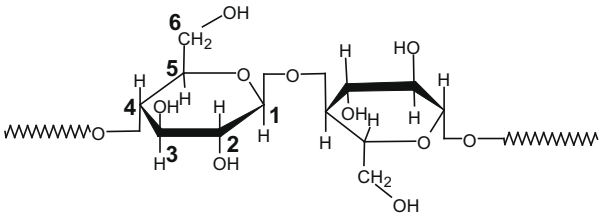
Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR measurements were carried out using a Bruker Avance 400 spectrometer operating at 79.490 MHz. The samples were placed in 7 mm ZrO_2 rotors. Magic angle spinning was performed at a spinning rate of 3 kHz. All the spectra were recorded using a combination of cross-polarization, high-power proton decoupling and magic angle spinning methods. A 25 kHz spectral width, a 5 s repetition time, a 2.5 ms contact time and a proton decoupling field equivalent to 33 kHz were used.

2.5. Contact angle

Contact angle measurements were carried out by deposing a calibrated liquid (distilled water) drop on the pellets of modified cellulose fibres. The contact angle apparatus used was an OCA 15 from Dataphysics, equipped with a CCD camera, with a resolution of 752 × 582 square pixels, working at an acquisition rate of 4 images per second. Collected data was processed using OCA software.

2.6. X-ray photoelectron spectroscopy

The used XPS spectrometer was a XSAM800 (KRATOS) operating in the fixed analyser transmission (FAT) mode, with a pass energy of 20 eV and a nonmonochromatised Al Kα X-radiation (1486.7 eV). Data acquisition and treatment details are described elsewhere (Vilar, Boufi, Ferraria, & Botelho do Rego, 2007). The charge shift was corrected using as reference the binding energy of carbon atoms bound to a hydroxyl group in cellulose (Carbons "1" in Scheme 1), at 286.73 eV. X-ray source satellites were subtracted. For quantification purposes, sensitivity factors were 0.66 for O 1s, 0.25 for C 1s and 0.42 for N 1s.



Scheme 1.

2.7. Diffraction measurements

Wide angle X-ray scattering (WAXS) diffractograms were recorded using a Siemens powder diffractometer D 5000 operated at the Cu Kα wavelength of 1.542 Å. Measurements of diffracted intensities were made over the angular range of 7–40° (2θ) at ambient temperature, with an increment step of 0.1° and a rate of 1 step per 10 s.

The crystallinity index X_c is defined as the height of the crystalline diffraction at 22.7° relative to the total height of the peak measured from the linear baseline drawn from a diffraction angle of 10° to 30° (2θ).

3. Results and discussion

Surface modification of cellulose by the isocyanate derivative is well known and often used to generate carbamate. However, isocyanates, namely the aliphatic ones, are expensive, available only in a limited number of structures and extremely sensitive to water. In the present work, a relatively easy approach is used: the activation with CDI to graft under mild conditions different organic structures on cellulose substrate through carbamate, amide and urea linkages.

In the first part of the paper an aliphatic amine is used as a model to show the occurrence of the condensation reaction on cellulose fibres previously treated with CDI.

Fig. 1 compares the FTIR spectrum of the unmodified fibres (spectrum 0) with the spectrum of CDI treated fibres (spectrum 1) and the one obtained after the interaction of the ensued CDI-treated cellulose with hexadecylamine (spectrum 2). Spectrum 0 shows the characteristic bands of cellulose skeleton at 1455, and 1420 cm^{-1} assigned to —OH in plane bending and CH_2 symmetric bending respectively. In the region 1200–1000 cm^{-1}, we find the fingerprint of the carbohydrate cycle at 1160, 1110 and 1060–1030 cm^{-1} corresponding to C—O—C asymmetric stretching, ring asymmetric stretching, and C—O stretching, respectively. The peak at 1635 cm^{-1} is related to the OH bending of water tightly absorbed on cellulose. In spectrum 1, two peaks emerged at 1760 and 1660 cm^{-1} assigned to the imidazole ester $\nu_{C=O}$ and to C=C and C=N stretching modes of the imidazole heterocycle. The disappearance of these two bands in spectrum 2 allied with the appearance of peaks at 1740 and 1530 cm^{-1} assignable to C=O stretching and NH deformation, respectively, confirmed the occurrence of the condensation reaction between the imidazole ester and the amino function according to Scheme 2.

The CP-MAS spectra obtained prior to and after the chemical modification are shown in Fig. 2. The starting cellulose fibres display the typical peaks of cellulose backbone at 65.5, (71.8+ 74.9), 89.1 and (104–105) ppm relative to the carbons C6, C2—C3—C5, C4 and C1, respectively. The small broad lines at about 63 and 85 ppm are the contribution of the disordered regions for the C6 and C4 carbons, respectively. The emergence of new peaks at 14, 23, 33 and 154 ppm assigned to the carbon atoms of terminal CH_3, CH_2 in β position relatively to CH_3, the internal methyl of the aminohexadecane chain and to the CO of the carbamate linkage, confirmed the C16NH2 condensation reaction at the surface according to the Scheme 2. One can notice that the cellulose peaks did not undergo significant change after the modification reaction confirming, again, that the heterogeneous condensation did not bring any modification to the morphology and the crystallinity of the cellulose substrate.

3.1. Grafting of multifunctional amine

In a previous study (Vilar et al., 2007), we have shown that surface treatment of cellulose film by aromatic diisocyanate leaves the second isocyanate function available for further chemical modifi-

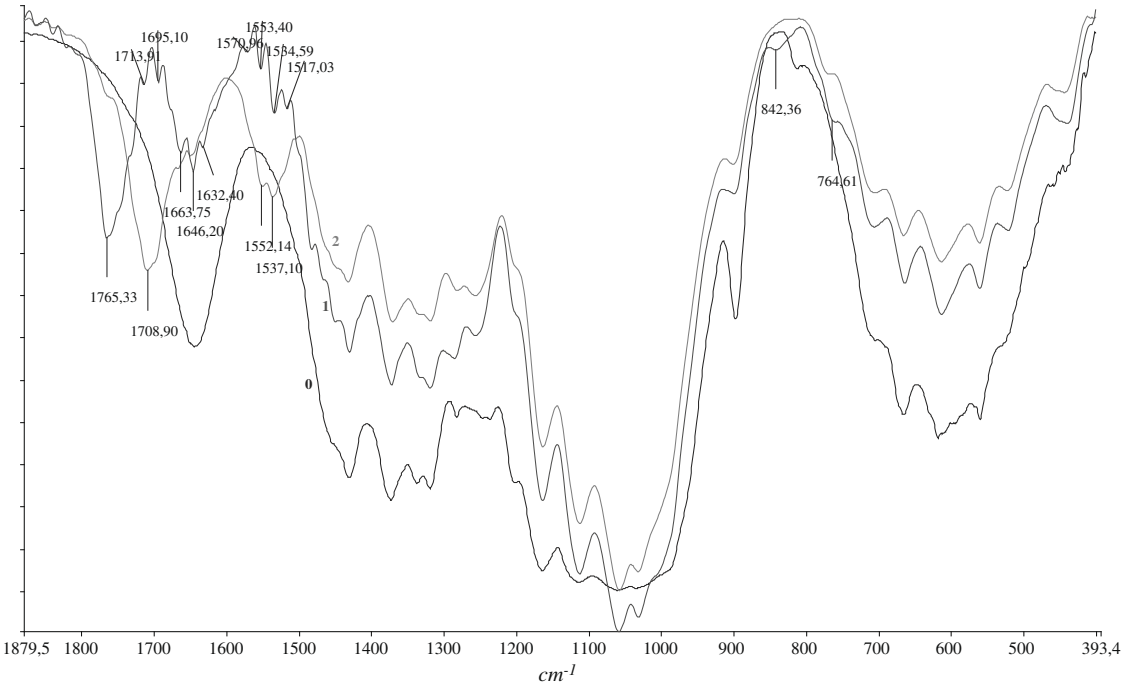
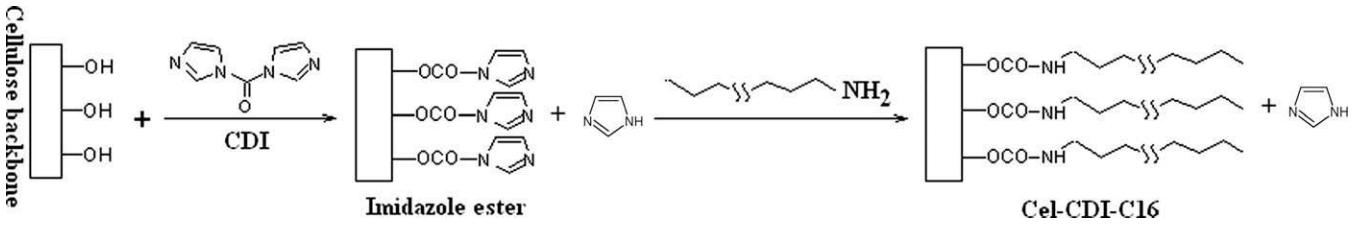


Fig. 1. FTIR spectra of virgin cellulose (0), activated fibers by CDI (1) and modified cellulose fibers with an amine in C16 (2).



Scheme 2. Chemical reaction of activated cellulose fibers by CDI with aliphatic amine in C16.

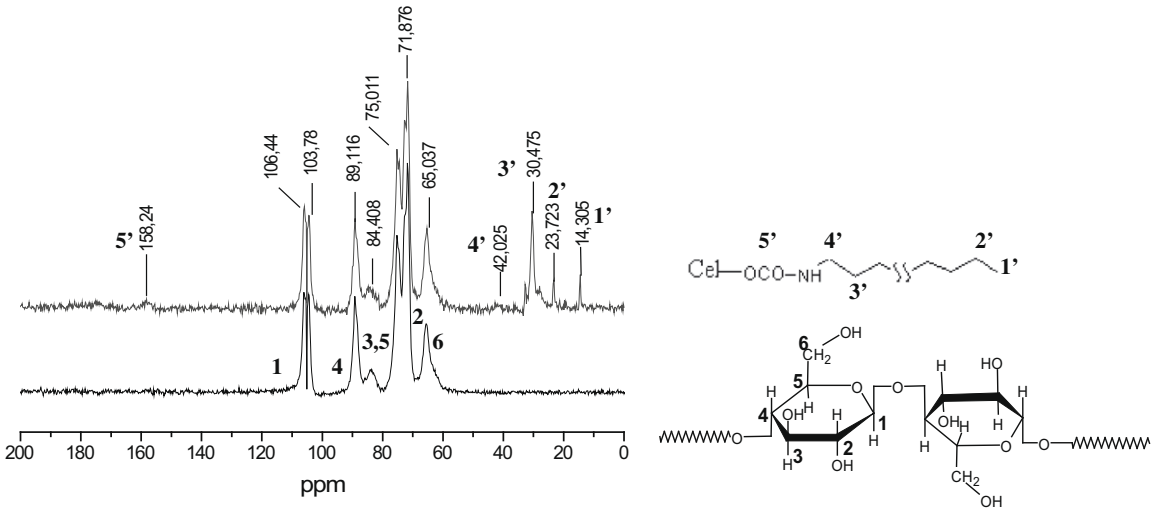


Fig. 2. NMR spectra of virgin cellulose and the modified fibers by an aliphatic amine in C16 Cel-CDI-NHC16.

cation. In the present work, we will show that CDI enables a wide range of possibilities of modification when used together with difunctional or polyfunctional amino derivatives. The following modification sequence was investigated:

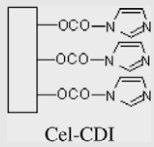
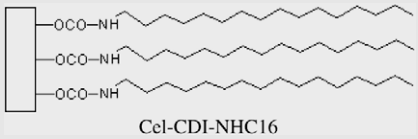
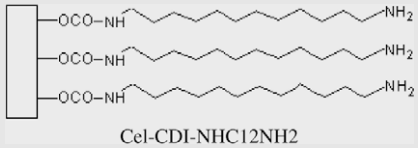
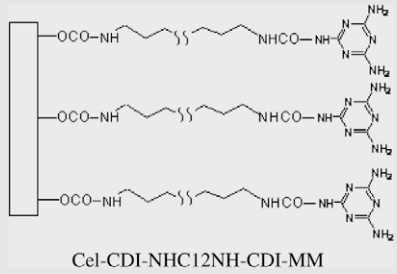
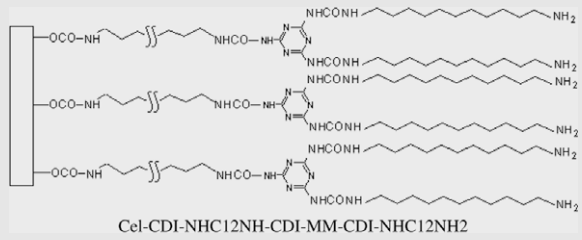
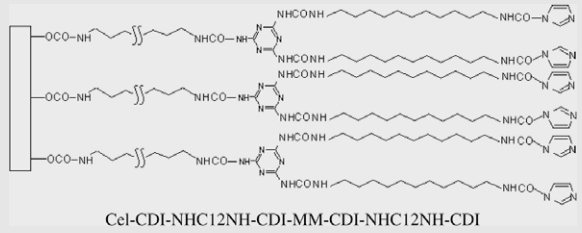
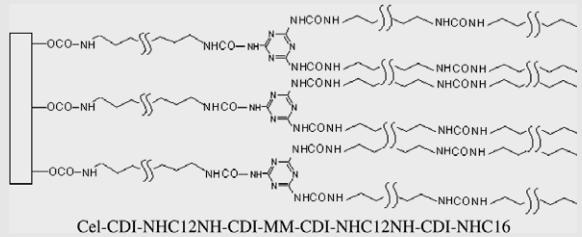
I. Cel-CDI: cellulose fibres activated by CDI.
II. Cel-CDI-NHC12NH2: result of the reaction of the 1,12-diaminododecane with a cellulose fibre previously CDI activated.
III. Cel-CDI-NHC12NH-CDI-MM: result of the reaction of melamine with the product obtained in II after activation with CDI.
IV. Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH2: result of the reaction of 1,12-diaminododecane with fibres obtained in III after treatment with CDI.
V. Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH-CDI: result of the reaction of CDI with fibres obtained in IV.
VI. Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH-CDI-NHC16: result of the reaction of hexadecylamine with the product obtained in V.

The ideal structures of the different intermediate samples are collected in Table 1. Fig. 3 shows FTIR spectra corresponding to the product issued from each modification sequence.

In spectrum A the typical bands of imidazole ester at 1770 and 1660 cm^{-1} are clearly shown. In spectrum B, the disappearance of the band at 1770 and its replacement with one at 1710 cm^{-1} is indicative of the amino group condensation with the imidazole ester giving rise to a carbamate linkage as described above. In spectrum C, the emergence of three bands in the ranges 1430–1460, 1530–1550 and 1620–1660 cm^{-1}, typical of the melamine moiety, confirmed its anchoring on the fibres surface. The bands at 1430–1460 and 1530–1550 cm^{-1} are associated to the triazine ring structure, while the one at 1620–1660 cm^{-1} is relative to NH_2 stretching vibration (Socrates, 1994). The amide I and amide II bands expected to appear at 1650 and 1520–1550 cm^{-1}, respectively, are probably overlapped with the melamine bands. The sharp medium intensity band centred at 820 cm^{-1}, typical of the triazine ring out-of-plane bending vibration (Socrates, 1994), attested also for the presence of the melamine cycle in samples III, IV, V and VI. In spectrum D, the conversion of the broad band at 1620-1660 cm^{-1} to a sharp one at 1660 cm^{-1} indicates that the terminal NH_2 groups of melamine ring have been involved in the condensation reaction with 1,12-diaminododecane after activation with CDI. One can notice that the bands at 1710, 1550 and 1430–1460 cm^{-1} remained unchanged. The treatment of the ensuing product in step V with CDI (spectrum E) generates new bands at 1770, 1635 and 1624 cm^{-1} attributed to the CO, C=C and C=N stretching vibration of the imidazole carboxamide resulting from the condensation of the terminal NH_2 group of 1,12-diaminododecane with CDI. One cannot exclude the reaction of CDI with buried hydroxyl groups of the cellulose fibres or residual unreacted surface hydroxyl. However, we consider that this hypothesis is unlikely given the heterogeneous character of the reaction, the low polarity of the solvent used and the low accessibility of those hydroxyl groups after the different reaction sequence. The reaction of the product resulting from step V with hexadecylamine leads to the disappearance of the bands at 1770, 1635 and 1624 cm^{-1} which are replaced by a shoulder at 1620 cm^{-1}, probably associated to the amide I band of the aliphatic urea group ensuing from the condensation of the hexadecylamine on the imidazole carboxamide.

The different evolutions observed on the FTIR spectra when difunctional or trifunctional amines are added to the grafting are in agreement with the occurrence of the condensation reaction

Table 1
Ideal structures of different modified cellulose samples.

Modified fibers structures and abbreviation	Numbering
 Cel-CDI	(I)
 Cel-CDI-NHC16	–
 Cel-CDI-NHC12NH2	(II)
 Cel-CDI-NHC12NH-CDI-MM	(III)
 Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH2	(IV)
 Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH-CDI	(V)
 Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH-CDI-NHC16	(VI)

through one terminal amine leaving the other one(s) available for further reaction. Additional evidence of the "living" character of the terminal amino groups is provided in the following section.

The CP-MAS ^{13}C NMR analysis was performed for two consecutive modification sequences: Cel-CDI-NHC12NH2 and Cel-CDI-NHC12NH-CDI-C16 are shown in Fig. 4. In the spectrum of Cel-CDI-NHC12NH2, besides the signals of the cellulose backbone, the presence of the peaks at 30 and 41 ppm assigned to the methylene carbon of the diaminododecane moiety and the peaks at 151 ppm confirmed the occurrence of the grafting reaction. New peaks appeared at 14, 23, 32 and 149 ppm in the spectrum of Cel-CDI-NHC12NH-CDI-NHC16 typical of the terminal CH_3, CH_2 in β position relatively to CH_3, the internal methyl of the hexadecylamine chain and to the CO of the urea linkage, respectively. This fact attests that the second terminal NH_2 function of the attached diaminododecane, after its conversion to carboxamide imidazole, by the action of CDI, suffered a condensation reaction with hexadecaneamine.

3.2. Surface properties

Contact angle measurements of liquid droplets on material surfaces are used to characterize surface properties of modified fibres to provide information regarding the evolution of hydrophilic/hydrophobic character induced by the different functionalizations. The dynamic change of the contact angle versus time of a drop of water on the surface of the fibres mildly pressed to provide uniform surface are shown in Fig. 5a. The low contact angle value of original fibres, about 25°, results from high hydrophilic character of the surface as a consequence of the high density of the surface hydroxyl group on cellulose fibres. The fibres treated with CDI followed by 1-aminododecane reached a contact angle about 91° denoting a highly hydrophobic surface which is the sign that the long aliphatic chains thoroughly hide the cellulose surface hydroxyl groups. The evolution of the contact angle after the above modification sequence I to VI is also depicted in Fig. 5: after step II the contact angle starts at a value close to 80° and rapidly drops to 25° after 1 s. The same trend is noticed after step III. However, one can notice that the time before the drop starts to be absorbed by the substrate is higher after step IV. In fact, given the presence of the terminal amino group in 1,12-diaminododecane or in melamine, we should expect a relatively polar surface with a low contact angle for the samples II and III. This discrepancy can be rationalised if we assume that the changing from a relatively hydrophobic surface to a highly hydrophilic one, is due to the involvement of the terminal amino groups in strong intermolecular interaction, through hydrogen bonding, between them or, more likely, with polar groups in cellulose surface or carbamate linkage. Those terminal groups are, thus, less available to share interaction with drop water molecules at the beginning of the experiment. With time, water drop induces the orientation of these groups towards the air-polymer interface to become more accessible to establish interaction with liquid water molecules. Indeed, it is reported that the surface properties of polymeric materials are dictated by the surface configuration of the molecule and their atoms spatial arrangement at the top surface (Yasuda & Okuno, 1994). Despite the expected presence of the amino groups on the sample IV surface, the contact angle starts at 80° and reaches a constant value at 70° after 10 s. The relatively high contact angle could be ascribed to the high proportion of methylene groups with respect to the amino one, i.e, 24 CH_2 against at least four amino groups. The hydrophobic effect imparted by these groups contributes to dilute the polar contribution of the terminal NH_2. Here again, the contact angle starts at a higher value and declines after several seconds after the drop deposition. However, thanks to the high proportion of the methylene groups the decay is more attenuated then previously. At the sixth functionalization step, the surface becomes fully hydrophobic with a constant contact angle reaching 95° even after several minutes after deposing the water droplet, which suggests a high level of surface coverage with alkyl chains issuing from the condensation

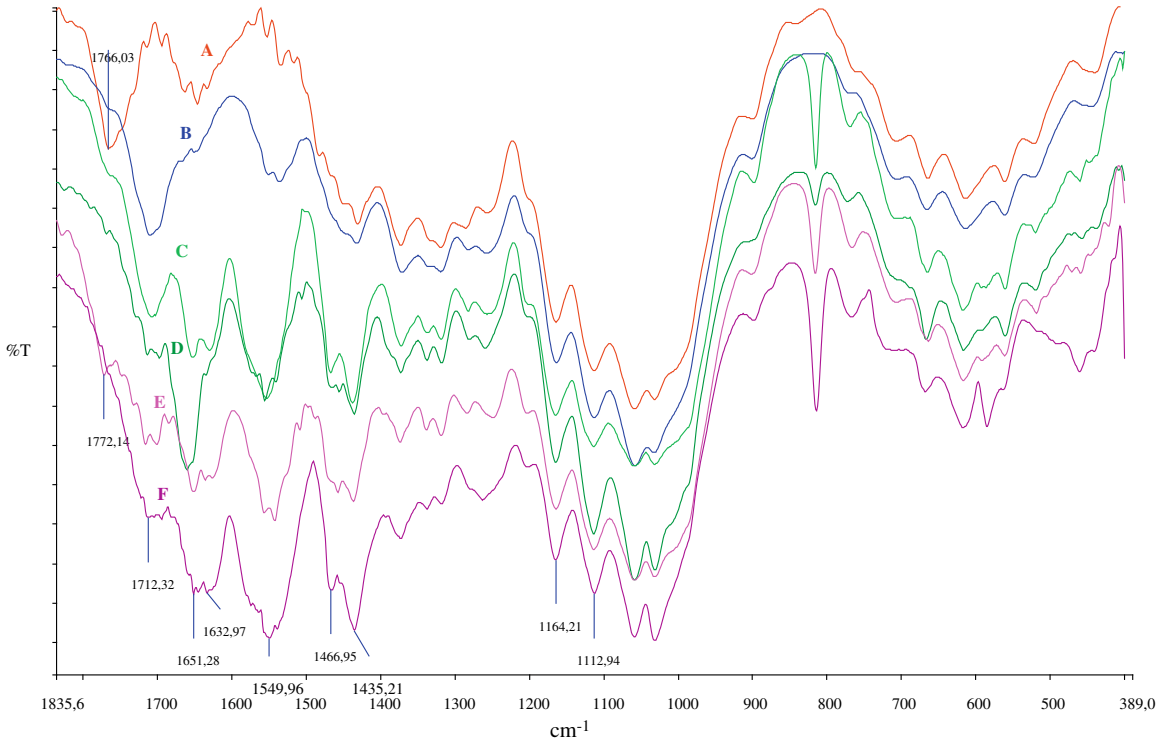


Fig. 3. FTIR spectra of: (A: sample (I)), (B: sample (II)), (C: sample (III)), (D: sample (IV)), (E: sample (V)) and (F: sample (VI)).

of the melamine terminal amino groups with acyl imidazolides intermediates. If one excludes the reaction of the terminal amine of melamine or 1,12-diaminododecane with a high efficiency then we could not expect such a high contact angle value.

The same trend is observed for the evolution of the contact angle when we change water by formamide as a probe (Fig. 5b). This supports the above rationalization regarding the orientation of the appended group on the surface.

3.3. XPS analysis

Samples II, III, IV and VI were analysed by XPS (Fig. 6) together with the sample resulting from the fibres treatment with CDI followed by 1-aminododecane (Cel-CDI-NHC12, not included in Table 1 and here denoted sample IIa) also studied by the contact angle technique. C 1s regions were fitted with 5 peaks. Fittings were performed using XPSPeak software. Constrains were: (a) the binding energy (BE) difference between the aliphatic peak (BE = 285 eV) and the cellulosic ones (BE = 286.7 and 288.1 eV) were kept constant (ΔBE = 1.7 and 3.1 eV); (b) the areas ratio between the two cellulosic peaks was kept equal to 5; (c) all the peaks were constrained to have the same FWHM and the same Lorentzian percentage. Peaks were assigned to aliphatic carbon at 285 eV, cellulose carbon, C—O and O—C—O centred at 286.73 and 288.06 eV, respectively, carbon from carbamate (—O—(C=O)—N—) groups centred at 289.5 ± 0.1 eV in samples II and IIa or carbon

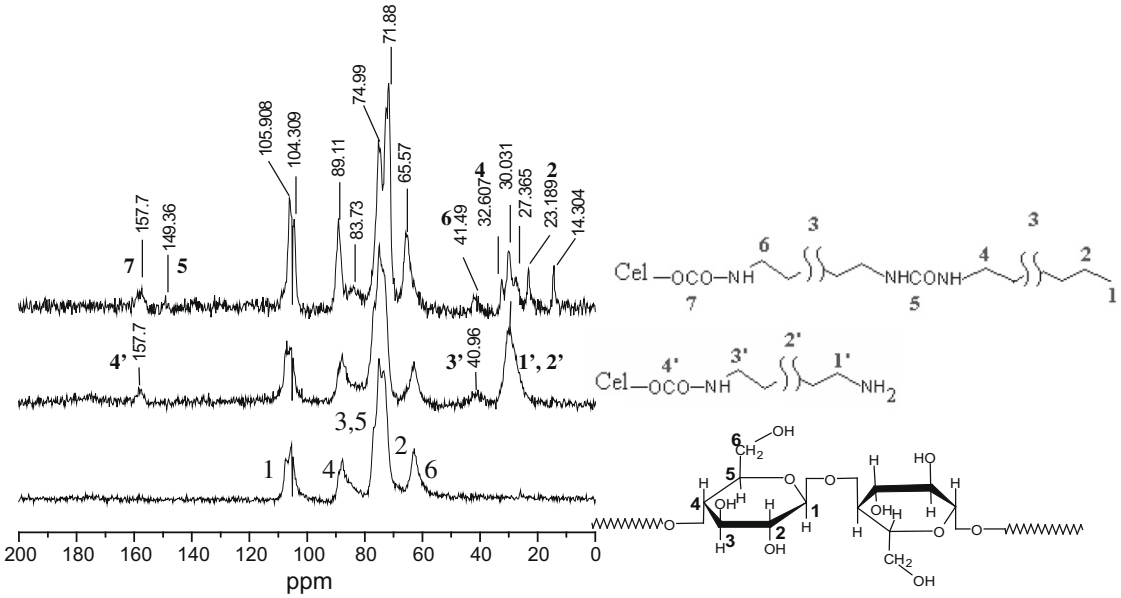


Fig. 4. NMR spectra of virgin cellulose fibers , Cel-CDI-C12NH and Cel-CDI-NHC12NH-CDI-NHC16.

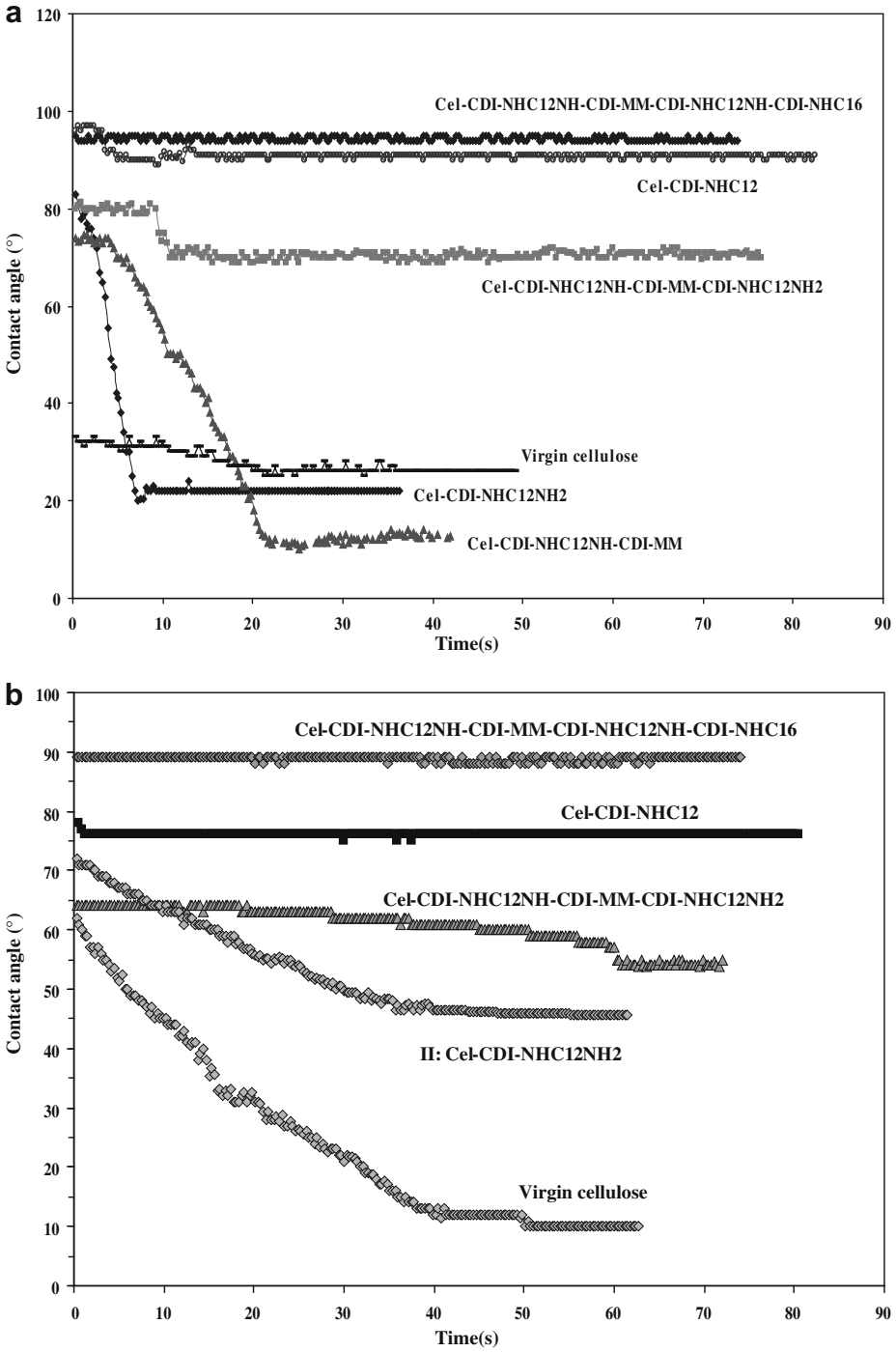


Fig. 5. Evolution of contact angle versus time of virgin cellulose and the different modified samples (a) using water, and (b) formamide as a probe.

from urea (—N—(C=O)—N—) groups centred at 288.8 ± 0.1 eV in the other samples, and carbon in C—N centred between 285.5 and 286.1 eV depending on the sample. Samples II and IIa display very similar qualitative and quantitative results in XPS. In both, C 1s is dominated by the peaks assigned to cellulose. However, and besides the aliphatic carbons, C 1s also presents the contribution of carbon in carbamate groups (peak at 289.5 ± 0.1 eV) and singly bound to both terminal amine nitrogen C—N centred at ~286 eV. Since the amount of nitrogen in sample II should be twice the amount in sample IIa and half of nitrogen atoms should be in the extreme surface not suffering any photoelectron attenuation, the ratio C/N "seen" in sample II should be much smaller (by a factor less than 1/2) than in sample IIa. The experimental C/N ratio is 24 in sample IIa and 20 in sample II (it was expected to be less than 12). These results are compatible with most of the NH_2 unreacted groups being buried and explaining also the relatively high initial value of water contact angle on both surfaces.

In sample III, peaks assigned to cellulose are now more attenuated. The peak centred at higher binding energy (288.9 V) is assigned to carbon in urethane groups that link the outermost melamine to the diamine. It is expected to have also carbamate groups as in the previous sample, but since these groups are buried deep in the organic layer the signal is attenuated and they are not clearly detected. At BE = 287.4 ± 0.2 eV it is expectable to have the

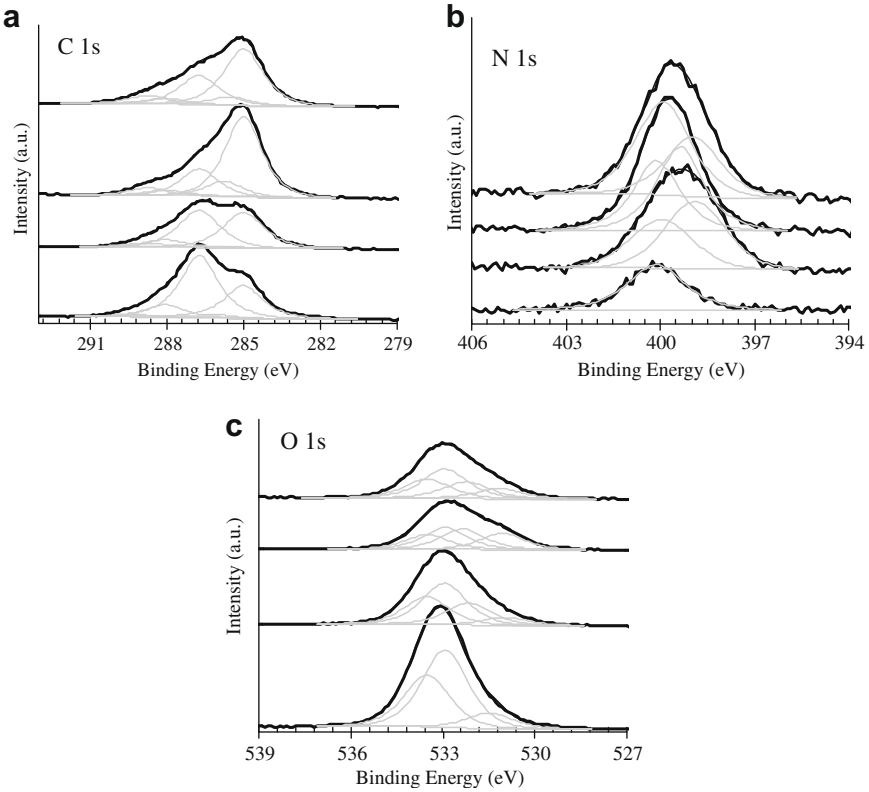


Fig. 6. XPS regions (a) C 1s, (b) N 1s and (c) O 1s of (from bottom to top) Cel-CDI-NHC12NH2; Cel-CDI-NHC12NH-CDI-MM; Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH2; Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH-CDI-NHC16.

melamine carbon contribution. However, it is almost impossible to distinguish it from the cellulose contribution.

In sample IV, C 1s is dominated by the peak assigned to aliphatic carbons. Carbons from cellulose and urethane groups are also detected.

C 1s of sample VI is similar to the previous one; however, even with an extra and longer aliphatic chain, the relative intensity of aliphatic carbons does not increase as expected: it even decreases!

Samples II and IIa show N 1s regions with one single peak centred at 400.1 ± 0.1 eV that corresponds mainly to the nitrogen singly bound to carbon. N 1s for all the other samples presents 2 peaks centred at 398.9 ± 0.2 (N1) and 400.0 ± 0.2 eV (N2). The first one is assigned to nitrogen in the melamine ring; the second one to nitrogen in amine groups and carbamate and/or urea groups. The relative importance of the two components varies from sample to sample (see Table 2). In sample II, N1 component is absent since no melamine was yet grafted. In sample III, the N1/N2 ratio is maximal, as expected, since melamine is the aminated outermost group. For samples IV and VI the N1/N2 ratio is decreasing, since the amino groups from the diamines being grafted, cover the melamine ring nitrogen.

O 1s was fitted with two components at 532.93 and 533.51 eV assigned to C—O and C—O—C in cellulose, respectively. Also 1 or 2 peaks between 531.0 and 532.4 eV corresponding to oxygen in carbonyl groups under different chemical environments (carbamate groups in Cel-CDI-NHC12 and Cel-CDI-NHC12NH2 plus urea in the other samples) were fitted. The cellulose components are predominant in samples IIa and II but their relative importance decreases in sample III, and even more in sample IV; but it slightly increases in sample VI.

The quantitative expression of these results is contained in Table 2. Ratio C/O_{cell} is a good ratio to attest for the increasing thickness of the layer on cellulose as the functionalisation proceeds. In fact, in the O 1s region of cellulose, no other components are expected whereas, in the C 1s region of cellulose components, also the contribution of carbons bound to nitrogen is expected. Therefore, O 1s components assigned to cellulose are a better parameter to measure the amount of cellulose. The first row of Table 2 shows that the cellulose coverage increases from sample II to sample IV but decreases when the last functionalization with the aliphatic amine chain in C16, CH_3 terminated, is achieved. In the same table, the C_{cell}/O_{cell} is added. This parameter, in the absence of other components in the cellulose C 1s region, should be 1.2. And, in fact, it is the obtained value for samples where no

Table 2
XPS quantitative results.

Samples	IIa	II	III	IV	VI
Atomic composition (%)					
C 1s 1 (aliphatic)	39.0	29.4	41.5	59.3	52.4
C 1s 2 (C—N)	2.4	2.8	2.0	11.1	7.7
C 1s 3 (C—O in cellulose)	46.9	55.0	43.5	19.9	26.8
C 1s 4 (O—C—O in cell)	9.4	11.0	8.7	4.0	5.4
C 1s 5 (O—C=O group)	2.4	1.9	4.3	5.6	7.7
Binding energy (eV)					
C 1s 1	285.0	285.0	285.0	285.0	285.0
C 1s 2	286.0	286.0	286.1	285.7	285.5
C 1s 3	286.7	286.7	286.7	286.7	286.7
C 1s 4	288.1	288.1	288.1	288.1	288.1
C 1s 5	289.6	289.4	288.8	288.7	288.7
Atomic ratio					
N/O_{cell}	0.1	0.1	0.4	1.1	0.8
C/O_{cell}	2.1	1.8	2.7	7.3	4.5
C_{cell}/O_{cell}	1.2	1.2	1.4	1.8	1.5
N1/N2		0	1.4	1.2	0.6
$N1/O_{cell}$			0.2	0.6	0.3

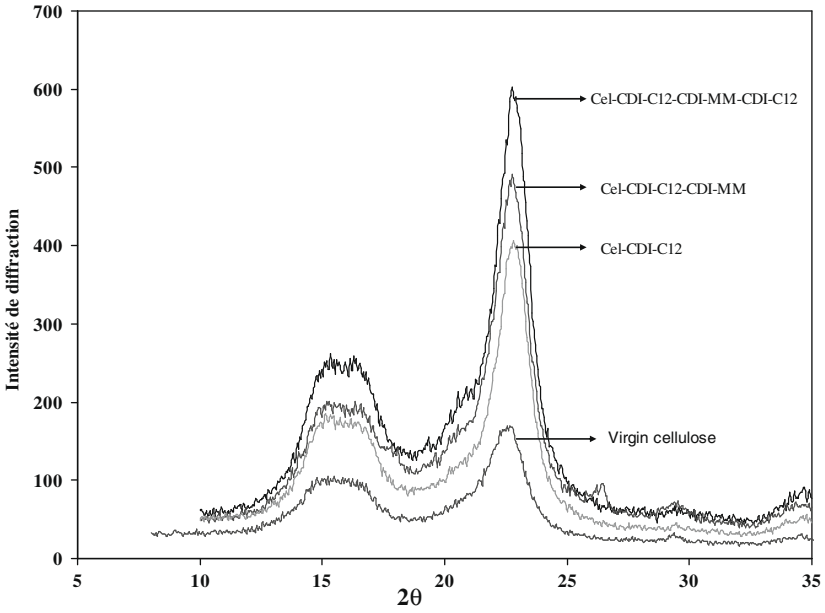


Fig. 7. X-ray diffraction patterns of original cellulose fibers and Cel-CDI-NHC12NH2, Cel-CDI-NHC12NH-CDI-MM, Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH2 and Cel-CDI-NHC12NH-CDI-MM-CDI-NHC12NH-CDI-NHC16.

melamine exists and a single functionalization was performed (samples II and IIa). In all the other samples that ratio is larger than 1.2 which is compatible with the growing of a layer over the surface: O 1s photoelectrons escape depth is shorter than the C 1s photoelectrons escape depth; therefore O 1s photoelectrons are more attenuated than the C 1s ones and the ratio C_{cell}/O_{cell} increases. Once again, this parameter confirms that the sample where the maximum cellulose coverage is attained is sample IV. However, a contribution of the melamine carbon to the increase of this parameter cannot be completely discarded (see above).

Nitrogen amount should increase at each grafting step since it exists both in the activating CDI molecule and in the diamine or monoamine chains. Once again, its XPS maximum value (measured as the ratio N/O_{cell}) is attained for sample IV and not for sample VI.

All the observations are consistant in indicating that the functionalization is successful till sample IV. However, in the last sample a poorer coverage of cellulose is consistently displayed which, at a first sight, contradicts results obtained from the contact angle measurement.

Combination of XPS and contact angle results provide a very clear illustration of molecular strategies to minimize surface energy: in samples where the more "external" groups are polar groups, the polar extremity, having a large surface energy, tends to become buried. This allows the polar group (NH_2 or melamine) to use all their possibilities of polar (Keesom) and hydrogen bond interactions with other neighbouring similar groups or with the carbamate, or urea depending on the case or, even, with unreacted cellulose hydroxyl groups. The consequence of this strategy is that the aliphatic chain bearing the polar group is far from its straight configuration in order to bury the free polar extremity. And since it is far from being perpendicular to the surface, any photoelectron escaping from the cellulose is attenuated by the "curved" aliphatic chain. Hence, simultaneously, we see more aliphatic carbon than should be seen if the chains stood perpendicular to the surface, and less cellulose carbon (and oxygen) and also less contributions from the polar groups containing nitrogen. Upon the reaction of the terminal CDI activated NH_2 group with hexadecylamine, the curved chains are likely to adopt a more extended conformation, given the linear structure of the hydrocarbon chains bearing 16 methylene groups and their tendency to adopt a stretched conformation at the solid/air interface.. This straight conformation creates channels allowing for the cellulose photoelectrons to escape to the XPS analyser giving quantitative results that suggest that the surface is less covered. Rotating the sample so the analysed photoelectrons escape the surface at 30° greatly increases the ratio between the aliphatic and the cellulosic carbon (from 1.7 at 90° to 2.3 at 30°) confirming this picture. This analysis was drawn as if the surface was flat. In fact, since the diameter of the fibres is of the order of a few microns, more than thousand times the length of the chains, most part of the surface "seen" by the XPS behaves as if it was flat. Simultaneously, this brush-pin like structure made of hydrophobic long chains provides an effect similar to the well known lotus flower effect explaining the high angle contact of the surface.

The quantitative XPS results were also used to estimate the degree of cellulose hydroxyl groups substitution (DS) defined as the number of hydroxyl groups substituted by glucose unit. Several groups or elements can be used for the estimation, the general formula used being:

$$\mathrm{DS} = \frac{\text{amount of groups/number of occurrences by substitution}}{\text{amount of cellulosic carbon}/6} \quad (1)$$

For a given sample, we can compute DS using more than one set of data. For instance, for sample II we can use

$$\mathrm{DS} = \frac{\text{O—C=O atomic }\%/1}{\text{cellulosic(C—O + O—C—O)}\%/6} \quad \text{or}$$

$$\mathrm{DS} = \frac{\text{N atomic }\%/2}{\text{cellulosic(C—O + O—C—O)}\%/6}$$

The obtained values were 0.2 ± 0.03. This value would be rather low if the substitution degree was uniform in depth. However, if we take into account that the availability of deeper cellulosic hydroxyls is much reduced, and since this is a mean value for several cellulosic layers, the fiber surface DS should be much higher. In fact, for samples where the length of grafted chains increases, and, thence fewer cellulose layers are probed by XPS, DS value increases reaching the value of 0.42 ± 0.05 for sample IV.

To investigate the effect of the different modification reaction on the crystallinity degree of cellulose fibres, Wide angle X-ray diffraction was used to evaluate crystallinity index. The X-ray

diffraction patterns shown in Fig. 7 revealed the presence of three peaks at $2\theta = 15°$; 17° and 22.7° typical of cellulose I form. Moreover, for the different samples, the crystallinity index is maintained roughly constant (in a range from 87% to 90%) in line with the above hypothesis according to which the chemical modification occurs only on the amorphous phase and the external surface of the fibres accessible to the solvent.

4. Conclusions

Surface grafting of different amino derivatives under mild condition was achieved using CDI as an activator agent. The surface activation of cellulose fibres under heterogeneous condition with CDI generates an imidazole ester derivative that facilitates the grafting of the aliphatic amine through carbamate linkage. The occurrence of the condensation reaction was evidenced by FTIR, NMR and XPS. Different sequences of modification could be accomplished using difunctional or trifunctional amines. It was shown that the reaction on the CDI activated cellulose substrate proceeds through the condensation of a single amine group leaving the second terminal amine function available for further reaction. This latter one could again be activated by CDI to generate carboxamide imidazole and undergo condensation with aliphatic amine or diamine. This strategy enables wide latitude of target surface functionalisation and opens a novel way of achieving molecular architecture on cellulose substrate.

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